Supporting information

Dynamic Control of Racemization Rate Through E–Z Photoisomerization of Azobenzene and Subsequent Partial Photoresolution Under Circular Polarized Light

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Contents

1. Synthesis

2,2-Bis[4{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}-3-nitrophenyl]propane 3. 2,2´-Dinitro-4,4´-isopropylidenediphenol (2.14 g, 6.72 mmol) was obtained by nitration of bisphenol A; 1-[2-(2-bromoethoxy)ethoxy]-4-nitrobenzene (3.9 g, 13.44 mmol) was synthesized from the reaction of 4-nitrophenol and bis(2-bromoethyl) ether in dry DMF (30 mL) containing potassium carbonate (1.86 g,13.44 mmol) at 110 °C under N_2 for 23 h. The reaction mixture was added to water and extracted several times with methylene chloride. The organic layer was washed with water, dried (anhydrous $MgSO_4$), and evaporated to dryness under reduced pressure. The residue was purified through chromatography (SiO_2; CH_2Cl_2) to give **3** as a light-yellow viscous liquid (4.75 g, 96%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.3 Hz, 4H), 7.71 (d, *J* = 2.5 Hz, 2H), 7.28 (dd, *J* = 2.5, 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 9.3 Hz, 4H), 4.22-4.27 (m, 8H), 3.96–4.02 (m, 8H), 1.68 (s, 6H).

2,2-Bis{4-{2-{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}ethoxy}-3-nitrophenyl}propane 4. Using the same procedure as that described for the synthesis of **3**, except that toluene-4-sulfonic acid 2-{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}ethyl ester was used instead of 1-[2-(2-bromoethoxy)ethoxy]-4-nitrobenzene, compound **4** was synthesized and isolated as light-yellow viscous liquid (96%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.3 Hz, 4H), 7.70 (d, *J* = 2.5 Hz, 2H), 7.28 (dd, *J* = 2.5, 9.1 Hz, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 6.98 (d, J = 9.3 Hz, 4H), 4.20–4.25 (m, 8H), 3.90 (t, *J* = 4.7 Hz, 8H), 3.72–3.79 (m, 8H), 1.68 (s, 6H).

Compound 1. A solution of 2,2-bis[4{2-[2-(4-nitrophenoxy)ethoxy]ethoxy}-3-nitrophenyl]propane (**3**, 2.7 g, 3.6 mmol) in dry THF (200 mL) was added dropwise over 19 h to a suspension of $LiAlH_4$ (1.39 g, 35 mmol) in THF (300 mL) under a nitrogen atmosphere. The reaction mixture was heated under reflux during the addition of the tetranitro compound and then the mixture was maintained at room temperature for 14 h. After the reaction mixture had been cooled to 0 °C, water was added carefully. The precipitate was filtered off and the solvent was removed through evaporation. The residual orange solid was dissolved in ethyl acetate, washed with water, and then the solvent was evaporated. The residue was purified through chromatography (SiO_2; CH_2Cl_2/EtOAc, 10:1) to give **1** as orange crystals (33 mg, 1.5%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 9.0 Hz, 4H), 7.38 (dd, *J* = 2.5, 8.4 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.73 (d, *J* = 2.5 Hz, 2H), 4.56 (ddd, *J* =

1.9, 6.6, 13.5 Hz, 2H), 4.37 (ddd, *J* = 1.9, 5.2, 13.5 Hz, 2H), 3.94–3.99 (m, 2H), 3.71–3.86 (m, 4H), 3.48–3.60 (m, 6H), 1.71 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 154.9, 148.9, 148.2, 143.7, 126.9, 124.4, 118.3, 118.3, 115.1, 72.4, 71.1, 69.1, 69.1, 44.0, 28.7; ESIMS *m/z* 609.3 ($M + H^+$), 631.3 ($M + Na^+$). Anal. Calcd for $C_{35}H_{36}N_4O_6$: C, 69.06; H, 5.96; N, 9.20. Found. C, 69.28; H, 6.13; N, 9.00.

Compound 2. Using the same procedure as that described for the synthesis of compound **1**, except that compound **4** was used instead of compound **3**, compound **2** was synthesized and isolated as orange crystals (3.6%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 2.5, 8.4 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 4H), 7.06 (d, *J* = 9.0 Hz, 4H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 2.5 Hz, 2H), 4.51 (ddd, *J* = 1.4, 6.8, 13.5 Hz, 2H), 4.25–4.40 (m, 6H), 3.84 (ddd, *J* = 1.7, 5.1, 11.7 Hz, 2H), 3.65–3.73 (m, 6H), 3.45–3.51 (m, 2H), 3.28–3.42 (m, 6H), 1.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 153.4, 147.0, 146.9, 144.1, 127.1, 124.3, 121.8, 116.7, 116.2, 72.3, 71.3, 70.8, 70.6, 69.4, 68.0, 43.4, 29.9; ESIMS *m/z* 697.3 ($M + H^+$), 719.3 ($M + Na^+$). Anal. Calcd for $C_{39}H_{44}N_4O_8$: C, 67.23; H, 6.36; N, 8.04. Found. C, 66.99; H, 6.37; N, 7.85.

