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

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A novel photochromic organogelator possessing [2.2]paracyclophane-bridged imidazole dimer unit with four hydrogen bonding urea arms was obtained. Irradiating UV light to benzene solution of the photochromic organogelator, rapid photochromism from colorless to green is observed. From the transient vis–NIR absorption measurement, a characteristic absorption around 400 nm and a broad absorption from 500 to 1000 nm can be attributed to the colored species. The half-life of the colored species is 243 ms at 298 K. In cyclohexane, the organogel was successfully formed, which was characterized by SEM observation and IR spectroscopy and showed fast photochromism even in the gel phase.

## 1. Introduction

Photoresponsive organogels are recognized as a new class of stimuli-responsive material [1–4], which enables photoinduced morphological change, including shape deformation [5–11] and sol–gel transition [12–18]. In the last decade, many systems [19–28] with conventional photochromic moiety as photoreactive module were proposed. However, of particular concern is that it takes over a minute to exhibit the morphological change because the response to light originates from photochromic reaction rate of the photochrome. In order to realize real-time photoinduced morphological control, which allows simultaneous deformation only under irradiation, an inherently fast photochromic system in solution should be applied into orgenogel systems.

We have recently developed a unique series of photochromic molecules based on [2.2]paracyclophane-bridged imidazole dimer, which allows instantaneous coloration upon exposure to UV light and rapid fading in the dark [29–31]. The half-life of the colored species derived from the homolytic photocleavage of the C–N bond of imidazole dimer unit is within the order of milliseconds in solution. Another remarkable aspect of the photochromism of such imidazole dimer systems is photogeneration of imidazolyl radicals with an unpaired electron [32–34], which could modulate the magnetic property simply by turning the optical stimulation on and off. Our accumulated previous research has been focused on the control of the simultaneous color change in solution, such as photosensitivity, reaction kinetics, and controlling colors of the photogenerated radical species by modifying the electronic structure. Hence, we consider the fast photochromic [2.2]paracyclophane-bridged imidazole dimer to be a promising switching component for fast photoinduced morphological change; simultaneous morphological control only under light irradiation is expected to produce a new class of photo-oriented intelligent materials system. Herein, we focused on the unique photochromic behavior of the [2.2]paracyclophane-bridged imidazole dimer unit even in organogel.

## 2. Experimental

### 2.1. General

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 (Wakogel® C-300). All reagents were purchased from TCI, Wako Co. Ltd., Aldrich Chemical Company, Inc, and ACROS Organics, and were used without further purification. All reaction solvents were distilled on the appropriate drying reagents prior to use. The NMR spectra were recorded on a JMN-ECP500A (JEOL) spectrometer,

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and the chemical shifts are quoted in ppm relative to tetramethylsilane. The IR spectra were obtained by IRPrestige-21 (Shimadzu). The FAB mass spectra were measured with an MStation MS-700 (JEOL) spectrometer by using 3-nitrobenzyl alcohol as a matrix. Scanning electron microscopy (SEM) was performed on a JEOL model JSM-6301F FE-SEM operating at 8 kV. Pt was deposited on the sample before observation using a JFC 1300 Auto Fine Coater (JEOL).

### *2.2. Experimental detail for laser flash photolysis*

The laser flash photolysis experiments were carried out with a Unisoku TSP-1000 time-resolved spectrophotometer. A Continuum Minilite II Nd:YAG (Q-switched) laser with the third harmonic at 355 nm (ca. 8 mJ per 5 ns pulse) was employed for the excitation light. The probe beam from an OSRAM HLX64623 halogen lamp was guided with an optical fiber scope to be arranged in an orientation perpendicular to the exciting laser beam. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a prior to the laser flash photolysis experiments.

### *2.3. Experimental detail for characterization of the organogel*

The organogel in cyclohexane was deposited on the waveguide surface by drop casting and covered with glass plate to prevent evaporation of the solvent. Absorption spectrum of the organogel of **1** was measured by Fastevert S-2600 Soma Kougaku multichannel spectrometer equipped with surface and interface stage (System Instruments Co., Ltd.) under irradiating UV light with Keyence UV-400 series UV-LED (UV-50H type), equipped with a UV-L6 lens unit (365 nm, irradiation power 300 mW/cm$^2$).

