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Gelation or Crystallization? Subtle Valance of Structural Factors for Assembly of DBA Derivatives with Methyl Esters[**]

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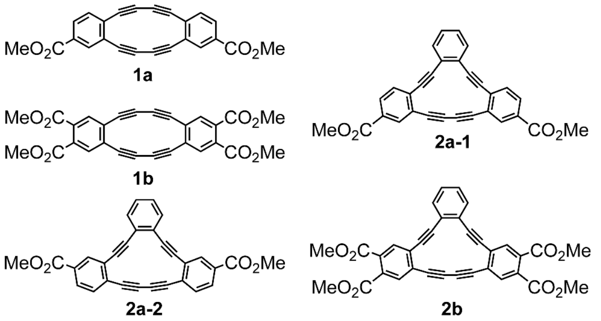
Morphology of molecular aggregates is crucially affected by molecular shape and intermolecular interactions. In 2009, we reported unusual gelation behaviour of a curved-butadiynl-bridged cyclic pi-conjugated molecule, octadehydrodibenzo[12]annulene ([12]DBA), possessing two methyl ester groups in noncentrosymmetric positions. Aggregation of the [12]DBA derivative occurred anisotropically to give crystalline nanofibers, which finally form a organogel. To investigate aggregation behaviour of the related analoges, we synthesized octadehydrotribenzo[14]annulene ([14]DBA) derivatives with two and four methyl ester groups and revealed that the [14]DBAs gave no gels but crystals, in which the molecules are stacked without unidirectional manner but with alternate way. The results indicate that gelation and crystallization of the present molecular system is laid on subtle balance of molecular shape and intermolecular interactions.

Introduction

One dimensionally pi-stacked fibrous assemblies have been one of attractive supramolecular architectures because they are expected to show exotic optoelectronic properties originating in a morphology with high aspect ratio.[1-8] Organo- or hydrogels based on such pi-stacked fibers are thus promising candidates of optoelectronically active soft materials.[9-13] Generally, a design principle of low molecular weight organic gelators with optoelectronic properties is to introduce long alkyl or alcoxy chains with hydrogen bonding moieties into periphery of a rigid pi-conjugated functional core. The resulting molecules can aggregate via phase segregation of rigid and flexible parts, combined with directional intermolecular interactions such as pi-pi stacking and hydrogen bonds, to give anisotropically-grown supramolecular fibers, which then form a three-dimensional network to hold solvent molecules within it. The principle is quite universal, and thus, is widely applied by huge numbers of pi-conjugated systems.

On the other hand, in 2009 we reported that butadiyne-bridged acene like pi-conjugated molecule so-called octadehydrodibenzo[12]annulene ([12]DBA) derivative[14] possessing two methyl ester groups **1a** (Scheme 1) exhibited excellent gelation ability for chlorinated solvents such as 1,2-dichloroethane.[15,16] The phenomenon is quite unusual because the compound has neither long substituent groups, steroidal groups, or hydrogen bonding groups but just two methyl ester groups at noncentrosymmetric positions. Such simple molecule, however, yielded organogel, successfully.



Scheme 1. Octadehydrodibenzo[12]annulene ([12]DBA) derivatives **1a** and **1b** and octadehydrotribenzo[14]annulene ([14]DBA) derivatives **2a-1**, **2a-2**, and **2b**.

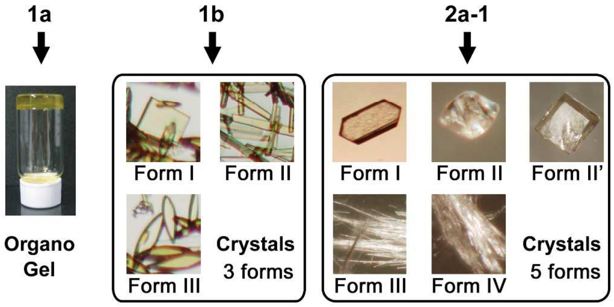


Figure 1. Aggregation status of DBAs **1a**, **1b** and **2a-1**.