2. NMR spectra

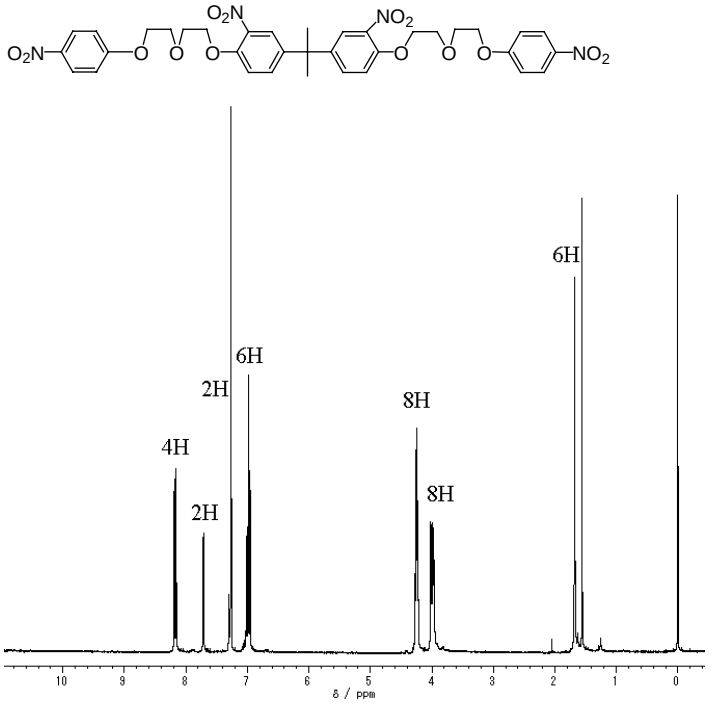


Figure S1. ^{1}H-NMR spectrum of **3**.

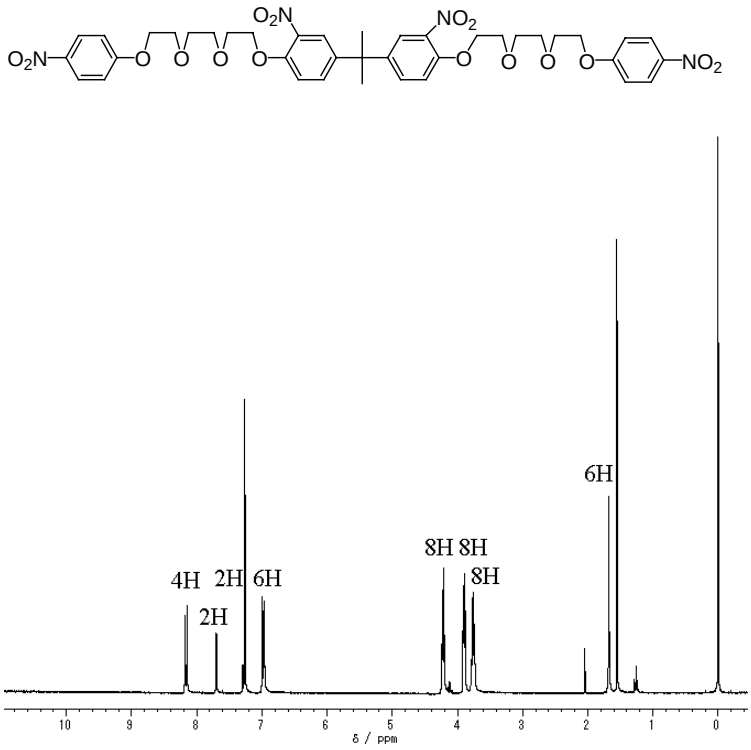


Figure S2. ^{1}H-NMR spectrum of **4**.

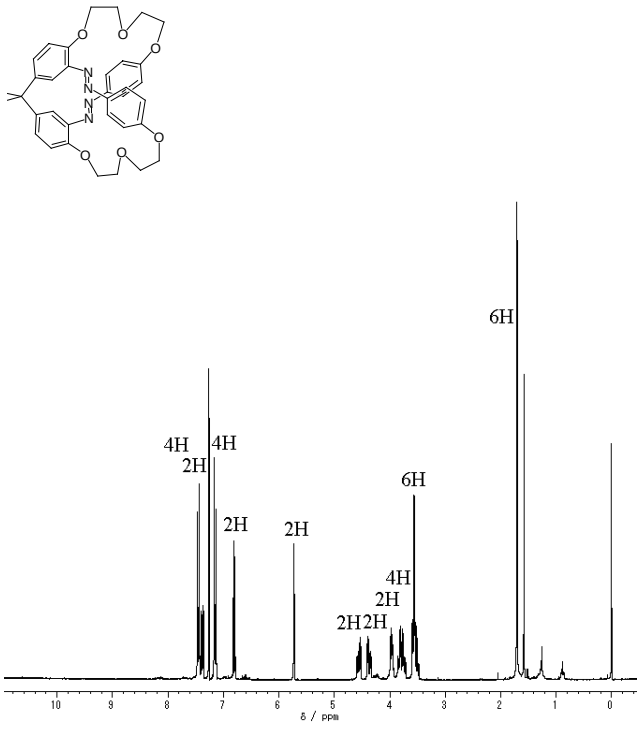


Figure S3. ^{1}H-NMR spectrum of **1**.

