

Electronic supplementary information (ESI)

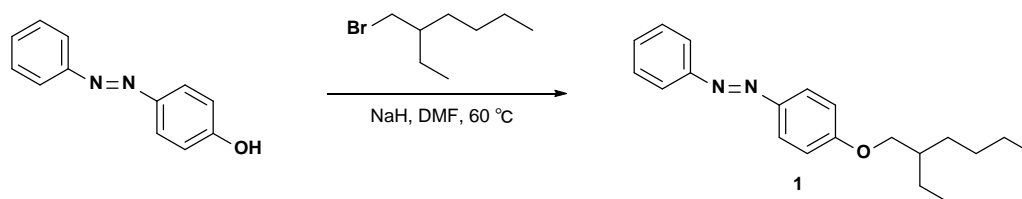
A Liquid Azobenzene as Solvent-Free Solar Thermal Fuel

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General. Reagents were obtained from commercial source and used without further purification. Photoirradiation was conducted by an Asahi Spectra MAX-150 xenon lamp (5 mW/cm² at 365 nm) for tracking of spectral changes and cyclability test. An Ushio USH-500SC super high pressure UV lamp (40 mW/cm²) with an Ushio BPF-365-1 365 nm bandpass filter was employed for the color change observation, determination of isomerization enthalpy, and measurement of shear viscosity. ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker AV300M spectrometer. High-resolution mass spectra (HRMS) were obtained using a Bruker micrOTOF-QIII. UV-Vis absorption spectra were measured on a Hamamatsu PMA-12 photonic multichannel analyzer equipped with a JASCO LUS-373 deuterium-halogen light source. DSC was performed on a Mettler Toledo DSC1 for measurements of isomerization enthalpy and a Seiko instruments inc. DSC6100 for measurement of thermal behavior. Shear viscosity was measured using an Anton Paar MCR 302 rheometer.



Scheme S1. Synthesis of compound **1**.

Synthesis of 1. To a solution of 4-(phenylazo)phenol (15.00 g, 76 mmol) in dehydrated DMF (300 mL) was added NaH (50% dispersion in mineral oil) (4.36 g, 114 mmol) portionwise under nitrogen atmosphere at 0 °C. After stirring at room temperature for 30 minutes, 1-bromo-2-ethylhexane (20 mL, 91 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to 60 °C and stirred for 5 h. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate. The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was washed with water and brine, and then dried over anhydrous Na₂SO₄. After filtration and evaporation, the resulting residue was purified by column chromatography (hexane to hexane/ethyl acetate = 20:1 to hexane/ethyl acetate = 10:1) to give compound **1** (22.21 g, 99%). ¹H-NMR (300 MHz, CDCl₃) δ 7.80-8.00 (m, 4H), 7.35-7.55 (m, 3H), 6.95-7.05 (m, 2H), 3.85-4.00 (m, 2H), 1.65-1.85 (m, 1H), 1.20-1.60 (m, 8H), 0.80-1.00 (m, 6H); ¹³C-NMR (75 MHz, CDCl₃) δ 162.04, 152.95, 146.98, 130.20, 128.98, 124.73, 122.55, 114.80, 71.03, 39.46, 30.59, 29.12, 23.95, 23.02, 14.01, 11.11; HRMS (ESI) Calcd for C₂₀H₂₇N₂O [M+H]⁺: 311.2188. Found: 311.2120; Elem. Anal. Calcd for C₂₀H₂₆N₂O: C, 77.38; H, 8.44; N, 9.02. Found: C, 77.27; H, 8.38; N, 9.19.

