

# Photoreversible supramolecular polymer formation†

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**Particle sizes of a supramolecular polymer composed of diarylethene having two quadruple hydrogen bonding moieties were changed photoreversibly.**

Supramolecular polymers have been attracting much attention as new materials since they exhibit novel characteristics compared with conventional polymers.<sup>1</sup> Supramolecular polymers are composed of small monomers and mostly the monomers are connected by multiple hydrogen bonding. One of the features of such polymers is that they are under thermodynamic equilibrium, hence the stability of the supramolecular polymer is dependent on external stimuli such as temperature and medium. Therefore, supramolecular polymers are called “reversible polymers”. Indeed, change of the external stimuli, for example temperature, affect the association of monomers since supramolecular formation is thermally reversible.<sup>1</sup> As another example, photoinduced dissociation of the supramolecular polymer has been accomplished.<sup>2</sup> However, these systems utilize the change of association of hydrogen bonding of the corresponding monomers “one-way” by the external stimuli and a supramolecular polymer with a “reversible switch” has not yet been reported.

Switching of supramolecular formation has been widely studied and reported.<sup>3</sup> A photoswitch is the one of the most attractive switches for supramolecules since it is not necessary to add any substrate but to irradiate with light as an external stimulus. So, fully reversible switching can be achieved by photoirradiation. Among photochromic compounds, dithienylethenes are thermally irreversible and highly fatigue resistant.<sup>5a</sup> Therefore artificial receptors having a photochromic dithienylethene moiety as a photoreversible switch have been reported.<sup>3–5</sup>

These facts encouraged us to develop a photoswitchable supramolecular polymer which reversibly changes molecular weight and polymeric form by photoirradiation. Here we demonstrate photoreversible supramolecular polymer formation formed by intermolecular multiple hydrogen bonding by use of a dithienylethene photoswitch.

Fig. 1 shows the concept for a photoswitchable supramolecular polymer. The molecule has two ureidopyrimidinone groups at both sides. These groups perform DDAA type (or DADA type, D: proton donor, A: proton acceptor) “quadruple hydrogen bonding” inter- or intramolecularly.<sup>1</sup> The open form of the dithienylethene photoswitch is flexible and has two conformations, anti-parallel conformation **1a** and parallel conformation **1a'**. These conformations exchange slowly at ambient temperature.<sup>4</sup> For example, two conformations of the similar dithienylethene

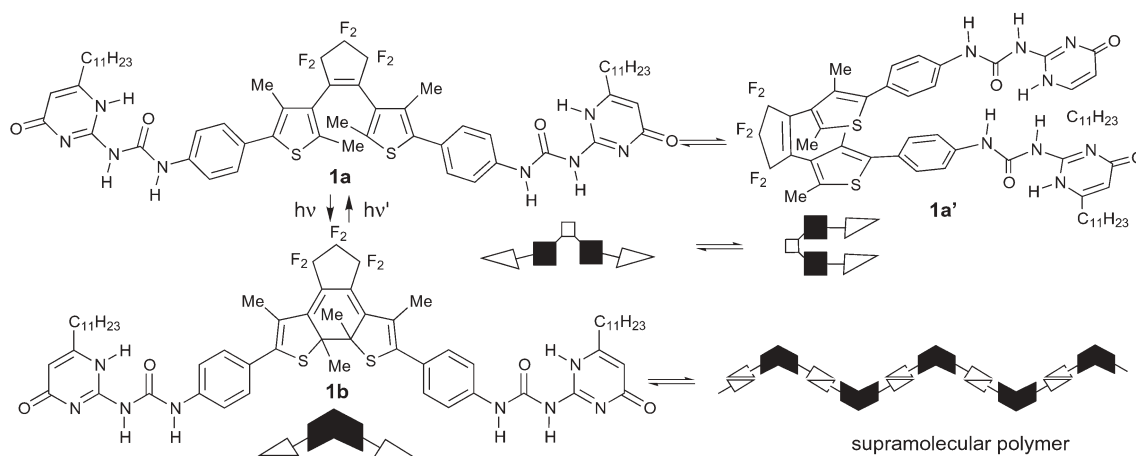
exchange 50 times per second at 80 °C, this is slower than the NMR timescale therefore one can observe both spectra in <sup>1</sup>H NMR at ambient temperature.<sup>4</sup> The supramolecule composed of the open form is assumed to be relatively unstable since the supramolecular formation may accompany the large entropy loss due to the loss of flexibility and the molecular weight of the supramolecule is expected to be small. On the other hand, the photogenerated closed form has a rigid structure. Hence, the supramolecular polymer composed of the closed form is assumed to be stable and the number of the associated monomers will be large. These processes are reversibly photoswitchable upon irradiation with light having different wavelengths according to the photochromic reaction.

