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Reversible On–Off Photoswitching of Hydrogen Bonding for Self-Assembled Fibers Comprising Physical Gels

Masaya Moriyama, Norihiro Mizoshita, and Takashi Kato*

Department of Chemistry and Biotechnology,
School of Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656

Received January 5, 2006; E-mail: kato@chiral.t.u-tokyo.ac.jp

We report on photo-stimulated reversible association and dissociation of hydrogen bonding for self-assembled fibers comprising physical gels. The gels are formed by a hydrogen-bonded gelator containing photochromic azobenzene moieties. The photoswitching of hydrogen bonding is caused by the changes of molecular polarity for the azobenzene moieties.

Hydrogen bonding is a non-covalent intermolecular interaction, which plays a key role in supramolecular chemistry due to its dynamic nature.[1] The development of hydrogen-bonded materials exhibiting stimuli- and environment-responsive properties has attracted attention in the field of materials and supramolecular chemistry.[1] For example, hydrogen bonding can be switched by external stimuli such as temperature,[2] pH,[3] and metal ions.[4] Light should also be one of the most effective stimuli because its intensity and wavelength can be tuned to control the dynamic behavior of hydrogen bonding. Our intention is to develop new stimuli-responsive hydrogen-bonded materials. Physical gels can be one of the representative stimuli-responsive materials. A variety of solvents, common organic, aqueous and liquid crystalline solvents, have been gelated through hydrogen bonding[5] as well as π–π interactions,[6] dipole–dipole interactions,[7] and van der Waals interactions.[8] The physical gels show thermoreversible gel–sol transitions. For the photo-responsive gel–sol transitions, cholesterol and anthracene derivatives were used as the gelators.[6c,8] Their aggregation is driven by van der Waals and π–π interactions. In contrast, a few materials have also been reported as photo-responsive hydrogen-bonded physical gels.[9,10] We first reported the distinct photo-stimulated reversible on–off switching of the hydrogen bonding (gel–sol transition), inducing structural changes in liquid crystalline (LC) physical gels.[10,11] The nematic LC gels based on a hydrogen-bonded gelator **1** consisting of bis(acylamino)cyclohexane and photochromic azobenzene moieties transform to the LC sol state upon UV irradiation. The *trans*-to-*cis* photoisomerization of the azobenzenes induces a gel–sol transition with dissociation of the hydrogen bonds. The *cis*-to-*trans* back isomerization induced photochemically and thermally leads to gelation with the recovery of the hydrogen bonds. Recently, Tamaoki and co-workers also reported the photoinduced gel–sol transitions of organogels based on a cholesterol-type gelator having hydrogen-bonding urethane and azobenzene moieties.[12] However, the mechanism of the photoinduced gel–sol transition has not yet been discussed. The light-induced gel–sol transition is not always observed for the physical gels using a photochromic gelator containing azobenzene moieties.[13] Here, we report on the photoinduced reversible on–off switching of the hydrogen bonding in the physical gels consisting of gelator **1** (Chart 1). The mechanism of the switching is also discussed.

We have found that hydrogen-bonded compound **1** containing *trans*-azobenzene moieties (*trans*-**1**) gelates organic solvents, cyclohexanone and dodecylbenzene. Figure 1a shows a photograph of the gel state of *trans*-**1** ($20\,\mathrm{g\,L^{-1}}$) in cyclohexanone at room temperature. The gel is translucent and is orange due to the azobenzene chromophore. The gel–sol transition temperature of the cyclohexanone gel at the concentration of $20\,\mathrm{g\,L^{-1}}$ is 60 °C.

UV irradiation ($\lambda = 365\,\mathrm{nm}$) of the gel induces a gel–sol transition as shown in Fig. 1b. In this stage, the *trans*-to-*cis* photoisomerization of azobenzene moieties of **1** is observed in the UV–vis absorption spectra (Figs. 2a and 2b). For the gel state before irradiation, the baseline of the spectrum is in

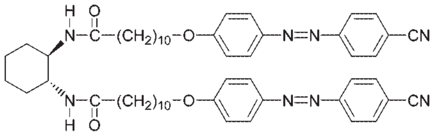

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Chart 1.

