Supplementary Material (ESI) for Chemical Communications

Photoisomerization of Azobenzene Gel by Pulsed Laser Irradiation

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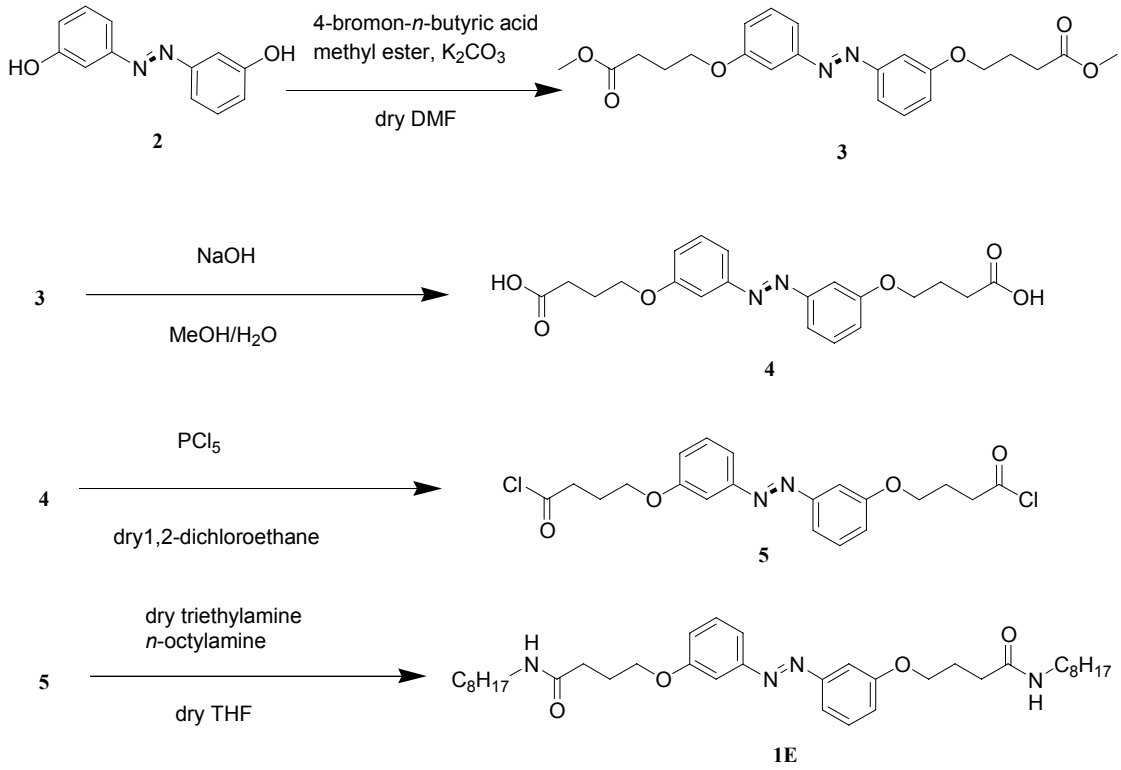
Table of contents

Experimental general remarks. All solvents used were reagent grade and were distilled before use. Reagents were purchased from Aldrich, TCI, Wako, or Nacalai Tesque and used without purification. ^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz) spectrometer at ambient temperature. Chemical shifts are denoted in δ units (ppm) relative to the solvent signals $CHCl_3$ (^{1}H NMR: δ= 7.24 ppm, ^{13}C: δ= 77.0 ppm). IR spectra were measured on a HORIBA FT-710. Mass spectra (FAB-MS) were obtained from a JEOL JMS-GC mate II using 3-nitrobenzyl alcohol and glycerol as the matrix. Melting points were measured on BUCHI B-545, and absorption spectra were measured on an HITACHI U-3500 spectrophotometer. Visible light was irradiated by a 500 W Xe-arc lamp (USHIO SX-Ul501XQ). Scanning electron microscopes (JEOL JSM-5200 and JSM-5410) and an optical microscope (Leica DMLP) were used to study the surface microstructure of the gels. The IR spectra were monitored on an HOROBA FT-710 IR spectrophotometer. All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto, 63-210 mesh). For the absorption spectral measurements, optical cells with 0.5-mm, and 1-cm light pass lengths were used for the absorption spectral measurements of the gels and the solutions, respectively.

