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Mirror Image Nanostructures of New Chromogenic Azobenzene Gels by Introduction of Alanine Moiety

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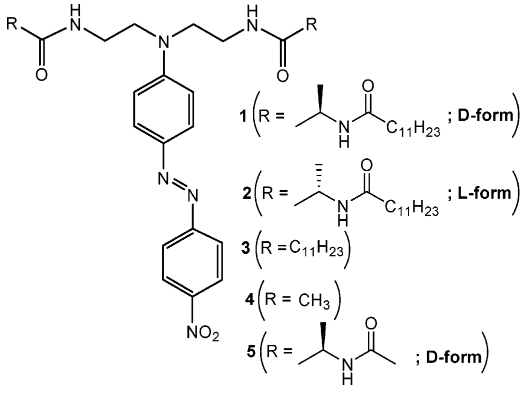
Self-assembly is a powerful tool to prepare functional molecular materials.[1−5] One example is a fibrous molecular assembly in organic solvents, which leads to the formation of physical organogels. In these materials, noncovalent interactions such as hydrogen bonding,[2−6] lipophilic,[7] and $\pi-\pi$ interactions[1d,8] derive such one-dimensional assembly of gelators. Among these interactions, hydrogen bonding or $\pi-\pi$ aromatic stacking is known to be one of the most predominant interactions to govern the gelation. Furthermore, these gelators often have functional groups involved in molecular interactions with chiral groups,[3,4,6d−e] which allows the self-assembled helical structures to be applicable in various fields such as asymmetric catalyst,[9] sensors,[10] and biomolecular separation.[11] For example, cyclohexane diamine[6d] and diurea[6f] derivatives having chiral centers at the amino groups are known to be efficient gelators within one-dimensional self-assembly by the hydrogen bonding.

Table 1. Gelation Ability[a] of 1−5 in Organic Solvents

solvent	1	2	3	4	5
ethyl acetate	I	I	G	S	I
tetrahydrofuran	G	G	G	S	I
methanol	G	G	S	S	PG
n-butanol	G	G	S	S	PG
cyclohexane	I	I	I	S	I
n-hexane	I	I	I	S	I
benzene	G	G	PG	S	I
toluene	G	G	G	S	I
p-xylene	G	G	S	S	I
m-xylene	G	G	S	S	I
chloroform	I	I	I	S	I
acetic acid	PG	PG	G	S	S

[a] Gelator = 5.0 wt %. G, stable gel formed at room temperature; S, soluble; I, insoluble; PG, partially gelatinized.

The stereochemical series of amino acid groups not only act as an effective unit to the helical morphological control of the self-assembly but also give a deriving force to form the self-assembled organogel by the intermolecular hydrogen-bonding interaction. With those objects in mind, we have newly synthesized a stereochemical series of *p*-nitro-azobenzene-coupled bis-alanines **1**, **2**, and **5** as shown in SI Schemes 1 and 2 (see Supporting Information).[12] Compounds **3** and **4** in the absence of alanine units or long-chain alkyl groups were synthesized as references to confirm the critical roles for the intermolecular hydrogen-bonding interaction of the numbers of amide groups and the hydrophobic interaction between alkyl chain groups in gel formation, respectively. We herewith report on morphological control and the self-assembled behaviors of the organogels **1**−**3**, respectively.



To test the gelation, **1**−**5** are heated in a sealed glass tube until the solid is dissolved, and then they are cooled to room temperature (Table 1). It is necessary for the sample to be highly viscous in the macroscopic manifestation. Interest-

