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Hydrogen bonded molecular assembly by reversible cyclization reaction of anthracene†

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A hydrogen bonded molecular assembly of 2-ureido-4(1*H*)-pyrimidinone was constructed by utilizing an anthracene photodimerization reaction.

The study of the control of the conformation of a supramolecular structure is of importance in developing functionalized materials in nanotechnology. In particular, photochemical control of the material properties is an excellent approach, since photochemical reactions should occur only in the time domain of the excited state and in the space domain of the light irradiation. Furthermore, the reactions are controlled by the intensity and the wavelength of light.

In connection with the photochemical control of macromolecular structure, we have reported that a stilbene dendrimer of molecular weight as high as 6500 undergoes *trans*-to-*cis* isomerization with a quantum yield of 0.24.[1] The difference in molecular structure between the *trans*-form and the *cis*-form of the stilbene core should bring about the change of the whole conformation of the dendrimers.[1–4]

In the meantime, non-covalent interactions such as hydrogen bonding, π–π interaction, and metal–ligand interaction have been used to construct supramolecular assemblies in which it is possible to exhibit the function of switching, because the association character can be controlled by external stimulation such as temperature, pH, and light.[5] Especially, hydrogen bonding is a most useful interaction in self-assembly because of the directional and selective character of its association and its moderately high association constant.

Recently, Meijer *et al.* introduced the concept of using quadruple intermolecular hydrogen bonding to prepare the linear polymers formed by the self-assembly of two 2-ureido-4(1*H*)-pyrimidinone (UPy) units, which dimerize strongly in a solvent like $CHCl_3$ with a dimerization constant as high as > 10^6 M^{-1}.[6,7] Because of its high dimerization constant, one can use the UPy group to construct supramolecular systems having a varying photoresponsive chromophore.

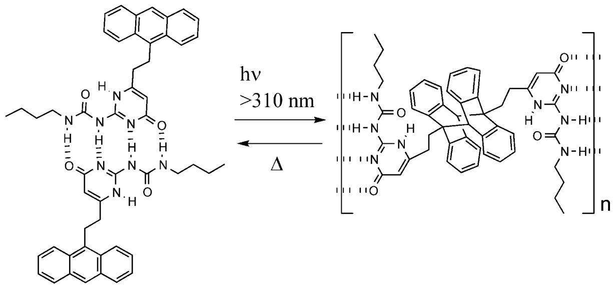
We have previously reported that UPy derivatives having a pyrene group or an *N*,*N*-dimethylaniline group undergo efficient excimer or exciplex formation even in dilute solution as low as 10^{-5} M in chloroform due to the formation of an intermolecular quadruple hydrogen bonded dimer.[8] We wish to report here the synthesis of a UPy derivative (**1**) having an anthracene ring (Scheme 1).‡ It is well known that anthracene derivatives undergo a [4 + 4] photocyclization reaction on irradiation.[9] The reaction can be used to connect and disconnect two molecules reversibly. Therefore, compound **1** is expected to undergo formation and dissociation of hydrogen bonded oligomer reversibly by photochemical and thermal processes.

Fig. 1 shows the absorption spectrum of **1** in chloroform. The absorption band assigned to the anthracene ring appeared at wavelength longer than 320 nm and at 258 nm. The change of the absorption spectrum on irradiation with a 150 W Xe lamp through a UV-31 filter is also shown in Fig. 1. The absorbance of the anthracene ring decreased with concomitant increase of absorbance around 280 nm. This spectrum change indicated that the anthracene ring in **1** underwent a [4 + 4] cyclization reaction on irradiation.[9]

The spectral change in ^{1}H NMR on irradiation with a 150 W Xe lamp through a UV-31 filter was also observed as shown in Fig. 2. The anthracene proton signal [δ 7.4 (m, 4H), 7.9 (d, 2H), 8.2 (d, 2H), 8.4 (s, 1H) ppm] disappeared and new multiplet peaks appeared at 6.8 ppm which were assigned to the proton of the *o*-xylene system. In addition, the peak of the anthryl methyl proton of **1** was observed at 4 ppm before irradiation, while that of the corresponding proton after irradiation was observed at 2.5 ppm. The change of ^{1}H NMR spectrum was consistent with the formation of an anthracene photodimer.[9] The NH proton peak that formed intermolecular hydrogen bonding broadened and finally disappeared on irradiation with light, indicating that the photodimer **2** is associated by intermolecular hydrogen bonding.