### *2.4. Synthesis*

#### *2.4.1. Synthesis of propoxyphthalimide-substituted benzil (**4**)*

4,4′-dihydroxybenzil **3** (501 mg, 2.07 mmol), *N*-bromopropylphthalimide (1.24 g, 4.62 mmol), and potassium carbonate (1.54 g, 11.1 mmol) were added to anhydrous DMF (7 mL), and the reaction mixture was heated at 65 °C for 5 h. After cooling to r.t., the reaction mixture was extracted with chloroform; the combined extracts were washed with water and brine. 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 colorless powder (712 mg; yield: 56.0%). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.87 (m, 8H), 7.73 (m, 4H), 6.84 (d, $J$ = 8.6 Hz, 4H), 4.11 (t, $J$ = 5.5 Hz, 4H), 3.92 (t, $J$ = 6.4 Hz, 4H), 2.22 (t, $J$ = 6.1 Hz, 4H); FAB-MS: *m*/*z* 617 [M + H]$^+$.

#### *2.4.2. Synthesis of propoxyphthalimide-substituted bisimidazole (**5**)*

**4** (2.27 g, 1.9 mmol), [2.2]paracyclophane-4,13-dicarbaldehyde (502 mg, 1.90 mmol) and ammonium acetate (2.16 g, 28.0 mmol) were refluxed in acetic acid (40 mL) for 24 h. After adding ammonium acetate (2.00 g, 25.9 mmol), the reaction mixture was heated for additional 24 h and was cooled to room temperature and was neutralized with aqueous $NH_3$. The resulting precipitate was filtered and washed with water. The crude mixture was purified with silica gel column chromatography using THF/hexane = 3/1 to 1/1 as eluent to give a yellow powder (1.35 g, 48.7%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 11.4 (s, 2H), 7.77 (m, 16H), 7.10 (m, 5H), 6.89 (d, $J$ = 9.2 Hz, 2H), 6.67 (d, $J$ = 7.9 Hz, 2H), 6.57 (m, 6H), 6.50 (d, $J$ = 9.2 Hz, 4H), 4.51 (m, 2H), 3.98–3.87 (m, 8H), 3.73 (m, 8H), 3.06 (m, 6H), 2.03 (m, 8H); FAB-MS: *m*/*z* 1458 [M + H]$^+$.

#### *2.4.3. Synthesis of urea-substituted [2.2]paracyclophane-bridged bisimidazole (**1H**)*

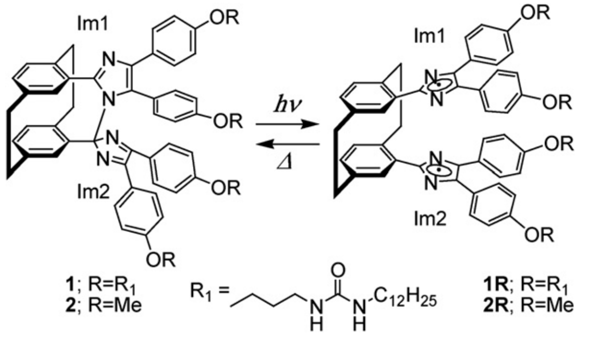
To a solution of **5** (210 mg, 0.144 mmol) was dissolved in THF (3 mL) was added 75% hydrazine hydrate (1 mL) and heated at 60 °C for 24 h. After addition of water, a colorless precipitation was formed and collected in *vacuo* to yield crude mixture of **6**, which was used without further purification because of its insolubility in common organic solvents. To a crude mixture of **6** in chloroform (50 mL) was added dodecyl isocyanate (0.500 g, 2.37 mmol) and the reaction mixture was refluxed for 24 h. After the solvent was removed in *vacuo*, the crude mixture was purified with silica gel column chromatography using chloroform to chloroform/methanol = 9/1 as eluent and further purified by reprecipitation in hexane to yield **1H** as a pale brown powder (0.201 g, 77%) and was used without further purification because of its large polarity. $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 11.4 (s, 2H), 7.20 (d, $J$ = 8.6 Hz, 4H), 7.08 (m, 2H), 6.97 (t, $J$ = 8.6 Hz, 4H), 6.69–6.59 (m, 12H), 5.93–5.82 (m, 8H), 3.93–3.87 (m, 2H), 3.14 (m, 8H), 2.96 (m, 8H), 1.81 (m, 8H), 1.34 (d, $J$ = 4.9 Hz, 8H), 1.23 (b, 80H), 0.84 (t, $J$ = 6.7 Hz, 12H); FAB-MS: *m*/*z* 1782 [M + H]$^+$.