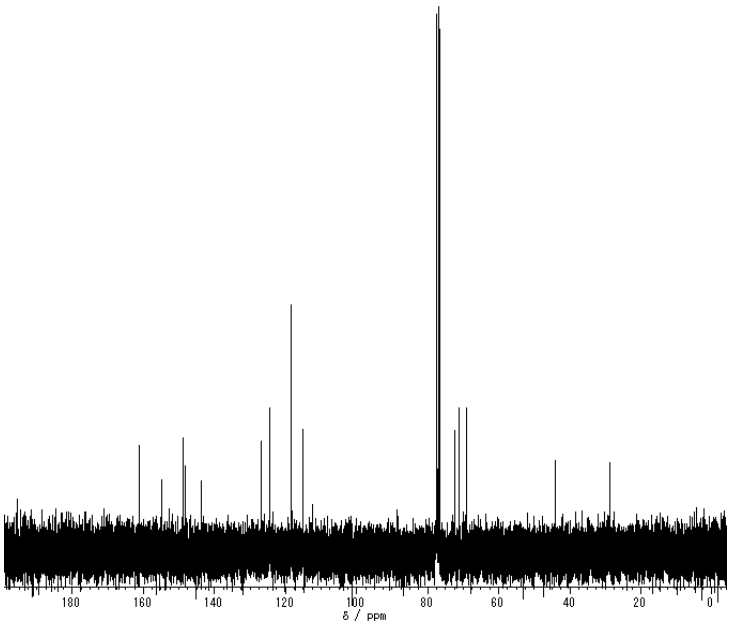


Figure S4. ^{13}C-NMR spectrum of **1**.

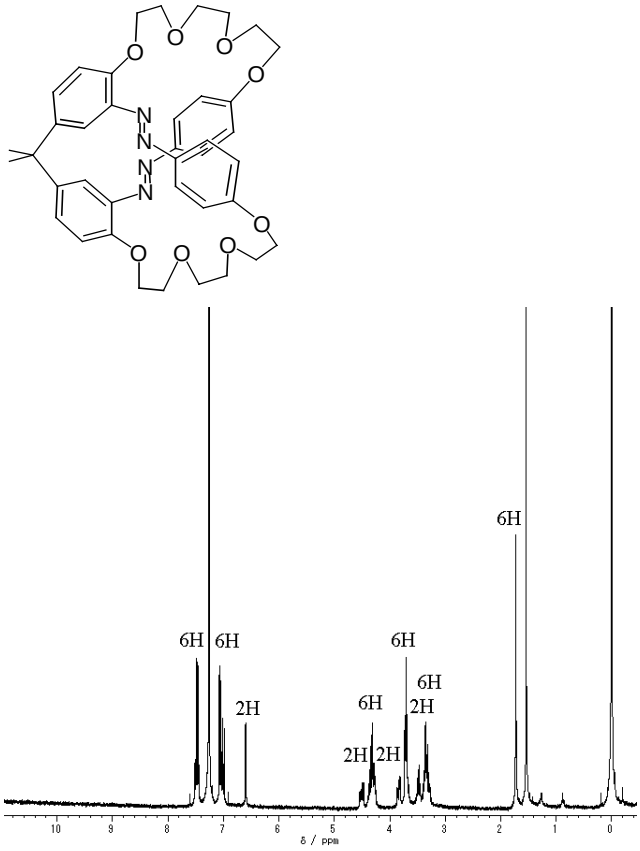


Figure S5. ^{1}H-NMR spectrum of **2**.

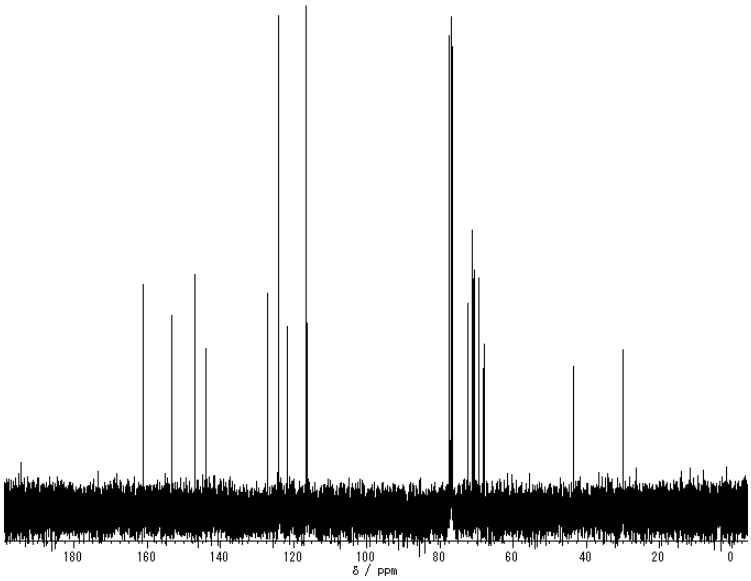


Figure S6. ^{13}C-NMR spectrum of **2**.

3. Crystal Structures

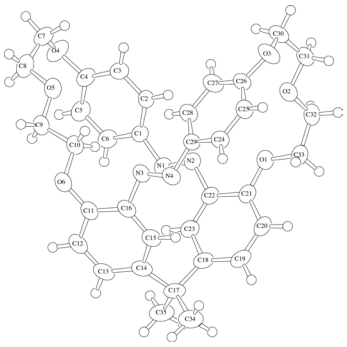


Figure S7. X-ray crystal Structure of *EE*-**1**.

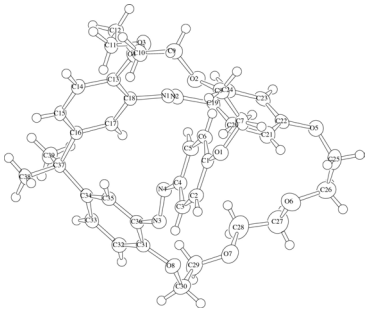


Figure S8. X-ray crystal Structure of *ZZ*-**1**.

