Supramolecular Chemistry

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Octadehydrodibenzo[12]annulene-Based Organogels: Two Methyl Ester Groups Prevent Crystallization and Promote Gelation**

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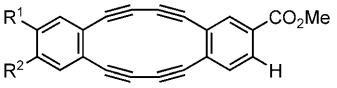
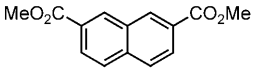
Recently, π-conjugated cyclic systems involving benzene rings and acetylene units, the dehydrobenzoannulenes (DBAs),[1,2] have attracted substantial interest from the viewpoint of acting as building blocks of supramolecular assemblies, along with their optoelectronic functionality, rigid, well-defined molecular structures, and extensively delocalized π electrons.[3–6] To date, a handful of superstructures based on triangular DBAs have been reported. They include one-dimensional (1D) fibrous superstructures in films from Diederich, Nielsen et al.[3] and Iyoda et al.,[4] micelles and liquid crystals from Tew et al.,[5] and two-dimensionally ordered networks at the liquid–solid interface from Tobe, De Feyter et al.[6] More recently, we also demonstrated that a single crystal composed of one-dimensionally π-stacked DBA exhibited highly anisotropic charge-carrier mobility.[7] However, superstructures of DBAs have not been extensively reported except for the case of crystals,[8] and there has been no report on organogels based on DBAs.[9] One of the reasons for the lack of DBA superstructures is that the affinity interactions between DBA rings are weaker than those of other systems, such as discotic graphene-like molecules, owing to weaker π–π interactions of DBA rings containing sp-hybridized carbon atoms.[3] Indeed, for gelators, strong and highly directional intermolecular interactions are required.

Herein, we describe the construction and structural characterization of an organogel derived from boomerang-shaped DBA **1** with methyl ester groups, which was designed according to the strategy detailed below.

For construction of organogels, it is generally recognized that gelators have to satisfy the following three requirements: 1) formation of 1D fibrous aggregates through self-complementary and unidirectional intermolecular interactions,



1: $R^1 = CO_2Me$, $R^2 = H$
2: $R^1 = H$, $R^2 = CO_2Me$



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2) favorable cross-linking of 1D fibers to form 3D networked structures, and 3) some factors to prevent crystallization and to preserve metastable gel states. Based on these factors, the design of low-molecular-weight organic gelators (LMOGs) has been rationalized by introducing substituents that induce gelation, such as steroid skeletons and long alkyl chains.[10] These groups provide favorable van der Waals interactions and prevent crystallization (Figure 1a). In contrast, in our strategy we focused on a dipole–dipole interaction and molecular symmetry (Figure 1b), though a strategy based on dipole–dipole interactions was considered by Ajayaghosh et al.[11] We applied the following two strategies to design DBA-based gelators: 1) to increase intermolecular affinity of DBAs, highly-polarized substituents should be introduced in the periphery;[3] and 2) to align the molecules anisotropically and exclusively in a certain direction, the molecule should be asymmetrized into a curved shape, such as the banana-shape structure applied in liquid crystals.[12] We therefore designed the boomerang-shaped DBA **1** described herein, which has two methyl ester moieties in *syn* positions.

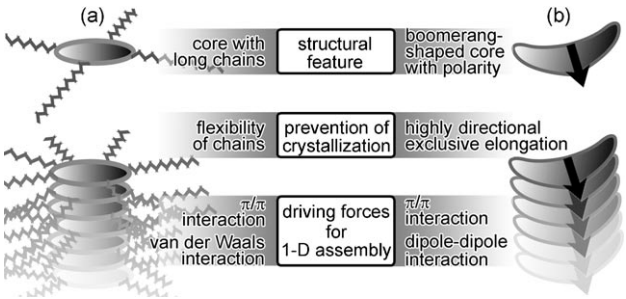

Figure 1. A comparison of the one-dimensional assembly of π-conjugated systems. a) Conventional typical system, with long alkyl chains. b) Present system, with an asymmetric boomerang shape and having polar substituents.

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When freshly purified **1** (synthesized according to Scheme S1 in the Supporting Information) was dissolved in chloroform, gelation successfully occurred, in contrast to many cases of methyl ester substituted π-conjugated molecules,[13] including DBA,[8d] which usually gave crystalline precipitates. The detailed gelation ability of **1** was then investigated in various organic solvents (Table 1). Chloroalkanes as solvent tend to result in transparent gels (Figure 2a) with excellent CGC values (0.11% for 1,2-dichloroethane, and T_g values of about 30°C). Aromatic solvents yield opaque gels with excellent CGCs (0.36–0.42% and T_g of 43–44°C). DBA **1** was insoluble or provided jelly precipitates in polar solvents.