Synthesis of 3,3'(-bis[{(*N*-octylamino)carbonyl}propoxy]azobenzene 1E

3,3'-Bis[{(*N*-octylamino)carbonyl}propoxy]azobenzene **1E** was prepared from 3,3'-dinitroazobenzene[S1] based on the route in Scheme S1.



Scheme S1. Synthetic route from **2** to azobenzene derivative **1E**

Compound 3 To a mixture of 0.46 g (2.1 mmol) of 3, 3'-dihydroxyazobenzene (**2**) and 15 ml of DMF anhydrous, 0.89 g (6.4 mmol) of anhydrous K_2CO_3 and 0.93 g (5.1 mmol) of 4-bromo-*n*-butyric acid methyl ester were added and stirred for 5 h at 75 ^oC. After the reaction was over, water was added at room temperature. Then the reaction mixture was extracted with chloroform (50 ml × 2). The combined organic layer was washed with 5% NaOH aq. (50 ml × 4) and water (50 ml × 3), successively. The solution was dried over Na_2CO_3 anhydrous, and the solvent was removed in

reduced pressure to obtain 0.69 g (1.7 mmol) of **3** in 81% yields (mp. 96.8-97.6 ^{o}C).

3: ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.16 (tt, 4H, *J*=7.3, 6.0 Hz , -CH_2), 2.56 (t, 4H, *J*=7.3 Hz , -CH_2), 3.70(s, 6H, -OCH_3), 4.10(t, 4H, *J*=6.0 Hz, -CH_2), 7.02(ddd, 2H, *J*=8.1, 1.7, 1.0 Hz, -Ar), 7.41(dd, 2H, *J*=8.1, 7.8 Hz, -Ar), 7.42(dd, 2H, *J*=2.6, 1.7 Hz, -Ar), 7.55(ddd, 2H, *J*=7.8, 2.6, 1.0 Hz, -Ar) ; MS (TOF-MS): 415.5 $[M+1H]^+$ (calcd: 414.5).

Compound 4. To a methanol solution containing 0.38 g (0.92 mmol) of **3**, 8 ml of 2 N NaOH aq. was added and stirred for 1 h at 40 ^{o}C. After the removal of the solvent, 20 ml of chloroform and 20 ml of water were added to the mixture. Then the solution was acidified to pH 3 by the addition of 3 M HCl. The mixture was extracted with chloroform (20 ml × 3) and the combined organic layer was washed with water (20 ml × 3). The solution was dried over Na_2SO_4 anhydrous and the solvent was removed in reduced pressure to obtain 0.29 g (0.75 mmol) of **4** as a yellow crystals in 82% yields (mp. 174.0-174.8 ^{o}C).

4: ^{1}H NMR (400 MHz, DMSO-d_6): δ=1.98(tt, 4H, *J*=7.2, 6.6 Hz , -CH_2), 2.42(t, 4H, *J*=7.2 Hz , -CH_2), 4.09(t, 4H, *J*=6.6 Hz, -CH_2), 7.15(ddd, 2H, *J*=6.5, 1.9, 1.6 Hz, -Ar), 7.40(dd, 2H, *J*=2.0, 1.6 Hz, -Ar), 7.50(dd, 2H, *J*=7.8, 6.5 Hz, -Ar), 7.55(ddd, 2H, *J*=7.8, 2.0, 1.9 Hz, -Ar) , 12.16(s, 2H, -COOH) . ; MS:386 (M^+)

Compound 1. To a 1, 2-dichloroethane anhydrous solution (20 ml) containing 1.00 g (2.6 mmol) of diacid **4**, 1.36 g (6.5 mmol) of phosphorous pentachloride was added at 0 ^{o}C in a dry argon gas atmosphere. The mixture was refluxed for 2 h to obtain a red solution. Acid chloride **5** was used without isolation after it was cooled to 0 ^{o}C. To the solution, 20 ml of a 1, 2-dichloroethane anhydrous solution containing 0.78 g (7.8 mmol) of triethylamine and 0.67 g (5.2 mmol) of *n*-octylamine were added at 0