A dithienylethene having two hydrogen bonding sites **1a** was synthesized and purified by using size exclusion chromatography using CHCl<sub>3</sub> as eluent.‡ The absorption spectral change upon irradiation with 366 nm light is shown in Fig. 2. A colorless solution of the open form **1a** ( $1.12 \times 10^{-4}$  mol dm<sup>-3</sup> in CHCl<sub>3</sub>) turned to a violet solution by UV irradiation, indicating that **1a** changed into the photoisomer **1b**. Visible irradiation (>540 nm) returned the initial spectrum, therefore compound **1** is photochromic.

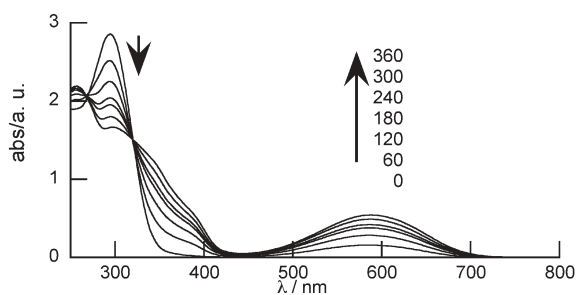
At the concentration of **1a** in CHCl<sub>3</sub> for measuring absorption spectra at 25 °C ( $1.12 \times 10^{-4}$  mol dm<sup>-3</sup>), the reversible conversion by irradiating with UV and visible light could be carried out without precipitation. However, when the concentration of **1a** in chloroform was increased to  $2.0 \times 10^{-4}$  mol dm<sup>-3</sup>, a blue solid was precipitated when **1a** solution was irradiated with UV light. This phenomenon revealed that the photogenerated closed form **1b** highly aggregated and the formed supramolecule has poor solubility in CHCl<sub>3</sub> at this temperature. While the open form **1a** can be dissolved in chloroform up to  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>. Except for CHCl<sub>3</sub>, we could not find any other suitable solvent for dissolving compound **1a**.

The <sup>1</sup>H NMR spectrum of the open form **1a** in CDCl<sub>3</sub> (300 MHz,  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup>, 25 °C) indicated three kinds of acidic protons at 12.3, 12.5 and 13.0 ppm and their intensity ratio was 1 : 1 : 1. These protons can be assigned as the protons at urea moieties (each two protons) and pyrimidinone moieties (each one proton). The chemical shifts of these protons did not change upon changing the concentration between  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> and  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>. The chemical shifts of the acidic protons of the open form **1a** were independent from this concentration region. It is assumed that the acid protons took part in intramolecular hydrogen bonding or the chemical shifts were not affected in this concentration range due to high association. The <sup>1</sup>H NMR spectrum showed that only one of the conformations was dominant since only two kinds of the methyl protons of thiophene rings were found in the spectrum. The quantum yield for the

† Electronic supplementary information (ESI) available: NMR spectrum of **1a**. See <http://www.rsc.org/suppdata/cc/b4/b415114c/>  
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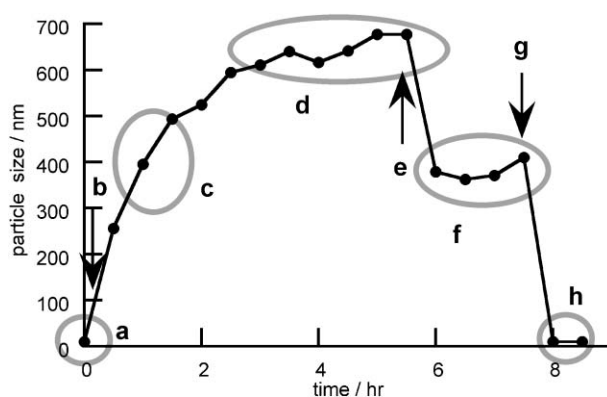
**Fig. 1** Concept for photoswitchable supramolecular polymer.