#### *2.4.4. Synthesis of urea-substituted [2.2]paracyclophane-bridged imidazole dimer (**1**)*

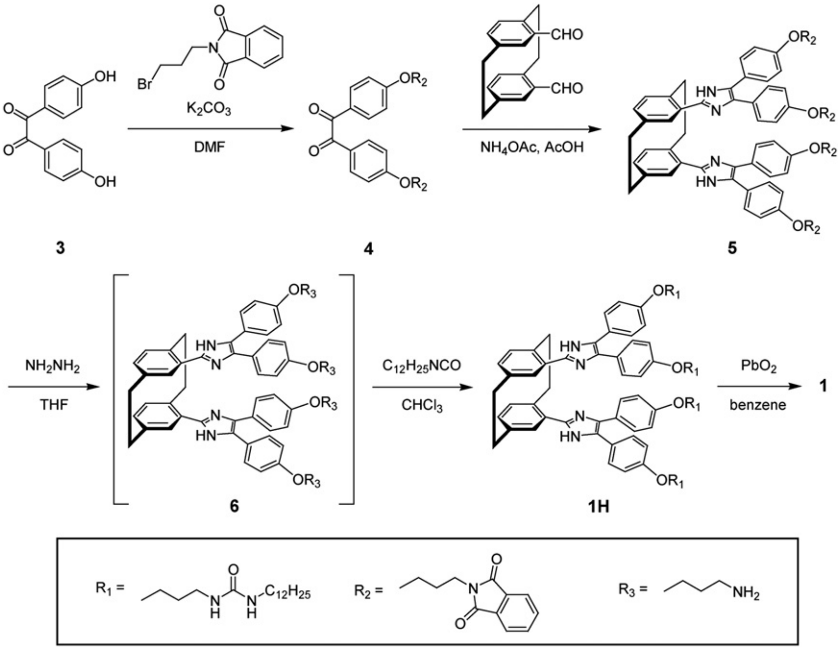
All manipulations were carried out with the exclusion of light. Under nitrogen, **1H** (0.060 g, 0.058 mmol) and lead(IV) oxide was refluxed in benzene (30 mL) and ethanol (5 mL) for 24 h. The reaction mixture was filtered over Celite and the filtrate was evaporated to dryness. The crude product was purified with reprecipitation in hexane to yield **1** (82.5 mg, 60%). $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$: 7.25 (t, $J$ = 7.3 Hz, 3H), 7.13 (t, $J$ = 8.2 Hz, 3H), 7.03 (d, $J$ = 8.6 Hz, 2H), 6.94 (d, $J$ = 8.6 Hz, 3H), 6.82 (d, $J$ = 8.6 Hz, 2H), 6.64 (m, 6H), 6.50 (m, 3H), 5.88–5.72 (m, 8H), 4.34 (m, 1H), 4.03–3.68 (m, 8H), 3.15–3.04 (m, 7H), 2.94 (m, 8H), 1.83–1.69 (m, 8H), 1.33–1.15 (br, 88H), 0.73 (t, $J$ = 6.1 Hz, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$: 167.8, 164.3, 161.2, 161.1, 159.6, 159.5, 159.3, 159.1, 158.5, 157.5, 147.1, 143.6, 141.2, 141.0, 139.9, 137.8, 137.3, 137.202, 137.198, 136.1, 135.0, 134.9, 134.7, 134.2, 133.8, 133.3, 133.0, 132.9, 131.9, 131.5, 128.2, 127.3, 127.1, 124.1, 123.9, 123.3, 114.7, 114.0, 113.9, 113.5, 111.6, 65.9, 65.7, 65.6, 40.7, 40.4, 40.2, 40.0, 37.3, 37.2, 37.1, 37.0, 36.9, 35.4, 34.5, 34.1, 32.0, 30.6, 30.4, 29.8, 29.6, 27.2, 22.8, 22.8, 12.3, 12.4; FAB-MS: *m*/*z* 1780 [M + H]$^+$.

## 3. Results and discussion

We designed a novel photochromic organogelator with [2.2]paracyclophane-bridged imidazole dimer (**1**), possessing tetrapodal urea arms at its termini (Scheme 1). Compound **1** was synthesized in five steps from 4,4′-dihydroxybenzil (**3**) (Scheme 2). After introduction of *N*-propylphthalimide unit *via* Williamson reaction in 56% yield, the phthalimide-substituted benzil (**4**) was reacted



Scheme 1.