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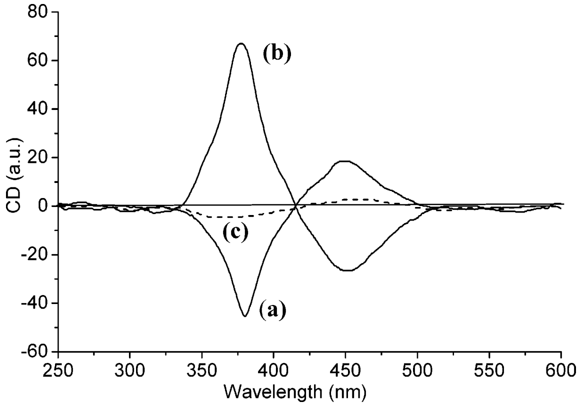

Figure 1. CD spectra of (a) **1** and (b) **2** in gel phase and (c) **1** in DMSO solution phase.

ingly, commonly, the alanine-appended azobenzene gelators **1** and **2** showed seven "G" (stable gel) marks with such as alcoholic and aromatic solvents, one "PG" (partially gel) marks, and four "I" (insoluble) marks, indicating that **1** and **2** act as versatile gelator of various organic solvents.

On the other hand, **3** exhibited four G marks, four S marks, one PG, and three I marks. These results support the view that the multiple intermolecular hydrogen-bonding sites introduced in **1** and **2** play an important role as a driving force to form the gels in various organic solvents. **4** and **5** exhibited 12 S and 2 PG marks due to the relatively high and low solubility, respectively. These findings strongly imply that long-chain alkyl groups are necessary for the formation of the gels in various organic solvents.

To characterize the helical aggregation mode in the organogel phase, we observed CD spectra of acetonitrile gels **1**−**3**. The $\lambda_{\max}$ in the UV absorption spectra of **1** and **2** appear at around 425 nm. In the CD spectra, $\lambda_{\theta=0}$ value appears at about 422 nm with which one can thus assign the CD bands arising from the exciton coupling. The CD spectrum of the self-assembled **1** exhibits a positive sign for the first Cotton effect (Figure 1a), indicating that the dipole moments are oriented in a clockwise direction in the aggregate of the gelator. In contrast, self-assembled **2** gives a negative sign (Figure 1b), implicating an anticlockwise direction. These CD spectra of **1** and **2** clearly support the view that the aggregates form with right- and left-handed helical structures, respectively. The CD intensity in the sol sample of **1** was much weaker than those obtained from the gel sample of **1** (Figure 1c). It is quite often found that a well-ordered chromophoric aggregate in the gel phase gives CD intensities much stronger than less ordered ones in sol phase in cholesterol-based gelators. The acetonitile gel **3** is, however, CD-silent even in high concentration of gel, supporting again that chiral arrangement of **1** and **2** is mainly due to the alanine moieties.

To obtain visual insights into the aggregation mode, we obtained the xerogel structures of the acetonitrile gels **1**−**3** by SEM. Figure 2, panels a and b, shows SEM images of the xerogels **1** and **2**, respectively, in which the right-handed and the left-handed helical fibers of 500−1000 nm diameter and micrometers in length are indicated. So, it is certain that the macroscopic helicities of the alanine-appended gels **1** and **2** are directly reflected from the microscopic helicities of them. Furthermore, these findings imply that the macroscopic helical direction of superstructures of the alanine-appended chromogenic gels is effectively tunable by enantiomeric amino acid units. On the other hand, the xerogel **3** exhibits the linear fiber structure with 50−200 nm diameter and micrometers in length (Figure 2c).

To obtain more detailed information about the self-assembled structures, FT-IR, powder-XRD, and ^{1}H NMR spectra were measured. In the FT-IR spectra of the *p*-xylene gels **1** and **2**, the characteristic peaks appeared at 3286 and 1638 cm^{-1}. These peaks are assignable to N−H and C═O stretching vibrations, respectively, attributable to the strong intermolecular H-bonding interactions between amide carbonyl groups, which is quite similar to the case of the solid-state (1640 cm^{-1}). In *p*-xylene solution, however, the stretching bands of the amide group for both gelators **1** and **2** appeared at 1656 cm^{-1}, indicating that the strong H-bonding networks formed in gel state are disentangled in the solution state (Supporting Information Figure S1).