4. HPLC

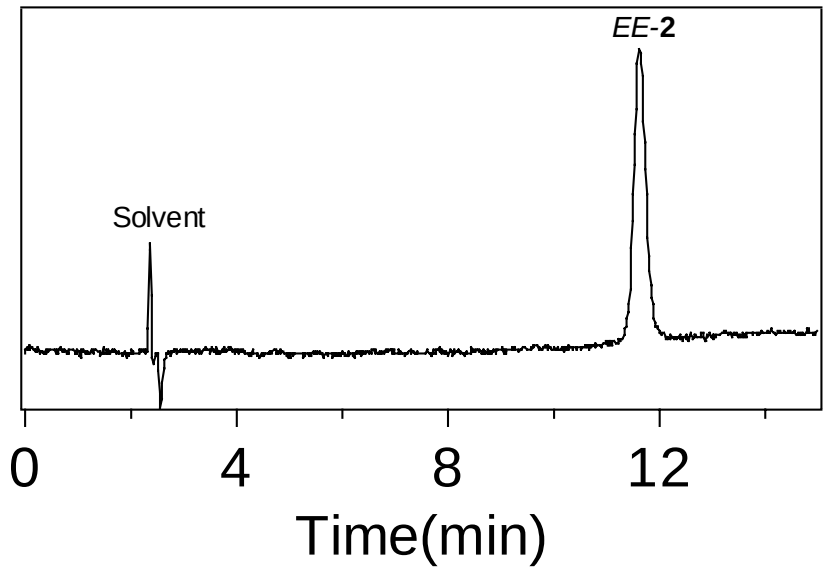


Figure S9. HPLC chart of *EE*-**2** before irradiation. ODS-80Ts CH_3CN/H_2O=80/20.

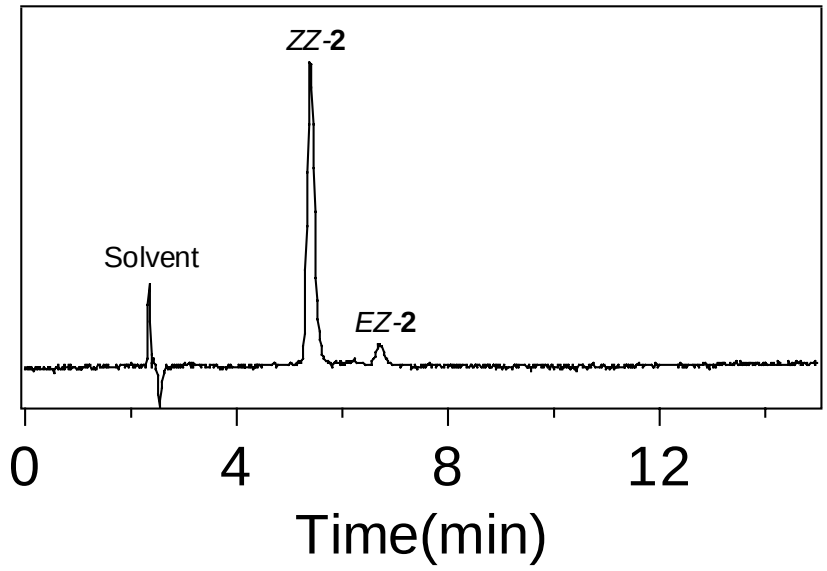


Figure S10. HPLC chart of the mixture of isomers after irradiation of racemic *EE*-**2** at 366 nm. ODS-80Ts CH_3CN/H_2O=80/20.

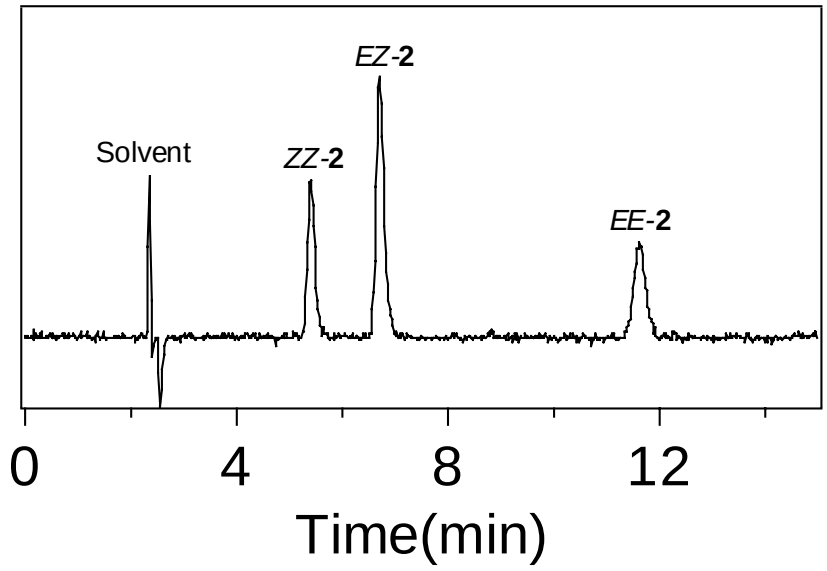


Figure S11. HPLC chart of the mixture of isomers after irradiation of *EE*-**2** at 436 nm. ODS-80Ts CH_3CN/H_2O=80/20.

