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Ultrafast dynamics of an azobenzene-containing molecular shuttle based on a rotaxane

Matthew M. Sartin,[†,a] Masahisa Osawa,[‡,a] Satoshi Takeuchi,[ǂ,a,b] Tahei Tahara[*,a,b]

[a]Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
[b]Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

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[a] *Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[b] *Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
† Present address: Onto Innovation, Bend, Oregon, 97701, USA
‡ Present address: Department of Applied Chemistry, Nippon Institute of Technology, Gakuendai, 4-1, Saitama 345-8501, Japan
ǂ Present address: Graduate School of Science, University of Hyogo, 3-2-1 Koto, Kamigori, Ako 678-1297, Japan
* Corresponding author.
E-mail:address: tahei@riken.jp (T. Tahara)

1. Experimental section

Materials

All chemicals were purchased from Tokyo Chemical Industries or FUJIFILM Wako Pure Chemical Co and used as received.

Synthesis

The first step of Rotaxane/Reference synthesis was performed according to a procedure found elsewhere in the literature,[1] while the remaining steps were similar to those described in the original report of Rotaxane/Reference synthesis.[2]

4,4'-dihydroxyazobenzene (DHAB). A mixture of 4-nitrophenol (5 g, 36 mmol), KOH (25g, 450 mmol), and water was heated to 120 °C and left stirring for 1 hour. The temperature was then increased from 120 °C to 180 °C, with 10 minute waits every 10 °C. From 180 °C to 200 °C, the interval was reduced to 5 °C. At 200 °C, small bubbles evolved slowly from the mixture as it turned dark brown. This continued for 30 min. Upon conclusion of the reaction, the mixture was dissolved in water, which was then acidified to a pH between 1 and 3, using concentrated HCl. The product was extracted using 300 mL diethyl ether. These solutions were combined and concentrated. A brown powder was then precipitated from the solution, using hexane, and the precipitate was purified on a silica column using 1:1 ethyl acetate/hexane as the eluent, to give DHAB as a mixture of red and brown flakes (0.54 g, 2.52 mmol, 14%). ^{1}H NMR (300 MHz, DMSO-d_6, TMS): δ 10.12 (s, 2H, OH), 7.71 (d, J = 8.7 Hz, 4H, ArH), 6.91 (d, J = 8.7 Hz, 4H, ArH). HRMS(EI) *m/z* Calcd for $C_{12}H_{10}N_2O_2$ (M^+): 214.074; Found: 214.074. Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 66.99; H, 4.78; N, 12.94%.

4,4'-Bis(2-bromoethoxy)azobenzene (DBrEAB). 1 g (4.67 mmol) of DHAB was dissolved in 100 mL acetone, with 8.8 g CH_2Br_2 (50.1 mmol). 2.7 g K_2CO_3 was added to the mixture, which was then refluxed at 75 °C for 48 h. The solution was then evaporated to dryness to remove CH_2Br_2. The resulting solid was treated in as described in the previous report. The precipitate was extracted using 3x 50 mL $CHCl_3$. These extracts were combined, washed three times with 75 mL water. The chloroform solution was filtered and then evaporated. The orange precipitate was recrystallized twice from 2:1 $CHCl_3$/EtOH to yield orange crystals (0.72 g, 1.68 mmol, 28%) ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.88 (d, J = 8.8 Hz, 4H, ArH), 7.01 (d, J = 8.8, 4H, ArH), 4.37 (t, J = 6.5 Hz, 4H, methylene), 3.68 (t, J = 6.3 Hz, 4H, methylene). HRMS(EI) *m/z* Calcd for $C_{16}H_{16}Br_2N_2O_2$ (M+): 425.958, Found: 425.958. Anal. Calcd for $C_{16}H_{16}Br_2N_2O_2$: C, 44.89; H, 3.77; N, 6.54. Found: C, 44.56; H, 3.71; N, 6.40%.

