# Photoresponsive Fluorescence Color Change Derived from TICT in an Organogel System

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A novel gelator containing 9-(9′-acridyl)carbazole (TICT probe) and azobenzene within a molecule was synthesized and the photoresponsive gel properties were investigated by spectroscopic analyses; it showed an interesting photoinduced fluorescence wavelength change, which leads to a potential development toward a new type of optical information materials.

Stimuli-responsive materials are expected to be components of industrially valuable products such as switches, and sensors.[1] It is a prerequisite for these materials to integrate a function that can change their properties in response to various input signals such as redox potential, light, and temperature. Supramolecular materials attract particular attention due to the ease in designing stimuli-responsive functions arising from the dynamic nature of their noncovalent interactions.[2] Low molecular-weight gels (LMWGs), which can be classified as a supramolecular systems, show a reversible sol–gel phase transition as a result of thermal or light stimuli. In addition, LMWGs form well-ordered fibrous superstructures driven by multiple, weak interactions such as dipole–dipole, van der Waals, and hydrogen-bonding interactions.[3] It seems undoubted, therefore, that alignment of functional substances in LMWG systems is a promising approach to obtain novel electrical, optical, and thermal properties.[4] Controlling these properties by light frequently provide important breakthroughs in development of these stimuli-responsive materials.

Herein, we report the design of a new photoresponsive fluorescence color change in an organogel system. This fluorescence color change is driven by twisted intramolecular charge transfer (TICT),[5] which tends to appear in polar solvents with a low-energy fluorescence band.

We previously reported that a fluorescence color of *p*-dimethylaminobenzoate (*p*-DMAB)-appended cholesterol-based gelators shifts to a high-energy fluorescence band in response to a phase transition from sol to gel, because the molecular twisting is suppressed by stacking of gelator molecules.[6] The trigger to induce the phase transition in this system was a thermal stimulus. In the present work, we utilize a light stimulus to induce the sol–gel phase transition (Figure 1). Therefore, this strategy is classified into a light input–light readout system, enabling us to realize the photoinduced multicolor fluorescence change.

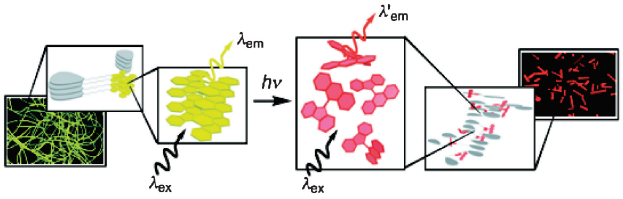


**Figure 1.** A schematic representation of a photoinduced fluorescence color change ($\lambda'_{em} > \lambda_{em}$) in the sol–gel system.

It is known that the fluorescence readout is advantageous when photochromic materials are applied to data storage devices because of its nondestructive nature.[7] Our new system presented here satisfies this prerequisite for the design of data storage devices.

Our molecular design for the azobenzene-appended 3,4,5-tris(*n*-dodecyloxy)benzoylamide-based gelator **1** (photoresponsive organogelator) coupled with the 9-(9′-acridyl)carbazole moiety (TICT dye; the fluorescence spectra of the reference compound in various solvents are shown in Figure S1.)[8] is shown in Figure 2. Compound **1** (mp: 149–150 °C) was synthesized by the reaction of **2** with **3** in the presence of cesium carbonate and identified by $^1$H NMR and MALDI-TOF mass spectral evidence and elemental analysis (yield 65%; the synthetic route is shown in Scheme S1).[8]

We evaluated the gelation ability of compound **1** (4.0–10 g·dm$^{-3}$) in various organic solvents by a "stable-to-inversion of a test tube" method. As shown in Table S1,[8] **1** gelates hexane, *p*-xylene, ethyl acetate, etc. It should be noted that **1** can form a gel even in 1-decanol, which has moderate solvent polarity where **1** may give low-energy fluorescence arising from TICT. On the other hand, **1** should show high-energy fluorescence arising from the inhibition of TICT due to rotational suppression of the C–N bond between two aryl groups in the gel phase.

To obtain visual images of **1** aggregates in the gels, we observed the **1** + 1-decanol gel and the **1** + *p*-xylene gel with a transmission electron microscope (TEM). As expected, fibrous aggregates were observed in both solvents (Figure 3): the fibers are composed of one-dimensionally assembled **1** less than 50 nm in width and more than several μm in length.

