Electronic Supplementary Information (ESI)

Light-driven twisting behaviour of chiral cyclic compounds

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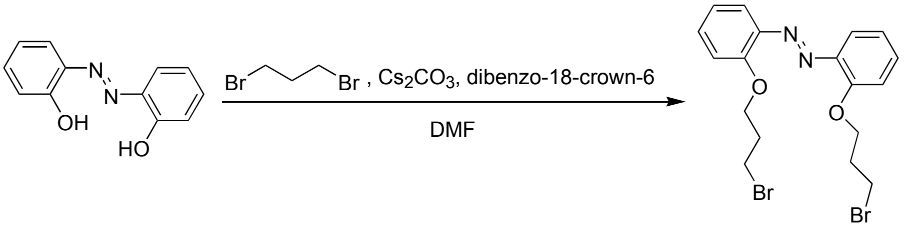
Experimental section

Unless otherwise noted, materials and solvents were purchased from commercial suppliers and were used without further purification. 2,2'-dihydroxyazobenzene, 1,3-dibromopropane, dibenzo-18-crown-6, (*R*)-2,2'-dihydroxy-1,1'-binaphthyl, (*S*)-2,2'-dihydroxy-1,1'-binaphthyl were purchased from Tokyo Kasei Kogyo Co. Ltd. Cesium carbonate and anhydrous *N,N*-dimethylformamide were purchased from Kanto Kagaku Co. Ltd. A Nematic liquid crystal (LC), ZLI-3282 (nematic-isotropic transition temperature: 101 °C), was purchased from Merck Ltd. Japan. The compounds synthesized were identified by means of ^{1}H NMR (JEOL AL400), EI mass spectroscopy (JEOL SX-102), and elemental analysis. Absorption spectra were measured using a JASCO V-530. CD spectra were obtained using a JASCO J-720. Morphological changes were examined by differential scanning calorimeter (PerkinElmer DSC7) and X-ray diffractometry (Rigaku RINT 2100). Thin films of **(*R*)-Azo** and **(*S*)-Azo** were obtained by spin-coating at a rate of 1,000 rpm for 30 s with 1 wt% solution in chloroform onto a fused silica substrate. The solvent was removed under reduced pressure at room temperature. Sample thickness (~ 100 nm) was checked by a Dektak surface profiler. The samples were irradiated at 365 nm (6 mW/cm^2) or 436 nm (14 mW/cm^2) from a 120W high-pressure mercury lamp (Asahi Spectra REX-120) through glass filters (Asahi Spectra HQBP365 or HQBP436).

Materials

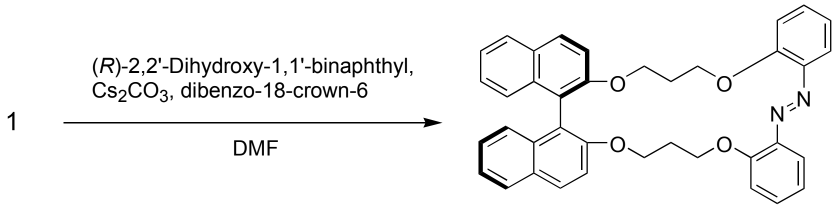


1

2,2'-bis(3-bromopropoxy)azobenzene (**1**)

2,2'-Dihydroxyazobenzene (0.5 g, 2.3 mmol), cesium carbonate (2.25 g, 6.9 mmol), and dibenzo-18-crown-6 (0.25 g, 0.69 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (50 ml). After stirring 20 min, 1,3-dibromopropane (4.64 g, 23 mmol) was added to the solution. The mixture was stirred at room temperature for 72 h under nitrogen. The crude product was extracted with methylene chloride and water, and then washed with brine before drying over anhydrous magnesium sulfate. After evaporation of the solvent, the solid residue was dissolved in toluene for purification by flash column chromatography on silica gel with a solvent gradient ranging from 0 to 1 % acetone in toluene to yield **1** (0.73 g, 69%). ^{1}H–NMR (400 MHz, $CDCl_3$): δ (ppm) 2.39-2.45 (m, 4H, Ph-OCH_2**CH_2**CH_2Br), 3.69 (t, 4H, Ph-OCH_2CH_2**CH_2**Br), 4.34 (t, 4H, Ph-OC**H_2**CH_2CH_2Br), 7.02-7.08 (m, 2H, aromatic rings), 7.11 (d, 4H, aromatic rings), 7.39-7.43 (m, 2H aromatic rings), 7.63 (d, 2H, aromatic rings).