4,4'-Bis(4-(4'-pyridyl)pyridinium-2-ethoxy)azobenzene dibromide (DBpyEAB). DBpyEAB was prepared following the previously published procedure. Briefly, 0.4 g (0.7 mmol) DBrEAB and

0.8 g (5.1 mmol) 4,4'-bipyridyl were dissolved in 6 mL DMF and stirred for 24 h. The product was washed with DMF then ether, to give DBpyEAB as a yellow powder (67%). ^{1}H NMR (300 MHz, DMSO-d_6, TMS): 9.31 (d, J = 6.6 Hz, 4H, PyH), 8.88 (d, J = 5.9 Hz, 4H, PyH), 8.68 (d, J = 7.0 Hz, 4H, PyH), 8.05 (d, J = 5.5 Hz, 4H, PyH), 7.83 (d, J = 8.8 Hz, 4H, ArH), 7.12 (d, J = 9.2 Hz, 4H, ArH), 5.13 (br., 4H, methylene), 4.67 (br., 4H, methylene). HRMS(ESI) *m/z* Calcd for $C_{36}H_{32}Br_2N_6O_2$ ([M-Br]+): 659.1765, Found: 659.1760. Anal. Calcd for $C_{36}H_{32}Br_2N_6O_2$+2.7H_2O: C, 55.17; H, 4.74; N, 10.73. Found: C, 54.88; H, 4.77; N, 10.58%. The inclusion of water in the elemental analysis is justified based on the hygroscopicity of this material.

4,4'-Bis(4-(4'-(2,4-dinitrophenyl)pyridinium)pyridinium-2-ethoxy)-azobenzene tetraperchlorate (Reference). 0.22 g (0.29 mmol) DBpyEAB was partly dissolved in 30 mL water by heating to 85 °C, while stirring for 1h. To this solution was added 20 mg tetra-*n*-butyl ammonium perchlorate (TBAP) and 1 g (5.37 mmol) 2,4-dinitrofluorobenzene. The reaction mixture was stirred at 85 °C for 72 h. The product was then filtered, and the solution part was washed 4x with 50 mL $CHCl_3$. 1.5 g $NaClO_4$ was then added to precipitate Reference as a brown sludge. Overnight vacuum-drying yielded a dark yellow powder (0.2 g, 0.15 mmol, 51%). ^{1}H NMR (300 MHz, D_2O): 9.71 (d, J = 7.3 Hz, 4H, PyH), 9.54 (d, J = 6.7 Hz, 4H, PyH), 9.18 (d, J = 2.9 Hz, 2H, ArH), 9.09 (d, J = 6.7 Hz, 4H, PyH), 9.03 (dd, J = 8.4 Hz, 2H, ArH), 8.97 (d, J = 7.2 Hz, 4H, PyH), 8.45, (d, J = 8.7, 2H, ArH), 7.85 (d, J = 8.7 Hz, 4H, ArH), 7.15 (d, J = 9.2 Hz, 4H, ArH), 5.23 (br., 4H, methylene), 4.72 (br., 4H, methylene). HRMS(ESI) *m/z* Calcd for $C_{48}H_{38}Cl_4N_{10}O_{26}$ ([M-ClO_4]+): 1211.1228, Found: 1211.1235. Calcd for ([M-2ClO_4]2+): 556.078, Found: 556.073. Anal. Calcd for $C_{48}H_{38}Cl_4N_{10}O_{26}$+3$H_2O$: C, 42.18; H, 3.25; N, 10.25. Found: C, 41.83; H, 3.23; N, 10.07%. The inclusion of water in the elemental analysis is justified based on the hygroscopicity of this material.