^{o}C and stirred for 24 h at room temperature. To the reaction mixture, 100 ml of chloroform was added and the combined organic layer was successively washed with 0.5 N HCl (100 ml×3) and water (100 ml×3). The solution was dried over Na_2CO_3 anhydrous, and the solvent was removed in reduced pressure to obtain 2.9 g (4.7 mmol) of **1** as a crude product. The recrystallization of the crude product of **1E** was performed from the mixture of chloroform and methanol (50/50 v/v), followed by recrystalizations from 2-propanol to obtain 0.85 g of pure **1E** as yellow crystals (mp. 145.0 -145.8 ^{o}C).

^{1}H-NMR(400MHz, $CDCl_3$) δ=0.86 (t, 6H, J = 6.9 Hz), 1.16-1.33 (m, 20H), 1.46 (quin, 4H, J = 6.9 Hz), 2.17 (quin, 4H, J = 6.9 Hz), 2.41 (t, 4H J = 6.9 Hz), 3.24 (q, 4H, J = 6.9 Hz), 4.10 (t, 4H, J = 6.9 Hz), 5.50 (t, 2H, J = 6.9 Hz, NH), 7.02 (ddd, 2H, J= 8.0, 2.4, 0.8 Hz), 7.418 (t, 2H, J = 8.0 Hz), 7.424 (dd, 2H, J= 2.4, 1.6 Hz), 7.55 (ddd, 2H, J =8.0, 1.6, 0.8 Hz); FAB-MS(NBA):m/z: 609 [M+1]. Anal. Calcd for $C_{36}H_{56}N_4O_4$: C, 71.00; H, 9.29; N, 9.20. Found: C, 71.02; H, 9.21; N, 9.16.

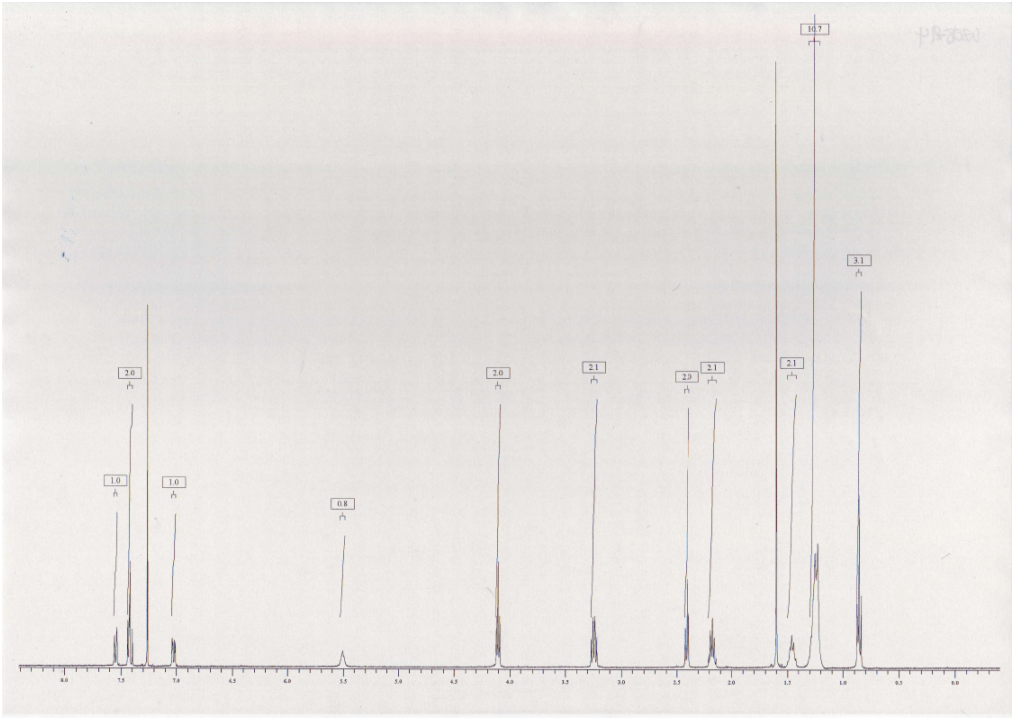


Fig. S1. ^{1}H NMR of **1E** in $CDCl_3$.