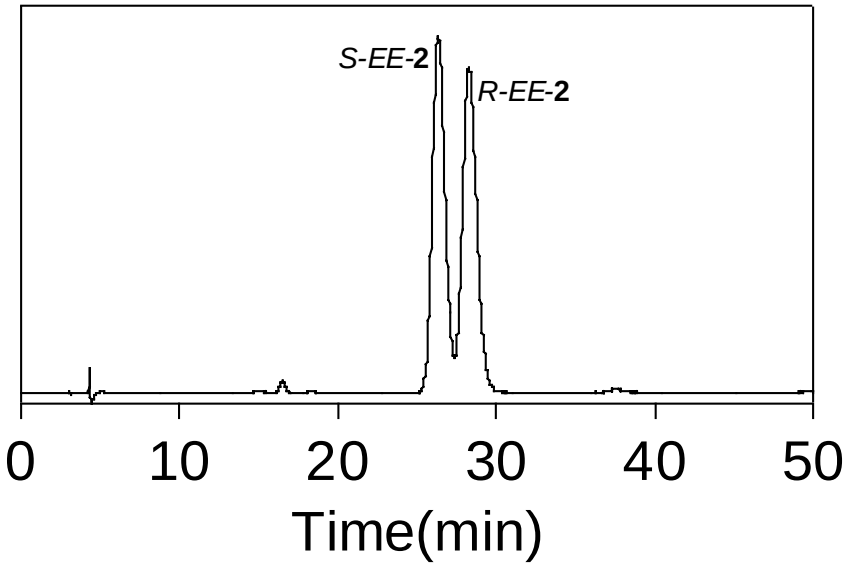


Figure S12. HPLC chart of racemic *EE*-**2** before irradiation. Chiral column AD-H Hex/IPA=80/20.

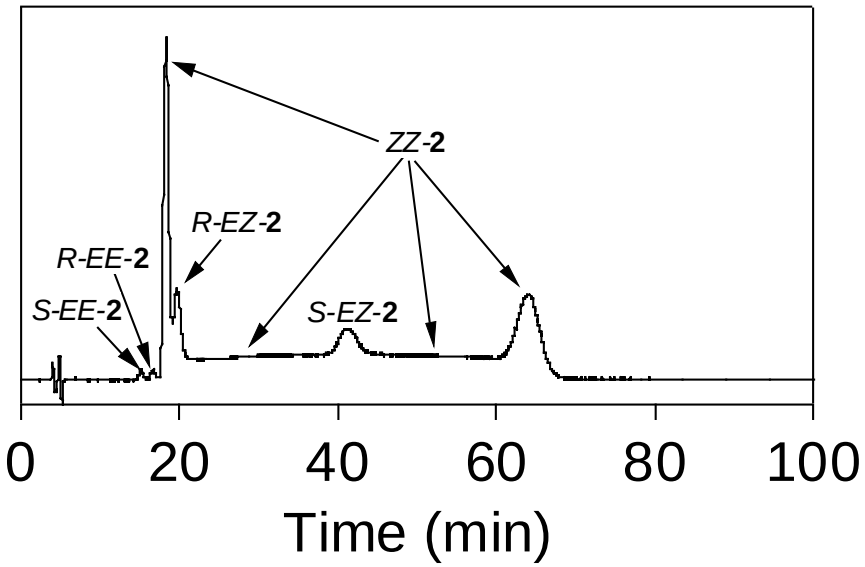


Figure S13. HPLC chart the mixture of isomers after irradiation of racemic *EE*-**2** at 366 nm. Chiral column AD-H Hex/IPA=40/60. "The resolution of the two peaks for the enantiomers of the *Z*,*Z* isomer did not approach the base line, but instead formed a plateau, obviously caused by molecules that had inverted their enanitiomeric configuration during resolution and then traveled at the speed of the antipode."

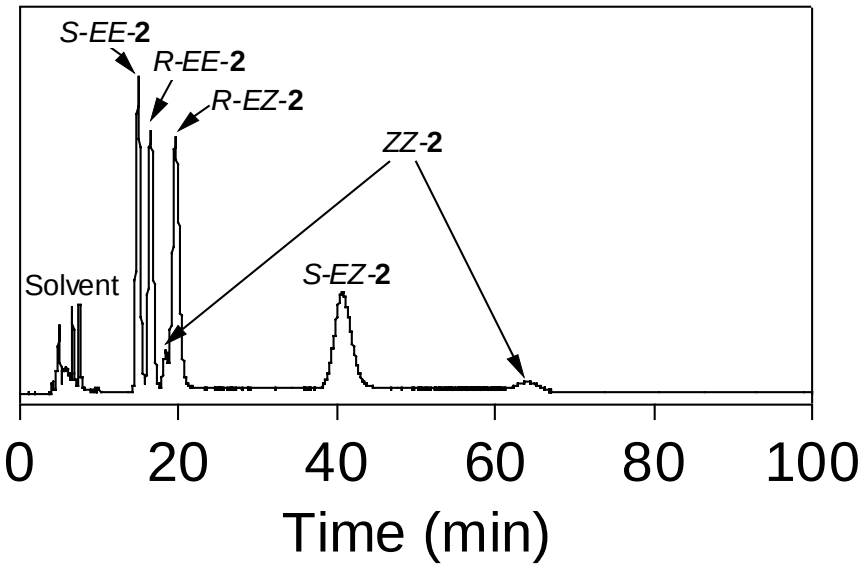


Figure S14. HPLC chart of the mixture of isomers after irradiation of racemic *EE*-**2** at 436 nm. Chiral column AD-H Hex/IPA=40/60.