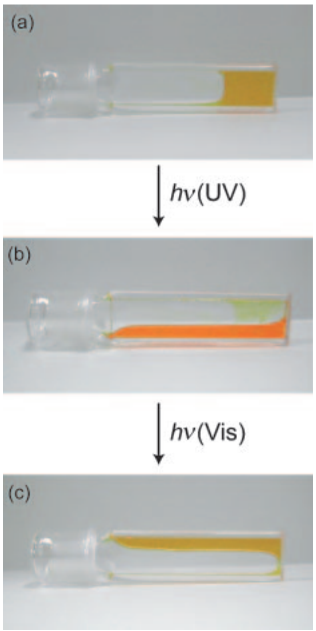

Fig. 1. Photographs of **1** in cyclohexanone ($20\,\mathrm{g\,L^{-1}}$). (a) Gel state before irradiation. (b) Sol state after UV light irradiation of the gel for 2 h. (c) Gel state after visible light irradiation of the sol for 1 h.

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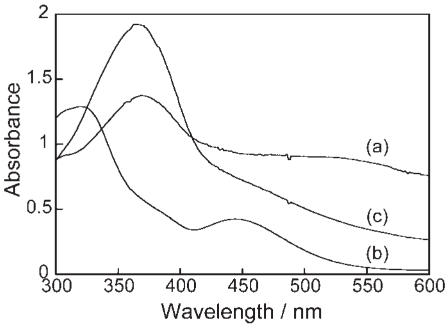

Fig. 2. UV–vis absorption spectra of the gel of **1** in cyclohexanone ($20\,g\,L^{-1}$). (a) The gel state before UV light irradiation. (b) Sol state after UV light irradiation for 10 min. (c) The gel state after visible light irradiation of the sol for 5 min at rt.

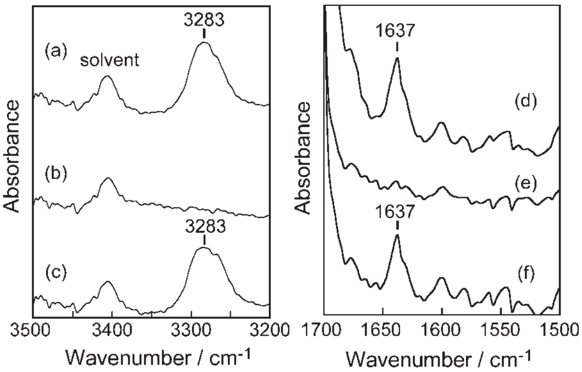

Fig. 3. IR spectra of **1** in cyclohexanone ($20\,g\,L^{-1}$) in the region of 3500–3200 (a–c) and 1700–1500 cm^{-1} (d–f) at rt. (a and d) Gel state before UV light irradiation. (b and e) Sol state after UV light irradiation for 10 min. (c and f) Gel state after visible light irradiation of the sol for 5 min.

a higher position due to light scattering (Fig. 2a). After UV irradiation, which induces the sol state, the baseline of the spectrum descends with a decrease in the π–π^* absorption band of the *trans*-azobenzenes at around 370 nm and with an increase in the n–π^* band of the *cis*-azobenzenes at around 450 nm. Subsequent visible light irradiation ($\lambda = 436$ nm) of the sol causes gelation again with the *cis*-to-*trans* back isomerization of the azobenzene units. Figure 1c shows a photographic image of the gel obtained by visible irradiation, which exhibits the re-gelation of the materials. In the UV–vis absorption spectrum shown in Fig. 2c, the π–π^* absorption band of the *trans*-**1** recovers. These results show that the light stimuli via *trans*–*cis* photoisomerization of azobenzenes in the gelator induce the reversible gel–sol transitions.

The photoinduced changes in the hydrogen bonds of **1** in the cyclohexanone gels have been examined by infrared (IR) spectroscopy. Figure 3 shows the IR spectra of **1** in cyclohexanone ($20\,g\,L^{-1}$) observed before and after photoirradiation. For the gel state before UV irradiation, the N–H and C=O stretching bands due to the amide units of **1** are observed at 3283 and 1637 cm^{-1}, respectively, which indicates the formation of intermolecular hydrogen bonds (Figs. 3a and 3d). After UV irradiation, for the sol state, the N–H stretching band of the hydrogen bonds shifts to quite a broad and weak band at around 3400 cm^{-1} and the C=O stretching band disappears (Figs. 3b and 3e). The disappearance of the C=O band is due to the overlap with the band of solvent.[14] Subsequent visible light irradiation of the sol state induces the shifts of the N–H and C=O bands back to the positions at 3283 and 1637 cm^{-1}, respectively (Figs. 3c and 3f). These positional changes of the IR bands obviously indicate the dissociation of the hydrogen bonds in the sol state and recovery in the gel state. The on and off states of the hydrogen bonding can be switched by selective-wavelength irradiations.