Critical gelation concentration

A typical gelation experiment was performed by carefully weighing 1.0 mg of compound in a 2 ml vial (diameter 10 mm) with a screw cap and the addition of 0.100 ml of the appropriate solvent. The vial was sealed tightly and heated until the compound dissolved, at which time the vial was cooled to room temperature. Gelation is considered to have occurred when a homogeneous solid material is obtained that does not exhibit gravitational flow (inverted test tube method). The minimal gelation concentration can be obtained by dilution of this sample with subsequent volumes of 0.100 ml of solvent until a homogeneous material is no longer obtained.

Gelation properties of azobenzene 1E

The gelation behavior for azo compound **1E** was examined in a number of solvents ranging from apolar to polar. The solvents used are listed in Table S1 based on the commonly used $E_T(30)$ scale for solvent polarity[S2] with the critical gelation concentrations (cgcs).[S3] Compound **1E** was only gelated by decaline with a minimum gelation concentration of 2.4 mg/ml. The absorption spectrum of the decaline gel is shown in Fig. 2 (main Text). The absorption maximum of the band appeared at 303 nm, which is 15 nm blue-shifted compared with that in the chloroform solution. The shift was attributed to the formation of H-aggregate.

Table S1. Gelation properties of azobenzene **1E** in organic solvents

Solvent	**1E**
Hexane	I
Cyclohexane	VS
Benzene	P
Decaline (mixture of *cis-,trans-*)	G(2.4)
trans-Decaline	G(2.4)
Toluene	P
1,4-Dioxane	S
n-Butyl acetate	P
Di-*n*-butyl ether	VS
Cyclohexanone	S
Chloroform	S
1,2-Dichloroethane	P
o-Dichlorobenzene	VS
Chlorobenzene	P
THF	S
2-Propanol	P
Acetonitrile	P
H_2O	I

G: gelation, P: precipitation, I: insoluble, S: soluble, VS: viscous solution,
( ) =minimum gelation concentration in mg/ml

Light irradiation apparatus

A handy UV lamp (TOPCON Fi5L (λ= 365 nm) and an UV-LED (UV-400, KEYENCE) with an UV-50H attachment (λ= 365 nm) were used as continuous UV light sources. The light intensities (and photon densities) in the system were measured by USHIO UIT-250 attached with a UVD-S365 and determined to be 6.0×10^{-3} J/mm^2 (1.82×10^{13} photon/s•mm^2) and 10.32 J/mm^2 (3.13×10^{16} photon/s•mm^2), respectively. A nanosecond laser photolysis system (DCR-3, Quanta-Ray) with a repetitive Q-switched Nd^{3+}: YAG laser was used for the laser flash photolysis. The third harmonic (355 nm) with 6 ns fwhm and 2.75×10^{-3} J/mm^2 were used for the excitation of the *E*-azobenzene derivative in the gel state. The excitation pulse was focused onto a spot with a diameter of ca. 1.8 mm (photon density; 8.18×10^{23} photon/s•mm^2). The repeating cycles were less than 1 Hz. The intensity of the nanosecond pulse laser power was monitored on OPHIR F150A. Visible light irradiation was carried out using a USHIO Xe arc lamp SX-Ul501XQ by a cut-off filter TOSHIBA Y-41.

Transient absorption spectral measurement of the decalin (mixture of *cis*-, *trans*-) gel of 1E.

A laser photolysis system combined with the above Q-switched Nd^{3+}:YAG laser, pulsed Xe amp, and a gated multichannel photodiode array (Hamamatsu, PMA-50 system) with a polychromator (Acton, M4197) was used to measure the nanosecond-millisecond transient absorption spectra. The setup of the system is shown in Fig. S2.

