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A Fully Photoreversible Supramolecular Polymer Having a Diarylethene Photoswitch

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The particle size of a supramolecular polymer composed of a diarylethene photoswitch and two quadruple hydrogen-bonding sites having C_{17} chain changes photoreversibly in tetrahydrofuran at room temperature, while that in a $CHCl_3$ solution is not photoreversible but is reversible with the assistance of heat.

Supramolecular polymers have been attracting much attention recently since they are a novel material that may rival conventional macromolecules.[1] One of the most important differences between supramolecular polymers and conventional macromolecules is reversibility. A supramolecular polymer can be associated and/or dissociated with external stimuli such as temperature change, solvent polarity change, and the addition of chemical substances.[1] Some reports have been presented on the photoswitching of hydrogen-bonded supramolecular polymers; however, the switching was not fully photoreversible, and formation or decomposition of the supramolecule took place with heating since the photoswitches were composed of thermally reversible azobenzene.[2] One report indicates a photoswitchable self-assembly with diarylethene photoswitch, but it failed to show a significant viscosity change.[3] We have previously reported a supramolecular polymer that has a thermally irreversible diarylethene as a photoswitch **1**.[4] The supramolecular formation of **1** was photoreversible; however, the dissociation was stepwise. With the assistance of heat, it has become possible to switch between monomer and supramolecular polymers with photoirradiation. This phenomenon is due to stable intermolecular quadruple hydrogen bonding and requires high temperatures to fully dissociate such strong binding. Moreover, the compound that we have reported was difficult to dissolve in most organic solvents except for chloroform or a mixture of chloroform and ethanol. Therefore, fully photoreversible supramolecular formation has not yet been accomplished, and this fact has encouraged us to develop a fully photoreversible supramolecular polymer in solution.

Figure 1 shows a schematic for photochromic diarylethene that has two quadruple hydrogen-bonding sites. To enhance the solubility, we have introduced two C_{17} chains at the ureidopyrimidinone moieties shown as compound **2**.[5] In this system, since the open form is flexible and can form weak intramolecular hydrogen bonding, the supramolecule would be difficult to form. On the other hand, in the closed form, which is generated from the open form upon irradiation with UV light, the diarylethene moiety takes place at the site of the cyclization reaction, and two hydrogen-bonding moieties would be fixed at both sides. Therefore, intermolecular hydrogen bonding becomes possible and a supramolecular polymer would be formed. Alternate irradiation of UV (330 ± 20 nm) and visible light (>460 nm) reversibly changed the absorption spectra of a $CHCl_3$ solution of **2**, showing that compound **2** is photochromic.[5] Since the absorption spectrum of the solution of the closed form **2b** did not change when it was stored in the dark at room temperature, the closed form **2b** was thermally stable at room temperature.

The ratio of the open form **2a** to the closed form **2b** in the photostationary state at 330 ± 20 nm was >99:1, which was determined with ^1H NMR spectroscopy. In contrast to the diarylethene with hydrogen bonding sites, on which we have previously reported,[4] the solubility of **2a** in organic solvents improved. For example, **2a** can be dissolved in THF and a nonpolar solvent such as toluene.

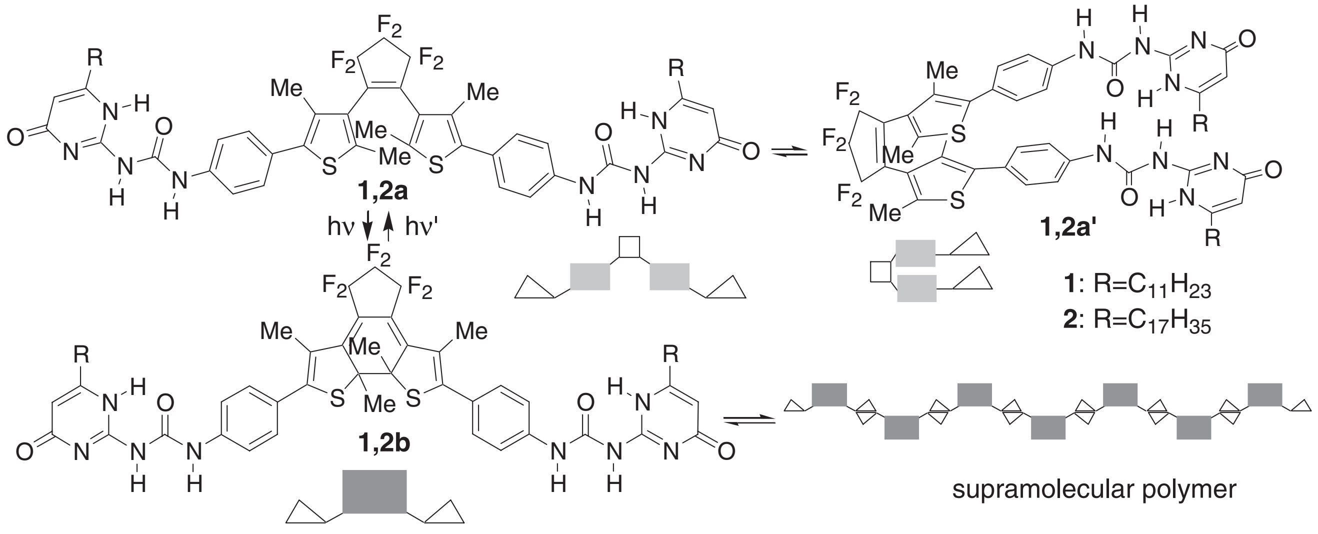

Figure 1. Photoreversible supramolecular formation.

