Supporting Information for:

Photochromic organogel based on [2.2]paracyclophane-bridged imidazole dimer with tetrapodal urea moieties

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1. Synthesis

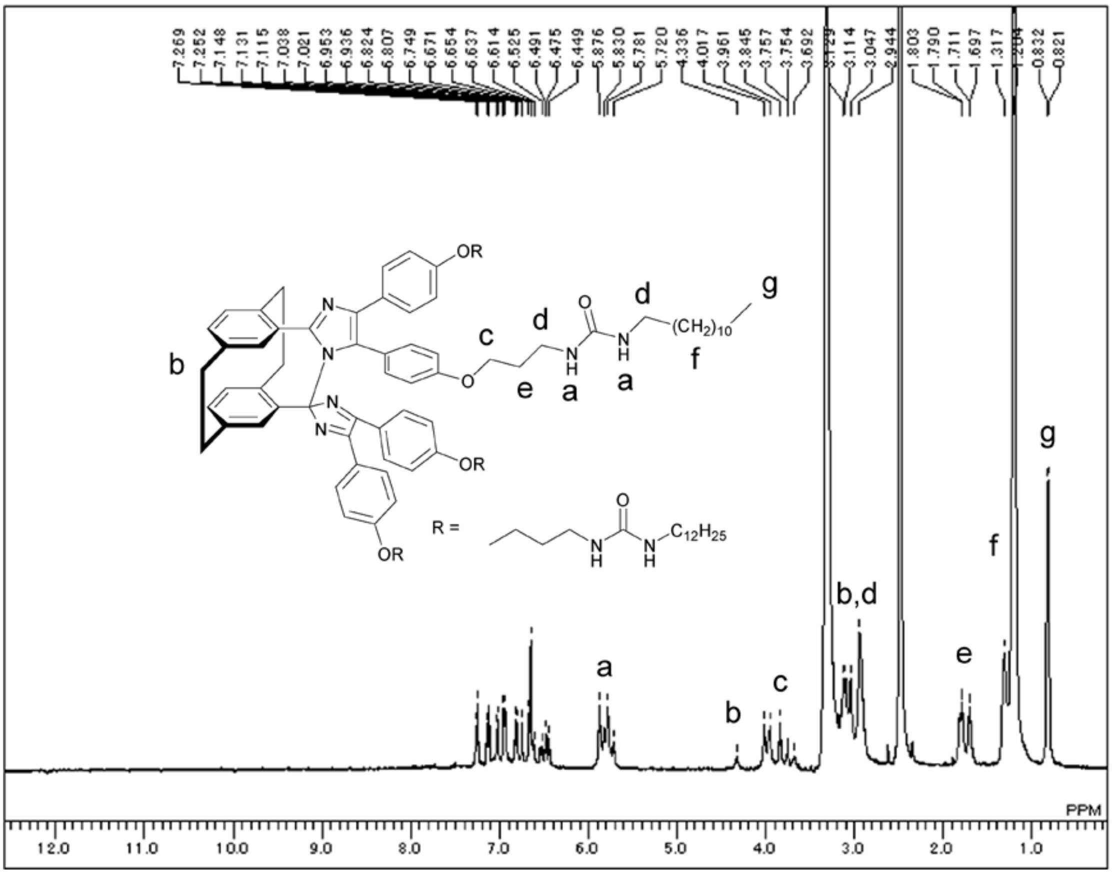
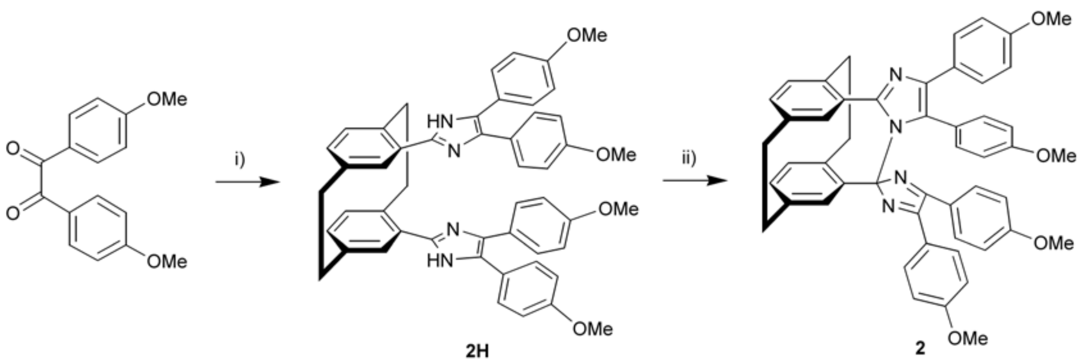


Figure S1. ^{1}H-NMR spectrum of **1** in DMSO-d_6.