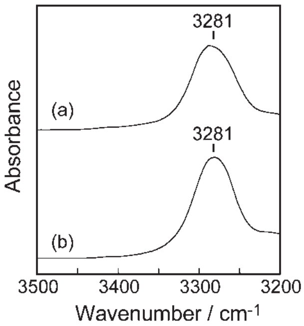

Fig. 4. IR spectra of *trans*-**1** (a) and *cis*-rich solid (b) at rt.

In the *trans*–*cis* photoisomerization of the azobenzenes, molecular polarity changes as well as molecular shape. Therefore, two possible mechanisms can be considered for the photoinduced on–off switching of the hydrogen bonding; one is the steric effect of the *trans*- and *cis*-azobenzene conformation, and the other is the solubility change of the gelator induced by the change in molecular polarity due to photoisomerization. To study the mechanism, we have measured the IR spectra of *cis*-**1**. The *cis*-rich solid sample was prepared by the spontaneous evaporation of solvent from a dichloromethane solution of *trans*-**1** under UV irradiation at room temperature. The sample includes ca. 75% of *cis*-**1**, which is estimated on the basis of the UV–vis absorption spectra. The IR spectra of *trans*-**1** and the *cis*-rich sample are shown in Fig. 4. The stretching bands of hydrogen-bonded N–H moieties are observed at 3281 cm^{-1} in both spectra. These results indicate that not only *trans*-**1**, but also *cis*-**1** can form hydrogen bonds even if the azobenzene moieties have a bent molecular shape.

Compound **1** also gelates dodecylbenzene, which has lower polarity than cyclohexanone. To a concentrated chloroform solution of **1** ($100\,g\,L^{-1}$) under UV light exposure, dodecylbenzene and cyclohexanone were added. Although no gelation was observed for the sample containing cyclohexanone, gelation did occur in the sample containing dodecylbenzene. This result shows that *cis*-**1** can gelate dodecylbenzene by the formation of hydrogen bonds. For azobenzenes, it is known that the molecular polarity of the *cis*-isomer is higher than that of the *trans*. Seki reported that the Langmuir monolayers of the polymers having azobenzene units at the air–water interface exhibit area expansion and contraction upon UV and visible irradiation.[15] This deformation of the monolayers was caused by a change in the contact with the water surface, which was due to the polarity change of the azobenzenes in the *trans*–*cis* photoisomerization process. The change in the molecular polarity of azobenzene moieties would induce the change in solubility of **1** in the solvents. The photoinduced on–off switching of hydrogen bonding in these physical gels is caused by the solubility change of hydrogen-bonded compounds, which is due to the photoisomerization of azobenzenes.

The photochromic hydrogen-bonded gelator, *trans*-**1**, having the azobenzene moieties gelates organic solvents such as cyclohexanone and dodecylbenzene. UV light irradiation of the cyclohexanone gel induces *trans*-to-*cis* photoisomerization of azobenzene units of the gelator, leading to the transition from the gel to the sol state. Subsequent visible light irradiation of the sol causes re-gelation with *cis*-to-*trans* photoisomerization of the azobenzenes. In the IR spectra of the materials, the positions of the N–H and C=O stretching bands of amide moieties shift after the irradiation, which indicates that light stimuli can induce the association and dissociation of the hydrogen bonding. Such photoinduced behavior of the hydrogen bonding is not observed in the dodecylbenzene. The polarity of the solvent should affect the solubility of the photo-generated *cis*-**1**. The polarity change of the azobenzenes in **1** should be a key factor in the induction of the photo-stimulated on–off switching of the hydrogen bonding.

Experimental

Materials. Compound **1** was synthesized by a previously reported method.[10]

Preparation of Gels. The physical gels were prepared by mixing the solvent and the gelator **1**. The mixtures were heated to isotropic states and then cooled to room temperature. The obtained mixtures in a quartz cell (thickness: 1 mm) were used for the macroscopic observation. For spectroscopic measurements, the mixtures were sandwiched between two CaF_2 substrates.

Photoirradiation. A high pressure mercury lamp (Ushio, 500 W) with the appropriate glass filters (Asahi Technoglass UV-35+UVD-36C (λ: 365 nm) and Y-43+V-44 (λ: 436 nm)) was employed as an irradiation source. The light intensities were 24 and 50 mW cm^{-2} for irradiation of the samples sandwiched in the CaF_2 substrates and held in the quartz cell, respectively.

Measurements of UV–Vis and IR Spectra. UV–vis absorption spectra were recorded by an Agilent 8453 spectrometer. IR spectra were measured by a JASCO FT/IR-660Plus spectrometer connected to an Irtron IRT-30 microscope unit.

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