**Fig. 2** Absorption spectral change of **1** ( $1.12 \times 10^{-4}$  mol  $\text{dm}^{-3}$  in  $\text{CHCl}_3$ ) upon irradiation with 366 nm light. Numbers denote irradiation time in seconds.

photocyclization reaction was estimated as 0.26.<sup>6</sup> The cyclization quantum yield is known to be dependent on the ratio of the anti-parallel conformation, therefore the anti-parallel conformation was more stable than parallel conformation in this condition.<sup>4b,6</sup> Thus the anti-parallel conformation of the open form is assumed to form the small supramolecule which is soluble in  $\text{CHCl}_3$ . The small supramolecule formation is due to the flexibility of the open form. In addition, the undetectable amount of the parallel conformation could act as a “stopper” and prevent the formation of a large supramolecule.

Fig. 3 shows the average particle size change of **1**, which was estimated by dynamic light scattering (DLS) measurements, upon irradiation with UV and visible light (in  $\text{CHCl}_3$ -ethanol (97 : 3),  $1.22 \times 10^{-4}$  mol  $\text{dm}^{-3}$ , 25 °C).<sup>§</sup> Under these conditions, no precipitation took place after UV irradiation. The particle size of the open form **1a** in this condition could not be estimated by our DLS instrument (Fig. 3, a). The minimum limit of the measurable particle size of our DLS instrument is about 10 nm, therefore we assumed that the average size of the particle was smaller than 10 nm. From the  $^1\text{H}$  NMR study the open form also formed a supramolecule, therefore the open form **1a** existed as not supramolecular polymer but as a small supramolecule in these conditions. After UV irradiation (Fig. 3, b), the particle size gradually increased (Fig. 3, c) at 25 °C and after 3 h that became constant and was about 650 nm (Fig. 3, d). The length of the closed form **1b** monomer is about 3 nm and the molecular weight



**Fig. 3** Particle size change of the supramolecule upon irradiation with UV and visible light. Meanings of the symbols are indicated in the text.

of **1b** is estimated as about 1200, then the photogenerated supramolecular polymer is assumed to be composed of at least 200 monomers and the molecular weight of the supramolecule was estimated as more than  $2.5 \times 10^5$  in this condition. Visible irradiation decolorized the solution and the closed form **1b** returned to the open form **1a** (Fig. 3, e). The particle size estimated by DLS was decreased by visible irradiation from 650 nm to 400 nm (Fig. 3, f). This decrease is due to the flexibility of the open form **1a** since **1a** is a thermodynamic mixture of the long anti-parallel and the short parallel conformations (Fig. 1). The supramolecule formed in the closed form was maintained even after photoisomerization under these conditions since it may take long time to reach the thermodynamic equilibrium of the supramolecule of the open form **1a** due to the strong multiple hydrogen bonding. Hence, this state is assignable to the large supramolecule of the open form without thermodynamic equilibrium. After heating the solution at 60 °C for 30 min (Fig. 3, g), the particle size returned to the initial state (<10 nm) (Fig. 3, h). This phenomenon indicated that the open form reached thermodynamic equilibrium upon heating. That is to say, heating accelerated the dissociation of the large supramolecule and the small supramolecule composed of the open form was generated. The molecular weight of the supramolecular polymer composed of

the closed form was assumed to be increased and the highly associated supramolecular polymer could not be dissolved in these conditions.

The photoreversible supramolecular formation has been accomplished by the photochromic dithienylethene bearing two hydrogen bonding moieties with the aid of heating.

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## Notes and references

‡ Compound **1a**, colorless solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C, 300 MHz, TMS)  $\delta$  0.85 (m, 6H), 1.24 (m, 32H), 1.66 (m, 4H), 2.06 (s, 6H), 2.36 (m, 4H), 2.49 (s, 6H), 5.94 (s, 2H), 7.34 (d, 2H,  $J = 8\text{Hz}$ ), 7.72 (d, 2H,  $J = 8\text{Hz}$ ), 12.30 (s, 2H), 12.36 (s, 2H), 13.06 (s, 2H); ESI-TOF MS  $m/z$  579.3871

( $\text{M} + 2\text{H}^+$ ).  $^1\text{H}$  NMR spectrum of the closed form **1b** could not be measured due to its low solubility.

§ DLS measurements were performed with Otsuka Electronics ELS-800 at the Analytical Research Center for Experimental Sciences in Saga University.

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