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Self-assembled organogels based on two-component system

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ABSTRACT

Organogels were produced by the self-assembly of two organogelators, 3,5-bis(dodecanoylamino)-benzoic acid and aromatic amines, in nonaromatic hydrocarbon solvents, through hydrogen bonding, aromatic stacking, and van der Waals interactions. 3,5-Bis(dodecanoylamino)benzoic acid has one carboxylic acid group for hydrogen bonding with amines and two alkylamide groups that can participate in interlayer hydrogen bonding and van der Waals interactions. The shape and size of the aromatic amines have a significant effect on the gel properties as well as their structures. A variety of organogels were realized by forming complexes of 3,5-bis(dodecanoylamino)benzoic acid and various amines with an aromatic group in nonaromatic hydrocarbon solvents.

1. Introduction

Gels are materials that are frequently encountered but seldom understood. Gelation is a well-known phenomenon, and gels are used in a variety of fields such as hydrometallurgy, cosmetics, food processing, lubrication, the recovery of spilled crude oil, and drug delivery.[1] Recently, organogelation that takes place through the self-assembly of low molecular weight gelators (LMWG) in organic solvent has attracted considerable attention.[2,3] The structure of aggregates in gels is determined by the direction and strength of the intermolecular interactions associated with the aggregation process. Gelator molecules self-assemble through noncovalent interactions such as hydrogen bonds, π–π interactions, solvophobic effects, and van der Waals forces, which play important roles in determining the gelation characteristics and the structures of the gels. The gelation process is accompanied by the one-dimensional growth of a gelator in various types of fibers,[4] helices,[5] and tubes.[6] In order to control the structures and properties of organogels, synthetic amphiphilic molecules have been used as gelators, because many biological systems comprise a variety of amphiphiles, exhibiting three-dimensionally ordered phases.[7] However, very little is known about the mechanism of gel formation and the influence of the gelator structure on gel behavior.

In contrast to single LMWG gel systems, new gelation systems using two components have been developed.[8,9] The most important feature of these two-component systems is the ease with which the properties and structures of the gel can be modulated by changing the molar ratio of the two components or the structure of each component. Smith and co-workers reported excellent examples[8] in which a two-component gelator system enhances the tunability of gel-phase materials and in which the macroscopic properties and microstructural features of these gels can be controlled.

Here we report two-component gelator systems that can produce various types of organogels depending on amines (**1**–**5**) having aromatic cores. A two-component gel system consists of an (alkanoylamino)benzoic acid with an amphiphile group (**A**, **B**) and amines with aromatic cores (**1**–**5**) (Fig. 1). 3,5-Bis(dodecanoylamino)benzoic acid (**A**) has one carboxylic acid group for hydrogen bonding with amines and two alkylamide groups that can form interlayer hydrogen bonds and generate van der Waals forces. 4-(Dodecanoylamino)benzoic acid (**B**) has one carboxylic acid group for hydrogen bonding with amines and one alkylamide group that can form interlayer hydrogen bonds along with generating van der Waals forces. Furthermore, the aromatic groups of the amine component have different shapes and sizes, and are expected to show different packing patterns and strengths when assembled with the amphiphile group on compound **A** or **B**. Compound **6** was used as a control to determine if an aromatic moiety in the amine component has any effect on gelation.

2. Results and discussion

2.1. A computational calculation

The initial experiments were performed to see whether the complexes formed between the two components could make a discotic structure through hydrogen bonding and aromatic stacking interactions. In order to ascertain that 3,5-bis-(dodecanoylamino)benzoic acid (**A**) and 1,3,5-tris(4,5-dihydro-1*H*-imidazol-2-yl)benzene (**1**) could

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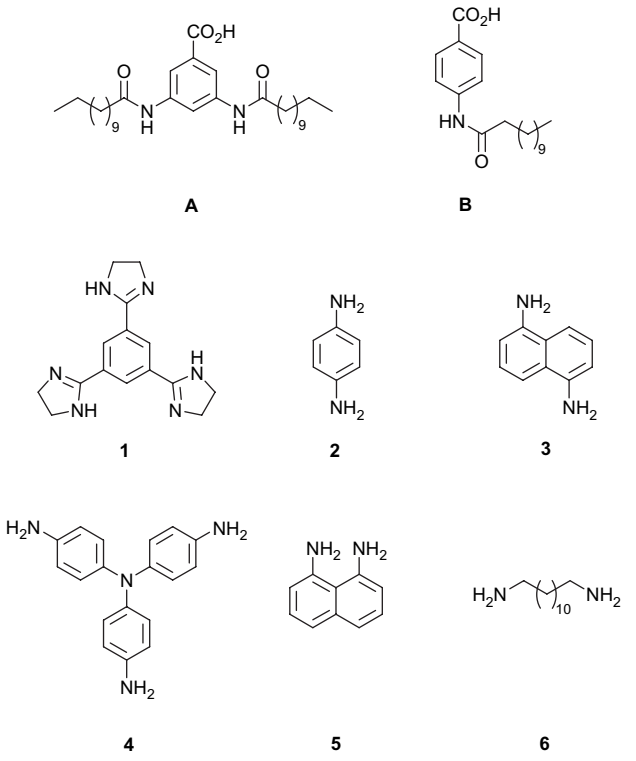

