

Electronic Supplementary Information (ESI)

**Non-Destructive Erasable Molecular Switches and Memory Using
Light-Driven Twisting Motions**

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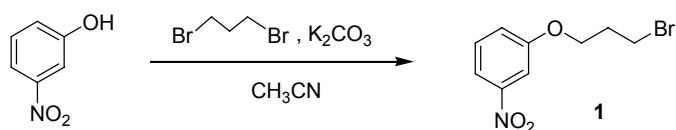
The synthesized compounds were identified by means of ^1H NMR spectroscopy (JEOL AL300 and AL400), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (PE Biosystems Voyager Elite), and elemental analysis. Optical rotations of the chiral cyclic compounds were measured using a JASCO DIP-370 polarimeter. Morphological changes were examined on Mettler hot-stages (models FP-90 and FP-82HT). Absorption spectra were measured using a JASCO V-530 spectrometer. Circular dichroism (CD) spectra were obtained using a JASCO J-720 spectrometer. The thermal behaviour of the compounds was examined on the same spectrometer equipped with a JASCO EHC-477. The thermal behaviour of the materials was also evaluated using differential scanning calorimetry (DSC; Perkin-Elmer DSC7, heating and cooling rate: $10\text{ }^\circ\text{C min}^{-1}$) and X-ray diffractometry (MacScience MXP21TA-PO). Crystal data for structure analyses, cell determination, and face indices of the crystal were collected on a diffractometer (RIGAKU AFC-8) with a charge-coupled device (CCD) detector (Saturn 70CCD) by using $\text{MoK}\alpha$ radiation. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Samples were irradiated at 365 nm (light intensity: 10 mW cm^{-2}) and 436 nm (10 mW cm^{-2}) using glass filters (Asahi Spectra HQBP365 and HQBP436, respectively) and a 120 W high-pressure mercury lamp (Asahi Spectra REX-120).

Thin films were fabricated by spin-coating a solution of the compound (1 wt%) in chloroform onto a fused silica substrate at a rate of 500 or 1000 rpm for 30 s. The films were annealed at $100\text{ }^\circ\text{C}$ for 30 min and then cooled to form a glassy state. The sample thickness was checked using a Dektak surface profiler. The orientational behaviour of the films was determined using a polarizing microscope (Nikon E600WPOL) equipped with a digital camera (Nikon CoolPix995).

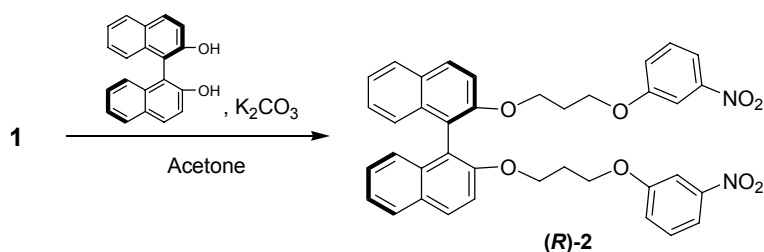
Synthesis of R3A and S3A

Unless otherwise noted, compounds and solvents were purchased from commercial suppliers and used without further purification. 3-Nitrophenol, 1,3-dibromopropane, (*R*)-2,2'-dihydroxy-1,1'-binaphthyl, and (*S*)-2,2'-dihydroxy-1,1'-binaphthyl were obtained from Tokyo Kasei Kogyo Co. Ltd. Lithium aluminum hydride, anhydrous acetonitrile, and anhydrous tetrahydrofuran were purchased from Kanto Kagaku Co. Ltd. Potassium carbonate and acetone were purchased from Junsei Kagaku Co., Ltd.