Scheme 2.

with [2.2]paracyclophane-4,13-dicarbaldehyde to form bisimidazole (**5**) in 49% yield. The four phthalimide moieties were cleaved by hydrazinolysis to yield the tetraamine as insoluble powders (**6**), which was reacted with an excess amount of dodecyl isocyanate to give the urea-substituted [2.2]paracyclophane-bridged bisimidazole (**1H**) in 77% yield. The precursor, **1H** was oxidized with lead (IV) oxide to afford the target urea-substituted [2.2]paracyclophane-bridged imidazole dimer (**1**) in 60% yield.

Irradiating UV light to benzene solution of **1**, rapid photochromism from colorless to green is observed. Under continuous irradiation, the benzene solution of **1** reaches the photostationary equilibrium, and the absorption decays rapidly following mono-exponential thermal bleaching kinetics after ceasing the irradiation. The complete bleaching is achieved within a few seconds which makes it possible to see the color change of the solution only where UV light is irradiated. Fig. 1a shows the transient vis–NIR absorption spectra of **1** in degassed benzene solution at 298 K measured by a nanosecond laser flash photolysis experiment. A characteristic absorption around 400 nm and a broad absorption from 500 to 1000 nm can be attributed to the colored species, **1R**. The half-life of the colored species is 243 ms at 298 K. The thermal recombination obeys first-order kinetics over the temperature range from 278 to 328 K as shown in Fig. 1b.

In order to study influence of the urea arms on the photochromic properties in solution, the identical unsubstituted segment **2**, which has four methoxy substituents, was prepared (Scheme S1) and its photochromic properties were also investigated. The half-life of the colored species is 220 ms at 298 K, which is comparable to that of **1** (243 ms) (Fig. 2). The absorption of the colored species, **2R**, generated by UV irradiation also gives similar spectrum with a broad absorption from 500 to 1000 nm to the absorption spectrum of **1R**. These results indicate that there are no substitution effects of the urea arms on the half-life and absorption spectrum of the colored species at 298 K (Figs. S3 and S4). The enthalpies and entropies of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively) for the thermal recombination of **1R** and **2R** were estimated from Eyring plots over the temperature range from 278 to 328 K. The Eyring plot gives a good straight line (Fig. 3 and Fig. S5), and the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values determined by least-square analysis of the Eyring plots are 55.1 kJ mol$^{-1}$ and $-55.3$ J K$^{-1}$ mol$^{-1}$, respectively. On the other hand, the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the recombination of **2R** are 63.5 kJ mol$^{-1}$ and $-22.4$ J K$^{-1}$ mol$^{-1}$, respectively. It should be noted that the smaller $\Delta S^{\ddagger}$ value for recombination of **1R** than that of **2R** is derived from introduction of the bulky urea arms, which brings steric hindrance between the imidazolyl radicals. Remarkably, below 288 K, the half-life of **1R** becomes smaller than that of **2R** (Fig. 4). For example, at 278 K, the half-life of **1R** is 1.14 s, which is smaller than that of **2R** (1.42 s). This is probably due to formation of inter/intramolecular hydrogen bonding network at low temperatures, resulting in the rigid environment around the photogenerated imidazolyl radicals. The entangled hydrogen bonding network as rigid environment gives restriction of molecular structural change for photochromic reaction; upon UV irradiation to generate the imidazolyl radical, one of the imidazole rings (Im1, Scheme 1) rotates to form face-to-face geometry with the other imidazole ring (Im2, Scheme 1) as the formation process of the imidazolyl radical colored species [29]. As a result, the closer distance between two imidazole rings allows accelerated recombination of the radical species to give the shorter half-life of **1R** than that of **2R**.

We investigated the gelation behavior of **1** for various common organic solvents by first dissolving **1** by heating, followed by cooling to room temperature. It can form a stable turbid gel in cyclohexane with more than 2.2 wt% (9.7 mM) (Fig. S6). The organogel dissolves into solution over 328 K to be transparent. Using other solvents such as acetonitrile, acetone, toluene, benzene and so on, no organogel formation is observed after heating–cooling cycles. The morphology of the xerogel prepared from **1** was investigated by field emission scanning electron microscopy (FE-SEM). From the FE-SEM observation, the cyclohexane gel forms three-dimensional entangled network structures consisting from sub-micrometer scale nanofibrous structures (Fig. 5). The fibers have several micrometers length and approximately 200 nm width, which can similarly be observed for xerogels composed of other urea-based organogelators [35–38]. The formation of the hydrogen bonding network through urea moieties is characterized by IR absorption bands which corresponds to the N–H stretching and the amide bands of urea unit

