# Effects of *ortho*-Phenyl Substitution on Molecular Arrangements of Octadehydrodibenzo[12]annulene

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To modulate assembly manners of octadehydrodibenzo[12]annulene ([12]DBA) core in solid state, we first synthesized *ortho*-phenyl-substituted derivative **2** and investigated the effects of the substituents on the molecular stacking manner of the [12]DBA core. [12]DBA **2** yielded four types of crystals, which differ from that of the parent compound: Namely, the guest-free crystal possessing an offset stacking manner (I-GF), the solvate with a edge-to-face arrangement (II), the solvates with zigzag  $\pi$ -stacked arrangements (III and III'), and the solvate with 1D  $\pi$ -stacked columnar arrangements (IV). In the crystals, the phenyl groups contribute to limiting the stacking geometry of the [12]DBA cores and to forming void spaces accommodating various guest species, allowing versatile molecular assembly manners hitherto known for [12]DBA derivatives. We revealed that the crystals showed structure dependent fluorescence and charge carrier behaviors.

It is a critical issue for developing organic and supramolecular electronic materials to regulate stacking manner of  $\pi$ -counjugated molecules.<sup>1</sup> Peripheric aryl substitution of  $\pi$ conjugated molecules is one effective way to modulate and control assembly of the molecules, because the substituents can force the  $\pi$ -conjugated cores to be packed into certain specific structures which are not achieved by the parent compounds. For example, tetracene crystallizes in herringbone fashion through CH- $\pi$  interactions,<sup>2</sup> while rubrene (5,6,11,12-tetraphenyltetracene) crystallizes into  $\pi$ -stacked and herringbone structure,<sup>3</sup> in which good  $\pi$ -overlap with interplanar distance of 3.7 Å is responsible for high mobility.<sup>4</sup> Nuckolls and co-workers also investigated the assembly in the crystalline state of a series of pentacenes that are substituted along their long edges with one to six aromatic rings.<sup>5</sup> More progressively, Okamoto, Matsuo, and co-workers achieved face-to-face  $\pi$ -stacking structures of phenyl- and perfluorophenyl-substituted tetracene to enhance charge carrier properties, where phenyl-perfluorophenyl stacking and C-H-F interaction effectively worked between neighboring molecules.<sup>6</sup> Furthermore, Jin, Fukushima, Aida, and co-workers revealed that two phenyl groups attached to one side of the hexabenzocoronene unit are essential for formation of exotic graphene tubes composed of amphiphilic hexabenzocoronene derivatives.<sup>7</sup>

Rigid, sterically-hindered aryl substituents can also provide an inclusion space capable of accommodating guest species, allowing lattice host–guest systems. In such systems, structures of the host framework often vary depending on the guest species. For example, Moorthy and co-workers demonstrated that tetraarylpyrene is capable of forming various solvates and cocrystals with different molecular arrangements, in which



Scheme 1. [12]DBA 1 and its *ortho*-phenyl-substituted derivative 2.

the guest molecules are accommodated in the void spaces composed of the aryl groups.<sup>8</sup> We also reported aryl-substituted hexadehydrotribenzo[12]annulene derivatives formed crystalline supramolecular architectures possessing both 1D  $\pi$ -stacking columns and inclusion channels (1D- $\pi$ SIC structure) accommodative aryl guest species.<sup>9</sup>

In this study, we planned to investigate aryl substitution effect on molecular arrangements of octadehydrodibenzo[12]annulene ([12]DBA) (Scheme 1).<sup>10</sup> The parent compound 1 was first synthesized by Eglinton and co-workers.<sup>11</sup> After that, a number of its derivatives were reported for motifs of carbonrich materials,<sup>12</sup> for a platform of optically and electronically functional systems conjugated with phthalocyanine,<sup>13</sup> Ru(II)coordinated dipyridophenazine,<sup>14</sup> and dimethoxynaphthalene,<sup>15</sup> for a building block of supramolecular architectures such as crystalline charge-transfer complexes,<sup>16</sup> gels,<sup>17</sup> supramolecular nanofibers,18 and 2D-networked assemblies on a surface,19 and for a potential monomer of topochemical polymerization in the solid state.<sup>16,19,20</sup> However, the [12]DBA derivative substituted by four phenyl groups at the ortho-positions of butadiyne moieties has not been known although the trimethylsilyl-substituted one was reported by Kira and co-workers.<sup>21</sup> Contrary to the parent [12]DBA 1 which assembles into only one inherent



**Figure 1.** Assembly of (a) parent  $\pi$ -system and (b) arylsubstituted  $\pi$ -system. The former yields only an inherent assembly structure, while the latter can provide versatile, unusual supramolecular architectures via (1) aggregation in a geometrically restricted manner and (2) inclusion of guest molecules, which would give lattice frameworks depending on the guest species.

form (Figure 1a), we expected that *ortho*-phenyl-substituted [12]DBA **2** could provide versatile, unusual supramolecular architectures via (1) aggregation in a geometrically-limited manner, such as stacking only along the long molecular axis with good  $\pi$ -overlap as observed for rubrene (Figure 1b-1), and/or (2) inclusion of guest molecules which would give various lattice frameworks depending on the guest species (Figure 1b-2).