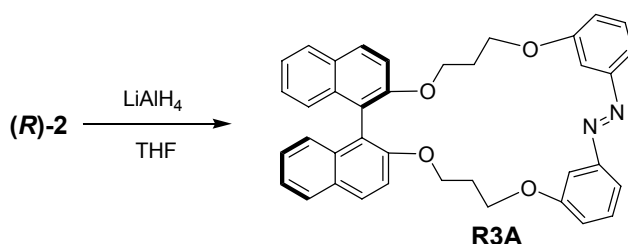
3-Nitro-1-(3-bromopropoxy)benzene (1)

To a solution of 3-nitrophenol (23.3 g, 167 mmol) and potassium carbonate (34.7 g, 251 mmol) in anhydrous acetonitrile (200 mL), 1,3-dibromopropane (270 g, 1.34 mol) was slowly added under nitrogen. The reaction mixture was heated under reflux for 24 h. The crude product was extracted with methylene chloride, and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the solid residue was purified by column chromatography on silica gel (eluent: methylene chloride/hexane = 1:1) to yield **1** (31.4 g, 73 %). ¹H NMR (300 MHz, CDCl₃): δ = 2.37 (quint, 2H, J = 6.3 Hz, Ar-OCH₂CH₂CH₂Br), 3.62 (t, 2H, J = 6.3 Hz, Ar-OCH₂CH₂CH₂Br), 4.20 (t, 2H, J = 6.3 Hz, Ar-OCH₂CH₂CH₂Br), 7.25 (dd, 1H, J = 8.4, 2.4 Hz, aromatic rings), 7.44 (dd, 1H, J = 16.2, 8.1 Hz, aromatic rings), 7.75 (d, 1H, J = 2.4 Hz, aromatic rings), 7.85 ppm (d, J = 8.1 Hz, 1H, aromatic rings).



(R)-2,2'-Bis[3-(3-nitrophenoxy)propoxy]-1,1'-binaphthyl ((R)-2)

To a solution of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (5.52 g, 19.3 mmol) and potassium carbonate (7.99 g, 75.9 mmol) in acetone (500 mL), **1** (10.0 g, 38.6 mol) was slowly added. The reaction mixture was heated under reflux for 24 h. The crude product was extracted with methylene chloride, and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the solid residue was purified by column chromatography on silica gel (eluent: methylene chloride) to yield (*R*)-**2** (9.70 g, 78 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 1.79 (t, 4H, J = 5.6 Hz, Ar-OCH₂CH₂CH₂O-binaphthyl), 3.51 (m, 4H, Ar-OCH₂CH₂CH₂O-binaphthyl), 4.10 (d, 4H, J = 5.6 Hz, Ar-OCH₂CH₂CH₂O-binaphthyl), 6.91 (d, 2H, J = 8.8 Hz, aromatic rings), 6.99 (d, 2H, J = 8.4 Hz, aromatic rings), 7.11 (dd, 2H, J = 14.4, 7.6 Hz, aromatic rings), 7.22 (dd, 2H, J = 14.4, 7.2 Hz, aromatic rings), 7.31 (s, 2H, aromatic rings), 7.50 (dd, 2H, J = 16.4, 8.4 Hz, aromatic rings), 7.57 (d, 2H, J = 9.0 Hz, aromatic rings), 7.78 (d, 2H, J = 7.2 Hz, aromatic rings), 7.86 (d, 2H, J = 8.0 Hz, aromatic rings), 8.00 ppm (d, 2H, J = 9.0 Hz, aromatic rings).