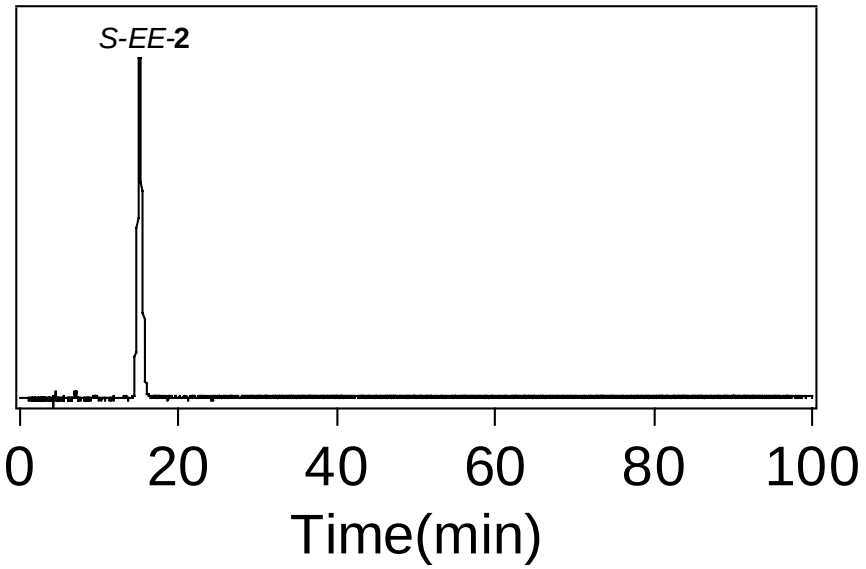


Figure S15. HPLC chart of enantiomeric pure *S*-*EE*-**2** before irradiation. Chiral column AD-H Hex/IPA=40/60.

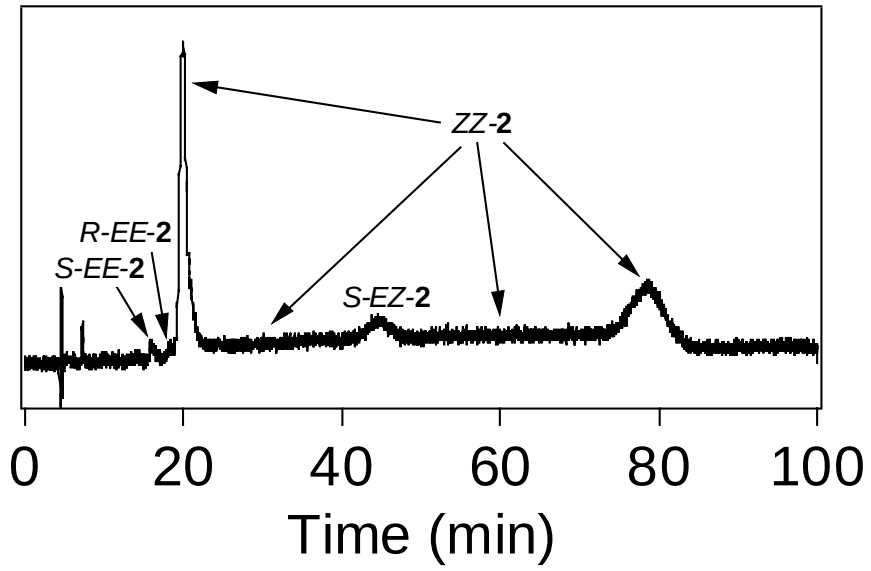


Figure S16. HPLC chart of the mixture of isomers after irradiation of the enantiomeric pure *S-EE*-**2** at 366nm for 3min. Chiral column AD-H Hex/IPA=40/60.

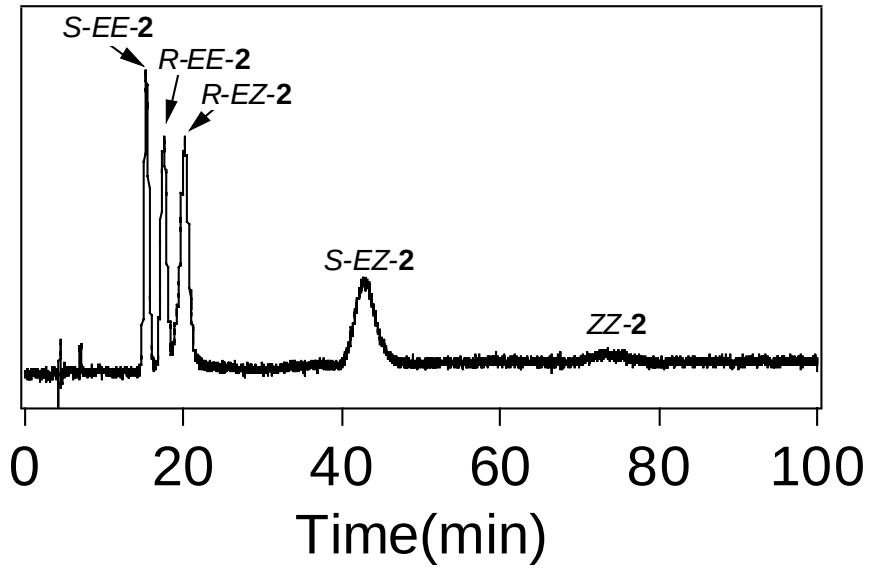


Figure S17. HPLC chart of the mixture of isomers after irradiation of the enantiomeric pure *S-EE*-**2** at 366nm for 3min followed by at 436 nm for 5 min. Chiral column AD-H Hex/IPA=40/60.