Herein, we describe synthesis of the *ortho*-aryl-substituted [12]DBA **2**, its crystal structures with or without guest molecules and structure-dependent optical and electrical properties. The present system is the first example for the [12]DBA derivatives to give such versatile molecular assembly manner, implying a rational way to modulate molecular arrangements not only of the [12]DBA but also of a wide range of  $\pi$ -conjugated molecules.

#### **Results and Discussion**

**Preparation and Crystallization of [12]DBA 2.** [12]DBA **2** was synthesized according to Scheme 2. Cross-coupling reaction of 1,2,3,4-tetrabromobenzene  $(3)^{22}$  with phenylboronic acid gave 1,4-disubstituted product **4** in 39% yield. Although Vollhardt and co-workers reported selective Sonogashira reaction of **3** with acetylene derivatives at 1,4-positions in high yields,<sup>23</sup> the present reaction resulted in moderate yield. Reaction of **4** with trimethylsilylacetylene in the presence of Pd(0) and ZnCl<sub>2</sub> at 100 °C gave diethynyl derivative **5** in 67% yield.<sup>24</sup> Desilylation of **5**, followed by Cu(II)-mediated oxidation cyclization gave dimer **2** together with trimer **6** in 51% and 28% yields, respectively.

Solutions of **2** dissolved in various organic solvents were evaporated slowly to give crystals with and without included solvent molecules. Their crystal data are listed in Table 1. The obtained twelve crystals can be classified into the following four forms according to [12]DBA's frameworks; **I**-GF: a guest-free crystal with an offset stacking manner, **II**(solv.): a solvate with an edge-to-face arrangement, **III**(solv.) and **III**'(solv.): solvates with zigzag  $\pi$ -stacked arrangements, and **IV**(solv.): a solvate with 1D  $\pi$ -stacked columnar arrangements, where included solvents are shown in the parenthesis. The detailed structures of the forms are described as follows.

Conformation of 2 in the Crystals. Regarding the conformation of the four phenyl groups, the crystals involve in total three conformers as shown in Figure 2: Conformers with (A) four phenyl groups twist into the same direction, (B) two phenyl groups bound to the same side of the long edge of [12]DBA core twist into the same direction, while the other two twist into the opposite direction, and (C) two phenyl groups bonding to the same phenylene ring twist in the same direction. Such various conformations of the phenyl groups allows 2 to access versatile packing arrangements. Table 2 lists the twisted angles of the phenyl groups of the conformers. Because of packing force, the observed angles become slightly smaller than the calculated value (46.7°) for  $D_2$ -symmetric conformer optimized at the B3LYP/6-31G\* level. The smallest averaged angle is observed in I-GF.

Crystal Structure of I-GF. [12]DBA 2 itself is packed with an offset stacking manner to yield guest-free (GF) crystal (I-GF) belonging to the space group  $P2_1/n$  (Figure 3a). The crystals were obtained by slow evaporation of chloroform, ethyl acetate, or mesitylene solution, although formation occurred accidentally and depended on the crystallization batches. It is surprising for us that 2 experiences the unexpected offset stacking, instead of slipped stacking along the long molecular axis as shown in Figure 1a, even though the [12]DBA core carries stericallyhindered phenyl groups. The substituted phenyl groups, which are staggered by 38.2-48.1° from the [12]DBA plane, are located on the adjacent [12]DBA planes (dihedral angles of the phenyl and the neighboring [12]DBA planes: 13.2°) to prevent the [12]DBA moieties from stacking with each other. The substituted phenyl groups are also contacted intermolecularly in twofold helical herringbone fashion (dihedral angle of the adjacent phenyl groups: 57.8°) as shown in Figure 3b.