Rotaxane. 1.0 g DBpyEAB (1.3 mmol) was partly dissolved in 60 mL water by stirring for 1 h at 75 °C. The solution was returned to room temperature, and 6.3 g (6.5 mmol) cyclodextrin was added and the mixture was stirred for 1 h. 2.4 g (13 mmol) 2,4-dinitrofluorobenzene was then added to the solution, and this was stirred at 25 °C for 72 hours. The solution was then washed 3x with 60 mL $CHCl_3$ each. To this solution was added 5 g NH_4PF_6, which was then filtered. The gummy, red precipitate was dissolved in 60 mL acetonitrile and filtered. 5 g tetraethylammonium perchlorate was added to the solution to produce an orange precipitate that was filtered. The precipitate was then dissolved in *ca*. 10 mL water. 5 g $NaClO_4$ was then added to produce Rotaxane as a gummy, orange material (mass 230 mg, 0.10 mmol, 8% yield). ^{1}H NMR (300 MHz, D_2O): 9.38-9.44 (m, 6H, PyH), 9.37 (d, J = 6.6 Hz, 2H, PyH), 9.34 (d, J = 7 Hz, 2H, PyH), 8.96 (dd, J = 8.4 Hz, 2H, ArH), 8.88 (d, J = 7.7 Hz, 2H, ArH), 8.85 (d, J = 7.7 Hz, 2H, ArH), 8.76 (d, J = 5.8 Hz, 4H, PyH), 8.30 (d, J = 8.4 Hz, 4H, ArH and AzoArH (paper reports distinct doublets for each species)), 7.65 (d, J = 8.8 Hz, 2H, azoArH), 7.33 (d, J = 8.4 Hz, 2H, azoArH), 7.23 (d, J = 9.1 Hz, 2H, azoArH), 5.27 (br., 4H, methylene), 4.95 (d, J = 2.9 Hz, 6H, CyD), 3.8-3.5 (m, 36H CyD).

Expected methylene resonances at 4.86 and 4.78 ppm and 18 CyD resonances were not observed, presumably due to overlapping bands. HRMS(ESI) *m/z* Calcd for $C_{84}H_{98}Cl_4N_{10}O_{56}$ ([M-2ClO_4]2+): 1042.246, Found: 1042.246. Calcd for ([M-3ClO_4]3+): 661.848, Found: 661.848. Anal. Calcd for $C_{84}H_{98}Cl_4N_{10}O_{56}$+1.8$H_2O$: C, 43.53; H, 4.43; N, 6.04. Found: C, 43.13; H, 4.52; N, 5.98%. The inclusion of water in the elemental analysis is justified based on the hygroscopicity of this material.

Methods

Steady-State absorption spectra

Steady-state absorption spectra of all samples were measured using a UV-Visible absorption spectrophotometer (U3310, Hitachi). The cis configurations of Rotaxane and Reference were prepared by irradiating the respective samples using 365 nm light from a UV hand lamp for 60 s.

Treatment of sample during time-resolved measurements

Rotaxane and Reference were dissolved in 1:1 water/acetonitrile for all experiments. The sample solution was flowed continuously for time-resolved measurements. Absorption spectra of the sample were periodically collected during measurements to assess the condition of the sample. The solution was changed when the sample isomerization exceeded 15%, as judged by the absorbance of the $\pi\pi^*$ absorption band (typically after about 10 hours).

Broadband femtosecond fluorescence upconversion measurements

For femtosecond time-resolved fluorescence measurements, sample solutions of 570 μM Reference and 470 μM Rotaxane were used. The time-resolved fluorescence signals were measured by the broadband fluorescence upconversion method, using a setup similar to one reported by Canizzo et al.[3] The light source was the output of a Ti:sapphire regenerative amplifier system (800 nm, 80 fs, 8 mJ, 1 kHz; Legend Elite Duo-F, Coherent). A portion of the amplifier output (4 mJ) was used to pump an optical parametric amplifier (Topas-C, Light Conversion), and the fourth harmonic of the signal output was used as the excitation pulse at 375 nm. The excitation pulse was attenuated to 250 nJ in energy, and focused onto a 0.5-mm pathlength, fused silica flow cell, through which the sample solution was flowed using a rotary pump. Fluorescence of the sample was collimated and refocused onto a 0.3-mm-thick BBO crystal using a pair of parabolic mirrors. A colored-glass filter was placed in the path of the fluorescence to remove scattered light from the excitation. Another fraction of the amplifier output was attenuated to 13 μJ and used as a gate pulse. The gate pulse was sent down a variable-length delay stage and then focused onto the BBO crystal, so that it spatially overlapped the fluorescence spot. The fluorescence was upconverted by Type II sum-frequency mixing with the gate pulse in the BBO crystal. The upconverted signal was passed through an iris to remove most of the fluorescence. Further filtering was achieved by dispersing the upconverted signal in a prism and spatially filtering with a blade,