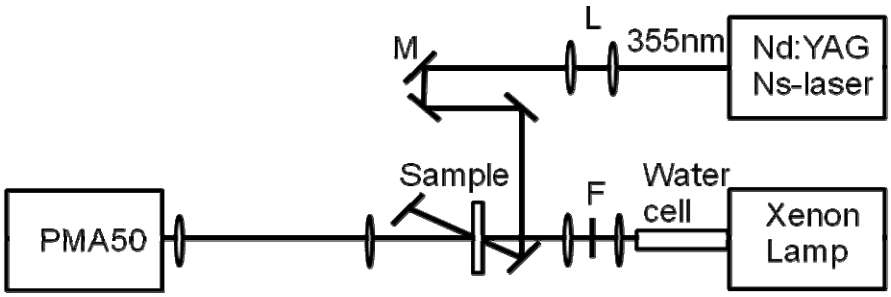


Fig. S2 Schematic of laser-probe transient absorption apparatus: 355-nm pump laser (Nd:YAG), Photo-Multichannel-Analyzer-50 (PMA50), mirror (M), filter (F), and lens (L). Beam diameter was changed by two focus lenses (100 mm and 50 mm, respectively). Water cell was placed in front of Xenon lamp to prohibit the thermal effect.

Absorption spectra of decaline gel of 1E after UV light

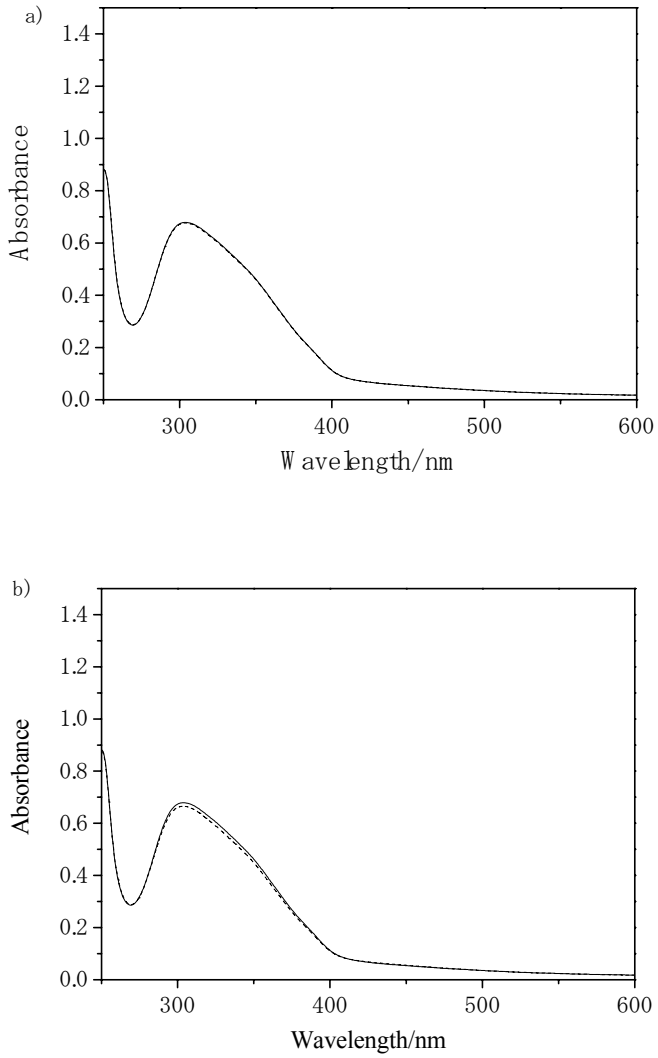


Fig. S3 (a) Absorption spectra of (mixture of *cis*-, *trans*-) decaline gel of **1E** (2.5 mg/ml) solid line: before UV light irradiation, broken line; after UV light (TOPCN, Fi5L, 1×10^{-5} W/mm^2, 1.82×10^{13} photon/s•mm^2, λ = 365 nm) irradiation; (b) Absorption spectra of (mixture of *cis*-, *trans*-) decalin gel of **1E** (2.5 mg/ml) solid line: before UV light irradiation, broken line; after UV light (KEYENCE, UV-LED UV-400 attached with UV-50H, 1.72×10^{-2} W/mm^2, 3.13×10^{16} photon/s•mm^2, λ= 365 nm) irradiation.