To understand the H-bonding and the $\pi-\pi$ stacking interactions operating in the self-assembled structures, we carried out ab initio calculations and molecular modeling. The molecules **1** and **2** are our main interest, but the molecules are quite large. So, we carried out ab initio calculations for molecule **5** to obtained energy minimized geometry using a suite of Gaussian 98 programs.[13] The interplanar distance between two azobenzene moieties is about 4.6 Å, and the interatomic distance in the H-bonding between the oxygen and nitrogen atoms should be less than 3.4 Å. These values are close to the typical distances in $\pi-\pi$ stacking and H-bonding (see Supporting Information Figure S2). Thus, the H-bonding and $\pi-\pi$ stacking interactions are operating to facilitate the helical assembled structures.

The X-ray diffraction (XRD) patterns of **1**−**3** were measured to obtain the information on the molecular packing

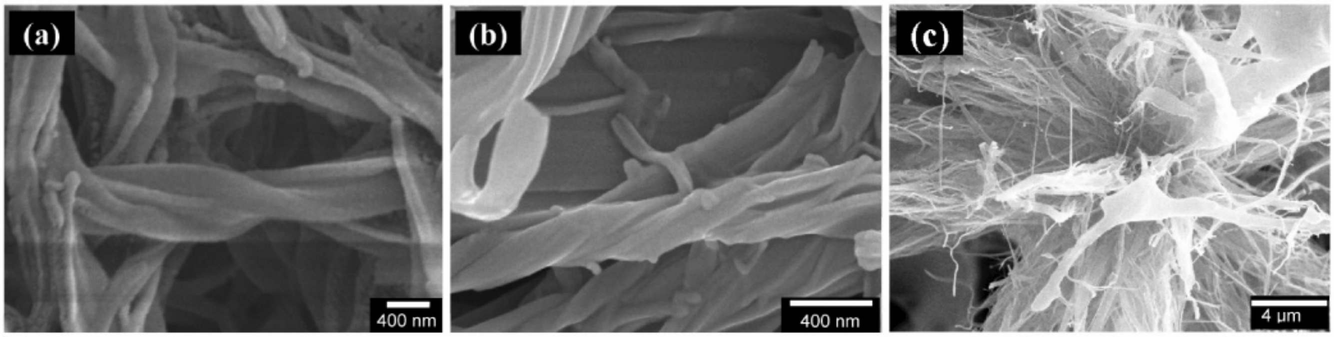

Figure 2. SEM images of acetonitrile gels obtained from (a) **1**, (b) **2**, and (c) **3**.

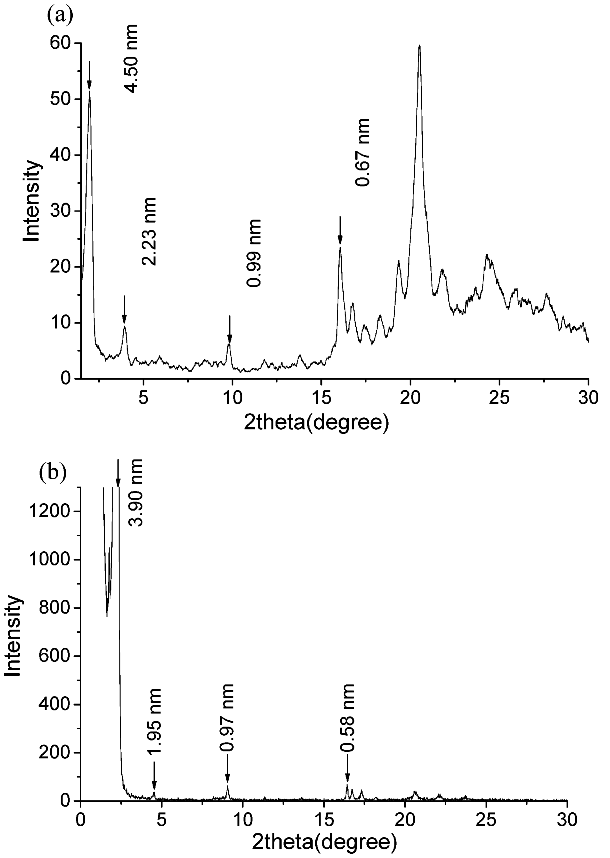

Figure 3. Powder XRD patterns of xerogels (a) **1** and (b) **3**.