Figure 1. Molecular structures of organogelators.

form a stable 3:1 complex, computational calculation was performed with compound **1** and 3,5-bis(acetylamino)benzoic acid (simplified model compound of 3,5-bis(dodecanoylamino)benzoic acid for: **A′**) in a chloroform solvation model using MacroModel 7.0.[10] The two-dimensional 3:1 complex of compounds **A′** and **1** (**A′$_3$1$_1$**) was formed by intermolecular hydrogen bonds between imidazolium groups and carboxylates. The self-assembled structure composed of 1,3,5-tris(4,5-dihydro-1*H*-imidazol-2-yl)benzene and carboxylic acids through charged H-bonds is widely known.[11] This complex was envisioned as a model structure of a hydrogen-bonded and aromatic-stacked polymeric structure (Fig. 2). It shows that all the aromatic rings were stacked well with some amide groups of compound **A′** forming interlayer H-bonds. When the solvent polarity was changed to nonpolar, it allowed a strengthening of the intermolecular and interlayer H-bonds. It also shows a good possibility that the **A$_3$1$_1$** complexes can form long fibrous structures in nonpolar solvents such as cyclohexane and decalin.

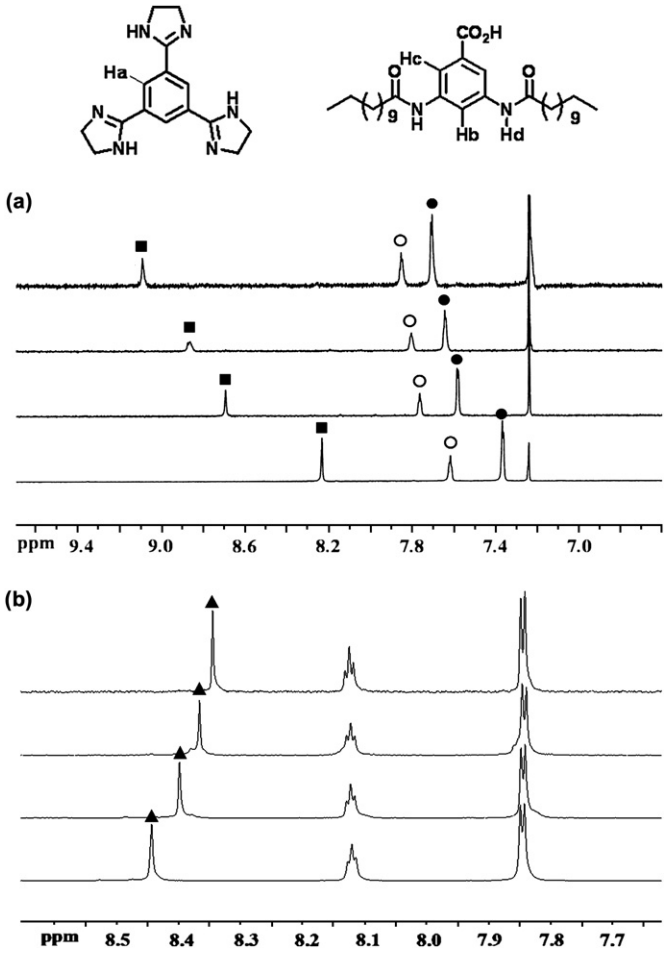

Figure 3. (a) ^{1}H NMR spectra of the 3:1 complex of compounds **A** and **1** in various polarities. The solvent ratio of $CDCl_3$–CD_3OD (v/v) from the bottom to top: 1:2 to 6:2. All the aromatic protons were shifted downfield (H_a=filled square, H_b=filled circle, H_c=open circle). (b) ^{1}H NMR spectra of the 3:1 complex of compounds **A** and **1** in DMSO-d_6 at 350 K. The concentration of **A$_3$1$_1$** from the bottom to top: 20 mM, 10 mM, 5 mM, 1 mM. Amide protons were shifted downfield (H_d=filled triangle).