**Crystal Structure of the Form II.** Recrystallization from a chloroform solution gave a solvate  $II(CHCl_3)$  belonging to the space group  $P2_1/c$ , concomitantly with the crystals I-GF. Contrary to I-GF,  $II(CHCl_3)$  has a phase-separated structure: namely, the crystal has a layer composed of the [12]DBA core and that of the substituted phenyl parts (Figure 4a). The [12]DBA cores form a porous sheet motif through face-to-edge (CH- $\pi$ ) interactions at the short edges of the [12]DBA core (angle between [12]DBA planes: 73.8°) (Figure 4b). The void spaces accommodate chloroform molecules with a 1:1 host/



**Figure 2.** Molecular conformations of **2** in crystals of (a) **I**-GF, (b) **II**(CHCl<sub>3</sub>), (c) **III**(DCM), and (d) **IV**(DCM). The signs + and – indicate the rotation direction of the substituted phenyl groups as shown in (e). The crystals **II**(CHCl<sub>3</sub>) and **IV**(DCM) contain two crystallographically independent molecules (molecules 1 and 2). Conformer A, in which four phenyl groups twist into the same direction. Comformer B, in which two phenyl groups bonded to the same side of the long edge of the [12]DBA core twist into the same direction, while the other two twist into the opposite direction. Conformer C, in which two phenyl groups bonded to the same phenylene ring twist into the same direction. The structures are drawn with thermal ellipsoids with 50% probability except for (b) **II**(CHCl<sub>3</sub>), which is with 75% probability.

guest ratio. It is well known that significant dispersion force works between chlorine atoms of the chloroform and  $\pi$ -conjugated plane.<sup>25</sup> Therefore, such interaction is one of the factors

to give the present structure. The substituted phenyl groups form densely-packed sheet motif as shown in Figure 4c. The phenyl groups bonded to one [12]DBA layer, colored with

Table 1. Cryst	al Data for the	Obtained Cry	stals of 2									
	I-GF	II(CH <sub>3</sub> Cl)	III(DCM)	III(Tol)	III(o-Xyl)	III(m-Xyl)	III(p-Xyl)	III(Mes)	III'(THF)	IV(DCM)	IV(AcOEt)	IV(DCE)
Formula	$C_{A}H_{2A}$	$C_{44}H_{24}$ .	$C_{44}H_{24}$ .	C44H24•	$C_{44}H_{24}$ .	$C_{44}H_{24}$ .	C44H24•	$C_{44}H_{24}$ .	C44H24•	C44H24•	$C_{44}H_{24}.$	$C_{44}H_{24}$ .
	+7	CHC1 <sub>3</sub>	$2(CH_2CI_2)$	$C_{7}H_{8}$	$C_8H_{10}$	$C_8H_{10}$	$C_8H_{10}$	$2(C_9H_{12})$	$2(C_4H_8O)$	$CH_2Cl_2$	$0.5(C_4H_8O_2)$	$C_2H_4CI_2$
FW	552.67	672.00	722.48	644.81	658.84	658.84	658.84	793.06	696.89	637.61	596.68	651.63
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic	triclinic
Space groups	$P2_{1/n}$	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/c}$	$P2_1/c$	$P2_{1/c}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
$a/ m{\AA}$	13.4772(3)	10.7613(2)	14.5319(2)	14.1739(5)	14.0972(3)	14.2286(1)	14.2286(3)	18.7774(3)	7.58129(14)	9.82703(18)	9.7334(2)	9.8513(3)
$b/ m \AA$	7.41843(13)	9.8037(2)	16.06830(10)	16.0597(5)	16.3866(3)	16.0855(2)	16.0855(2)	16.0362(3)	15.9505(3)	12.4881(2)	12.2960(2)	12.8635(3)
$c/ m \AA$	14.6222(3)	47.3370(9)	7.58740(10)	7.6334(3)	7.5894(2)	7.6021(3)	7.6021(1)	7.48966(14)	16.0043(3)	14.3466(3)	14.1912(3)	14.2181(6)
$lpha/^{\circ}$	90	06	06	90	06	90	60	90	75.9310(9)	76.9900(7)	77.2390(8)	78.000(2)
$eta/^\circ$	101.8606(10)	90.6117(12)	96.1307(4)	100.7220(17)	96.9516(7)	100.7910(6)	100.7910(6)	94.7555(9)	83.8540(9)	81.9390(7)	81.8460(9)	84.0343(18)
$\gamma/^{\circ}$	90	06	06	90	06	90	60	90	89.6170(9)	68.0990(7)	68.9100(16)	67.208(2)
$V/Å^3$	1430.71(5)	4993.80(17)	1761.55(4)	1707.25(9)	1740.30(7)	1709.16(7)	1709.16(5)	2247.52(7)	1866.10(6)	1588.54(5)	1541.89(5)	1624.21(10)
Ζ	2	9	2	2	2	2	2	2	2	2	2	2
No. (collected)	15498	48487	21745	17271	15632	15400	11851	25550	19467	26425	10176	8841
No. (unique)	2605	13397	2635	3107	3001	2885	2833	4084	6611	5721	5831	5101
$R_{ m int}$	0.047	0.066	0.040	0.1066	0.030	0.033	0.032	0.0455	0.0747	0.058	0.044	0.063
$d/\mathrm{gcm^{-3}}$	1.283	1.341	1.589	1.254	1.257	1.280	1.280	1.172	1.240	1.333	1.285	1.332
R1	0.0554	0.0663	0.0454	0.1034	0.0470	0.0459	0.0374	0.0483	0.1246	0.0494	0.0575	0.0714
Rw	0.1937	0.1758	0.1175	0.2927	0.1327	0.1205	0.1009	0.1330	0.3764	0.1457	0.1643	0.2395
GOF	1.073	1.035	1.058	1.082	1.088	1.071	1.092	1.045	1.216	1.079	1.030	1.077
T/K	213	100	213	213	153	153	153	153	213	213	100	213
CCDC	940772	964560	940773	964566	964563	964562	964564	964561	964565	940774	940775	940776