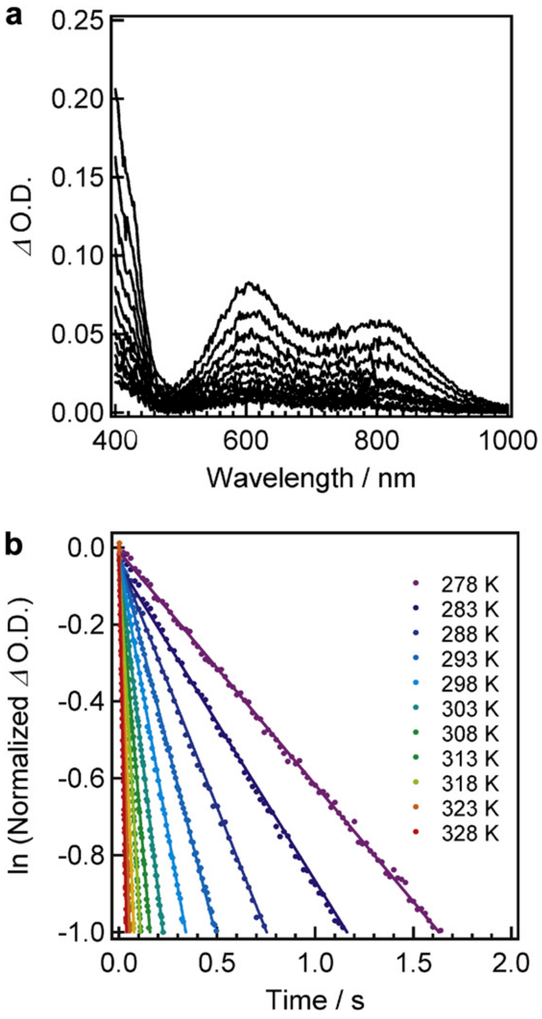


**Fig. 1.** (a) Transient vis–NIR absorption spectra of **1** in degassed benzene solution ($9.7 \times 10^{-5}$ M, 10 mm light-path length) at 298 K. Each of the spectra was recorded at 80 ms intervals after excitation with a nanosecond laser pulse (excitation wavelength, 355 nm; pulse width, 5 ns; power, 8 mJ/pulse). (b) Decay profiles of the colored species generated from **1** monitored at 400 nm in degassed benzene solution. The measurements were performed in the temperature range from 278 to 328 K.

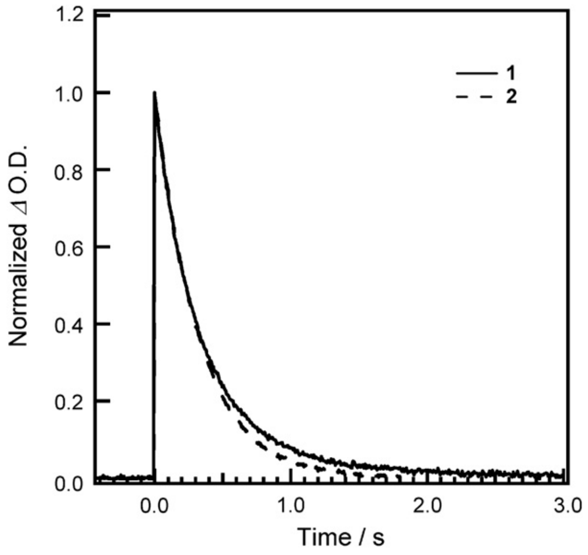


**Fig. 2.** Decay profiles of the colored species generated from **1** to **2** monitored at 400 nm in degassed benzene solution at 298 K.