2.2. NMR experiments

The discotic structures and gel formation were confirmed by strong hydrogen bonds and aromatic stacking interaction in the **A$_3$1$_1$** complex, which were identified by polarity-dependent and concentration-dependent NMR spectroscopy. However, because the **A$_3$1$_1$** complex is highly insoluble in nonpolar solvents such as

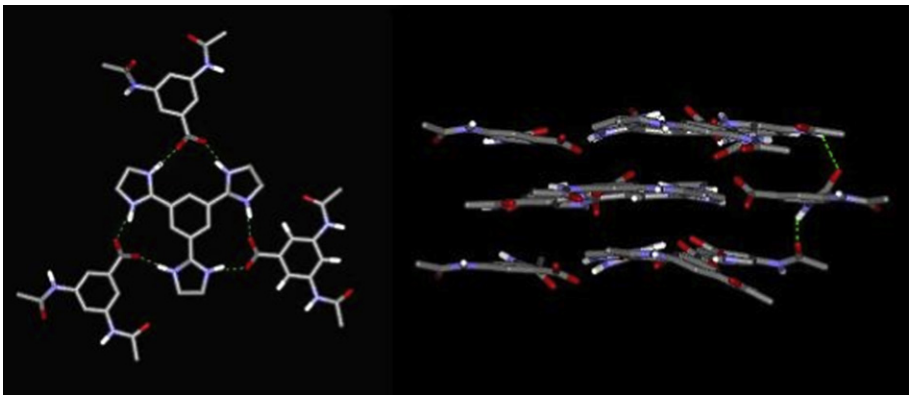

Figure 2. Global minimized 1:3 complex structure of tris(imidazoline) and 3,5-bis(acetylamino)benzoic acid (**A′**, simplified model compound of 3,5-bis(dodecanoylamino)benzoic acid) in a chloroform solvation model, MacroModel 7.0. (left) Top view of 1:3 complex. (right) Side view of the complexes with interlayer hydrogen bonds.

Table 1
Gelation ability of self-assembled gelators in different solvents

	Hexane	Cyclohexane	Decalin	Toluene	CH_3CN	*i*-PrOH
$\mathbf{A_3 1_1}$	G[a]	G	G	S[b]	S	S
$\mathbf{A_2 2_1}$	PG[c]	G	G	PG	S	S
$\mathbf{A_2 3_1}$	P[d]	G	G	P	P	S
$\mathbf{A_3 4_1}$	P	G	G	S	P	S
$\mathbf{A_2 5_1}$	P	G	G	P	P	S
$\mathbf{A_2 6_1}$	P	PG	PG	S	P	S
$\mathbf{B_3 1_1}$	P	P	P	P	P	P

[a] G=gel.
[b] S=soluble.
[c] PG=partial gel.
[d] P=precipitate.

cyclohexane, chloroform, dichloromethane, or acetonitrile, methanol was used as the solubilizing solvent. The solvent polarity was varied by changing the methanol and chloroform composition (Fig. 3a). NMR spectroscopy showed that the aromatic protons of compound **1** shifted downfield ($\Delta\delta$(ppm)=+0.95) and the aromatic protons of compound **A** also shifted downfield ($\Delta\delta$(ppm)=+0.21, +0.11) with increasing proportion of chloroform in the methanol solution. Computational modeling studies show that the polymeric aromatic cores should be D_3 symmetric in a nonpolar solvent of chloroform, not the displaced π–π stacked structure. This is evidently shown in polarity-dependent ^{1}H NMR spectra: while a displaced π–π stacked structure should lead to a low magnetic field