Crystal Data for the Obtained Crystals of 2

Table 2. Conformation of the Substituted Phenyl Groups

Crystal	Twisted angles <sup>a)</sup>	Conformer <sup>b)</sup>
I-GF	38.23-48.11 (43.21)	С
II(CH <sub>3</sub> Cl)	37.45-56.55 (48.45)	A, B <sup>c)</sup>
III(DCM)	44.79-46.79 (45.75)	В
III(Tol)	44.15-46.57 (45.36)	В
III(o-Xyl)	42.73-46.46 (44.59)	В
III( <i>m</i> -Xyl)	45.65-46.23 (45.94)	В
III(p-Xyl)	44.61-45.63 (45.12)	В
III(Mes)	44.28-45.27 (44.78)	В
III′(THF)	44.20-46.40 (45.19)	В
IV(DCM)	42.05-45.98 (44.51)	C, C <sup>c)</sup>
IV(AcOEt)	41.86-45.35 (43.59)	C, C <sup>c)</sup>
IV(DCE)	40.87-46.77 (43.91)	C, C <sup>c)</sup>

a) Averaged values are shown in parentheses. b) Detailed structures of the conformers are given in Figure 2. c) Two crystallographically independent molecules are included in the unite cell.



**Figure 3.** Crystal structure of **I**-GF. (a) Packing diagrams viewed from the *b* and *c* axes. (b) Twofold helical arrangements of the substituent phenyl groups.

green, are in meshing engagement with those bonded to the next [12]DBA layer, colored with yellow, to form the densely-packed sheet structure. The nearly orthogonal contact of the phenyl groups (the dihedral angle and distance between centers of the phenyl groups are 81.8–87.1° and 4.86–5.06 Å, respectively) should contribute the stabilization of the crystal.<sup>26</sup>

**Crystal Structure of the Forms III and III'.** Crystallization from dichoromethane gave crystals **III**(DCM) and **IV**(DCM) concomitantly or either of them depending on the crystallization batches. **III**(DCM) belongs to the space group  $P2_1/c$ . The [12]DBA molecules stack into a zigzag fashion through  $\pi$ - $\pi$  interaction between the fused benzene moieties (the closest stacking distance: 3.40 Å) as shown in Figure 5a, and through face-to-edge (CH- $\pi$ ) interactions between substituted phenyl groups (dihedral angle: 74.5°) as shown in Figure 5b. Dichloromethane molecules are accommodated between the layers with a host/guest ratio of 1:2.

Interestingly, the zigzag-stacked layer structure observed here are revealed to be tolerant for guest species included



Figure 4. Crystal structure of  $II(CHCl_3)$ . (a) Packing diagram viewed from the *b* axis, (b) the [12]DBA layer, and (c) the phenyl layer, in which the phenyl groups bound to the [12]DBA layer (green) and those to the next DBA layer (yellow) are densely packed in orthogonal fashion. The guest molecule is disordered in two positions, one of which is shown in orange.