(*R*)-2,2’-bis{3-(2’’-phenoxy)propoxy}-1’’-azo-1,1’-binaphthyl (**(*R*)-Azo**)



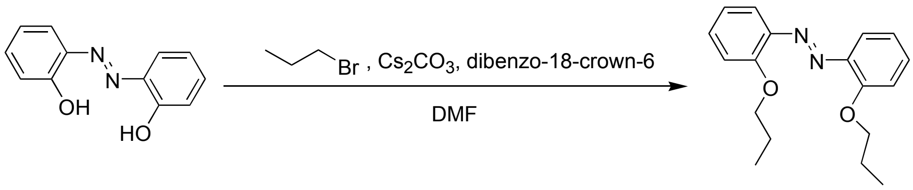
(*R*)-Azo

(*R*)-2,2’-Dihydroxy-1,1’-binaphthyl (0.63 g, 2.2 mmol), cesium carbonate (3.6 g, 11 mmol), and dibenzo-18-crown-6 (0.4 g, 1.1 mmol) were dissolved in anhydrous *N,N*-dimethyl formamide (300 ml). After stirring 20 min, **1** (1.0 g, 2.2 mmol) was added to the solution. The mixture was stirred at room temperature for 72 h under nitrogen. The crude product was extracted with methylene chloride and water, and then washed with brine before drying over anhydrous magnesium sulfate. After evaporation of the solvent, the solid residue was dissolved in toluene for purification by flash column chromatography on silica gel with a solvent gradient ranging from 0 to 2 % acetone in toluene. Furthermore, the product was purified by size exclusion chromatography (Shodex KF-5001) with only chloroform. The second fraction was collected and evaporated to dryness, to afford **(*R*)-Azo** (0.3 g, 24%). ^{1}H–NMR (400 MHz, $CDCl_3$): δ (ppm) 1.77-1.94 (m, 4H, Ph-OCH_2**CH_2**CH_2O-binaphthyl), 3.48-4.21 (m, 8H, Ph-OC**H_2**CH_2CH_2O-binaphthyl and Ph-OCH_2CH_2**CH_2**O-binaphthyl), 6.75 (d, 2H, aromatic rings), 7.01-7.23 (m, 8H, aromatic rings), 7.30-7.34 (m, 4H, aromatic rings), 7.56 (d, 2H, aromatic rings). EI-MS: m/z = 580 $[M]^+$. Anal. Calc. for $C_{38}H_{32}N_2O_4$: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.52; H, 5.55; N, 4.80.

(*S*)-2,2'-bis{3-(2''-phenoxy)propoxy}-1''-azo-1,1'-binaphthyl ((***S***)**-Azo**)

(***S***)**-Azo** was prepared from **1** in a similar method to that described for (***R***)**-Azo**. Yield: 24%. EI-MS: m/z = 580 $[M]^+$. Anal. Calc. for $C_{38}H_{32}N_2O_4$: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.52; H, 5.54; N, 4.80.

2,2'-dipropoxyazobenzene (a model compound of (***R***)**-Azo** and (***S***)**-Azo**)