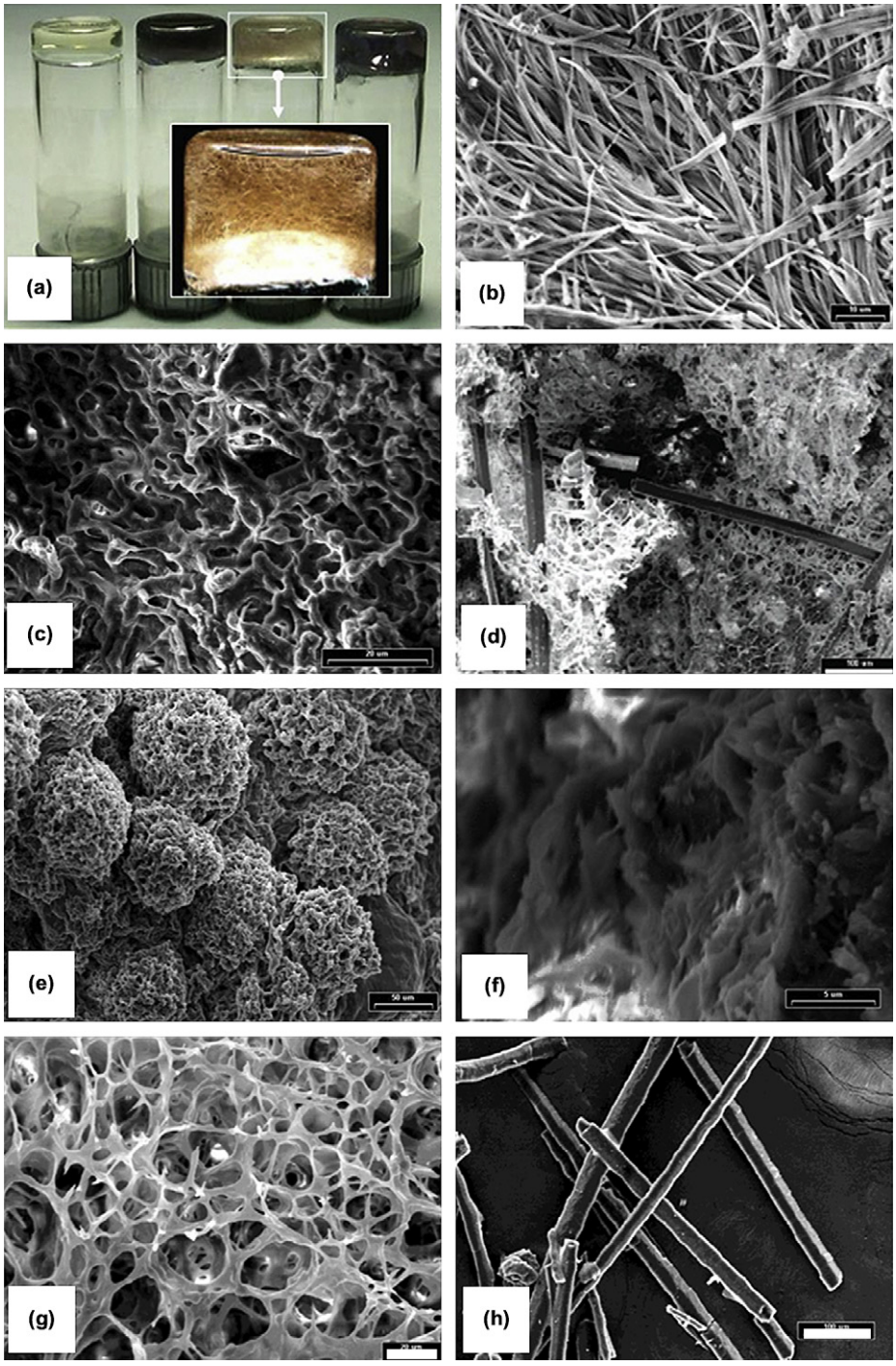

Figure 4. (a) Image of the organogels in cyclohexane (20 mM, 2.28–3.68% w/v). SEM images, (b) $\mathbf{A_3 1_1}$ in hexane (scale bar=10 μm), (c) $\mathbf{A_2 2_1}$ in cyclohexane (20 μm), (d) $\mathbf{A_2 3_1}$ in cyclohexane (100 μm), (e) $\mathbf{A_2 5_1}$ in cyclohexane (50 μm), (f) $\mathbf{A_3 4_1}$ in cyclohexane (5 μm), (g) the fibrous network structures from $\mathbf{A_2 3_1}$ (20 μm), (h) separated tubular structure from $\mathbf{A_2 3_1}$ (100 μm), in cyclohexane.