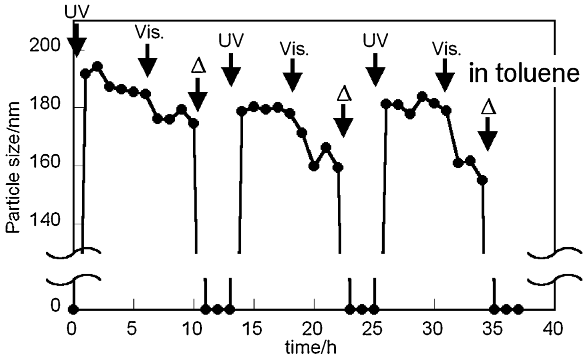

Figure 2. Particle size change of the supramolecule upon irradiation with UV and visible light in a toluene solution (20 °C, [**2**] = 3.0 × 10^{-4} mol dm^{-3}).

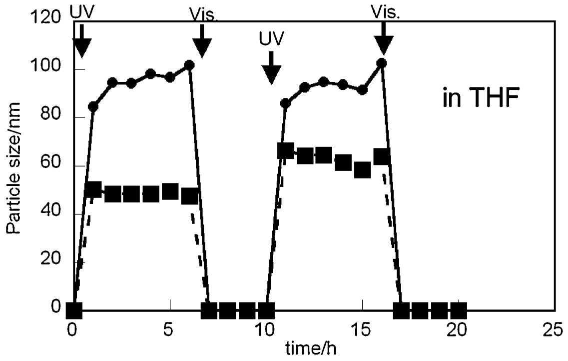

Figure 3. Particle size change of the supramolecule upon irradiation with UV and visible light in THF solutions (20 °C, circles: [**2**] = 3.0 × 10^{-4} mol dm^{-3}, squares: [**2**] = 2.0 × 10^{-4} mol dm^{-3}).

Measurements of the particle size changes of toluene and THF solutions of **2a** were performed with dynamic light scattering, the results of which are shown in Figures 2 and 3.[6] As shown in Figure 2, in a toluene solution, the particle size of the supramolecular polymer increased drastically according to the photocyclization reaction upon irradiation with UV light; hence, the color of the solution turned to blue-violet. Finally, the particle size reached about 180 nm. The length of compound **2b** was about 3 nm, at which point more than 60 molecules formed the supramolecular polymer. The particle size and the absorption spectrum were maintained when the solution was stored in the dark. Upon visible irradiation, the solution became colorless, and the ring-opening reaction took place. However, the particle size decreased slightly and did not return to its initial value. This can be explained by the stable multiple hydrogen bonding in a nonpolar solvent such as toluene, as we have previously reported.[4] The supramolecular polymer composed of the open form was, therefore, present in this conditions. After the solution was heated at 70 °C for 1 h, the supramolecular polymer dissociated, and the particle size returned to its initial value (<10 nm). These particle size changes were repeated at least 5 times. The system reached thermodynamic equilibrium after obtaining the activation energy by heating.

Figure 3 shows the particle size change of a THF solution of compound **2**. The particle size of the supramolecular polymer of the closed form **2b** in THF was about 90 nm, which was almost half of that in toluene despite having similar concentrations. Since the hydrogen bonding is weakened in a polar solvent such as THF, the particle size became smaller than that in toluene. The particle size did not change in the dark at the same temperature. Upon visible irradiation, the solution became colorless, and compound **2** returned to the open form **2a**. Simultaneously, the particle size decreased to its initial value. These phenomena were caused by the high polarity of the solvent. In the higher polar solvent (THF), the quadruple hydrogen bonding become weakened compared with that in the lower polar solvent ($CHCl_3$). Therefore, the dissociation of the hydrogen bonding became faster in a THF solution. Substitution of C_{11} chain of **1** with C_{17} chain enhanced the solubility of **2** in the polar solvents like THF. The particle size was also dependent on the concentration of the solution due to the intermolecular hydrogen bonding, as the particle size in the concentrated solution (3.0 × 10^{-4} mol dm^{-3}) was almost 1.5 times larger than that in the dilute solution (2.0 × 10^{-4} mol dm^{-3}). Nevertheless, fully photoreversible supramolecular formation at room temperature was accomplished.

In summary, a THF solution of diarylethene having two quadruple hydrogen-bonding sites changes the particle size fully photoreversibly at room temperature.

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References and Notes

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5 Synthesis of the compounds will be shown elsewhere. Compound **1a**: colorless powder, mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 13.01 (s, 2H, pyrimidinone N–H), 12.34 (s, 2H, urea N–H), 12.28 (s, 2H, urea N–H), 7.72 (d, $J = 8$ Hz, 4H; benzene-H), 7.34 (d, $J = 8$ Hz, 4H, benzene-H), 5.93 (s, 2H, pyrimidinone-H), 2.49 (s, 4H, alkyl-H), 2.36 (s, 6H, thiophene-H), 2.06 (s, 6H, thiophene-H), 1.60 (m, 4H, alkyl-H), 1.29–1.16 (m, 56H, alkyl-H), 0.86–0.83 (m, 6H, alkyl-H); Anal. Calcd for $C_{73}H_{98}F_6N_8O_4S_2\cdot 2H_2O$: C, 64.20; H, 7.53; N, 8.20%. Found: C, 64.18; H, 7.16; N, 8.10%. ^{1}H NMR spectrum and absorption spectral change upon irradiation with UV light are shown in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Website, http://www.csj.jp/journals/chem-lett/index.html.

6 Dynamic light scattering measurements were performed with an Otsuka Electronics ELS-800 and the minimum limit for the measurement is 10 nm.