as well as by a 340 nm short-pass filter, which was used to remove any residual fluorescence. Then, the filtered signal was focused onto the entrance slit of a spectrograph (HR-320, Jobin Yvon), where the signal was spectrally dispersed and imaged onto a liquid-nitrogen cooled CCD camera (PyLoN, Princeton Instruments). Continuous rotation of the BBO crystal during the accumulation time allowed phase-matching of each wavelength component of the fluorescence, and hence the simultaneous collection of the entire fluorescence spectrum. Fluorescence detection at the magic angle was achieved by rotating the polarization of the excitation pulse with respect to the gate polarization. Kinetic traces of the S_1 fluorescence were obtained, with the BBO crystal tuned to phase match 660 nm fluorescence with the 800 nm gate pulse. Each data point is the average of two exposures of 5 minutes each. The time resolution of this experiment was estimated to be 180 fs by measuring upconverted Raman scattering of the solvent.

Femtosecond time-resolved absorption

For femtosecond time-resolved absorption measurements in the visible region, Rotaxane was prepared at 400 μM and Reference was prepared at 270 μM in 1:1 water/acetonitrile. The sample solutions were diluted by a factor of four for measurements in the near ultraviolet region to avoid strong absorption of the probe pulse. The time-resolved spectra observed in two spectral regions were scaled to overlap with one another and then combined to obtain the time-resolved absorption spectra presented.

The light source used for the femtosecond time-resolved absorption experiments was the output of a Ti:sapphire regenerative amplifier system (800 nm, 80 fs, 1.2 mJ, 1 kHz; Legend Elite, Coherent). Most of the fundamental output of the amplifier was used to drive an optical parametric amplifier (Topas-C, Light Conversion), and the fourth harmonic of the resulting signal component was used as the pump pulse at 345 nm. A tiny residual fraction of the amplifier output was focused onto a continuously translating CaF_2 plate to generate a white-light continuum pulse that spectrally covers the near-ultraviolet region and the entire visible region. The continuum pulse was split into two parts, and they were used as probe and reference pulses. Both the pump and probe pulses were focused and spatially overlapped together in a 1-mm-thick sample cell. The energy of the pump pulse was reduced to 170 nJ at the sample position, and the pump polarization was set at the magic angle with respect to the probe polarization. The reference pulse, as well as the probe pulse passing through the sample cell, were fiber-coupled into a spectrograph (500is/sm, Chromex), where they were spectrally dispersed and imaged onto different vertical positions of a CCD camera (PIXIS-400F, Princeton Instruments). The probe and reference spectra of each group of five laser shots were read out at a repetition rate of 100 Hz. The chirp characteristic of the white light probe pulse was examined by optical Kerr effect measurements for the solvent, and it was used to determine the time origin at each probe wavelength. The instrumental time resolution was estimated to be 110 fs from the fwhm of the stimulated Raman gain signal of the solvent.