To investigate the morphology of the gels, air-dried representative samples (a transparent gel in 1,2-dichloroethane, an opaque gel in benzene, and a jelly precipitate in acetone) were subjected to scanning electron microscopy (SEM) measurements. The gel in 1,2-dichloroethane has intricately intertwined retiform structures, which are provided from bundle of tape-like fibrils of about 60 nm of width (Figure 2b). The gel in benzene has a similar morphology (Figure 2c). The jelly precipitate from acetone also has a fibrous structure, although the solvent could not be retained (Figure 2d). Atomic force microscopy measurements also support the results (Supporting Information, Figure S1). These results indicate that **1** prefers to form fibrous superstructures.

Table 1: Gelation properties of **1** in selected organic solvents.

Solvent	State	CGC[a] [wt%]	T_g[b] [°C]
dichloromethane	G(T)[c]	0.24	28
chloroform	G(T)	0.30	25
1,2-dichloroethane	G(T)	0.11	32
benzene	G(O)[d]	0.36	43
chlorobenzene	G(O)	0.42	44
toluene	G(O)	0.31	43
methyl benzoate	G(O)	0.38	44
THF	G(O)	0.51	44
1,4-dioxane	G(O)	0.36	39
acetone	P[e]		
ethyl acetate	P		
triethylamine	I[f]		
ethanol	I		
diethyl ether	I		

[a] CGC: critical gelation concentration. [b] T_g: gel–sol dissociation temperature under CGC conditions. [c] G(T) = transparent gel. [d] G(O) = opaque gel. [e] P = jelly precipitate. [f] I = insoluble.

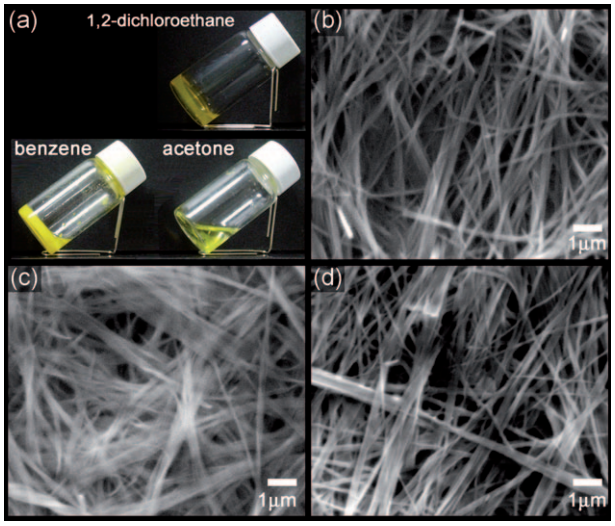

Figure 2. Optical photographs of the gels and precipitate of **1** (a), and SEM images obtained from the air-dried gels and precipitate (b–d). b) Transparent gel in 1,2-dichloroethane, c) opaque gel in benzene, and d) jelly precipitate in acetone. Scale bars: 1 μm.

To obtain information pertaining to the gelation behavior of **1** and the molecular arrangement in the fibrous superstructures, temperature-dependent UV/Vis spectra of **1** were measured in 1,2-dichloroethane solutions having concentrations of 5.0×10^{-3} and 5.0×10^{-4} M. The former concentration exceeds the CGC of 3.9×10^{-3} M, whereas the latter has a much lower value. The gel was subjected to UV/Vis spectroscopy at temperatures ranging from −5 to 40°C (Figure 3a). Upon degeneration of the gel by heating, the intensity of the absorption bands ranging from 345 to 440 nm increased, indicating that an aggregate forms by π–π interactions between the annulene rings. It should be noted that the weak shoulder at about 510 nm gradually decays, and the band at 484 nm becomes less discernable with increasing temperature. The decreasing band is attributed to the energetically favored supramolecular structure in the gel, while the increasing band is ascribable to the monomeric species. Absorbance intensities at 355, 372, 440, and 510 nm are plotted versus temperature (Figure 3a, inset). The temperature at the end of the change corresponds to the T_g value