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[**] DBA = Dehydrobenzoannulene

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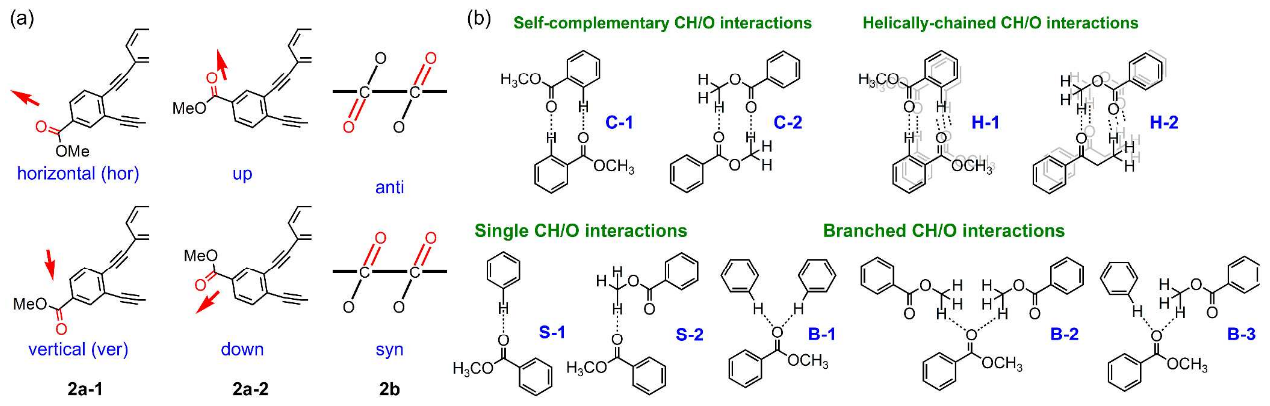


Figure 2. Structural factors providing varied molecular packing of [12]- and [14]DBA derivatives. (a) Conformational flexibility of methyl ester groups. (b) Weak hydrogen bonds (CH/O interactions) with various manners formed among methoxycarbonylphenyl moieties.

Inspired by gelation of **1a**, we have started investigating assembly behaviour of its analogue. We then synthesized [12]DBA derivative with four methyl ester groups **1b** and octadehydrotribenzo[14]annulene ([14]DBA) derivatives with two methyl ester groups **2a-1**, which has more expanded pi-conjugated core. As a result, [12]DBA **1b** was revealed to give no gels but crystals with three polymorphic forms.[17] [14]DBA **2a-1** was also revealed to yield as many as five polymorphic crystalline forms,[18] one of which formed a fragile gelly materials at low temperature (−19 °C).[19] The observed polymorphs of **1b** and **2a-1** were provided from flexibility of the methyl ester group regarding with its conformations and intermolecular interactions as shown in Figure 2. Namely, rotational flexibility of the methyl ester can provide conformers (Figure 2a), bringing about changes of dipole moments of the molecule and electrostatic potential surface on the molecule. Moreover, the carbonyl oxygen atom in the group can provide weak and less directional CH/O interactions[20-22] with electrostatically-positive hydrogen atoms (Figure 2b), allowing the molecules to pack into various arrangements.

In this manuscript, we describe synthesis and molecular assemblies of other two analogues, **2a-2** and **2b**. [14]DBA **2a-2** has two methyl ester groups in different positions from those of **2a-1**. [14]DBA **2b** has four methyl ester groups similar to **1b**. These systematic series enable us to consider correlation between assembly behaviour, molecular shape, and intermolecular interaction such as weak hydrogen bonds.

Experimental

Synthesis of Acyclic Tetrayne 4a. 1,2-bis(trimethylsilylethynyl)benzene (500 mg, 1.85 mmol) and anhydrous K_2CO_3 (2.56 g, 18.5 mmol) in methanol/ether (32/8 mL) was stirred at room temperature for 1 h. The mixture was extracted with dichloromethane and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to yield 1,2-diethynylbenznene as a yellow oil. The product was used in the next reaction without further purification. The oil was added to a mixture of **3a** (1.46 g, 4.07 mmol), $Pd(PPh_3)_4$ (107 mg, 92.5 μmol), CuI (35.0 mg, 185 μmol), and triisopropylamine (1.3 mL) in deoxygenated anhydrous tetrahydrofuran (THF) (17 mL) under nitrogen atmosphere. After stirred over night at room temperature, the reaction mixture was concentrated in vacuo. The mixture was extracted with dichloromethane and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (silica gel, chloroform / hexane = 10 / 1) gave **4a** (85.9 mg, 79%) as a yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.20 (d, J = 1.6 Hz, 2H, ArH), 7.93 (dd, J_1= 1.6 Hz, J_2= 8.1 Hz, 2H, ArH), 7.59 (m, 4H, ArH), 7.37 (m, 2H, ArH), 3.79 (s, 6H, OCH_3), 0.24 (s, 18H, SiCH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 165.8, 133.2, 132.2, 131.9, 129.7, 129.6, 128.8, 128.3, 126.3, 125.8, 102.6, 102.2, 92.8, 91.7, 52.2, -0.2 ppm.