2,2'-dihydroxyazobenzene (1.5 g, 7.0 mmol), cesium carbonate (5.5 g, 17 mmol), and dibenzo-18-crown-6 (0.6 g, 1.7 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (100 ml). After stirring 20 min, 1-bromopropane (2.07 g, 17 mmol) was added to the solution. The mixture was stirred at room temperature for 72 h under nitrogen. The crude product was extracted with methylene chloride and water, and then washed with brine before drying over anhydrous magnesium sulfate. After evaporation of the solvent, the solid residue was dissolved in toluene for purification by flash column chromatography on silica gel with a solvent gradient ranging from 0 to 1.5 % acetone in toluene to yield the molel compound (1.6 g, 75%). ^{1}H–NMR (400 MHz, $CDCl_3$): δ (ppm) 1.08 (t, 6H, Ph-$OCH_2CH_2C\mathbf{H_3}$), 1.89-1.95 (m, 4H, Ph-$OCH_2C\mathbf{H_2}CH_3$), 4.15 (t, 4H, Ph-$OC\mathbf{H_2}CH_2CH_2Br$), 6.97-7.08 (m, 4H, aromatic rings), 7.36-7.39 (m, 2H aromatic rings), 7.66 (d, 2H, aromatic rings). Anal. Calc. for $C_{19}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.47; H, 7.32; N, 9.29.

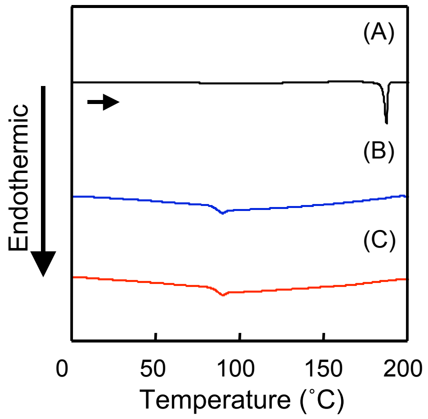


Figure S1. DSC thermograms of (***R***)**-Azo** on first (A), second (B), and third heating (C), respectively. Scan rate: 10 ˚C/min.

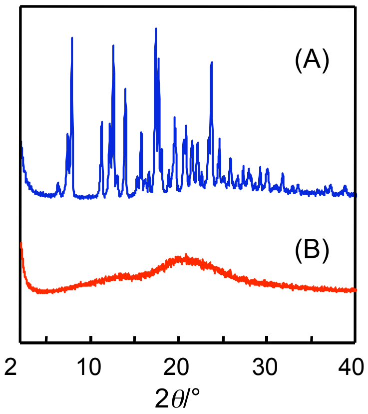


Figure S2. X-ray diffraction patterns of (***R***)**-Azo** at room temperature. (A) Before thermal treatment, (B) after thermal treatmant at 220 ˚C for 5min.

Thermodynamic parameters of *cis-trans* isomerization process

We investigated the thermal *cis-trans* isomerization process. For the thermal *cis-trans* isomerization,

$$\ln\frac{[cis]}{[cis]_0} = -kt \qquad (1)$$

where $[cis]$ and $[cis]_0$ are the concentrations of the *cis*-azobenzene at time t and time zero, and k is the rate constant for the thermal *cis-trans* isomerization. The first-order rate constant was determined by fitting the experimental data to the equation,

$$\ln\frac{A_\infty - A_t}{A_\infty - A_0} = -kt \qquad (2)$$

where A_t, A_0 and A_∞ are the absorbance at 365 nm at time t, time zero and infinite time, respectively. The first order plots according to eq. 2 for the *cis-trans* thermal isomerization of (***R***)**-Azo** and 2,2'-dipropoxyazobenzene as a model compound in 1,4-dioxane at various temperatures are shown in Figure S3.

Furthermore thermodynamic parameters such as enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were determined according to the Eyring equation:

$$k = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \qquad (3)$$

where R, k_B, and h are gas constant, Boltzmann constant, and Planck's constant, respectively. Substituting into eq. 3,

$$\ln\left(\frac{kh}{k_B T}\right) = -\frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R} \qquad (4)$$

Figure S4 shows Eyring plots for *cis* to *trans* thermal isomerization of **(*R*)-Azo** and 2,2'-dipropoxyazobenzene in 1,4-dioxane. The values of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ were obtained from an intersect and a slope, respectively, of the linear plot of $\ln(kh/k_BT)$ versus $1/T$ extrapolated to $T \rightarrow \infty$.