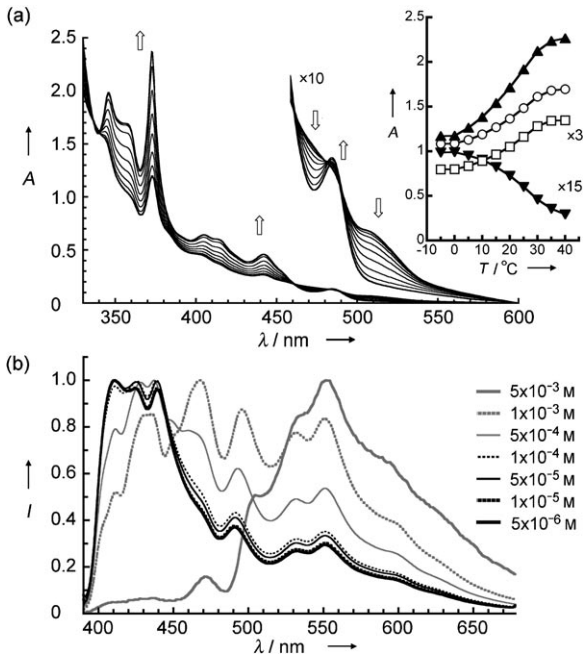

Figure 3. Changes in spectra of **1** in 1,2-dichloroethane. a) UV/Vis spectra recorded at various temperatures (−5 to 40°C) at a concentration of 5.0×10^{-3} M. b) Fluorescence spectra (λ_{ex} = 345 nm) for various concentrations (5.0×10^{-6} to 5.0×10^{-3} M) at 25°C. Inset shows absorbance changes at 355 (○), 372 (▲), 440 (□), and 510 (▼) nm.

determined above (32 °C). The spectral changes in 5.0×10^{-3} M solvent were not observed in the 5.0×10^{-4} M dilute solution (Supporting Information, Figure S2).

Concentration-dependent changes in fluorescence spectra were also determined. Figure 3b shows the normalized spectra in 1,2-dichloroethane solution at 25 °C. Upon increasing the concentration, bands at 411, 426, and 439 nm decay rapidly, and in particular for concentrations higher than 1.0×10^{-4} M, which is probably due to self-absorption. At 5.0×10^{-3} M, above the CGC, a very weak band with $\lambda_{max}=551$ nm remained ($\Phi_{em}<0.01$). The fluorescence band is probably due to the aggregated species, in which excitation energy migration efficiently occurs within and/or between the fibrous assemblies, as reported in the case of the oligo(*p*-phenylene vinylidene) (OPV) gels.[14] Time-resolved experiments for **1** in 1,2-dichloroethane (5.0×10^{-3} M) at −5 °C (Supporting Information, Figure S3) support this fact: the lifetime τ at 540 nm (1.5 ns) is shorter than that at 450 nm (2.4 ns).

To verify our strategy and characterize the fibrous superstructure in more detail, DBA **1** was compared with compounds **2** and **3**. DBA **2** is the *anti*-isomer of **1** (synthesized according to Scheme S2 in the Supporting Information). Naphthalene derivative **3** is formally derived by removing two diyne groups from **1**.

Noncentrosymmetric **1** has a dipole moment of 2.22–3.58 Debye along its short axis as it has $C2_v$ symmetry, whereas **2** in the $C2_h$ symmetric conformation has no dipole moment (Supporting Information, Figure S4). The difference in the dipole moment must affect the aggregation behavior. For **1**, molecular aggregation along the π-stacked direction should be significantly accelerated by dipole–dipole interactions. Such highly anisotropic growth of the aggregate should yield no crystals, but instead yield 1D fibrous aggregates, providing gelation. In contrast, the aggregation growth of **2** is expected to be less anisotropic than that of **1**, and results in a 3D crystalline superstructure. In fact, isomer **2** did not yield any gel-like materials under the same conditions as **1**, but did yield crystalline precipitates by cooling of a chloroform solution (Supporting Information, Figure S5).