Synthesis of Acyclic Tetrayne 4b. 1,2-bis(trimethylsilylethynyl)benzene (313 mg, 1.16 mmol) was desilylated by the same procedure described above. The product was added to a mixture of **3b** (1.40 g, 3.37 mmol), $Pd(PPh_3)_4$ (134 mg, 116 μmol), CuI (25 mg, 130 μmol), and triethylamine (50 mL) under nitrogen atmosphere. After stirred over night at 40 °C, the reaction mixture was concentrated in vacuo. The mixture was extracted with dichloromethane and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (silica gel, hexane / ethyl acetate = 10 / 1 to 6 / 4) followed by preparative HPLC gave **4b** (536 mg, 66%) as a dark yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 2H ArH), 7.83 (s, 2H, ArH), 7.62-7.59 (m, 2H, ArH), 7.40-7.38 (m, 2H, ArH), 3.91 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 0.22 (s, 18H, SiCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.2, 166.7, 132.8, 132.2, 131.6, 131.2, 129.0, 128.7, 128.5, 125.7, 103.0, 101.8, 95.0, 91.4, 53.04, 53.00 ppm.

Synthesis of [14]DBA 2a-2. A 1.0 M THF solution of tetrabutylammomium fluoride (0.32 mL) was added dropwise to a solution of **4a** (183 mg, 0.312 mmol) dissolved in THF (8.5 mL) at room temperature. After stirred for 1 h, the mixture was extracted with chloroform and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to yield a light brown solid. The resulting material was used for the following step without further purification. A drop of the product dissolved in pyridine (20 mL) was added into CuCl (309 mg, 3.12 mmol) dissolved in pyridine/methanol (160/160 mL) for 1h. After stirred for 2 h at room temperature, the reaction mixture was concentrated in vacuo. The mixture was extracted with chloroform and washed with water and brine. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. Purification by column chromatography (silica gel, dichloromethane) gave **2a-2** (102 mg, 74%) as a pale yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.51 (d, J = 1.6 Hz, 2H, ArH), 8.05 (dd, J_1= 1.6 Hz, J_2= 8.4 Hz, 2H, ArH), 7.95 (m, 2H, ArH), 7.64 (d, J= 8.1 Hz, 2H, ArH), 7.48 (m, 2H, ArH), 3.98 (s, 6H, OCH_3) ppm. ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 165.8, 136.2, 134.0, 130.2, 129.8, 129.3, 128.7, 128.4, 126.4, 123.1, 95.6, 92.2, 86.2, 82.5, 52.5 ppm. HR-MS (FAB) m/z calcd for $[M]^+$ $C_{30}H_{16}O_4$ 440.1049, found 440.1048.

Synthesis of [14]DBA 2b. 2b was synthesized according to the synthetic procedure of **2a-2** with starting from **4b** (930 mg, 1.32 mmol). Purification by column chromatography (silica gel, chloform), followed by preparative HPLC gave **2b** (296 mg, 40%) as a gray solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21(s, 2H, ArH), 7.97-7.95 (m, 2H+2H, ArH), 7.55-7.53 (m, 2H, ArH), 3.98 (s, 6H, OCH_3), 3.96 (s, 6H, OCH_3) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 166.8, 136.7, 133.6, 132.3, 132.1, 131.0, 130.2, 129.2, 125.0, 123.4, 96.9, 92.0, 85.7, 82.7, 53.3, 53.2 ppm. HR-MS (FAB) m/z calcd for $[M+H]^+$ $C_{34}H_{20}O_8$ 557.1237, found 557.1236.