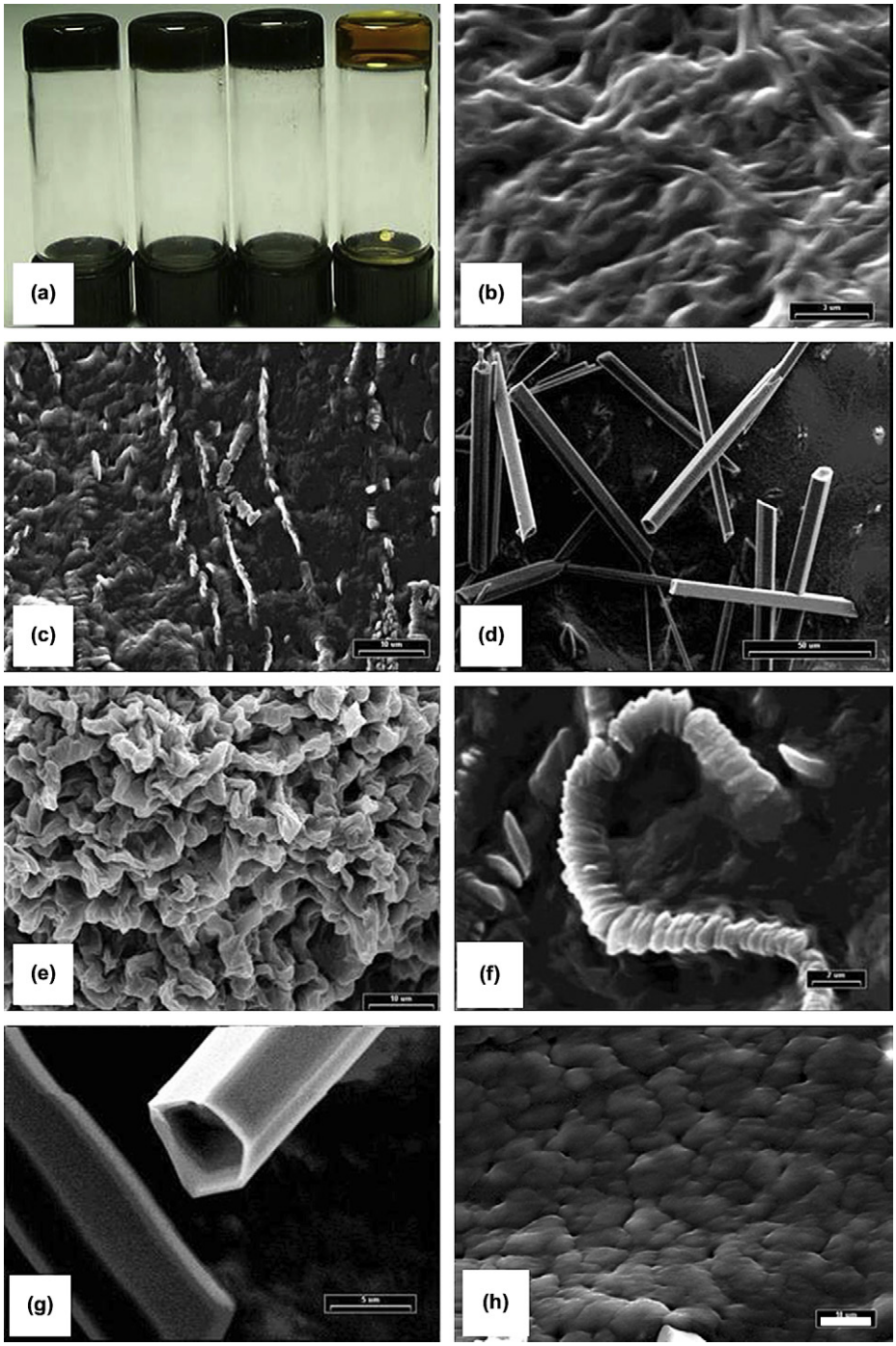

Figure 5. (a) Image of the organogels in decalin. SEM images, (b) $\mathbf{A_2 2_1}$ in decalin (scale bar=3 μm), (c) $\mathbf{A_3 4_1}$ in decalin (10 μm), (d) $\mathbf{A_2 3_1}$ in decalin (50 μm), (e) $\mathbf{A_2 5_1}$ in decalin (10 μm), (f) enlarged image of $\mathbf{A_2 4_1}$ (2 μm), (g) the tubular structure from $\mathbf{A_2 3_1}$ (100 μm) in decalin, (h) the gel medium from $\mathbf{A_2 3_1}$ (20 μm).

(upfield in a chemical shift) in lowering the polarity of the solvent, the chemical shift moved to the downfield, consistent with D_3 symmetric π–π stacked structure. ^{1}H NMR signals of the $\mathbf{A_3 1_1}$ complex are concentration-dependent in DMSO-d_6 (Fig. 3b). The amide proton signal (H_d) shifted downfield (δ(ppm)=+0.10) upon increasing the concentration from 1 mM to 20 mM, whereas the aromatic proton signals showed insignificant shift. This indicates that hydrogen bonding is a crucial factor for self-association and gel formation. These phenomena are attributable to an increase in the population of the π–π stacked, hydrogen-bonded oligomeric or polymeric structures of $\mathbf{A_3 1_1}$ in a nonpolar solvent.

2.3. Influence of solvent on gelation

The gelation tests were performed as follows: a weighed amount of each complex in an organic solvent (0.5 mL) was heated in a vial until the solid dissolved. The solution was then left to cool to room temperature in air. (The state of the phase was confirmed by visual observation.) Gel formation was observed during cooling or immediately after the cooling process. The powdered complex was insoluble in solvent but could be dissolved by gentle heating. Clear organogels were obtained after cooling to room temperature. The gelation behavior of the complexes was examined by dissolving