2. Femtosecond time-resolved fluorescence spectra of Reference and Rotaxane

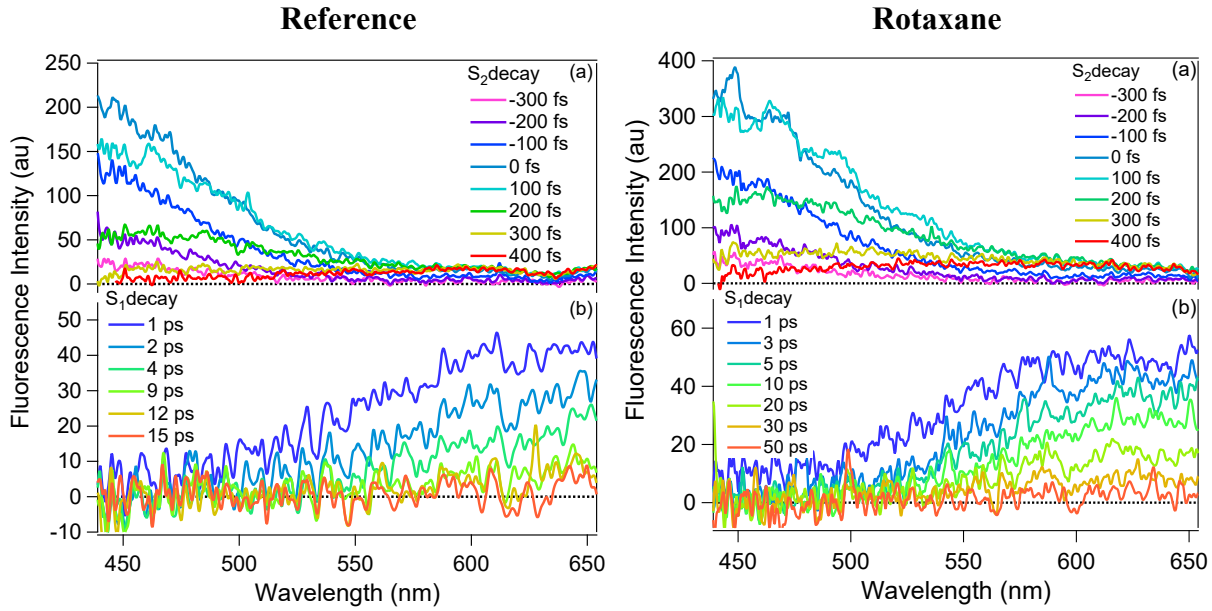

Figure S1. Representative time-resolved fluorescence spectra of (left) 570 µM Reference, (right) 470 µM Rotaxane in 1:1 water/acetonitrile, following excitation into the S_2 band at 375 nm. (a) Rise and decay of S_2 fluorescence (b) decay of S_1 fluorescence.

3. Comparison of long-lived features of time-resolved absorption spectra with the difference between the ground-state absorption spectra of cis and trans isomers

We compared the time-resolved absorption (TA) spectrum at 145 ps to the difference spectrum of the two isomers obtained by subtracting the ground-state absorption spectrum of trans Rotaxane from that of a solution of Rotaxane isomerized by irradiation at 365 nm for 1 min. An overlay of the TA spectrum at 145 ps with this difference spectrum is presented in Figure S2a. The difference spectrum shows a negative signal in the position of the ππ* absorption band, and a positive feature with a peak at 440 nm that indicates the formation of the cis isomer by irradiation. The bleach of the TA spectrum at 145 ps and that of the difference spectrum are similar, but the peak attributable to the cis isomer in the TA spectrum at 145 ps appears at 470 nm, rather than at the 440 nm observed in the difference spectrum. In addition, the TA spectrum at 145 ps shows an offset at wavelengths longer than 550 nm that is not present in the difference spectrum. Similar features are observed in the TA spectra of Reference (Figure S2b). These differences may indicate the involvement of processes that occur on time scales slower than the time window of the present measurements (~150 ps for Rotaxane and ~50 ps for Reference), which generate the fully-relaxed rotaxane with the azobenzene moiety in the cis configuration. However, we cannot exclude the possibility that these features represent a small amount of decomposition products that were generated during the prolonged exposure to the laser. Since the absorbance of these features is much smaller than the transient features being examined in this study, we do not discuss them further in this paper.