According to our strategy, boomerang-shaped ester **3** should also yield 1D fibrous aggregates as in the case of **1**. In contrary to the gelation found for **1**, however, slow evaporation of a solution of **3** dissolved in chloroform/methanol yielded crystalline precipitates that contain two polymorphic crystals: a majority being columnar crystals, and the remainder platelet crystals. Crystallographic analysis revealed that molecule in the former, which has a down–down carbonyl conformation (Figure 4a), arranges in a slipped π-stacked fashion (i.e., *J* aggregation),[15] whereas those in the latter, with an up–up conformation (Figure 4c), arrange in an alternately π-stacked fashion (i.e., *H* aggregation)[16] such as to cancel out their dipole moments. Thus, the up–up conformation is a key structure for the *J*-type stacking. Comparison of the powder X-ray diffraction (PXRD) patterns of the cryodried gel of **1** with that of the crystals of **3** revealed that the gel has a similar pattern to that of the *J*-type crystal, rather than the *H*-type (Figure 5). The peaks from the gel at $2\theta=14.8$, 15.5, 23.5, and 27.4° (*d* spacing: 6.1, 5.7, 3.8, and 3.3 Å, respectively) in Figure 5a correspond to the peaks of (010), (011), (10±1), and (11±1) planes of the *J*-type crystal in Figure 5b: the former two peaks are attributed to the periodic distances related to the molecular length along the shorter axis, and the latter two to the periodic distance in the π-stacking direction.[17] The peaks in the small angle region at $2\theta=4.3$, 6.6, and 9.2° (*d* spacing: 21.0, 13.5, and 10.8 Å) are related to the molecular length along the longer axis. Therefore, **1** is expected to arrange mainly in the *J*-aggregated fashion to form fibrous superstructures. The reason that **3** did not give a gel despite its desired 1D molecular arrangement is that exclusive 1D elongation of the superstructure did not occur because its aromatic core is smaller than that of **1**.

Interestingly, when the methyl groups in **1** were replaced by longer alkyl chains, such as ethyl, propyl, and butyl groups,[18] the resulting annulenes gave no organogels but rather crystalline precipitates. Preliminary X-ray crystallo-

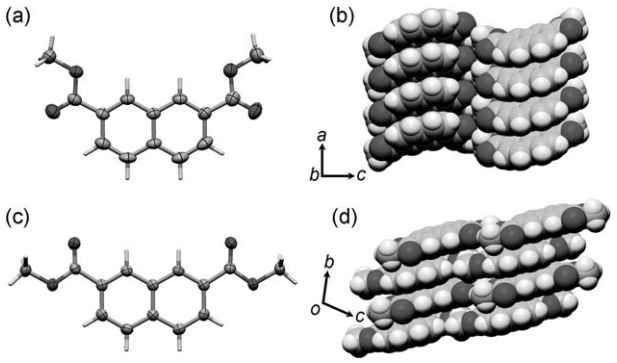

Figure 4. Crystal structures of **3**. Molecular conformations and packing diagrams for the *J*-type (a,b) and *H*-type (c,d) structures. Atoms in (a) and (c) are drawn as thermal ellipsoids with 50% probability, except for hydrogen atoms (sticks). Oxygen atoms are shown in dark gray.

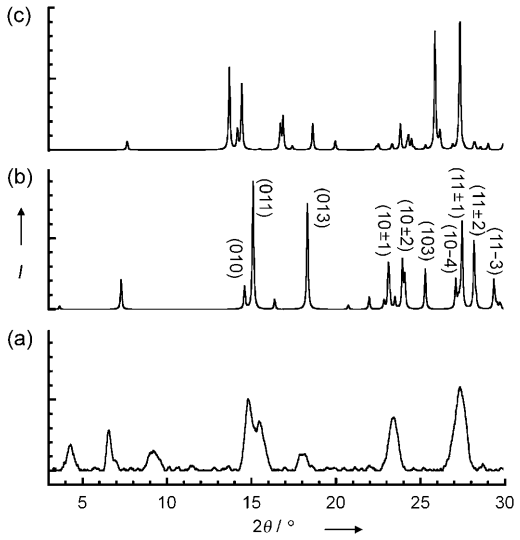

Figure 5. Comparison of the PXRD patterns between a) a cryodried gel of **1**, and b) the *J*-type and c) the *H*-type crystals of **3**. The patterns in (b) and (c) are simulated on the basis of the single-crystal diffraction data.

graphic analysis on single crystals of the ethyl and *n*-propyl ester derivatives revealed that the esters did not have a down–down conformation, and the DBAs no longer aggregated in the *J*-type assemblies owing to steric hindrance of the ester moieties (Supporting Information, Figure S7). Thus, methyl ester groups are also a crucial factor for gelation.

The gelation of **1** is assumed to occur in the following way. One appropriate conformer of **1**, that is, the down–down conformer, and having a boomerang-shaped structure, stacks along a certain direction, with uniform molecular directionality, by dipole–dipole and π–π interactions (Figure 6a).