Photodimer **2** was detected in the ESI-MS spectrum. The peaks of *m*/*z* at 851.46 and 1680.92 were assigned to be [M + Na]$^+$ and [2M + Na]$^+$ of compound **2**, respectively. Compound **2** has two UPy units in the molecule capable of forming hydrogen bonded polymer. Thus, observation of the signal of [2M + Na]$^+$ also indicated that compound **2** associates by intermolecular hydrogen bonding.

We examined the retroreaction as well. Compound **2** was dissolved in *o*-dichlorobenzene, and the absorption spectrum change was observed at the temperature of 125 °C. Fig. 3 shows the time development of the appearance of the absorption



1 dimer **2**

Scheme 1

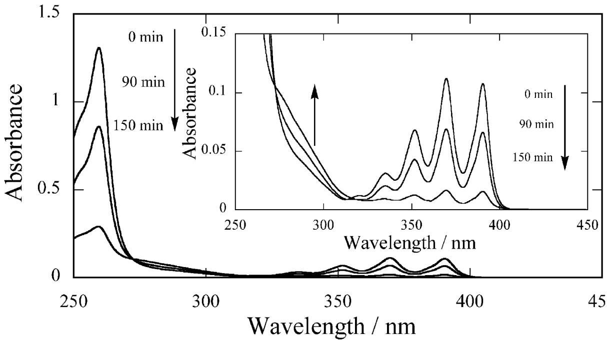


Fig. 1 Change of absorption spectrum of **1** (1×10^{-5} M) on irradiation with a 150 W Xe lamp through a UV-31 filter in chloroform.

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† Electronic supplementary information (ESI) available: thermal change of ^{1}H NMR spectrum of **2**. See http://www.rsc.org/suppdata/cc/b3/b304034h/

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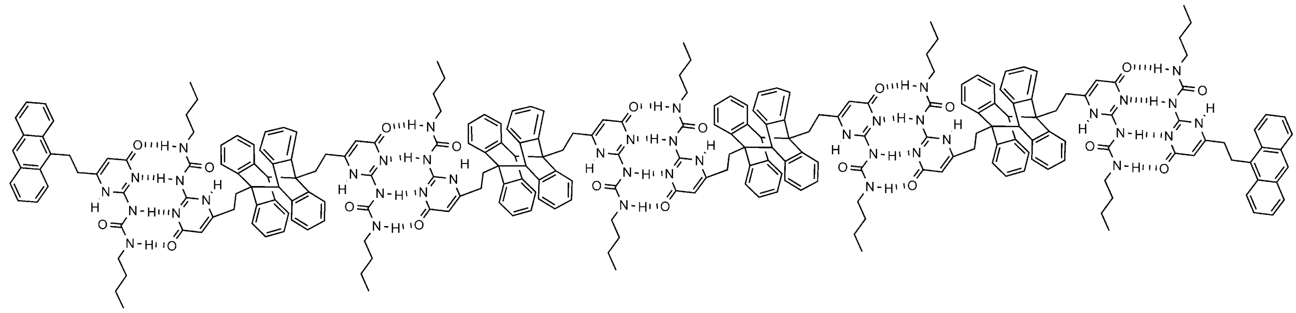

Fig. 4 Expected conformation of oligomer of **2** associated with **1** in 25 mM NMR sample solution.

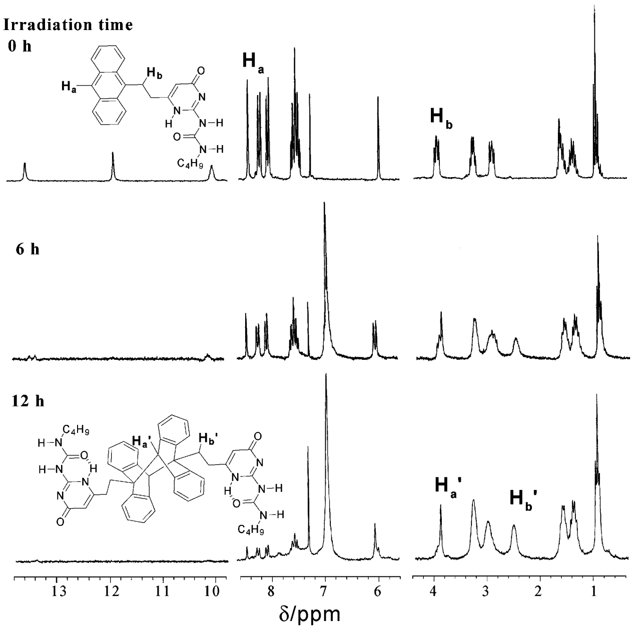

Fig. 2 Change of ^{1}H NMR spectrum of **1** (25 mM) in chloroform-d on irradiation with a 150 W Xe lamp through a UV-31 filter.