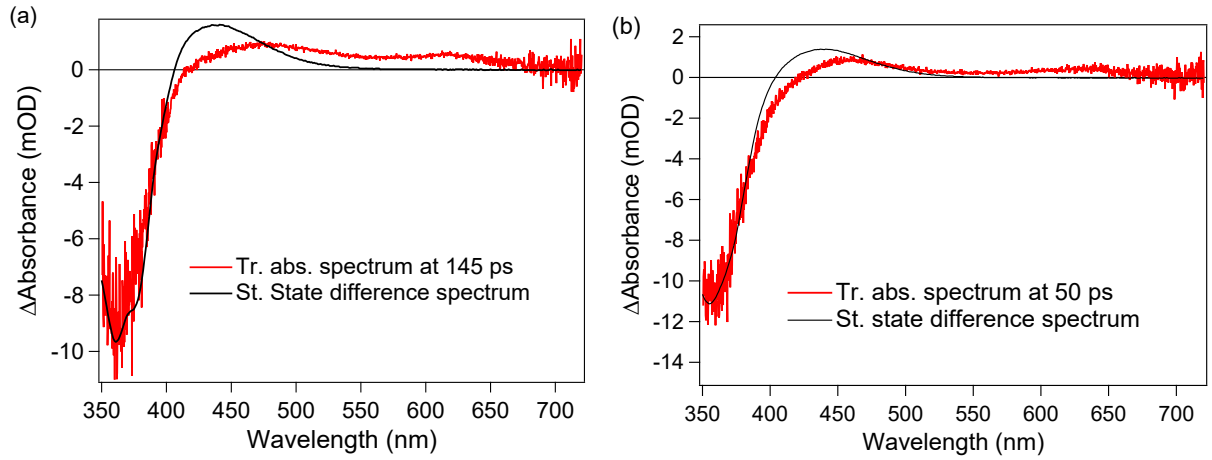

Figure S2. Femtosecond time-resolved absorption spectrum obtained at long time delay (red) and difference spectrum between the steady-state absorption spectra obtained before and after irradiation of the sample for 1 min (black). In both cases, the steady-state spectra have been scaled in order to overlap the bleach of the ππ* transition. (a) Rotaxane (b) Reference.

4. Femtosecond time-resolved absorption spectra of Reference and temporal traces at selected wavelengths

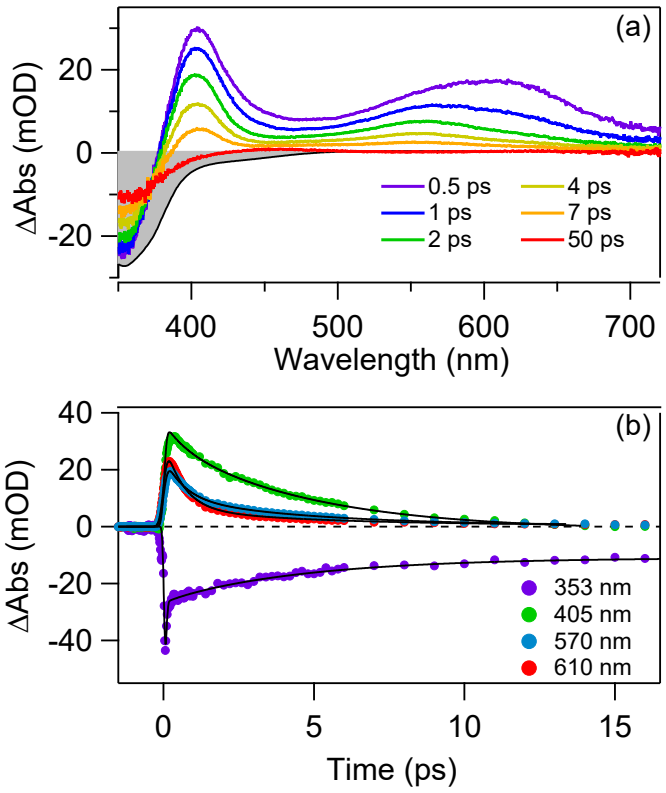

Figure S3. (a) Femtosecond time-resolved absorption spectra of Reference in 1:1 water/acetonitrile, following excitation at 345 nm. The spectral region at wavelengths shorter than 450 nm was obtained using 86 μM Reference solution, and that at longer wavelengths was obtained using 270 μM Reference solution and scaled to overlap the 86 μM data. The shaded area is the inverted absorption spectrum of Reference. (b) Temporal traces of the time-resolved absorption signals of Reference in 1:1 water/acetonitrile monitored at several wavelengths.