between the layers. Besides crystal III(DCM), 2 yields crystals III including toluene, o-xylene, m-xylene, p-xylene, 1,3,5trimethylbenzene (mesitylene), and tetrahydrofuran [III(Tol), III(o-Xyl), III(m-Xyl), III(p-Xyl), III(Mes), and III'(THF), respectively] as shown in Figure 6. III(DCM) includes dichloromethane with a 1:2 host/guest ratio, while III(Tol), III(o-Xyl), III(m-Xyl), and III(p-Xyl) with a 1:1 host/guest ratio. These crystals belong to the same space group  $P2_1/c$ and exhibit nearly identical lattice parameters including the a axis (14.1–14.5 Å) which corresponds to distance between layers. These results indicate that the void space did not strictly recognize molecular shapes of mono- or disubstituted benzene. Solvate of trisubstituted benzene III(Mes), which includes mesitylene with a DBA/guest ratio of 1:2 similar with III(DCM), belongs to the space group  $P2_1/c$ , while the lattice parameters differ from the formers. Particularly the *a* axis is elongated up to 18.8 Å. The solvate of THF also has the same zigzag layer motif with a 1:1 host/guest ratio. However, the layers are arranged in slightly slipped manner to give P1 crystal III'(THF). These results indicate that the zigzag layer composed of 2 can be applied for a platform of new crystalline host-guest systems.

**Crystal Structure of the Form IV.** The  $P\bar{1}$  crystal **IV**(DCM) accommodates dichloromethane in a 1:1 host/guest ratio. Two crystallographically independent molecules of **2** are alternately  $\pi$ -stacked to give a 1D columnar motif (Figure 7a). The DBAs in the column show slippage in the long axis direction and no significant slippage in the short axis due to steric effect of the phenyl groups (Figure 7b), in which dichloromethane molecules are accommodated in void spaces of the layer to form a densely packed layer structure similar to that in **II**(CHCl<sub>3</sub>) as shown in Figure 7c. In the layer, the adjacent phenyl groups are arranged nearly perpendicular with face-



Figure 5. Crystal structure of III(DCM). (a) Packing diagrams viewed from the a and c axes. (b) Arrangements of the substituted phenyl groups. The guest molecule is disordered in two positions, one of which is shown in orange.

to-edge contact (the dihedral angle:  $85.2-87.1^{\circ}$ ). This type of molecular arrangement was also obtained when ethyl acetate and dichloroethane were applied as solvents: **III**(AcOEt) and **III**(DCE), respectively. The crystal structures are shown in Figures S4 and S5.

**Examination of Topochemical Polymerization in Crystals IV.** Cyclic compounds containing more than one butadiyne



Figure 7. Crystal structure of IV(DCM). (a) Packing diagrams viewed from the *a* and *c* axes, (b) relative orientation of DBA 2 molecules in the column, (c) the layer structure composed of the phenyl groups colored green and guest molecules (dichloromethane) colored orange. The guest molecule is disordered in two positions, one of which is shown in orange.



**Figure 6.** Pacing diagrams of (a) **III**(DCM), (b) **III**(Tol), (c) **III**(*o*-Xyl), (d) **III**(*m*-Xyl), (e) **III**(*p*-Xyl), (f) **III**(Mes), and (g) **III**'(THF), in which the guest molecules are shown with the space-fill models colored orange. The guest molecule in **III**(DCM), **III**(Tol), **III**(*o*-Xyl), **III**(*m*-Xyl), and **III**(*p*-Xyl) is disordered in two positions, one of which is shown in orange.



Scheme 3. (a) Proposed ene-yne ladder polymer formed by topochemical polymerization of [12]DBA. Stacking manner of [12]DBA with slippage both in short and long axes directions (b) and only in long axis direction (c).

Table 3. Geometric Parameters of Crystals IV(DCM), IV(AcOEt), and  $IV(DCE)^{a}$ 

	Ideal	IV(DCM)	IV(AcOEt)	IV(DCE)
$d^{\rm b)}/{\rm \AA}$	4.9	4.84-4.99	4.79-4.95	4.86-4.99
$\theta^{ m c)}/^{\circ}$	45	49.4-48.9	48.0-47.6	51.4-52.1
$d_{1-4}^{\rm d)}/{\rm \AA}$	3.4	3.76-3.74	3.62-3.64	3.91-3.92

a) The respective value of parameters have ranges, because the crystals involve two crystallographically independent molecules. b) *d*: Stacking distance. c)  $\theta$ : slipping angle. d)  $d_{1-4}$ : C<sub>1-4</sub> distance.