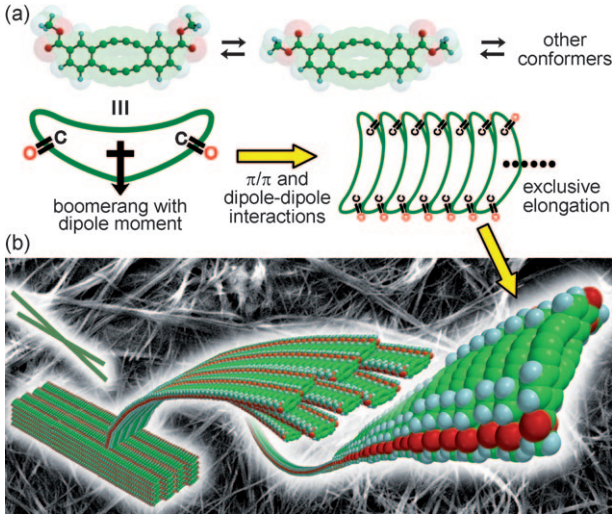

Figure 6. a) Representation of the formation of the 1D columnar superstructure by the boomerang-shaped molecules. b) The proposed superstructure in the gel of **1**.

Elongation takes place exclusively in the π-stacking direction because of effective dipole–dipole interactions to yield a 1D fibrous superstructure (Figure 6b). The fibers then construct a 3D network to form the gel.

In summary, we have described the formation and characterization of an organogel provided by boomerang-shaped DBA **1**, which was designed and synthesized based on the strategy that focuses on dipole–dipole interactions and asymmetrization of the molecule. Despite a lack of long alkyl chains but rather equipped with only two methyl ester groups, **1** acts as an excellent LMOG for various organic solvents. To the best of our knowledge, there has been no examples of LMOGs that have a π-conjugated core and only methyl ester groups.[19] As DBA **1** has a reactive distorted butadiyne moiety, **1** could undergo intermolecular reactions, such as polymerization, converting the self-assembled superstructures into covalently-bonded nanostructures. Current efforts are now focused on surveying the physical properties and conversion of the gel into polymeric materials.

Experimental Section

Preparation of gels**:** Compound **1**, along with an appropriate solvent, was placed in a test tube and sealed and heated until the compound was dissolved. The solution was then rapidly cooled to room temperature (in the cases of benzene and 1,4-dioxane) or −19 °C (for other solvents) and allowed to stand for 10–15 min. The formation of the gels was evaluated by determining whether they were stable to inversion in the test tube. The gel-destruction temperature was determined by the dropping-ball method (rate of temperature increase: ca. 1 °C min^{-1}). A glass ball weighing 0.18 g was placed on the gel surface, and the test tube was heated in a water bath. The temperature (T_g) was noted when the ball fell to the bottom of the test tube. See the Supporting Information for other detailed experiments.

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[15] Crystal data for the *J*-type crystal of **3**: $C_{14}H_{12}O_4$, $M_r = 244.25$, $a = 3.8914(5)$, $b = 6.0548(7)$, $c = 24.256(3)$ Å, $\beta = 90.532(6)$, $V = 571.47(11)$ Å^3, $T = 153$ K, monoclinic, space group $P2_1$ (No. 4), $Z = 2$, $\mu(Cu_{K\alpha})$ 0.871 mm^{-1}, $\rho_{calcd} = 1.419$ g cm^{-3}, 6540 collected, 2068 unique ($R_{int} = 0.075$) reflections. Final $R1 = 0.058$ ($I > 2.0\sigma(I)$) and $wR2 = 0.145$ (all data). CCDC 725719 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] Crystal data for the *H*-type crystal of **3**: $C_{14}H_{12}O_4$, $M_r = 244.25$, $a = 7.2916(5)$, $b = 7.5568(6)$, $c = 12.0759(12)$ Å, $\alpha = 102.755(5)$, $\beta = 93.669(4)$, $\gamma = 115.632(5)°$, $V = 574.40(8)$ Å^3, $T = 153$ K, triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $\mu(Cu_{K\alpha})$ 0.865 mm^{-1}, $\rho_{calcd} = 1.410$ g cm^{-3}, 6172 collected, 2053 unique ($R_{int} = 0.075$) reflections, Final $R1 = 0.058$ ($I > 2.0\sigma(I)$) and $wR2 = 0.164$ (all data). CCDC 725720 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] When absolute value of l in the (hkl) plane is larger than 1, for example (013), (10 ± 2), (103), (11 ± 2), and (11–3) in pattern (b), the corresponding peak was not or weakly observed in pattern (a), probably because of irregularly, slippage, and/or the limited dimension of the aggregate.

[18] Transesterification from the methyl ester to other esters was carried out concurrently with the Glaser reaction by using the corresponding alcohols in the cross-coupling reactions (see the Supporting Information).

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