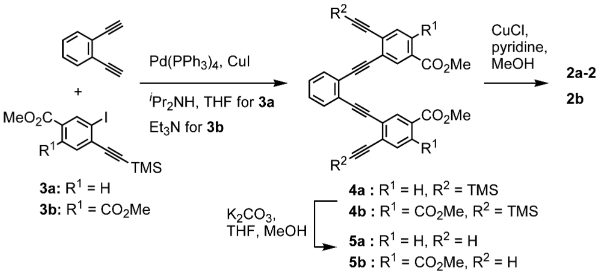
Crystallography. For crystal of **2a-2**, diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2-D area detector using graphite-monochromatized Cu-Kα radiation (λ = 1.54187 Å). The cell refinements were performed with software equipped in a Rigaku R-AXIS RAPID system. For crystal of **2b**, diffraction data were collected on a CCD (Rayonix/MX225HE) with the synchrotron radiation (λ = 0.8000 Å) monochromated by the fixed exit Si(111) double crystal. The cell refinements were performed with HKL2000 software.[23] Direct methods (SHELXD2013)[24] were used for the structure solution of the crystals. All calculations were performed with the observed reflections [I > 2σ(I)] with the program CrystalStructure crystallographic software packages,[25] except for refinement which was performed using Shelxl2013.[24] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

Results and discussion

[14]DBAs **2a-2** and **2b** were synthesized as shown in Scheme 2. Iodobenzene derivatives **3a** and **3b** were cross-coupled with the freshly-prepared *o*-diethynylbenzene in the presence of Pd(0) to give the corresponding acyclic tetrayne derivatives **4a** and **4b** in 79% and 66% yields, respectively. Desilylation of the tetraynes **4a** and **4b** followed by copper-mediated intramolecular oxdative cyclization gave dehydrobenzo[14]annlene derivative **2a-2** and **2b** in 74% and 40% yields for 2 steps, respectively.

Table 1. Crystal data for **2a-2** and **2b**.

	2a-2	**2b**
Formula	$C_{30}H_{16}O_4$	$C_{34}H_{20}O_8$
M_r	440.43	556.53
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$ (#33)	$P2_1/c$ (#14)
a/Å	21.2337(4)	9.8740(1)
b/Å	7.94640(14)	13.6348(1)
c/Å	25.6281(5)	19.5627(2)
α/°	90	90
β/°	90	91.5660(5)
γ/°	90	90
V/Å^3	4324.27(14)	2632.74(4)
Z / Z'	8 / 2	4 / 1
T / K	153	153
$d_{calcd.}$	1.353	1.404
GOF	1.08	1.05
Reflections collected	61425	14389
No. of unique data [$R_{(int)}$]	7884 [0.069]	4289 [0.035]
No. of data with $I > 2\sigma(I)$	4243	1731
R_1 ($I > 2\sigma(I)$)	0.077	0.099
Rw(all data)	0.249	0.319
CCDC[26]	1060477	1060476



Scheme 2. Synthesis of [14]DBAs **2a-2** and **2b**.

To investigate aggregation behaviour, the synthesized [14]DBAs **2a-2** and **2b** were then dissolved in various organic solvents with heating, followed by rapidly cooled to precipitate. The resultant aggregates were not gels but crystalline powders or needles. Single crystals of **2a-2** and **2b** suitable for X-ray crystallographic analysis were successfully obtained by slow evaporation of ethyl acetate and dichloromethane solutions, respectively.

[14]]DBA **2a-2** crystallized into the space group $Pna2_1$. Crystallographically independent two molecules with the up-down conformation of the carbonyl groups (coloured with yellow and blue) were stacked in an alternate arrangement with an averaged pi-stacking distance of 3.43 Å (planarity deviation of each of the DBA rings are upto 0.07Å and 0.10 Å) as shown in Figure 3a. The stacked dimer was stabilized with electrostatically favourable head-to-tale arrangements of the