in the cycle are intensively investigated because topochemical polymerization<sup>27-29</sup> occurring in their one-dimensionally stacked architectures can provide ladder- or tube-type ene-yne polymeric materials. The topochemical polymerization of a cyclic system is first achieved by Vollhardt, Youngs, and coworkers for crystals of octadehydrotribenzo[14]annulene in 1995.30 Subsequently, construction of 1D-stacked assemblies and their topochemical polymerization were reported by Shimizu's,<sup>29a</sup> Lauher's,<sup>29d</sup> and Morin's<sup>29e</sup> groups. [12]DBA is also a candidate for the monomer of the reaction (Scheme 3a). However, in spite of great efforts, there is no report of topochemical polymerization of [12]DBA derivatives. We carefully evaluated crystal structures of the [12]DBA derivatives reported, and consequently found in fact that the all [12]DBAs slipped in the shorter axis direction of the molecules as well as in the longer axis direction (Scheme 3b, also see Figure S1), except for phenanthrene annelated [12]DBA reported quite recently by Nakamura and co-workers.<sup>18</sup> The slippage in the short axis causes molecular assemblies unfavorable for topochemical polymerization, judging from the optimized structure of the expected ene-yne polymer (Figure S2). On the other hand, the IV crystals obtained in the present study possess desired 1D  $\pi$ -stacked columnar architecture with no slippage in the short axis direction but in longer axis direction (Scheme 3c).

Table 3 shows the geometric parameters of **IV** crystals, particularly **IV**(AcOEt) and **IV**(DCM), whose d,  $\theta$ , and  $d_{1-4}$  values are ranged in 4.79–4.99 Å, 47.6–52.1°, and 3.62–3.92 Å, respectively, where d,  $\theta$ , and  $d_{1-4}$  indicate stacking distance, slipping angle, and intermolecular distance between C1 and C4 atoms of butadyine moieties, respectively. These values

are close to the ideal values for topochemical polymerization; i.e., d = 4.9 Å,  $\theta = 45^{\circ}$ ,  $d_{1-4} = 3.4$  Å. Therefore, we examined topochemical polymerization on the crystals IV(DCM) and IV(AcOEt). First, to investigate heat-induced polymerization, the crystals IV(DCM) and IV(AcOEt), as well as III(DCM) as a reference, are subjected to differential scanning calorimetry (DSC), showing weak endothermic peaks at 108, 103, and 90 °C, respectively, and significant exothermic peaks at 294, 300, and 289 °C, respectively (Figure 8a). Thermal gravimetric (TG) analysis of the crystals indicates that the former peaks correspond to structural transformation due to guest desorption (Figure 8b). Furthermore, powder X-ray diffraction (PXRD) patterns of the crystals after the transformation agreed with that of I-GF (Figure S6). These results indicate that the crystals released the guest molecules upon heating, to transform into the guest-free form unsuitable for topochemical polymerization. The exothermic peaks at around 300 °C are probably attributed to thermal decomposition of the compound. Indeed, the resultant black materials show no PXRD signals and were insoluble in common organic solvents, preventing solution NMR analysis. Next, the polymerization at room temperature was attempted by  $\gamma$ -ray irradiation (81.1 Gy h<sup>-1</sup> for 24 h) or UV (Xe-ramp 300 W for 48 h) to the crystals IV(DCM) and IV(AcOEt). Surprisingly, however, the crystals showed no reaction and their structures remained under the reaction conditions. This significant stability implies that the reaction would require more precise and strict geometric conditions and/or that the phenyl groups densely-packed in the edge-toface fashion would not allow even subtle structural changes caused by topochemical polymerization.

Structure-Dependent Optical and Electrical Properties of the Crystals. Optical and electrical properties of the obtained crystals were investigated because a  $\pi$ -stacked arrangement of the [12]DBA core must strongly affect on them. Figure 9 and Table 4 show optical data of I-GF, III(DCM), and IV(DCM), as well as those of 2 in solution.<sup>31</sup> The fluorescence spectrum of crystal I-GF has an obvious vibrational structure with  $\lambda^{em}_{max} =$ 571 nm [ $\phi_F = 0.3\%$ ,  $\tau = 1.5$  ns (97%), and 9.8 ns (3%)], where  $\lambda^{em}_{max}$ ,  $\phi_F$ , and  $\tau$  denote wavelength at fluorescence maximum, fluorescence quantum yield, and fluorescence lifetime, respectively, similar to those observed in a solution state. Crystal III(DCM) also has an unambiguous vibrational spectrum with  $\lambda^{em}_{max} = 564$  nm [ $\phi_F = 1.3\%$ ,  $\tau = 1.8$  ns (22%), and 2.7 ns



**Figure 8.** Thermal analyses of the crystals **IV**(DCM) and **IV**(AcOEt), as well as **III**(DCM). (a) DSC curves, (b) TG curves.



**Figure 9.** Structure-dependent optical and electrical properties. (a) Fluorescence spectra of I-GF, III(DCM), and IV(DCM), as well as 2 in chloroform solution. (b) Anisotropic charge carrier behavior of IV(DCM) in  $\pi$  stacked and orthogonal direction (red and blue lines, respectively).