***trans*-(*R*)-2,2'-Bis[3-(3''-phenoxy)propoxy]-1''-azo-1,1'-binaphthyl (*trans*-**R3A**)**

To a solution of lithium aluminum hydride (3.6 g, 93 mmol) in anhydrous tetrahydrofuran (300 mL), (**R**)-**2** (6.0 g, 9.3 mol) was slowly added at 0 °C under nitrogen. The reaction mixture was stirred at room temperature for 24 h, and then heated under reflux for 24h. The crude product was extracted with methylene chloride, and then washed with brine before drying over anhydrous magnesium sulfate. The solvent was evaporated off under reduced pressure, and the solid residue was purified by column chromatography on silica gel (eluent: methylene chloride/hexane = 3:2). The fraction was collected and purified by preparative size exclusion chromatography (Shodex K5001, eluent: chloroform). The first fraction was collected and evaporated to dryness to afford *trans*-**R3A** (0.22 g, 4 %). ¹H NMR (300 MHz, DMSO-*d*₆): δ = 1.48 (m, 2H, Ar-OCH₂CH₂CH₂O-binaphthyl), 1.90 (m, 2H, Ar-OCH₂CH₂CH₂O-binaphthyl), 3.57 (m, 4H, Ar-OCH₂CH₂CH₂O-binaphthyl), 3.70 (t, 2H, *J* = 8.1 Hz, Ar-OCH₂CH₂CH₂O-binaphthyl), 4.41 (t, 2H, *J* = 6.9 Hz, Ar-OCH₂CH₂CH₂O-binaphthyl), 6.96 (d, 2H, *J* = 7.8 Hz, aromatic rings), 7.15 (m, 4H, aromatic rings), 7.39 (m, 10H, aromatic rings), 7.89 ppm (m, 4H, aromatic rings). Anal. Calcd. for C₃₈H₃₂N₂O₄: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.43; H, 5.61; N, 4.83. MALDI-TOF MS: *m/z* = 580.1 [*M*⁺].

***trans*-(*S*)-2,2'-Bis[3-(3''-phenoxy)propoxy]-1''-azo-1,1'-binaphthyl (*trans*-**S3A**)**

trans-**S3A** was prepared from (*S*)-2,2'-dihydroxy-1,1'-binaphthyl using a method similar to that described for *trans*-**R3A**. Yield: 4%. Anal. Calcd. for C₃₈H₃₂N₂O₄: C, 78.60; H, 5.55; N, 4.82. Found: C, 78.37; H, 5.55; N, 4.66. MALDI-TOF MS: *m/z* = 580.1 [*M*⁺].

trans-(*R*)-2,2'-Bis[3-(2''-phenoxy)propoxy]-1''-azo-1,1'-binaphthyl (*trans*-**R2A**) and *trans*-(*S*)-2,2'-Bis[3-(2''-phenoxy)propoxy]-1''-azo-1,1'-binaphthyl (*trans*-**S2A**) were synthesized as previously reported.^[1]

Determination of the Thermodynamic Parameters of *cis* to *trans* thermal back-isomerization^[2]

The thermal *cis-trans* back-isomerization process was investigated. For the thermal *cis-trans* back-isomerization,

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

where $[cis]$ and $[cis]_0$ are the concentrations of the *cis* azobenzene at time t and initially, respectively, 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,

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

where A_t , A_0 and A_∞ are the absorbance at 365 nm at time t , initially and at infinity, respectively. The first order plots according to eq. 2 for the *cis-trans* thermal isomerization of **R3A** in 1,4-dioxane and a neat film are shown in Figures S4 a) and S10 b), respectively.

The thermodynamic parameters such as enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were determined according to the Eyring equation:

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

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

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

Figure S4 b) shows Eyring plots for *cis* to *trans* thermal isomerization of **R3A** in 1,4-dioxane. The values of ΔS^\ddagger and ΔH^\ddagger were obtained from the intersect and slope, respectively, of the linear plot of $\ln(kh/k_B T)$ versus $1/T$ extrapolated to $T \rightarrow \infty$.

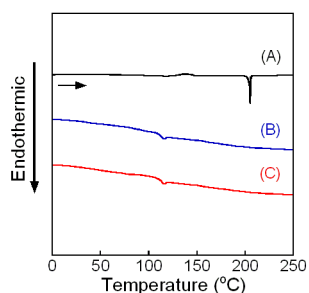


Figure S1. DSC thermograms of **R3A** on (A) first, (B) second, and (C) third heating cycles. Scan rate: 10 °C min⁻¹.

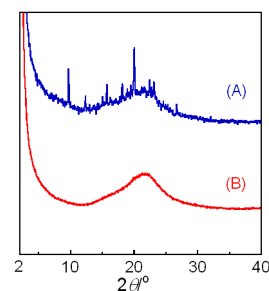


Figure S2. X-ray diffraction patterns of **R3A** at RT. (A) Before thermal treatment, and (B) after thermal treatment at 220 °C for 5 min.