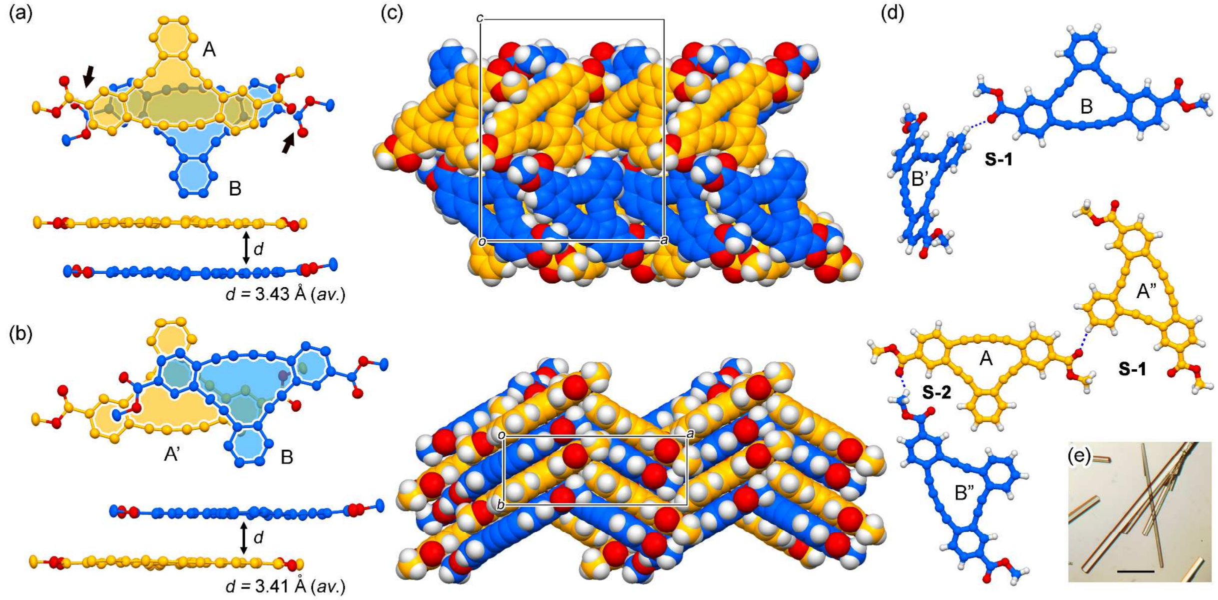


Figure 3. Crystal structure of **2a-2**. (a) Stacked dimer composed of crystallographically independent two molecules with 50% probability ellipsoid plot. (b) the other stacked pair with smaller overlap of the molecular planes. (c) Packing diagrams viewed from the *b* axis (top) and the *c* axis (bottom). (d) CH/O Contacts observed in the crystal. **S-1**: single CH/O interaction between the carbonyl oxygen and aromatic hydrogen atoms, **S-2**: single CH/O interaction between the carbonyl oxygen and methoxy hydrogen atoms. (e) Photograph of crystals of **2a-2**. Scale bar: 500 µm. Symmetry code: (A, B) *x*, *y*, *z*; (A') *x*, -1+*y*, *z*; (A'') 1-*x*, 3-*y*, 1/2+*z*; (B') 1/2-*x*, -1/2+*y*, 11/2+*z*; (B'') 1-*x*, 2-*y*, -1/2+*z*.