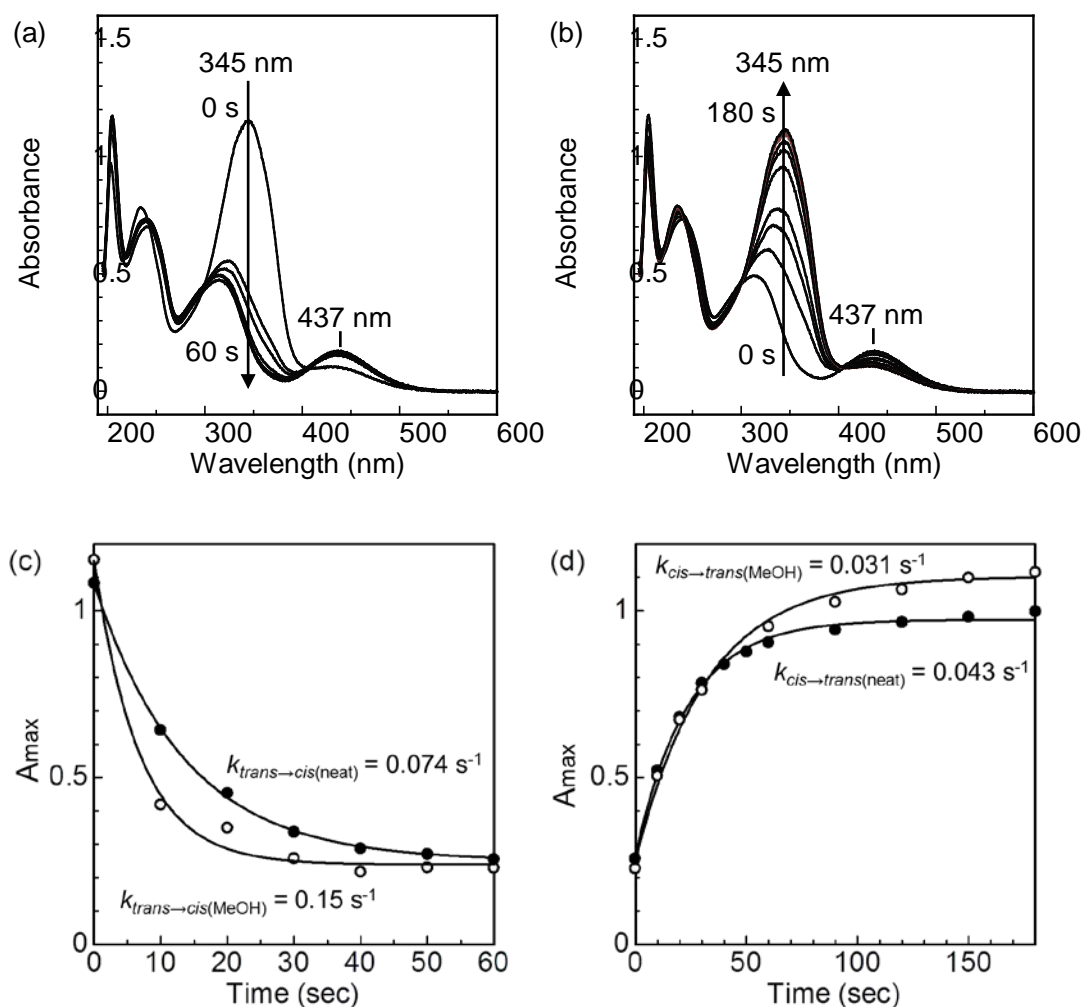


Fig. S1. UV-Vis absorption spectral changes of **1** upon irradiation (a) at 365 nm and (b) at 480 nm in methanol solutions (7.5×10^{-5} M). (c, d) Dependence of the peak absorbance on the irradiation time. (c) Irradiation at 365 nm, (d) Irradiation at 480 nm. (○) **1** in methanol (7.5×10^{-5} M), (●) in neat condition. Spectra of liquid **1** were obtained for thin liquid membranes prepared in between a quartz cell and a quartz plate. Rate constants of each reaction were determined by theoretical fitting according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-kt)$ where A_t , A_∞ and A_0 represent the absorbance at a irradiation time t , and at the photostationary state, and before irradiation, respectively.

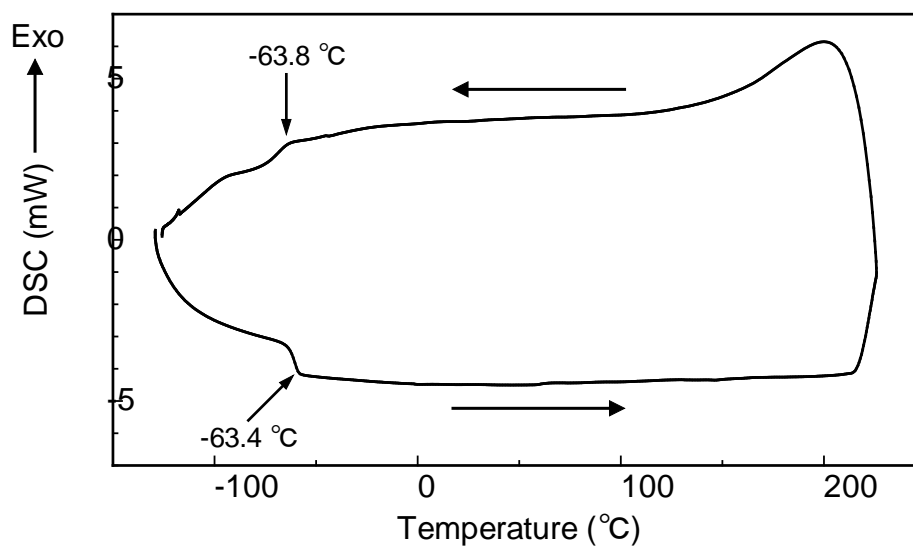


Fig. S2. DSC curve on a heating and cooling cycle for the second scan at 5 K·min⁻¹. Glass transition temperature was observable at around -63 °C.

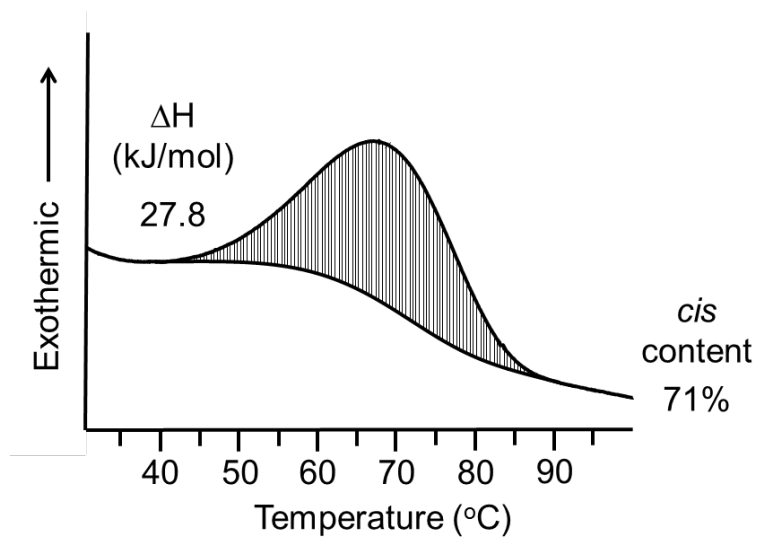


Fig. S3. DSC thermogram of *cis*-1. At a slow heating rate, 0.5 K·min⁻¹, lower peak temperature with a broad exothermic peak was obtained. The molar content of *cis* isomer was 71%.