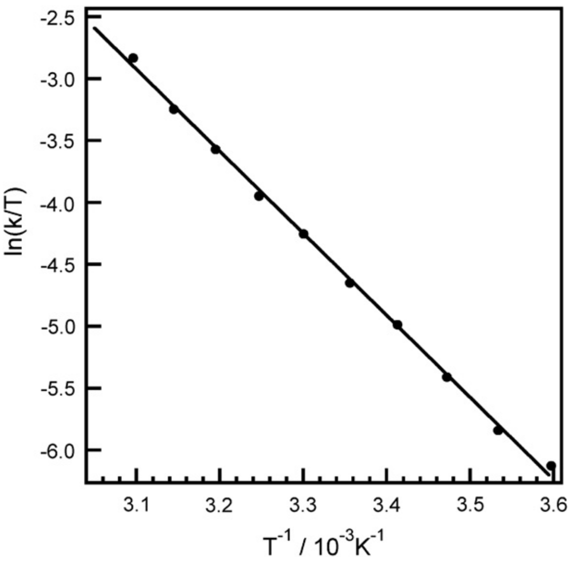


**Fig. 3.** Eyring plots for the thermal back-reaction of **1** in the temperature range from 278 to 328 K.

(Fig. 6). The solution of **1** in chloroform (8.4 mM) shows characteristic absorption bands for free amide moiety at 3409 and 1671 cm$^{-1}$ attributed to the N–H stretching and C=O stretching band, respectively. After transition to gel phase, the N–H stretching and C=O stretching bands are shifted to lower wavenumbers (3337 and 1611 cm$^{-1}$, respectively). According to the literature, this IR spectral shift is indicative for formation of the hydrogen bonds of adjacent urea groups of **1** [36–38].

Upon illumination at 365 nm, the organogel of **1** rapidly colorizes on the surface where UV light is illuminated and keeps the gel phase (Fig. S6). No significant phase transitions of the organogel during photoreaction are mainly due to internal filter effect with turbidity to inhibit total conversion; absorption and scattering of the UV light by **1** to prevent the photochromic reaction inside the organogel. When the light irradiation ceases, the colored part rapidly disappears to

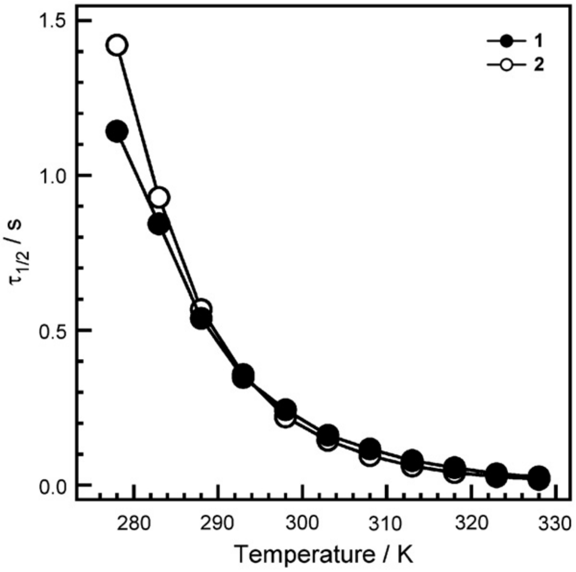


**Fig. 4.** Temperature dependence of the half-life of the colored species of **1** and **2** in degassed benzene determined from the measurements of the nanosecond laser flash photolysis experiment.

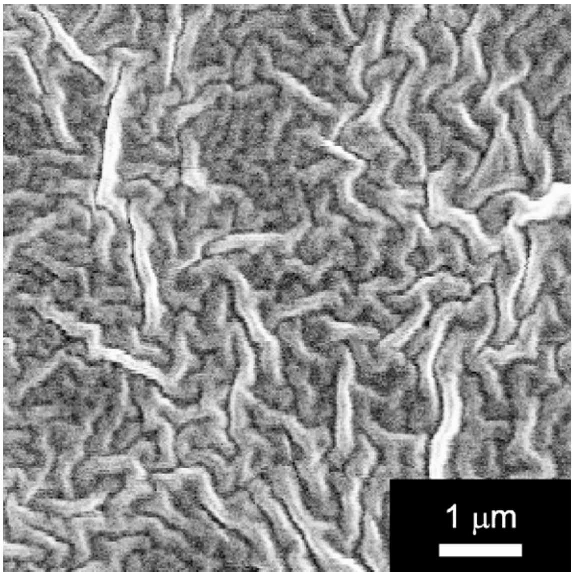


**Fig. 5.** SEM image of the xerogel of **1** prepared by dropping a cyclohexane gel (2.2 wt%) onto a silicon substrate, and then air-drying the organogel. Pt was deposited on the sample before observation.