Preparation of xerogel of 1E for SEM measurements

Xerogel of **1E** was prepared by storing the gel in a vacuum (desiccator) overnight at room temperature. The sample without nano pulsed laser irradiation was observed after gold vapor deposition. Another SEM sample after laser pulse irradiation was prepared as follows. The decaline gel of **1E** was mounted on the SEM stage loaded carbon tape and the nano second laser pulse (Quanta-Ray, DCR-3, λ= 355 nm) was irradiated followed by the evaporation of the solvent by storing the stage in the desiccators in the vacuum overnight at room temperature.

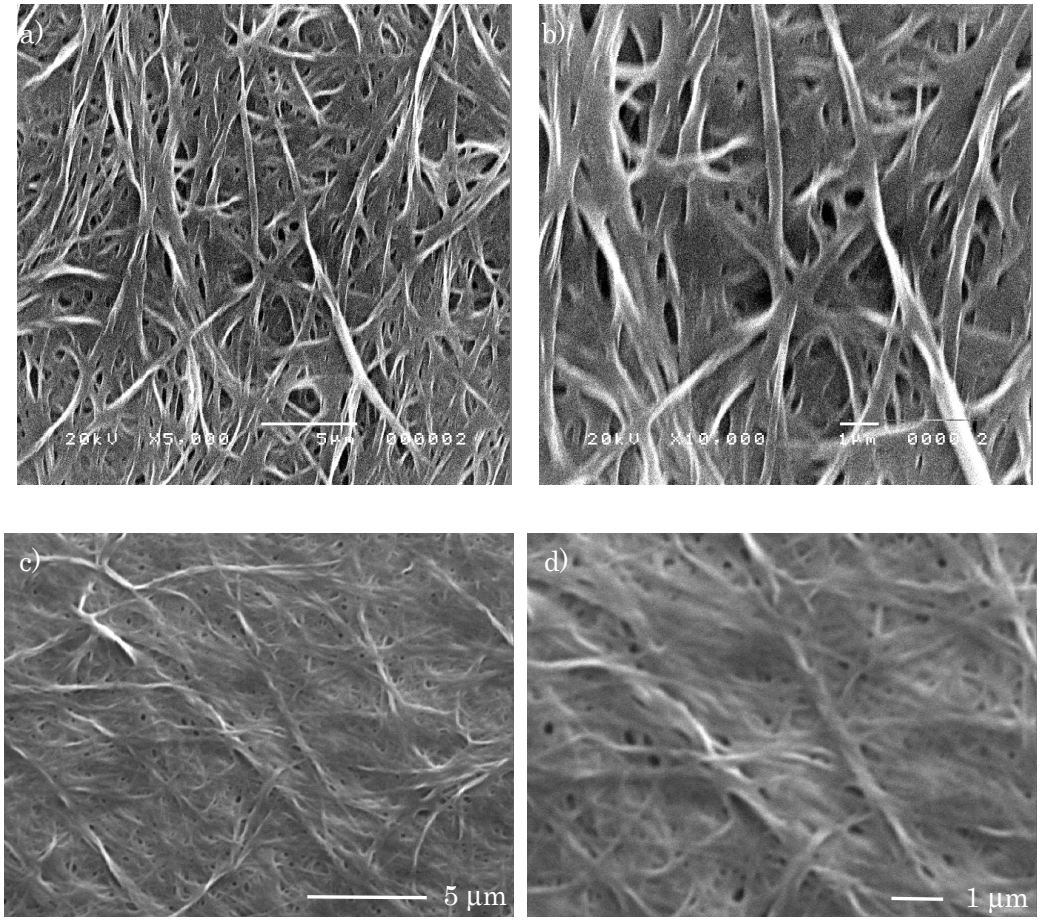


Fig. S4. SEM images of the surfaces of xerogels prepared from decaline (mixture of cis-, trans-) gel of **1E**: (a) before pulse laser irradiation (× 5000), (b) (× 10000); (c) after pulse laser irradiation λ = 355 nm, 4.68×10^{-3} J/mm^2•pulse, 5.47×10^{23} photon/s•mm^2, half time width 6 ns) (×5000); (d) ×10000

IR measurement of 1E in solution and in gel state.