Scheme S1



Reagents and condition: (i) [2.2]Paracyclophane-4,13-dicarbaldehyde, $AcONH_4$, AcOH, reflux, 12 h; (ii) $K_3[Fe(CN)_6]$, KOH aq., benzene, r.t., 5 h.

Synthesis of 2H.

4,4’-dimethoxybenzil (0.300 g, 1.11 mmol), [2.2]paracyclophane-4,13-dicarbaldehyde (150 mg, 0.567 mmol) and ammonium acetate (0.875 g, 11.4 mmol) were refluxed in acetic acid (40 mL) for 12 h. The reaction mixture was cooled to room temperature and was neutralized with aqueous NH_3. The resulting precipitate was extracted with dichloromethane, and the organic layer was dried over Na_2SO_4, and the solvent was removed in *vacuo*. The crude product was purified with silica gel column chromatography using chloroform as eluent to obtain pale yellow powder (202 mg; yield: 46.6%). ^{1}H-NMR (500 MHz, DMSO-d_6) δ : 11.4 (s, 2H), 7.21 (d, J = 8.6 Hz, 4H), 7.10 (d, J = 1.8 Hz 2H), 7.00 (d, J = 8.6 Hz, 4H), 6.97 (t, J = 8.6 Hz, 4H), 6.71–6.59 (m, 12H), 4.53 (dd, J = 11.9, 4.0 Hz, 2H), 3.73 (s, 6H), 3.68 (s, 6H), 3.14–3.01 (m, 6H); FAB-MS: *m/z* 765 $[M+H]^+$.

Synthesis of 2.

All manipulations were carried out with the exclusion of light. Under nitrogen, to a solution of **2H** (0.100 g, 0.131 mmol) in benzene (100 mL) was added the solution of potassium ferricyanide (0.988 g, 3.00 mmol) and KOH (0.432 g, 7.69 mmol) in water (100 mL), and the reaction mixture was vigorously stirred for 5 h. The organic layer was separated, exhaustively washed with water, and concentrated in *vacuo*. The crude product was purified with silica gel column chromatography using chloroform as eluent and further purified by reprecipitation in hexane to yield **1H** as a colorless powder (43 mg, 43%). ^{1}H-NMR (500 MHz, DMSO-d_6) δ : 7.28 (m, 3H), 7.15 (m, 3H), 7.04 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 3H), 6.86 (d, J = 8.6 Hz, 2H), 6.68 (m, 6H), 6.57 (dd, J = 6.8, 2.4 Hz, 1H), 6.48 (m, 2H), 4.34 (m,1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.65 (s, 3H), 3.58 (s, 3H), 3.14-2.94 (m, 7H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ : 167.5, 164.3, 161.7, 161.6, 159.3, 158.0, 146.9, 143.6, 141.3, 141.0, 139.4, 138.1, 137.5, 137.3, 136.1, 135.6, 134.8, 134.7, 134.0, 133.5, 132.5, 131.8, 131.5, 128.1, 127.5, 126.7, 124.7, 124.3, 123.8, 114.0, 113.43, 113.37, 113.2, 113.0, 111.6, 55.5, 55.4, 55.2, 55.1, 35.4, 35.3, 34.6, 34.2; FAB-MS: *m/z* 763[M+H]$^+$.