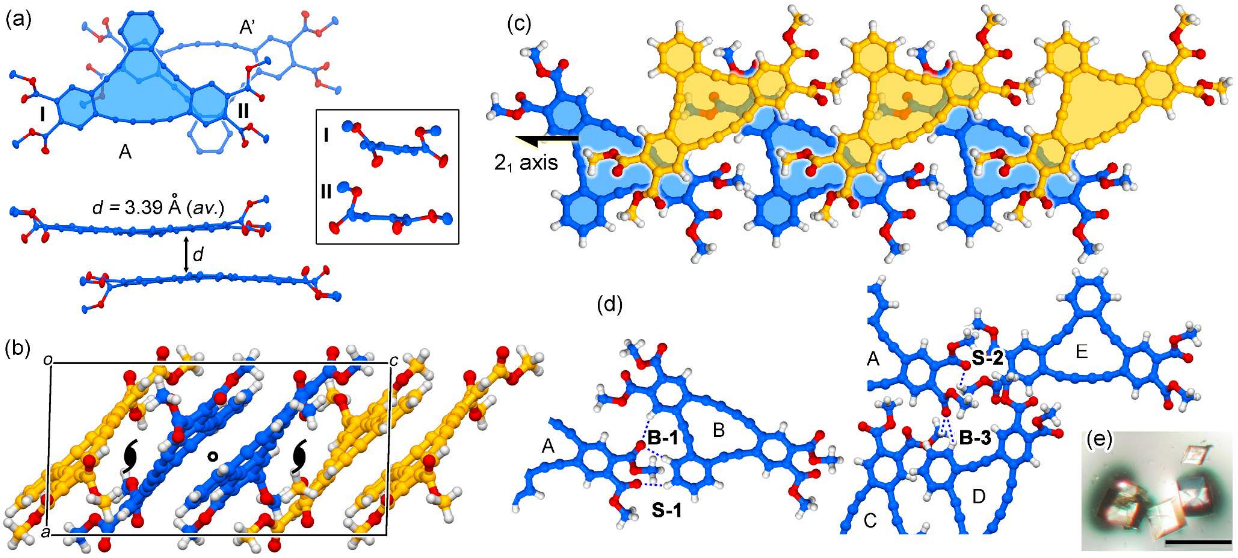


Figure 4. Crystal structure of **2b**. (a) Stacked dimer composed of inverted two molecules with 50% probability ellipsoid plot. (inset) conformation of the methyl phthalate moieties **I** and **II**. (b) Packing diagrams viewed from the *b* axis, in which the dimers colored with bule and yellow are related by twofold screw axis opperation. (c) Twofold helical motif running along the *b* axis. (d) CH/O Contacts observed in the crystal. **S-1**: single CH/O interaction between the carbonyl oxygen and aromatic hydrogen atoms, **S-2**: single CH/O interaction between the carbonyl oxygen and methoxy hydrogen atoms, **B-1**: branched CH/O interaction among the carbonyl oxygen and two aromatic hydrogen atoms, **B-3**: branched CH/O interaction among the carbonyl oxygen and aromatic and methoxy hydrogen atoms. (e) Photograph of crystals of **2b**. Scale bar: 250 µm. Symmetry code: (A) *x*, *y*, *z*; (A') 1-*x*, -*y*, -*z*; (B) *x*, -1+*y*, *z*; (C) -*x*, -1/2+*y*, 1/2-*z*; (D) -1+*x*, 1/2-*y*, 1/2+*z*; (E) -1+*x*, 1+*y*, *z*.

adjacent carbonyl groups, marked with arrows. This kind of carbonyl arrangements are often observed in crystalline states.[19] The dimer was stacked along the *b* axis with smaller overlap of the [14]DBA plane with the averaged interplanar distance of ca. 3.41 Å (Figure 3b,c). The slipping angle is 64.0°. The crystal exhibits the beta-type packing structure.[27] The

Table 2. Structural characteristics of the assembies of [12]- and [14]DBAs **1a**, **2a-1**, **2a-2**, **1b**, and **2b**.

compound	assembly status	morphology	conformation (stacking direction)	CH/O interaction	ref.
1a[a]	organo gel	nanofiber	ver-ver (Uni.)[c]	**S-2**	ref. 15, 16
2a-1	polymorphic crystals	**I**: plate	**I**: ver-ver (alt[d])	**I: B-1**, **S-1**	refs. 18, 19
	(5 forms)	**II**: block	**II**: ver-ver (others[e])	**II: S-2**	
	fragile gel at low temp.[b]	**II'**: block	**II'**: ver-ver(others[e])	**II': S-2**	
		III: thin needle	**III**: ver-ver (uni[c])	**III: B-1**, **C-1**	
		IV: thin needle	**IV**: hol-ver (uni[c])	**IV: B-1**, **C-1**	
2a-2	crystal	column	up-down (alt[d])	**S-1**, **S-2**	this work
1b	polymorphic crystals	**I**: plate	**I**: anti (-)[f]	**I: B-2**	ref.17
	(3 forms)	**II**: column	**II**: syn (-)[f]	**II: S-1**, **C-2**	
		III: spear	**III**: anti (-)[f]	**III: C-1**, **B-2**	
2b	crystal	block	syn (alt[c], others[e])	**S-1**, **S-2**, **B-1**, **B-3**	this work

a) Molecular conformation and packing manner of **1a** in the gel was estimated based on comparison between the observed powder X-ray diffraction pattern of the dried gel and that simulated for a model generated by the crystal structure prediction method. b) Fragile gel was formed only the 1,2-dichloroethane solution was rapidly cooled to -19 °C. c) "uni" indicates unidirectional stacking. d) "alt" indicates alternate stacking. e) "others" indicates stacking ways different from "alt" or "uni". (f) Stacking direction was not defined.

methyl ester groups form **S-1** and **S-2** CH/O contacts as shown in Figure 3d.

The alternate stacking manner of **2a-2** is the completely opposite to that of polymorphs III and IV of **2a-1**, in which the molecules slip and stack unidirectionally to give needle-like crystals with high aspect ratio (Figure 1). Crystalline habit of **2a-2**, on the other hand, is columnar shape with a relatively lower aspect ratio as shown in Figure 3e. Thus the position of the two methyl ester groups is crucial for stacking manner of [14]DBA core, and consequently, for crystalline habit.