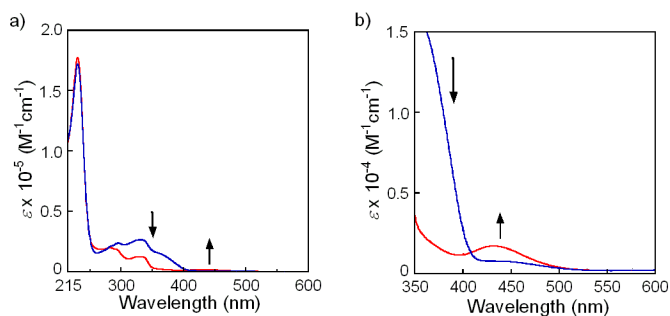


Figure S3. (a) Absorption spectra of **R3A** before (blue) and after irradiation (red) at 365 nm in 1,4-dioxane. (b) Zoom of (a) between 350 and 600 nm.

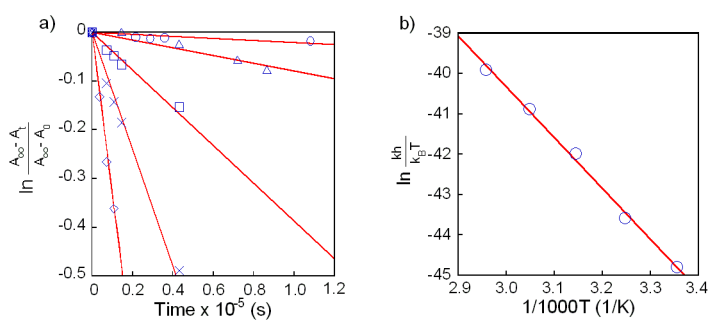


Figure S4. (a) First-order plots for *cis* to *trans* thermal backisomerization of **R3A** in 1,4-dioxane at (circles) 298K, (triangles) 308 K, (squares) 318 K, (crosses) 328 K, and (diamonds) 338 K. (b) Eyring plots for *cis* to *trans* thermal backisomerization of **R3A** in 1,4-dioxane.

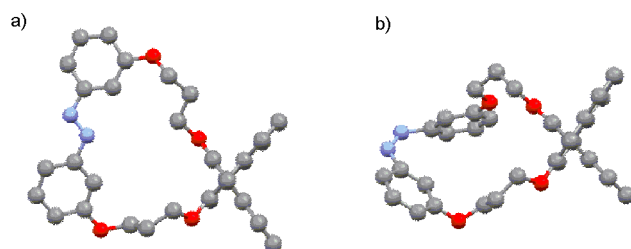


Figure S5. Lowest-Energy structures obtained by DFT calculations at the B3LYP/6-31G(d) level for *trans* (a) and *cis* form (b) of **R3A**.

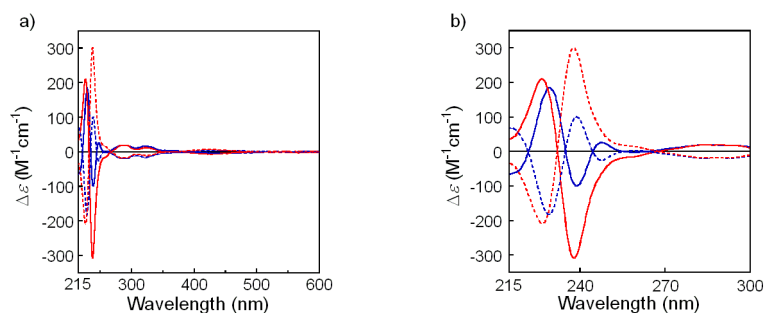


Figure S6. (a) CD spectra of **R3A** (solid line) and **S3A** (dotted line) in 1,4-dioxane before (blue) and after irradiation (red) at 365 nm. (b) Zoom of (a) between 215 and 300 nm.