5. Discussion of vibrational cooling in Rotaxane and Reference

The time constant of 3.5 ps was observed in the ground-state bleaching recovery dynamics monitored at 359 nm (Fig. 3b in the main text). This time constant is much shorter than that for vibrational cooling of a molecule in purely organic solvents, which typically show cooling times of ~10 ps. On the other hand, in water, where the hydrogen-bonding capability leads to rapid dissipation of excess energy, the vibrational cooling time becomes as short as 1 ps.[4] Because we use 1:1 water/acetonitrile mixture as solvent, it is reasonable to observe a vibrational cooling time in between those measured in pure organic solvents and pure water. Consistent with this assignment, the decay of the transient absorption spectrum at 406 nm (Figure 3b in the main text), which corresponds to the red edge of the ππ* band of the ground-state absorption, decays with time constants of 3.5 ps and 18 ps, like the bleach at 359 nm. The 18-ps component is ascribed to the decay from S_1B, and the 3.5-ps component matches the component in the bleach recovery that we attributed to vibrational cooling. Increased absorbance in the red edge region of the ground-state absorption is consistent with the electronic transition from the vibrationally hot ground state, and this increased absorbance decays as the vibrational cooling proceeds.[4] Based on this consideration, the 3.5-ps component of the bleach recovery at 359 nm as well as that in the decay of 406 nm band are safely attributed to the vibrational cooling process occurring in the ground state. For Reference, the decays in the ground-state bleach region and the red edge of the ππ* absorption can be fitted using only the 4.7 ps decay that corresponds to the decay from S_1B observed in the fluorescence upconversion measurements. Since Rotaxane and Reference have very similar structures around the azobenzene moiety, it is unlikely that the relaxation from the S_2 state follows a different path in Reference. Therefore, we think that we are unable to separately observe dynamics assignable to vibrational cooling of the ground state of Reference because the time constant for vibrational cooling is so similar to that for the relaxation from S_1B (4.7 ps) that the exponential fitting is not able to separate them.

As described in the main text, after excitation of the trans-azobenzene moiety to the ππ* S_2 state, a fraction of the population follows a non-reactive path back to the vibrationally hot ground state, and the other fraction follows a reactive path to isomerization on the nπ* S_1 potential surface. For the non-reactive path, the initially excited S_2 molecules relax to the vibrationally hot region of the S_1 surface, where they are then converted to a vibrationally hot ground state that relaxes with a time constant of 3.5 ps.[5-8] Using femtosecond time-resolved absorption, we found that the population of S_1A does not return directly to the initial ground state. Therefore, S_1A is on the reactive pathway, along with S_1B. S_1B is likely the quasi-stationary state on the S_1 potential surface that precedes a branching pathway between isomerization and deactivation to the initial ground state, and S_1A acts as a precursor quasi-stationary state for S_1B. A complete schematic of the process indicated by the present study is given in Fig. S4.

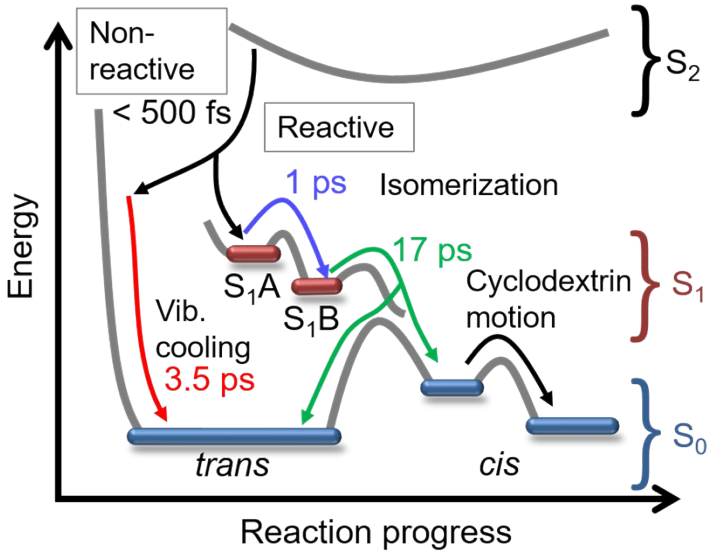

Figure S4. Potential surfaces depicting the pathways for relaxation and isomerization of Rotaxane following excitation into the S_2 band. The cyclodextrin motion is depicted as an additional process that follows isomerization.

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