IR spectra of the chloroform solution of **1E** were measured on HORIBA FT-710 spectrometer. The solution was poured into the IR cell made of mixed crystals of thallium iodide and thallium bromide. Xerogel was obtained by evaporation of the solvent from decaline gel of **1E** storing for 2 days under vacuum (2 hpa) at room temperature, and then the sample for IR measurement of xerogel **1E** was prepared by KBr method. NH band of **1E** in chloroform was observed at 3448 cm^{-1}, while that in xerogel was observed at 3303 cm^{-1}, respectively. The shift is attributable to the strong intermolecular hydrogen bonding in gel state.

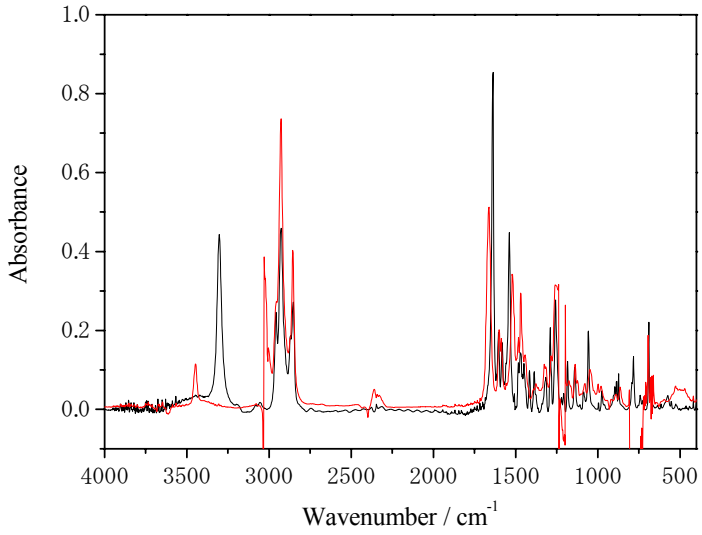


Fig. S5 NH bands of **1E** in IR spectra of Xerogel (black line) and in chloroform solution (1.12×10^{-2} M: red line).

Thermal recovery of 1E in solution and in gel state.

The thermal recovery of the **1Z** to **1E** in a decaline (mixture of *cis*-, *trans*-) solution or a 10% 2-propanol /decaline mixture was examined in a sealed quartz optical cell with 1 cm light pass. After 365 nm light irradiation, the cell was dipped into a water bath at elevated temperature and the recovery of the band attributable to the *trans*-isomer was monitored. The recovery was also monitored by ^{1}H NMR spectroscopy. The thermal recovery of **1E** in the gel state was monitored as follows. Decalin (mixture of *cis*-, *trans*-decalin) gel of **1E** was irradiated to the whole gel by UV pulse laser (355 nm pulse from Quanta-Ray, DCR-3) by changing the irradiation place. No thermal **1Z** to **1E** isomerization in gel state was observed at room temperature. (The thermal recovery in the solution was observed in solution as described in the main text.) The cell was then heated in a water bath, and the absorption spectral changes were monitored on a UV-vis spectrophotometer (Hitachi U-3500). The light intensity of the laser was monitored by Quanta-Ray DCR-3.

A control experiment also tried to recover the **1Z** to **1E** in decaline with lower concentration, but clear spectral changes were not observed due to the spontaneous gel formation of **1E**. Therefore a mixture (decaline: 2-propanol = 9: 1) was used as the solvent. After pulsed laser irradiation, the absorbance at 303 nm of **1E** in the gel state was reduced to 51% of the initial value, but only 17% of the absorbance was recovered after 30 h heating at the temperature shown in Fig. S7b. On the contrary, the absorbance at 317 nm in the solution was reduced to 37% of the initial value by UV light irradiation and gradually recovered with a half life of 192 min.