the complexes in various organic solvents (Table 1). Gelation did not occur in the polar protic/aprotic solvents such as acetonitrile and isopropyl alcohol. Because polar solvents might disturb the hydrogen bonds between carboxylic acid and amines, 3,5-bis(dodecanoylamino)benzoic acid and aromatic amines cannot form stable complexes. Moreover, gelation did not occur in aromatic solvents such as toluene. It appears that aromatic solvent molecules intrude into the complexes and disturb the assembly of the columnar structures. However, a 2:1 mixture of compound **A** and 1,12-diaminododecane **6** could not produce gels in any solvent system, presumably due to the absence of aromatic stacking interactions for the formation of columnar structures. This suggests that an aromatic group in the amine component plays an important role in the gelation of a two-component system. Compared with compound **A**, compound **B** has only one amide group and alkyl chain. Therefore, the lesser number of hydrogen bonds and weaker van der Waals force in the complexes with compound **B** presumably prohibited the gelation in all the solvents tested. Good gelation behavior was observed in nonaromatic hydrocarbon solvents such as cyclohexane and decalin. Gelation was not observed when only one of the two components was present. Therefore, a complex between compound **A** and an amine with an aromatic group is essential for gel formation.

2.4. Visual observation and SEM images

Clear organogels were obtained after cooling to room temperature (Fig. 4a). SEM images of xerogels prepared from complexes revealed the aggregation mode of the gelators. The aggregation patterns changed according to the shape of the aromatic groups. Figure 4b shows that the xerogels obtained from the gelator $\mathbf{A_3 1_1}$ in hexane consist mainly of three-dimensionally tangled, thick fiber bundles with diameters of 500–600 nm. These fiber bundles are not an uncommon occurrence. The xerogels from gelator $\mathbf{A_2 2_1}$ show winding fiber bundles with diameters ranging from 1 to 3 μm (Fig. 4c). In the case of $\mathbf{A_2 3_1}$, the fibrous structures in the gel medium, which were revealed to be microtubules, were observed with the naked eyes (Fig. 4a). Tube-like and fibrous structures were observed from gelator $\mathbf{A_2 3_1}$ (Fig. 4d).[9] The SEM image of $\mathbf{A_2 3_1}$ xerogel shows two distinct microstructures (fibrous and tubular structures). The fibrous network structures (Fig. 4g) contribute to the gelation of cyclohexane and the tubular structures pass through them. Microtubules can be separated by filtration after vigorously stirring diluted gels. In numerous cases, the microtubular structures collapse or lose their tubular function without a solvent. However, in this case, the separated microtubules retained their hollow tubular structures even without solvent molecules and were stable in air (Fig. 4h). The SEM images clearly show hollow tubular structures with uniform external diameters of 30–40 μm and wall thicknesses of 2–3 μm. The length of the longest tubule is 5 mm. The xerogels derived from 1,8-naphthalene diamine complex ($\mathbf{A_2 5_1}$) show a different aggregation mode. Aggregated fibers look like crumpled fabric, constituting a large spherical shaped body of 50 μm diameter (Figs. 4e and 5e). Remarkably fine fibrous structures were observed from $\mathbf{A_3 4_1}$ xerogels. They showed cotton-shaped superstructures (Fig. 4f). Upon using decalin solvent, the aggregation patterns dramatically changed in accordance with the shape of the aromatic groups. The SEM images of $\mathbf{A_2 2_1}$ and $\mathbf{A_2 5_1}$ in Figure 5b and e show similar structures, winding fiber bundles, and a large spherical shape body, in cyclohexane. Fig. 5c and f show an interesting aggregation shape. The SEM images of $\mathbf{A_3 4_1}$ in Figure 5c show helical and curved fibers with diameters of 0.8–1.2 μm. Close inspection indicates that the fibrous structures consist of disk-shaped aggregates. Gelators form disk shaped substructures and some are placed in an orderly fashion (Fig. 5f). We could also observe microtubules in the gel of $\mathbf{A_2 3_1}$ in decalin, which were smaller than those in the cyclohexane gel. The SEM images clearly show a hollow space (Fig. 5d and g). Microtubules have external diameters of 5–10 μm, lengths of 20–70 μm, and wall thicknesses of 0.5–1 μm. The microtubules formed in decalin are faceted, while those formed in cyclohexane show a round shape.

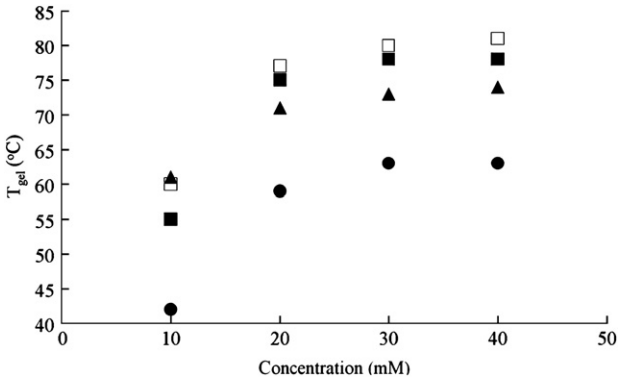

Figure 6. Effect of concentration on the gel–sol transition temperature of the gel in cyclohexane. Concentration is determined by moles of each complex per volume of cyclohexane. ($\mathbf{A_3 1_1}$=filled triangle, $\mathbf{A_2 2_1}$=filled circle, $\mathbf{A_2 3_1}$=filled square, $\mathbf{A_3 4_1}$=open square).