"We further confirmed the racemization of the *Z,Z* isomer through the observation that sequential irradiation of the enantiomeric pure (*S*)-*E,E*-**2** at 366 nm followed by at 436 nm led to the formation of the completely racemized mixture of *E,E* enantiomers."

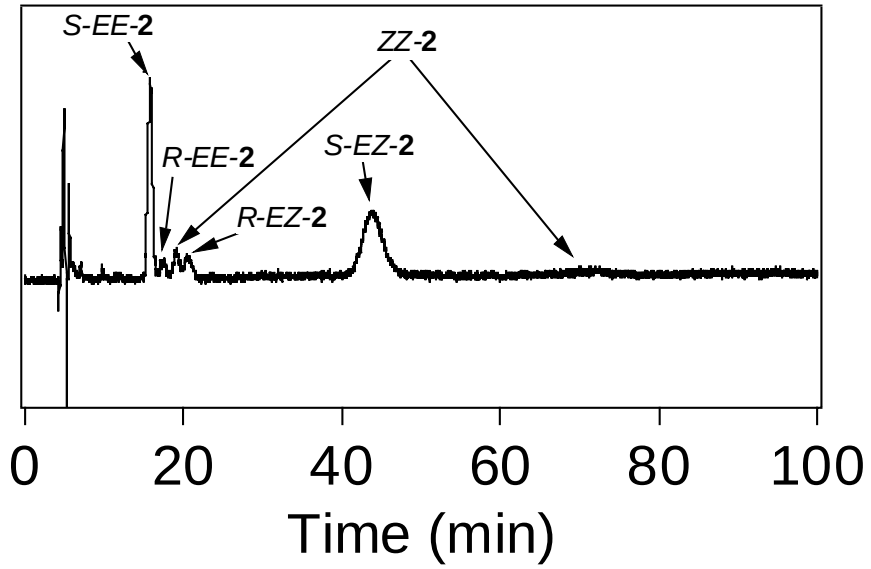


Figure S18. HPLC chart of the mixture of isomers after irradiation of the pure enantiomer *S-EE*-**2** at 436nm for 3min. Chiral column AD-H Hex/IPA=40/60. Peak areas: 35.2% (*S-EE*), 2.6% (*R-EE*), 48.1% (*S-EZ*), 4.5% (*R-EZ*), 5.1% (*S-ZZ*), 4.5% (*R-ZZ*).

"The chiral HPLC chromatogram of the photoreaction mixture of enantiomeric pure (*S*)-*E,E* at the early stage revealed that the peak areas for the *Z,Z* enantiomers were the same, while the peak area of one of the *E,Z* enantiomers was larger than that of the other; this result suggests that racemization of the *E,Z* isomer is much slower than that of the *Z,Z* isomer or thermally prohibited and occurred through sequential two-step photochemical reaction via *Z,Z* isomer."

5. CD spectra

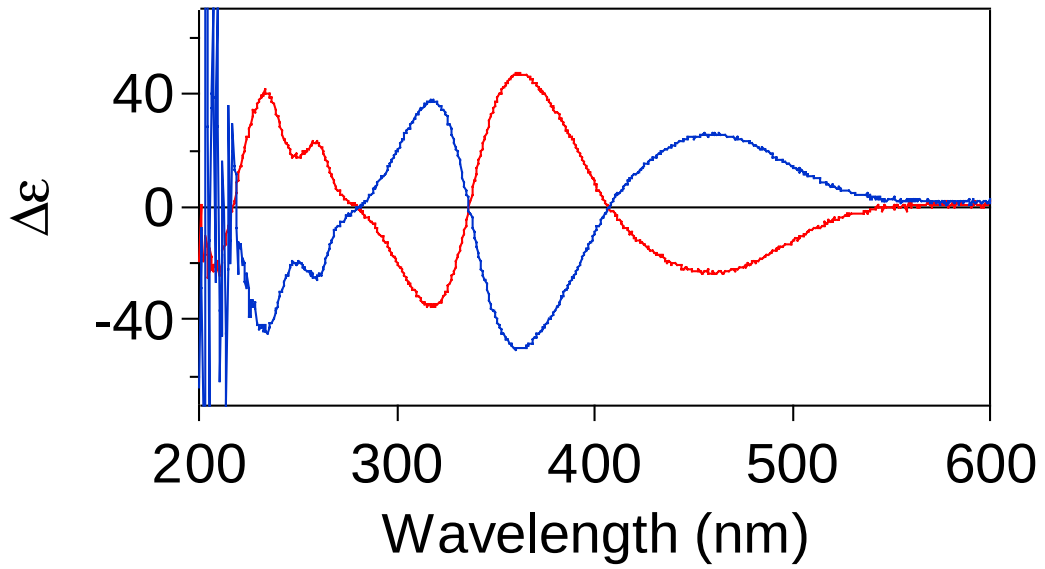


Figure S19. CD spectra of pure enantiomers of *EE*-**2**. The red and blue lines are the spectrum for the first ((*S*)-*EE*-**2**) and second ((*R*)-*EE*-**2**) eluents, respectively, under the HPLC with the chiral column.