Table 4.	Optical	Properties	of 2	in	Solution	and	Crystals
I-GF, I	II(DCM	), and IV(I	DCM)				

	$\lambda^{ m em}_{ m max}$ /nm	$\lambda^{ex}_{max}$ /nm	$\phi_{ ext{F}}$	τ /ns
<b>2</b> <sup>a)</sup>	557	248	0.012 <sup>b)</sup>	1.5 (96%), 4.2 (4%)
I-GF	571	469	0.003	1.5 (97%), 9.8 (3%)
III(DCM)	564	468	0.013	1.8 (22%), 2.7 (78%)
IV(DCM)	592	468	0.005	2.1 (60%), 3.2 (40%)

a) Measured in chloroform solution. b) Determined based on that of rhodamine G6 with  $\lambda^{ex} = 375$  nm.

(78%)]. Crystals **IV**(DCM), on the other hand, show weak, structureless spectra with  $\lambda^{\rm em}_{\rm max} = 591 \,\mathrm{nm} \ [\phi_{\rm F} = 0.5\%, \ \tau = 2.1 \,\mathrm{ns}$  (60%), and 3.2 ns (40%)], indicating that the molecular arrangements of the crystals **IV** provides a more stable excited state compared with the crystals **I-GF** and **III**, probably due to generation of species such as excited oligomers.

Charge carrier behavior of **IV**(DCM) was also investigated by flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurement,<sup>32</sup> revealing that the crystal **IV**(DCM) exhibited moderate photoconductivity ( $\phi \Sigma \mu = 2.9 \times 10^{-5}$ cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) along the crystallographic *a* axis, which corresponds to the  $\pi$ -stacked direction of the [12]DBA. The value is 2.7 times larger than those in the orthogonal axis ( $\phi \Sigma \mu =$  $1.1 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). The anisotropy of the conductivity is smaller than the columnar assembly of tribenzohexadehydro[12]annulene derivatives reported previously by our group,<sup>33</sup> indicating that the phenyl substituents staggered from the [12]DBA plane provide a pathway to charge carriers in the orthogonal directions.

### Conclusion

In this study, we synthesized an ortho-phenyl-substituted derivative of octadehydrodibenzo[12]annulene ([12]DBA 2) and investigated the effects of the arvl substituents on molecular stacking manner of the [12]DBA core. [12]DBA 2 yielded four types of crystalline lattices including a hitherto unknown form: the guest-free crystal possessing an offset stacking manner (I-GF), the solvate with an edge-to-face arrangement (II), the solvates with zigzag  $\pi$ -stacked arrangements of [12]DBA (III and III'), and the solvate with 1D  $\pi$ -stacked columnar arrangements of [12]DBA (IV). The substituted phenyl groups provided void spaces, in which various guest species are accommodated. Particularly, the zigzag  $\pi$ -stacked motif formed in III and III' is tolerant of guest species included between the layers, and therefore, can be a platform for a new crystalline host-guest system. Moreover, aggregation of [12]DBA cores is restricted by the phenyl groups, giving an unusual assembly in the crystal IV, that is, 1D  $\pi$ -stacked columnar architecture with no slippage in the short axis direction but in the longer axis direction. The structure has nearly ideal geometry for the topochemical polymerization. However, the anticipated polymeric material has not been obtained yet. The crystal with the 1D  $\pi$ -stacked motif exhibits broaden, redshifted fluorescence spectral profiles and anisotropic charge carrier behaviors ascribable to strong interaction between the  $\pi$ -orbitals of the adjacent [12]DBA cores. Finally, we conclude that ortho-substitution with phenyl groups, which provided

(1) aggregation with geometrically-restricted, unusual manner different from that of the parent [12]DBA and (2) inclusion of guest molecules which bring about formation of lattice frameworks depending on the guest species, can be a rational way to modulate molecular arrangements of the [12]DBA.

## Experimental

**General.** <sup>1</sup>H and <sup>13</sup>C spectra were measured with a JEOL spectrometer (270 or 400 MHz for <sup>1</sup>H and 67.5, 100, or 150 MHz for <sup>13</sup>C). Mass spectra data were obtained with a JEOL JMS-700 instrument or autoflex III Bruker. UV–vis spectra in solution were measured using a JASCO V-550 spectrometer. Emission spectra in solution were measured using a JASCO FP-6500 spectrofluorometer. The fluorescence decay times and lifetimes were obtained using HORIBA FluoroCube and the software (Data Station v.2.4 and DAS 6) supplied in the apparatus.