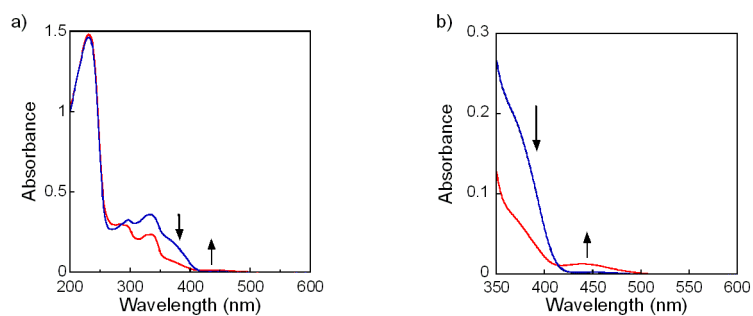


Figure S7. (a) Absorption spectra of **R3A** before (blue) and after irradiation (red) at 365 nm in a neat film. (b) Zoom of (a) between 350 and 600 nm.

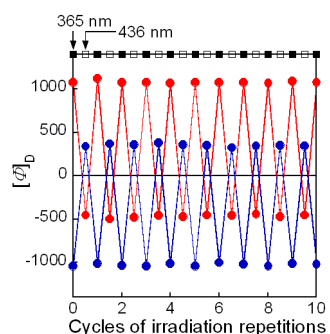


Figure S8. Chiroptical switching behaviour with non-destructive readout of $[\Phi]_D$ of **R3A** (red) and **S3A** (blue) in chloroform upon alternating irradiation at 365 nm (10 mW cm^{-2} , 500 s) and 436 nm (10 mW cm^{-2} , 500 s) at 20 °C. Monitoring wavelength: 589 nm.

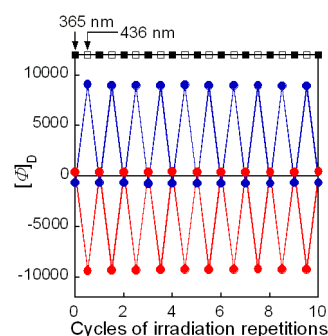


Figure S9. Chiroptical switching behaviour with non-destructive readout of $[\Phi]_D$ of **R2A** (red) and **S2A** (blue) in chloroform under alternating irradiation at 365 nm (10 mW cm^{-2} , 500 s) and 436 nm (10 mW cm^{-2} , 500 s) at 20 °C. Monitoring wavelength: 589 nm.

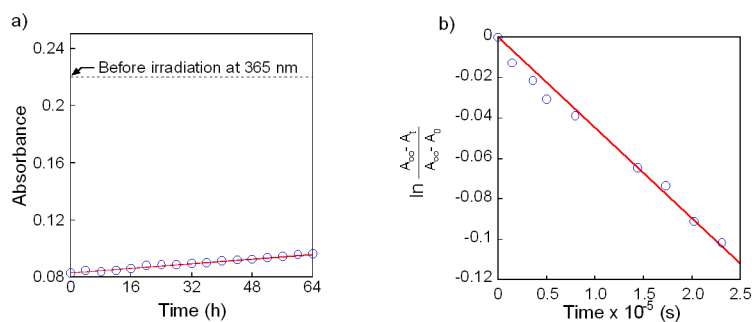


Figure S10. (a) Change in absorbance of the neat film of **R3A** kept in the dark after UV irradiation at 298K. Monitoring wavelength: 365 nm. (b) First-order plot for *cis-trans* thermal backisomerization of **R3A** in the neat film at 298K.

References

- [1] M. Kawamoto, T. Aoki and T. Wada, *Chem. Commun.* 2007, 930-932.
- [2] (a) D. A. McQuarrie and J. D. Simon, in *Physical Chemistry*, University Science Book, California, 1997; (b) H. Eyring, *Chem. Rev.* 1935, **17**, 65-77.