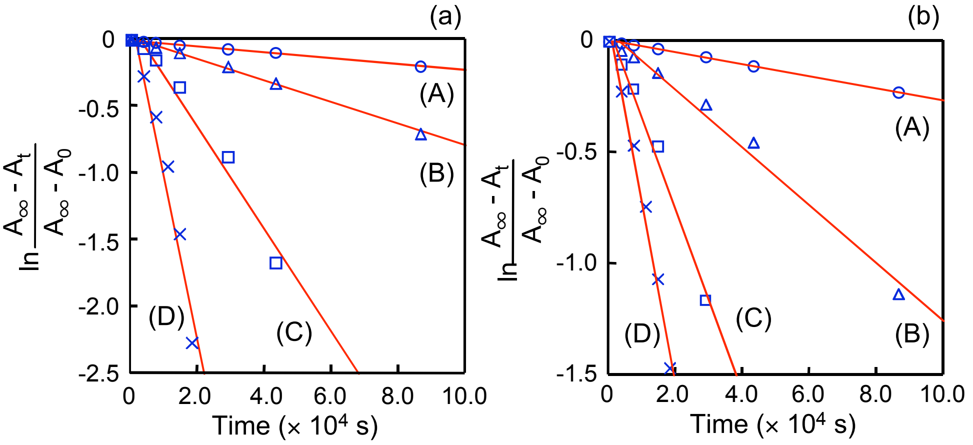


Figure S3. First-order plots for *cis* to *trans* thermal isomerization of **(*R*)-Azo** (a) and 2,2'-dipropoxyazobenzene (b) in 1,4-dioxane at various temperatures. (A) 25 ˚C, (B) 35 ˚C (C) 45 ˚C, and (D) 55 ˚C.

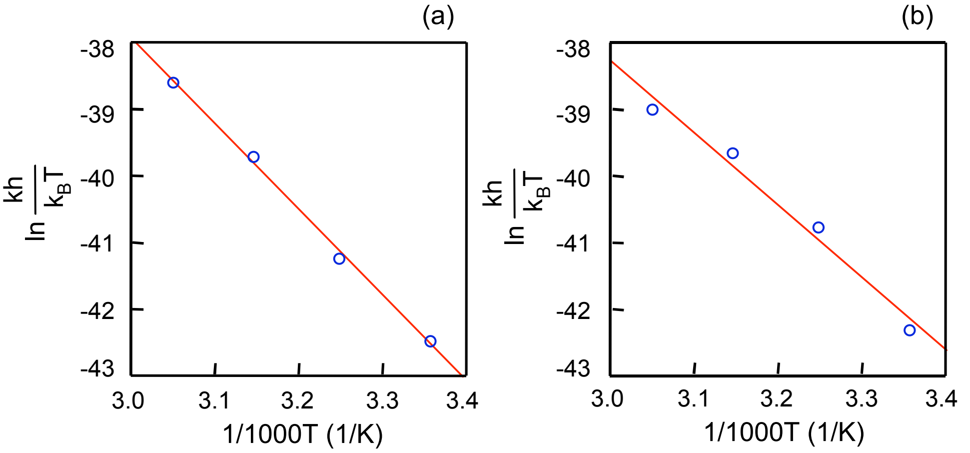


Figure S4. Eyring plots for *cis* to *trans* thermal isomerization of **(*R*)-Azo** (a) and 2,2'-dipropoxyazobenzene (b) in 1,4-dioxane.

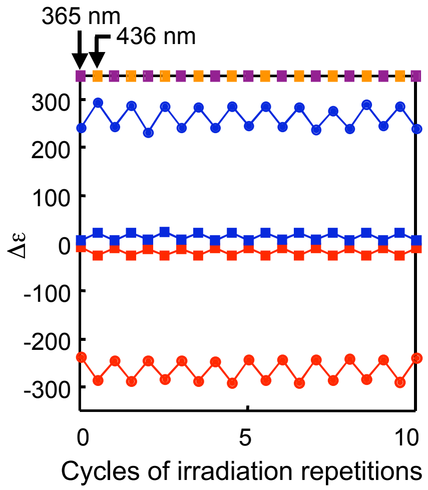


Figure S5. Switching behaviour of **(*R*)-Azo** (red) and **(*S*)-Azo** (blue) in 1,4-dioxane induced by irradiation with 365 nm (6 mW/cm^2, 20s) and 436 nm (14 mW/cm^2, 20s) at room temperature. Monitoring wavelength: 238 nm (circle) and 440 nm (square).