2.5. Sol–gel transition temperature (T_{gel})

The thermal stability of the organogels in cyclohexane was examined at various concentrations (Fig. 6). The temperature (gel-to-sol temperature, T_{gel}) at which the gels reverted to being solutions was investigated at various concentrations. The T_{gel} values increase with increasing molar concentration of the complexes and reach a horizontal region above a certain concentration. Although they have different shapes and sizes, all the complexes have a similar threshold concentration of approximately 25 mM. However, it is interesting that T_{gel} changes according to the size of the aromatic core. The T_{gel} values of complexes $\mathbf{A_3 1_1}$, $\mathbf{A_2 2_1}$, $\mathbf{A_2 3_1}$ and $\mathbf{A_3 4_1}$ were 74 °C, 63 °C, 78 °C and 81 °C at 40 mM, respectively. At all the concentrations investigated, the margin of T_{gel} was found to be approximately 15 °C between $\mathbf{A_2 2_1}$ and $\mathbf{A_2 3_1}$. A dramatic change in T_{gel} was observed by the addition of one aromatic ring. Therefore, it is likely that T_{gel} values increase with the increasing strength of aromatic stacking. $\mathbf{A_2 2_1}$ complexes form gels that are thermally more stable than $\mathbf{A_3 1_1}$ complexes, because compounds **1** and **2** have the same aromatic group but a different number of hydrogen bonding groups. As previously stated, some amide groups of compound **A** must form interlayer H-bonds to make hydrogen-bonded and aromatic-stacked polymeric structures.

3. Conclusions

We have developed a new gelation system for organic solvents by the self-assembly of aromatic amines and amphiphile groups. Various macroscopic shapes of organogels were realized by forming complexes of an amphiphile group (3,5-bis(dodecanoylamino) benzoic acid) and various amines with an aromatic group in nonaromatic hydrocarbon solvents. This study showed that the organogels can be formed by the appropriate combination of the basic building blocks and solvents that can provide sufficient hydrogen bonding and aromatic stacking interactions. A computational calculation and NMR experiments demonstrate that all the aromatic rings were stacked well with some amide groups of compound **A** forming interlayer H-bonds. It shows the possibility that the complexes can form long fibrous structures. The polymeric structures of the gel state can be changed according to the shape and size of the aromatic groups (three-dimensionally tangled, thick fiber bundles,

tube-like structures, helical structures formed by disk shape aggregates, etc.). The gels show well-defined thermoreversible sol–gel transitions and the T_{gel} values increased with the increasing strength of aromatic stacking. It is clear that the number of hydrogen bonds and aromatic stackings have a pronounced effect on the gelation properties and the microstructure of the gels. This two-component gelation approach could be useful for controlling the microscopic and macroscopic properties, and have potentially interesting applications.

4. Experimental section

4.1. Synthesis

4.1.1. General

All chemicals and solvents were purchased from Aldrich or Tokyo Kasei Chemicals, and were used as-received. Deuterated solvents were acquired from Cambridge Isotopic Laboratories and were used for NMR spectrometric measurements. All NMR spectra were recorded on a Bruker Advance DPX-300. All ^{1}H NMR and ^{13}C NMR were recorded in DMSO-d_6 at 298 K (spectral width: −1 to 14 ppm). The reference peaks were set to δ 2.49 and δ 39.51 ppm from tetramethylsilane for the ^{1}H and ^{13}C NMR spectra, respectively. The XWINNMR program was used for the pulse program.

4.1.2. 3,5-Diaminobenzoic acid methyl ester

HCl gas was bubbled into a solution of 3,5-diaminobenzoic acid (98%, Aldrich) (5.0 g, 32.9 mmol) in 150 mL of dry CH_3OH and stirred at 0 °C for 2 h. The resulting white precipitate was filtered and refluxed in 150 mL of dry CH_3OH for 4 h. All the volatile components were evaporated and the residue was basified with $NaHCO_3$ and filtered. The crude product was purified by recrystallization (CH_2Cl_2–hexane) to provide white solid (4.64 g, 85% yield).

^{1}H NMR (300 MHz, DMSO-d_6): 3.73 (3H, s), 4.99 (4H, s), 6.01 (1H, t, J=1.97 Hz), 6.41 (2H, d, J=1.95 Hz).