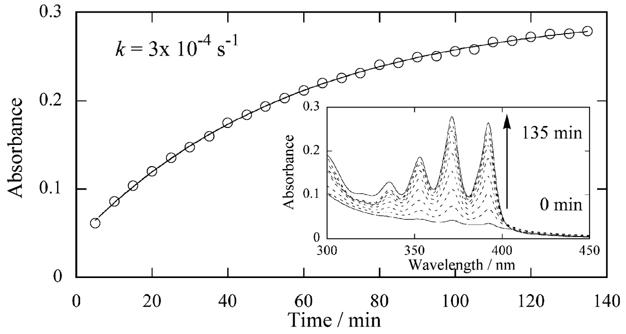

Fig. 3 Time development for thermal cycloreversion of anthracene photodimer in **2** (2×10^{-5} M) at 125 °C in *o*-dichlorobenzene.

assigned to the anthracene, and the rate constant of the retroreaction was determined to be 3×10^{-4} s^{-1} at 125 °C. The thermal conversion of the photodimer to the anthracene monomer was also observed in the ^{1}H NMR spectrum in DMSO-d$_6$, the conversion being complete in 15 min at 150 °C.

It is reported that the half-life, $t_{\frac{1}{2}}$, of the head-to-head photodimer of 9-methylanthracene ($t_{\frac{1}{2}}$ = 1 h at 38 °C) is very different from that of the head-to-tail photodimer ($t_{\frac{1}{2}}$ = 1 h at 149 °C).[9] On the basis of these results, compound **2** should exist in a head-to-tail conformation that facilely forms a hydrogen bonded polymer.

The formation of **2** on photoirradiation reached the plateau value of *ca.* 80% calculated from the integral of the proton signal in the NMR spectrum shown in Fig. 2, when the concentration of the starting material **1** was 25 mM. Further irradiation of the sample solution gave a precipitate, indicating that the solubility of the photodimer was less than 1×10^{-5} M in chloroform. This result clearly shows that the hydrogen bonded oligomer of **2** should exist as a structure having the monomer **1** at both ends as shown in Fig. 4.

We have demonstrated in this preliminary communication the possibility of constructing a reversible hydrogen bonded polymer by utilizing an anthracene photodimerization reaction and a thermal retroreaction.

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Notes and references

‡ Compound **1**: ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 0.88 (3H, t, J = 7.6 Hz), 1.32 (2H, m), 1.45 (2H, m), 2.78 (2H, m), 3.16 (2H, t, J = 6.8 Hz), 3.89 (2H, m), 5.91 (1H, s), 7.55 (4H, m), 8.10 (2H, d, J = 8.2 Hz), 8.35 (2H, d, J = 8.2 Hz), 8.52 (1H, s), 9.75 (1H, br), 11.6 (1H, br), 12.8 (1H, br) ppm. ESI-MS calcd for $C_{25}H_{26}N_4O_2$ [M + Na]$^+$ = 437.20, found 437.22.

Compound **2**: ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ 0.91 (6H, t, J = 7.2 Hz), 1.34 (4H, m), 1.49 (4H, m), 2.31 (4H, m), 3.00 (4H, m), 3.20 (4H, m), 3.98 (2H, s), 5.96 (2H, s), 6.79 (4H, t, J = 7.3 Hz), 6.85 (4H, t, J = 7.3 Hz), 6.96 (4H, d, J = 7.3 Hz), 7.09 (4H, d, J = 7.3 Hz), 9.69 (2H, br), 11.7 (2H, br), 12.8 (2H, br) ppm. ESI-MS calcd for $C_{50}H_{52}N_8O_4$ [M + Na]$^+$ = 851.40, found 851.46.

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