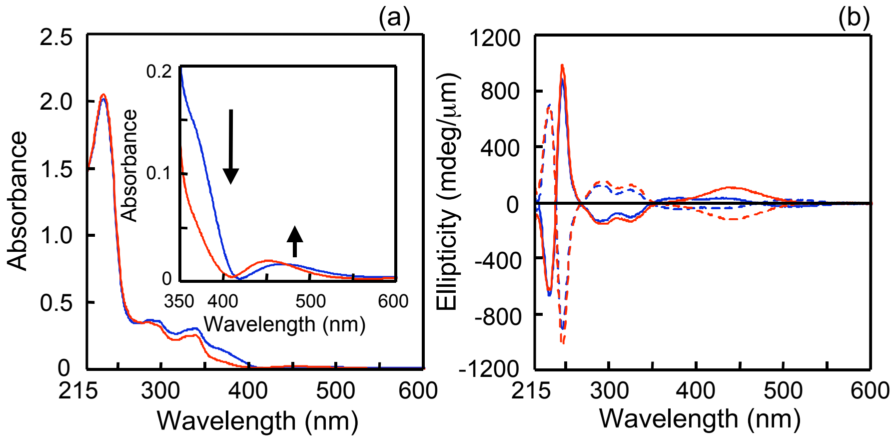


Figure S6. Absorption spectra of **(*R*)-Azo** (a) and CD spectra of **(*R*)-Azo** (dotted line) and **(*S*)-Azo** (solid line) (b) in thin films. (blue) Before irradiation, (red) just after irradiation at 365 nm (6 mW/cm^2) at room temperature. Film thickness: 100 nm.

Investigation of LC alignment behaviour in a wedge cell

Chiral cyclic compound-doped LC was mixed with ZLI-3282 (mixture of fluorophenylcyclohexane derivatives) at various concentrations (0.25 ~ 1 wt%) in a chloroform solution. The solvent was removed under reduced pressure at 40 ˚C. A wedge cell was composed of two glass substrates with rubbed polyimide layers. The thickness of the wedge cell was as follows: one was 10 μm and the other was 550 μm. Samples were filled with the mixture by capillary action at room temperature. Photoinduced orientation behaviour was determined with a polarizing microscope (Nikon E600WPOL) equipped with a digital camera (Nikon CoolPix995).

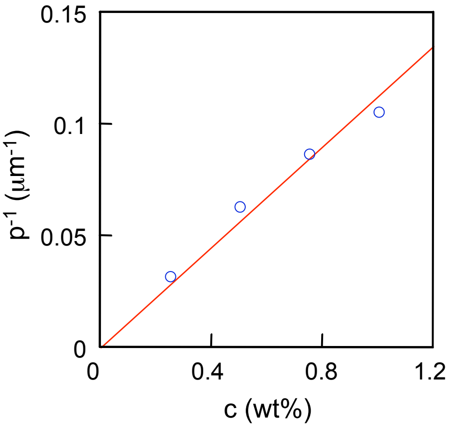


Figure S7. Helical pitch (p) as a function of concentration (c) of ***(R)*-Azo** in an LC host.

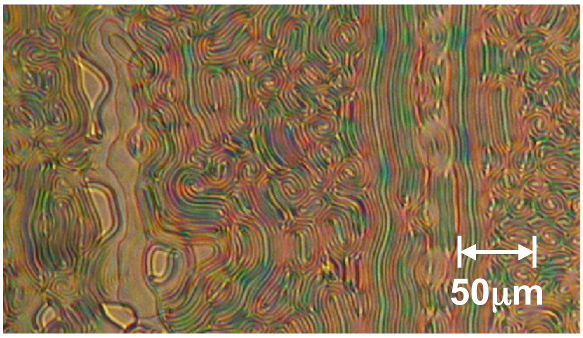


Figure S8. Photoinduced fingerprint texture in a wedge cell upon continuous UV irradiation at 365 nm.