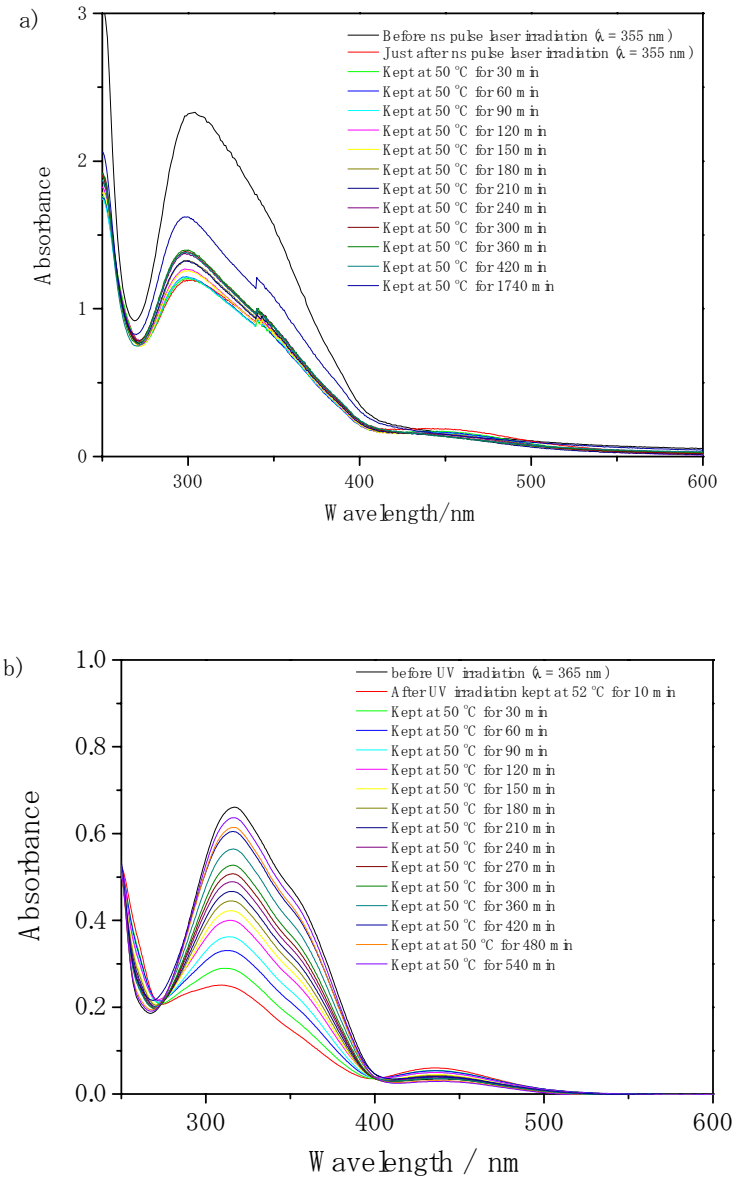


Fig. S6. Absorption spectral changes of thermal *Z* to *E* isomerization of **1E** in decaline gel (a), and in solution (decaline: 2-propanol = 9 : 1 v/v) (b) at 50 °C.

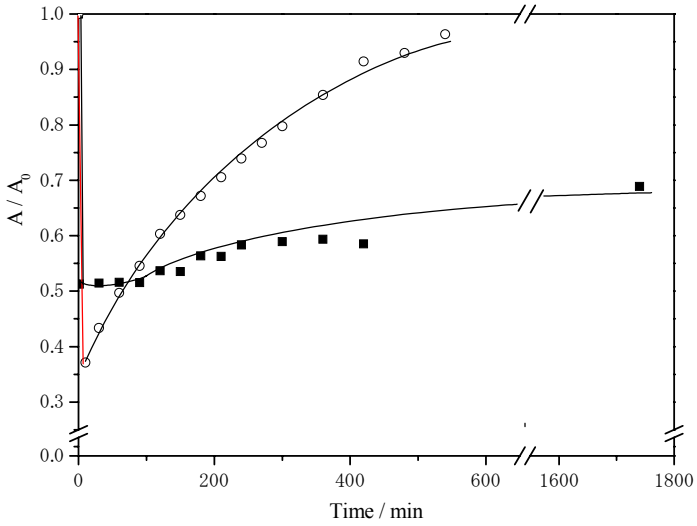


Fig. S7 Thermal recovery of absorbance of **1E** in a solution (decaline: 2-propanol = 9: 1; open circles) and decaline gel state (2.5 mg/ml; filled squares) at 50°C.

References

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