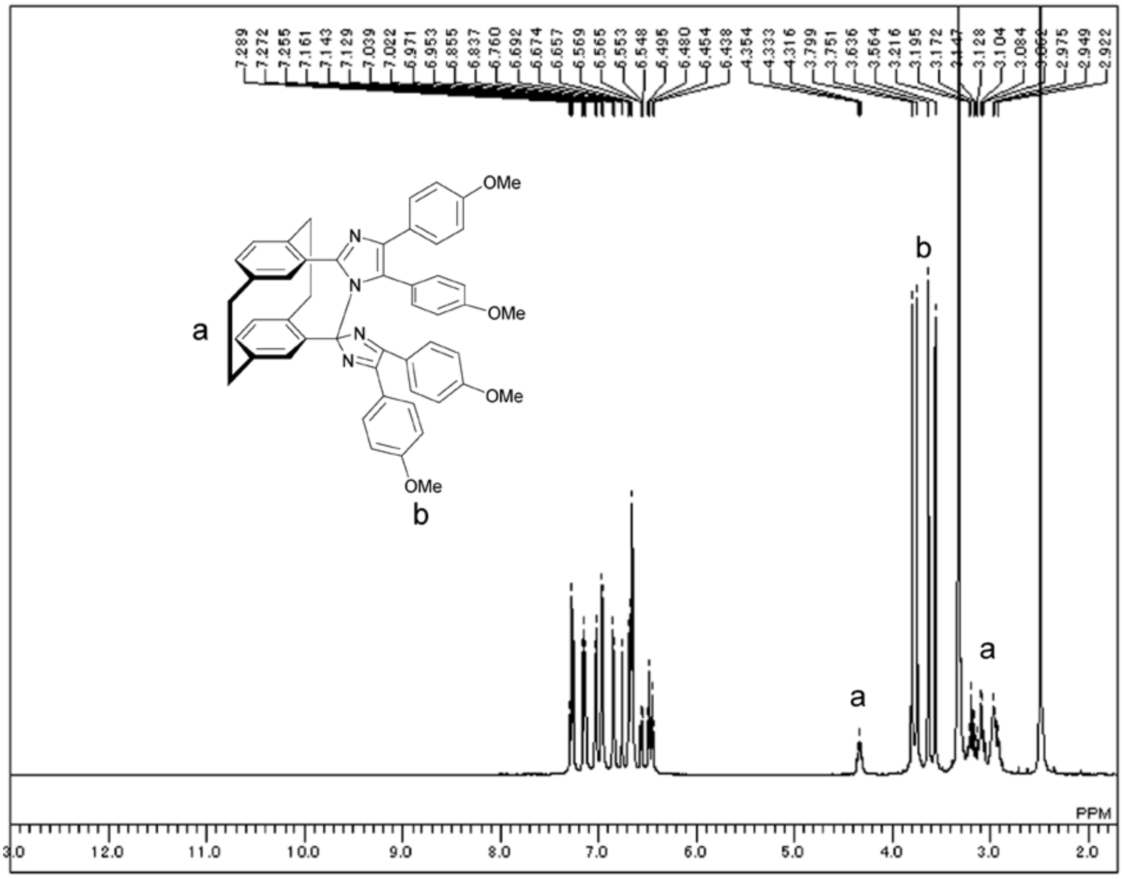


Figure S2. ^{1}H-NMR spectrum of **2** in DMSO-d_6.

2. Photochromic behavior of 2

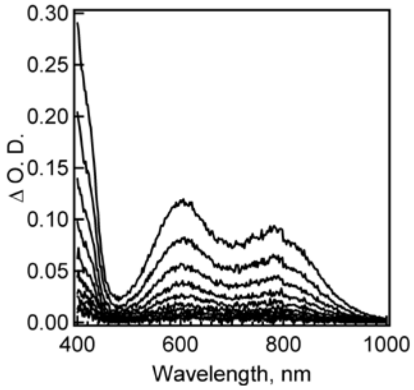


Figure S3. Transient vis–NIR absorption spectra of **2** in degassed benzene solution (9.7×10^{-5} M, 10 mm light-path length) at 298 K. Each of the spectra was recorded at 120 ms intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8 mJ/pulse).

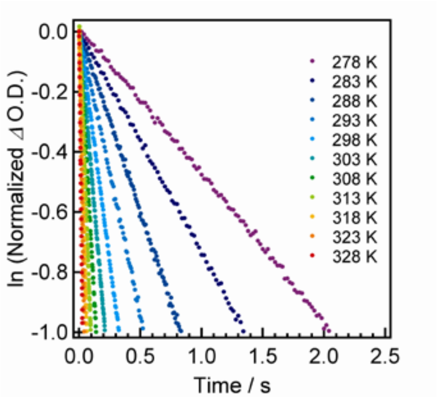


Figure S4. Decay profiles of the colored species generated from **2** monitored at 400 nm in degassed benzene solution. The measurements were performed in the temperature range from 278 to 328 K.

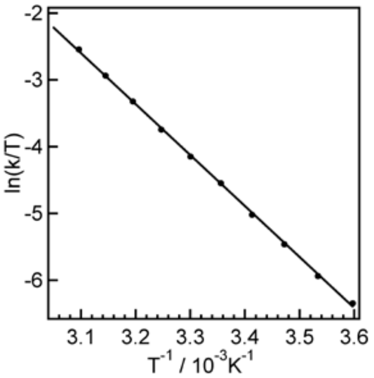


Figure S5. Eyring plots for the thermal back-reaction of **2** in the temperature range from 278 to 328 K.

3. Photochromism of the organogel

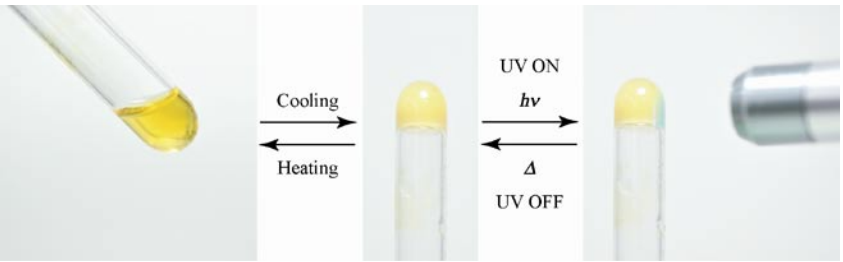


Figure S6. Photographic images of the photochromic gel system comprised of **1** in cyclohexane (2.2 wt%).