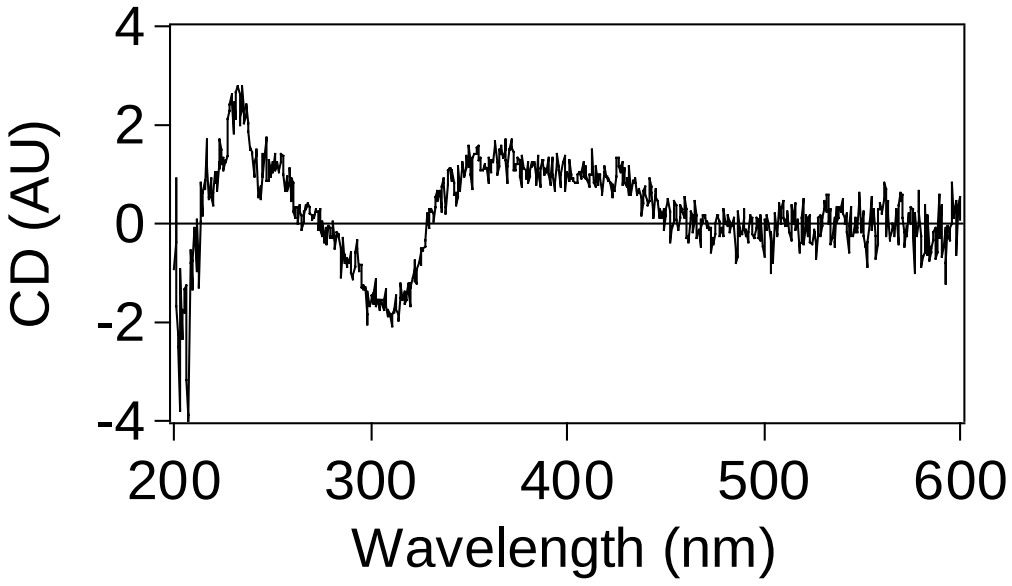
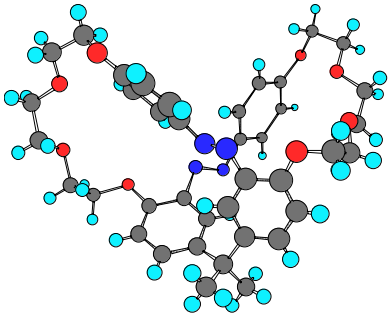
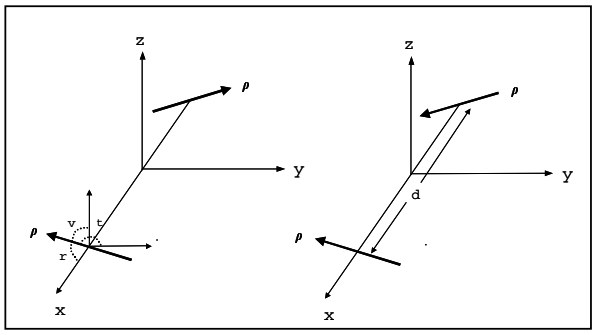


Figure S20. CD spectra of (*S*)-*EZ*-**2** isolated from an irradiated solution of the (*S*)-*E*,*E* -**2**. The concentration is not determined. The compound contains 10% of (*S*)-*E*,*E* -**2** as an impurity.

6. Determination of the Absolute Configuration of **2** Presenting a Specific CD Spectrum. We estimated the CD spectrum for (*S*)-*E*,*E*-**2** (its X-ray crystallographically derived solid state structure is presented below) by calculating the rotational strength *R* of the circular dichroism and the separation $\tilde{\nu}$ between the two transition state energies for the π–π* transition band at ca. 361 nm.





If two non-coplanar excitation moments ρ in a dissymmetric molecule are related by a two-fold rotation axis *z*, they couple to give resultant transitions having A and B symmetry in the group C_2 of the chromophoric system (Fig. S1).[2] The rotational strengths *R* of the two resultant transitions are equal in magnitude and opposed in sign, and they are given by

$$R_A = -R_B = \pi \nu d\rho^2 \cos v \cos t \qquad (1)$$

where ν is the wavenumber of the transition in the isolated chromophore.

The separation $\Delta\tilde{\nu}$ between the two transition energies is given by

$$\Delta\tilde{\nu} = \tilde{\nu}_A - \tilde{\nu}_B = 2\rho^2(\cos^2 v - \cos^2 t + 2\cos^2 r)/hcd^3 \qquad (2)$$

where h is Planck's constant and *c* is the velocity of light.

If it is assumed that the excitation moments of the two azobenzene chromophores are point dipoles located at the centers of the N=N double bonds, the distance *d* is 4.72 Å in **2** and the vertical, tangential, and radial cosines are +0.771, –0.628, and –0.194, respectively. Using these values, R_A, R_B, and $\Delta\tilde{\nu}$ can be calculated; their signs are determined to be negative, positive, and positive, respectively. These results indicate that (*S*)-*E*,*E*-**2** presents a positive Cotton effect for the π–π* transition band at ca. 361 nm.

7. References

1. Kitazawa, S.; Kimura, K.; Shono, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3253–3257.

Mason, S. F.; Vane, G. W. *J. Chem. Soc. (B)*, **1966**, 370–374.