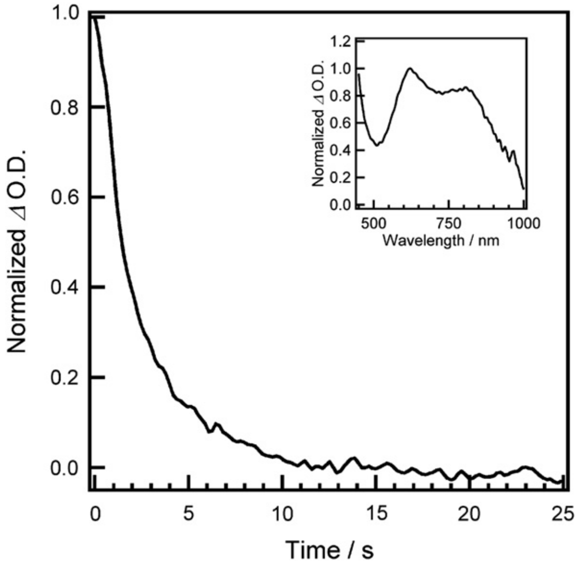


**Fig. 7.** Decay profile of the colored species of the organogel of **1** after UV light irradiation (365 nm). Inset shows vis–NIR absorption spectra of the colored species of organogel **1** normalized at 625 nm. The measurements were performed at room temperature with slab optical waveguide technique.

recover the colorless organogels. The absorption spectrum of the colored species of the turbid gel **1** was measured under UV light irradiation with slab optical waveguide technique instead of the conventional transmission absorption spectroscopy. In the gel phase, a similar absorption spectrum of the colored species to that in solution is observed with characteristic absorption bands around 600 and 800 nm (Fig. 7, inset). This indicates that the coloration under UV light irradiation is derived from the photogenerated imidazolyl radicals and there are small effects on the electronic state of the imidazolyl radical unit upon gelation. On the other hand, the thermal bleaching reaction does not obey first-order kinetics and half-life of the colored species of **1**, defined as the time with 50% of the normalized Δ O.D. (optical density), was estimated to be approximately 1.4 s at room temperature (Fig. 7). Considering that the half-life in benzene solution is 243 ms at 298 K, this deceleration of the recombination reaction is due to the contribution of the slow component, which can generally be observed in photochromic reaction in bulk level [39–43]. In other conventional photochromic gel systems, it takes over a minute to complete the photochromic reaction because the slower response to light originates from photochromic reaction rate of the photochrome. On the other hand, applying an inherently fast photochromic unit into organogel system, the photochromic reaction with orders of seconds even in organogel can be expected as a promising candidate for simultaneous photoinduced morphological transition only under light irradiation.

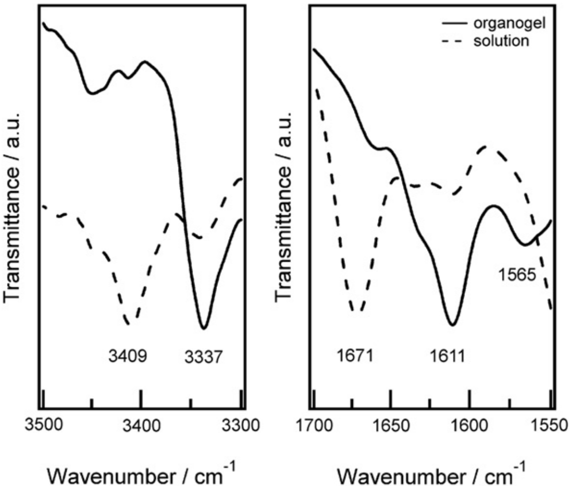


**Fig. 6.** FT–IR spectra of the organogel (solid lines, 9.7 mM in cyclohexane) and solution (dashed lines, 8.4 mM in chloroform) of **1**.

## 4. Conclusion

In conclusion, we have prepared a novel organogelator possessing [2.2]paracyclophane-bridged imidazole dimer as a photochromic unit. We demonstrated the inherently fast photochromic reactions, homolytic photocleavage of the C–N bond of imidazole dimer unit and recombination between the photogenerated imidazolyl radicals, took place even in the gel phase. We believe that the modification of this system makes it possible to realize simultaneous morphological/physicochemical control only under light irradiation, which will create a new class of photo-oriented intelligent materials system.

## Acknowledgement

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## Appendix. Supplementary data

Synthesis and photochromic property of **2**, NMR chart of **1** and **2** and the photograph of the organogel of **1** were included in the Supplementary materials. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.dyepig.200.03.019.

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