in these gels. The X-ray diffraction patterns of the xerogels **1**−**3** prepared from acetonitrile show periodical reflection peaks (Figure 3), an indication that **1**−**3** indeed assemble into a lamellar organization. The obtained long spacings (*d*) of xerogels **1** and **2** are 4.50, 2.23, 0.99, and 0.67 nm, corresponding to the ratio of 1:1/2:1/3:1/4. The 4.50 nm length is twice smaller than the extended molecular length of **1** and **2** (3.20 nm by the CPK molecular modeling) but larger than the length of one molecule. These results strongly suggest that the self-assembled organogels **1** and **2** form a bilayer structure with a relative large region interdigitated in terms of $\pi-\pi$ stacking between azobenzene moieties. In addition, the obtained long spacings (*d*) of the xerogel **3** (one molecular length: 2. 90 nm) are 3.90, 1.95, 0.97, and 0.58 nm, corresponding to the ratio of 1:1/2:1/3:1/4. This finding supports that organogel **3** maintains an interdigitated bilayer structure. The length of the bilayered structure of the self-assembled organogel **3** is much shorter than those of organogels **1** and **2** because the length of bilayered structure highly depends on the length of molecule.

For further probes about the $\pi-\pi$ stacking between azobenzene moieties, we have used two methods of ^{1}H NMR technique. First, temperature variable experiment in dilute gel state was conducted. Interestingly, in the aromatic region, there are two different species: aggregate and monomer. As shown in Figure 4a, aromatic peaks of aggregate **1** in dilute gel state appeared at 7.88 (d, $J = 8.3$ Hz), 7.68 (d, $J = 8.3$ Hz), 6.98 (d, $J = 8.3$ Hz), and 6.68 ppm (d, $J = 8.3$ Hz) whereas aromatic peaks of monomer **1** appeared at 8.37 (d, $J = 9.2$ Hz), 7.94 (d, $J = 9.2$ Hz), 7.83 (d, $J = 9.3$ Hz), and 7.00 ppm (d, $J = 9.3$ Hz). Upon heating, aromatic peak intensities of monomer **1** gradually increase whereas those of aggregate **1** decrease at 7.88, 7.68, 6.98, and 6.68 ppm because the chemical shift difference between aromatic protons H_a and H_d as well as H_b and H_c may arise from $\pi-\pi$ stacking and the hydrogen-bonding interactions. Second, the NOESY experiment was carried out with **1** in DMSO-d_6