Then, IR spectral analyses were conducted. The signal at 1636 cm$^{-1}$, which we assigned to C=O stretching vibration, shifted to 1642 cm$^{-1}$ by UV light irradiation; Figure S2[8] and Table S2.[8] This result indicates that the hydrogen bonds were weakened by UV light irradiation. Furthermore, the results of UV–vis spectral analyses indicate that the aggregates of **1** are dissociated by UV light irradiation (Figure S3).[8] From the ab-

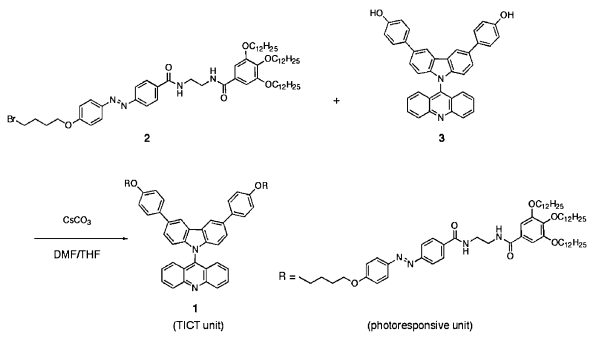


**Figure 2.** Synthesis and chemical structure of compound **1**: $CsCO_3$ (16 equiv), DMF/THF (4:3, v/v), 100 °C, 24 h, 65%.

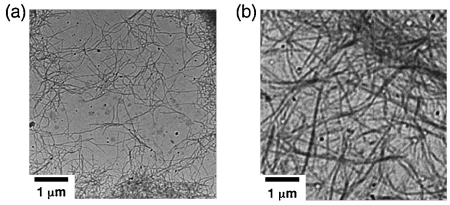


**Figure 3.** TEM images of the **1** gel (4.0 mM) and (b) *p*-xylene.

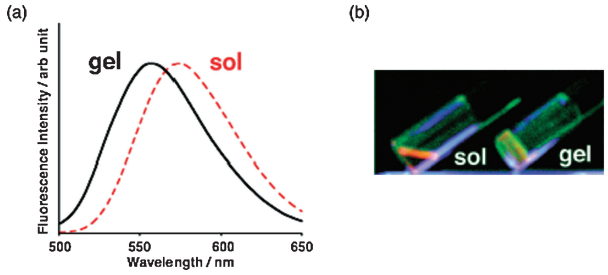


**Figure 4.** (a) Fluorescence spectra of **1**([**1**] = 4.0 mM, solvent: 1-decanol, $\lambda_{ex} = 350$ nm, optical path length: 1.0 mm, temperature: 25 °C.), (b) the image of **1** + 1-decanol sol and gel.

sorption spectral changes, the cis% of the photostationary state was estimated to be 60% in the sol state and 25% in the gel state.

We previously reported that a cholesterol appended *p*-DMAB derivative acts as an efficient gelator for various organic solvents.[6] The gel showed only the shorter wavelength fluorescence emission arising from the coplanar conformation independent of the solvent polarity, whereas the sol showed the conventional TICT fluorescence emission arising from the *p*-DMAB moiety. Since this methodology can be applied to our present work, fluorescence spectra of **1** were thoroughly examined both in the gel state and in the sol state.

We prepared the **1** + 1-decanol sol and the **1** + 1-decanol gel. Here, the "**1** + 1-decanol sol" was prepared by UV light irradiation in the cooling process after heating the 1-decanol solution of **1**. The fluorescence spectra of these samples are shown in Figure 4. A fluorescence maximum of the **1** + 1-decanol sol ($\lambda_{max} = 574$ nm) shifted to longer wavelength by 18 nm than that of the **1** + 1-decanol gel ($\lambda_{max} = 556$ nm: Figure 4a). As expected from this result, the light irradiation generated a fluorescence color change detectable by the naked eye (Figure 4b). As a reference experiment, we observed fluorescence spectra of **1** in *p*-xylene according to a similar method. A fluorescence maximum wavelength of the **1** + *p*-xylene sol ($\lambda_{max} = 545$ nm) was only 3 nm longer than that of the **1** + *p*-xylene gel ($\lambda_{max} = 542$ nm). This implies that the TICT effect can appear in 1-decanol that has higher solvent polarity than *p*-xylene. Utilizing these changes, we could demonstrate that visible light irradiation to the **1** + 1-decanol sol after UV light irradiation induces cis-to-trans isomerization and that the photo-induced isomerization cycle can be repeated at least five times (Figure S4).[8]

In conclusion, we have demonstrated that **1** acts as an efficient photoresponsive gelator, featuring photoinduced fluorescence change. The fluorescence maximum of **1** shifted to longer wavelength with change from the gel state to the sol state. Since **1** has photoresponsive substituents, this fluorescence color change can be induced not only by heating but also by UV light irradiation. We believe that the present organogel system has unique potentials to develop the novel photochemical soft materials from organogels.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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