4.1.3. 3,5-Bis(dodecanoylamino)benzoic acid

To a solution of 3,5-diaminobenzoic acid methyl ester (4 g, 24.1 mmol) in 150 mL of dry CH_2Cl_2 were added slowly dodecanoylchloride (>98%, TCI) (11.1 g, 50.6 mmol) and Et_3N (4.87 g, 48.1 mmol) by syringe. The resulting solution was stirred at 0 °C for 3 h. All the volatile components were evaporated and the residue was partitioned between CH_2Cl_2 and water. The organic phase was washed with water (×3) and then dried over Na_2SO_4. The white solid was treated with KOH (5.4 g, 96.3 mmol) and stirred in 150 mL of CH_3OH at room temperature for 10 h. Removal of CH_3OH followed by neutralization with 1 N HCl and filtration provided the crude product, which was purified by recrystallization (CH_3OH–CH_2Cl_2) to furnish white solid (9.82 g, 79% yield).

^{1}H NMR (300 MHz, DMSO-d_6): 0.85 (6H, t, J=6.61 Hz), 1.23 (32H, m), 1.57 (4H, m), 2.29 (4H, t, J=7.21 Hz), 7.87 (2H, d, J=1.29 Hz), 8.17 (1H, s), 10.02 (2H, s), 12.99 (1H, br s). ^{13}C NMR (75 MHz, DMSO-d_6): 171.95, 167.62, 140.14, 131.95, 115.04, 113.98, 36.82, 31.76, 29.48, 29.46, 29.39, 29.23, 29.19, 29.06, 25.56, 22.56, 14.41. HRMS (FAB): calculated ($C_{31}H_{53}N_2O_4$)=517.7728. Found=517.7755.

4.1.4. 1,3,5-Tris(4,5-dihydro-1H-imidazol-2-yl)benzene

A mixture of benzene-1,3,5-tricarboxylic acid (4.80 g, 22.84 mmol), ethylenediamine (5.03 mL, 75.38 mmol), ethylenediamine dihydrochloride (10.02 g, 75.38 mmol), *p*-toluenesulfonic acid (348 mg, 1.83 mmol), and ethylene glycol (30 mL) was heated to reflux for 3 h. About half of ethylene glycol was then slowly removed by distillation. The residual solution was concentrated to dryness at reduced pressure and was dissolved in a mixture of water (120 mL) and concd HCl (3 mL). Addition of 50% aqueous NaOH gave a yellow precipitate, which was purified by reprecipitation (4.6 g, 71.3% yield). The analytical data were in accordance with those reported in Ref. 11.

4.1.5. Tris(4-aminophenyl)amine

A mixture of tris(4-nitrophenyl)-amine (3.00 g, 7.89 mmol) and tin granules (27.0 g, 0.227 mol) in 12 N HCl (150 mL) was refluxed for 3 h. After cooling to room temperature, the insoluble residue was removed by filtration. The filtrate was diluted with distilled water. The aqueous solution was adjusted to pH 12 by the addition of NaOH and filtered. Volatiles were removed in vacuo to give a purple solid (1.12 g, 50.3% yield). The analytical data were in accordance with those reported in Ref. 12.

4.1.6. General method for the preparation of the gels

The aromatic cores (**1**–**6**) were mixed in a ratio of 3:1 or 2:1 with **1**. The mixtures were dissolved in $CHCl_3$ and MeOH (v/v=1:1). Clear solution was concentrated and dried in vacuo. These solids were used for the gelation test. These tests were performed by solubilizing a weighed amount of a mixture in a measured volume of the selected organic solvent (A_xN_1=20 mM in cyclohexane or decalin, N=**1**–**6**, x=2 or 3). The mixtures were heated until clear and cooled at room temperature. The minimum gel concentration of each gel is about 1.03% w/v (9 mM of complex) in cyclohexane. Samples for the cyclohexane gel and decalin gel images were dried in the air before examining SEM images. The solid in the vial was carefully picked up and applied to the polymer or stainless steel stubs by carbon tape. For the image of separated microtubules, filtered microtubules were dried in a vacuum and applied to polymer or stainless steel stubs by carbon tape. The T_{gel} values were measured using an inverted test tube method: a vial (diameter=1 cm) containing the gel was inverted and the temperature gradually increased to the point where the gel begins to flow.

4.2. Scanning electron microscopy

SEMs (scanning electron micrographs) were recorded using a JEOL JSM 5410LV. Dried gel samples were applied to polymer or stainless steel stubs by carbon tape. Prior to examination, the gels were coated with a thin gold layer by gold deposition (5 mA, 7 min).

Acknowledgements

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