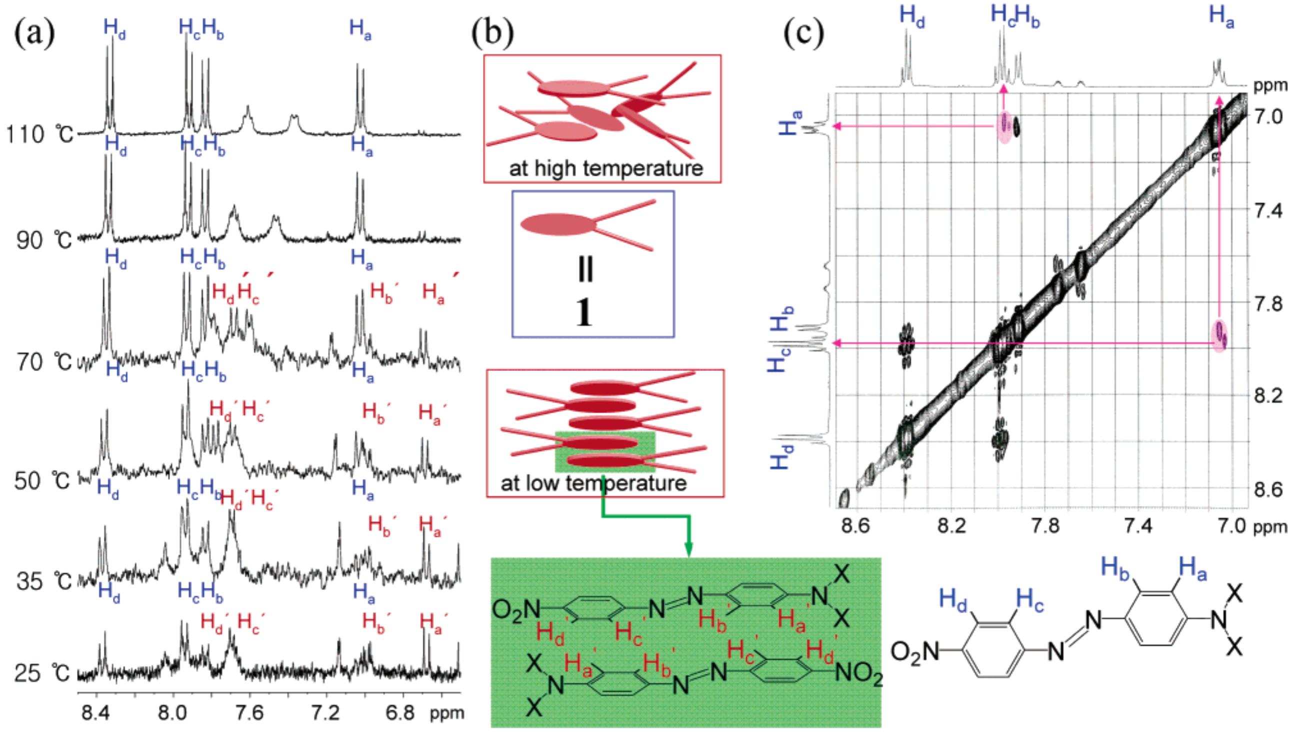

Figure 4. (a) Variable temperature ^{1}H NMR studies of the acetonitrile gel of **1**. (b) Proposed packing models of **1** at high and low temperatures. (c) NOESY spectrum of **1** at a concentration of 7.30 mmol in DMSO-d_6.

(Figure 4c). High concentration of **1** resulted in a number of additional NOE cross-peaks, especially between the azobenzene moieties, indicating that **1** is aggregated by $\pi-\pi$ stacking between azobenzene moieties. So, both NMR and XRD experiments gave a precise evidence for the B model structure (Supporting Information Figure S3 and see graphical abstract), almost fully stacked between azobenzene groups.

In conclusion, we reported the novel self-assembling behavior of organic gelators **1**−**3** having a chromogenic diazo group. These gels formed through intermolecular hydrogen-bonds, $\pi-\pi$ stacking, and hydrophobic interaction in various organic solvents. In particular, formation of intermolecular hydrogen bonds in the alanine unit plays an intrinsic role in their fiber self-assemblies along with an efficient gelation. The self-assembled morphological helicity can be easily controlled by alanine units. Thus, alanine-appended chromogenic gelators **1** and **2** are not only effective in gelation but also useful as a component of functional soft materials. This molecular design toward the control of hydrogen-bonded structures would serve a new approach for the development of low-molecular-weight gelators and various functional molecular materials.

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Supporting Information Available: Synthetic method of **1**, **2**, and **5**; FT-IR spectra of **1** in the organogel, solid, and solution states; proposed structures for molecular packing structures of organogels **1** and **2**; and assembled structures for eight molecules of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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