DBA **2b** crystallized into space group $P2_1/c$. Contrary to **2a-2**, the [14]DBA core is distorted with upto 0.25 Å of displacement from the means plane of the core, due to a steric effect of the ester moieties. The both dimethyl phthalate moieties (**I** and **II**) have the *syn*-conformation; dihedral angles of the carbonyl group against fused phenylene ring are 48.4° and 36.1° for **I** and 57.8° and 16.4° for **II** as shown in Figure 4a. This conformation is also observed in crystals of **1b**.[17] Two molecules form alternately-stacked dimer with an inversion center between them. Due to the steric hindrance of the methyl ester groups, overlapping of the [14]DBA cores is smaller than that of **2a-2**. The interplanar distance of the dimer is ca. 3.39 Å. As shown in Figure 4b, the neighbouring dimers in the packing diagram are related by twofold screw axis (2_1) operation. The 2_1 helical motif of **2b** were shown in Figure 4c, where no significant pi-interaction between the [14]DBA cores were observed, while the motif was stabilized by branched CH/O interaction involving one carbonyl group and two aromatic hydrogen atoms (type **B-1**) and by single CH/O interaction between a carbonyl group and an aromatic hydrogen atom (type **S-1**). In the crystal, the methyl ester groups participate in totally four kinds of CH/O interactions: **B-1**, **S-1**, **B-3**, and **S-2** as shown in Figure 4d. Crystalline habit of **2b** is rhombic block, indicating that crystal growth occurred less anisotropically (Figure 4e).

In Table 2, structural characteristics of the [12]- and [14]DBA derivatives are summarized. Based on the results, we can conclude the assembly behaviours of a series of dehydrobenzoannulene derivatives as followed:

1. When the molecules are stacked unidirectionally, the morphology of the resultant aggregates tends to be highly anisotropic, like fibre and thin needle. On the other hand, alternate stacking often yields high symmetric aggregation motifs, resulting in crystals with lower aspect ratio.
2. Methyl ester groups can provide wide range of CH/O interactions in terms of directionality and topology. This is one of remarkable factors for generation of polymorphic crystals. The present systems **2a-2** and **2b**, which yield one unique crystalline form at the present, also have potential to yield polymorphs in the future.[28-29]
3. Gelation behaviour of **2a** is quite specific among those of related compounds, which probably derived by subtle balance of molecular shape and intermolecular interactions.[30,31]

Conclusions

Two [14]DBA derivatives, analogs of a unusual gelator **1a**, were synthesized and their assembly behaviour was investigated. [14]DBA with two methyl ester groups **2a-2** gave a $Pna2_1$ crystal, in which the molecules are alternately stacked. [14]DBA with four methyl ester groups **2b** gave $P2_1/c$ crystal, in which the molecules are also stacked in alternate fashion. Because of the alternate stacking manner, crystals grow less anisotropic to yield no fibers or thin needles but columnar or block-like crystals. These results, in addition to assembly behaviours of other reported derivatives, indicate that appropriate positioning of the methyl ester groups is significantly important for changing molecular arrangements and consequently morphology of the crystalline products. Particularly, gelation behaviour of **1a** previously reported was achieved through quite specific balance of molecular shape and intermolecular interactions. Deep understanding and tuning of such valance, which is the next challenging target, is conducting in our laboratory.

Acknowledgements

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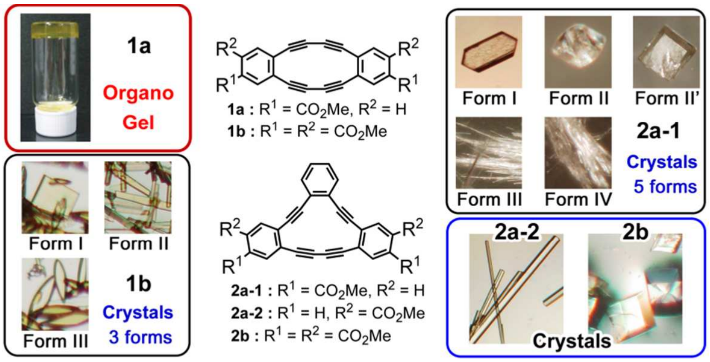
Notes and references

1 S. Laschat, A. Baro, N. Steinke, F. Giesselmann, *Angew. Chem. Int. Ed.* 2007, **46**, 4832-4887.
2 J. Wu, W. Pisula, K. Müllen, *Chem. Rev.* 2007, ***107***, 718-747.
3 L. Zang, Y. Che, J. S. Moore, *Acc. Chem. Res.* 2008, ***41***, 1596-1608.
4 T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev*. 2009, **109**, 5687–5754.
5 F. Würthner, T. E. Kaiser, C. R. Saha-Möller, *Angew. Chem. Int. Ed.* 2011, ***50***, 3376.
6 T. Aida, E. W. Meijer, S. I. Stupp, *Science*, 2012, **335**, 813–817.
7 B.-K. An, J. Gierschner, S. Y. Park, *Acc. Chem. Res.* 2012, **45**, 544–554.
8 H. Maeda, *Bull. Chem. Soc. Jpn.* 2013, **86**, 1359-1399.
9 A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res*. 2007, **40**, 644–656.
10 A. Dawn, T. Shiraki, S. Haraguchi, S. Tamaru, S. Shinkai, *Chem. Asian J*. 2011, **6**, 266–282.
11 A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, *Chem. Soc. Rev.* 2008, 37, 109–122.
12 S. S. Babu, S. Prasanthkumar, A. Ajayaghosh, *Angew. Chem.* Int. Ed. 2012, **51**, 1766–1776.
13 M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed, *Chem. Rev.* 2010, **110**, 1960–2004.
14 I. Hisaki, M. Sonoda, T. Tobe, *Eur. J. Org. Chem.* **2006**, 833-847
15 I. Hisaki, H. Shigemitsu, Y. Sakamoto, Y. Hasegawa, Y. Okajima, K. Nakano, N. Tohnai and M. Miyata, *Angew. Chem. Int. Ed.*, 2009, **48**, 5465-5469.
16 H. Shigemitsu, I. Hisaki, H. Senga, D. Yasumiya, T. S. Thakur, A. Saeki, S. Seki, N. Tohnai and M. Miyata, *Chem. Asian J.*, 2013, **8**, 1372-1376.
17 I. Hisaki, Y. Sakamoto, H. Shigemitsu, N. Tohanai and M. Miyata, *Cryst. Growth Des.*, 2009, **9**, 414-420.
18 I. Hisaki, E. Kometani, H. Shigemitsu, N. Tohnai and M. Miyata, *Cryst Growth Des*., 2011, **17**, 14348-14353.
19 H. Shigemitsu, I. Hisaki, E. Kometani, D. Yasumiya, Y. Sakamoto, K. Osaka, T. S. Thakur, A. Saeki, S. Seki, F. Kimura, T. Kimura, N. Tohnai and M. Miyata, *Chem. Eur. J.*, 2013, **19**, 15366-15377.
20 G. R. Desiraju, T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.
21 T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76.
22 G. R. Desiraju, *Chem. Commun*., 2005, 2995–3001.
23 HKL2000; Z. Otwinowski, W. Minor, *Methods Enzymol*. 1997, **276**, 307.
24 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, **2008**, *64*, 112.
25 Rigaku (2011). CrystalStructure. Versions 4.1. Rigaku Corporation, Tokyo, Japan.
26 CCDC 1060476 and 1060477 contain 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/.
27 G. R. Desiraju and A. Gavezzotti, *Acta. Crystallogra. Sect. B*, 1989, **45**, 473-482.
28 McCrone, W. C. *Polymorphism. In Physics and chemistry of the organic solid state*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Wiley In-terscience: New York, **1965**, pp. 725–767.
29 For Comprehensisve reports of recent polymorphs, see) H. G. Brittain, *J. Pharm. Sci.* 2007, **96**, 705–728; 2008, **97**, 3611–3636; 2009, **98**, 1617–1642; 2010, **99**, 3648–3664.
30 Orgnogelators without typical gelation inducing substituents, for example, see; a) B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song, S.-Y. Park, *J. Am. Chem. Soc.* 2004, **126**, 10232–10233; b) D. G. Velázquez, D. D. Díaz, Á. G. Ravelo, J. J. M. Tellado, *J. Am. Chem. Soc*. 2008, **130**, 7967–7973; c) X. Y. R. Lu, T. Xu, P. Xue, X. Liu, Y. Zhao, *Chem. Commun.* 2008, 453–455.
31 Another possible factor would be induced ring currents in the annulenic ring. [12]DBAs and [14]DBAs show anti-aromatic and aromatic characters, respectively, based on the ^{1}H NMR chemical shifts of the aromatic protons, see Table S1.



Aggregation of a series of strained dehydrobenzoannulene derivatives with methyl ester groups is revealed.