Single-Crystal X-ray Analysis. For crystals I-GF, III(Tol), III(Mes), III'(THF), and IV(DCM), diffraction data were collected on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu Ka radiation ( $\lambda = 1.54187$  Å). The cell refinements were performed with software equipped in a Rigaku R-AXIS RAPID system. For crystals II(CHCl<sub>3</sub>), III(DCM), III(*o*-Xyl), III(*p*-Xyl) III(*m*-Xyl), IV(AcOEt), IV(DCE), and 6, diffraction data were collected on a CCD (O315, ADSC) with the synchrotron radiation ( $\lambda = 0.7000$  or 0.8000 Å) monochromated by a fixed exit Si(111) double crystal. The cell refinements were performed with HKL2000 software.<sup>34</sup> Direct methods (SIR-2004<sup>35</sup> or SIR2008<sup>36</sup>) were used for the structure solution of the crystals. All calculations were performed with the observed reflections  $[I > 2\sigma(I)]$  with the program CrystalStructure crystallographic software packages,37 except for refinement, which was performed using SHELXL-97.38 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. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-940772 for I-GF, CCDC-964560 for II(CHCl<sub>3</sub>), CCDC-940773 for III(DCM), CCDC-964566 for III(Tol), CCDC-964563 for III(o-Xyl), CCDC-964562 for III(m-Xyl), CCDC-964564 for III(p-Xyl), CCDC-964561 for III(Mes), CCDC-964565 for III'(THF), CCDC-940774 for IV(DCM), CCDC-940775 for IV(AcOEt), CCDC-940776 for IV(DCE), and CCDC-940777 for compound 6. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

**Powder Diffraction X-ray Analysis.** PXRD data were collected on a Rigaku RINT-2000 using graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54187$  Å) at room temperature.

Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC) Measurement.<sup>32</sup> Nanosecond laser pulses from a Nd:YAG laser (third harmonic generation, THG (355 nm) from Spectra Physics, INDI, FWHM 5–8 ns) were used as excitation sources. The incident photon density of the laser was set at  $9.1 \times 10^{15}$  photons/cm<sup>2</sup>/pulse. For timeresolved microwave conductivity (TRMC) measurements, the microwave frequency and power were set at ca. 9.1 GHz and 3 mW, respectively, so that the motion of the charge carriers was not disturbed by the low electric field of the microwaves. The TRMC signal picked up by a diode (rise time <1 ns) is monitored with a digital oscilloscope. All the above experiments were carried out at room temperature. The photoconductivity is given by the equation  $\phi \Sigma \mu = (1/eAI_0F_{\text{light}})(\Delta P_r/P_r)$ , where  $\phi$ ,  $\Sigma \mu$ , *e*, *A*,  $I_0$ ,  $F_{\text{light}}$ ,  $P_r$ , and  $\Delta P_r$  denote photocarrier generation yield, the sum of the charge carrier mobilities, the unit charge of a single electron, the sensitivity factor (S<sup>-1</sup> cm), the incident photon density of an excitation laser (photon cm<sup>-2</sup>), the filling factor (cm<sup>-1</sup>), and the reflected microwave power and its change, respectively.

Synthesis of Terphenyl Derivative 4. A mixture of 1,2,3,4-tetrabromobenzene  $(3)^{22}$  (2.00 g, 5.08 mmol), phenylboronic acid (1.55 g, 2.7 mmol), [Pd(PPh\_3)\_4] (0.298 g, 0.254 mmol), Na<sub>2</sub>CO<sub>3</sub> (1.09 g, 10.1 mmol) in degassed 1,4-dioxane (15 mL), toluene (15 mL), and water (15 mL) was stirred for 24 h under reflux. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, and dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4/1), followed by rinsing with hexane to give 4 (759 mg, 39%) as a while solid.

4: mp: 121 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  7.48–7.39 (m, 10H), 7.29 (s, 2H). <sup>13</sup>C NMR (67.5 MHz, CDCL<sub>3</sub>):  $\delta$  144.5, 142.3, 129.7, 129.6, 128.4, 128.2, 127.0. HR-MS(FAB): calcd for C<sub>18</sub>H<sub>12</sub>Br<sub>2</sub> [M]<sup>+</sup> 387.9285; found 387.9280.

Synthesis of Diethynylterphenyl Derivative 5. A mixture of 4 (2.60 g, 6.70 mmol),  $[Pd(PPh_3)_4]$  (778 mg, 0.674 mmol), PPh<sub>3</sub> (370 mg, 1.41 mmol), ZnCl<sub>2</sub> (273 mg, 2.00 mmol), trimethylsilylacetylene (4.73 mL, 3.29 g, 33.5 mmol) in degassed piperidine (30 mL) and triethylamine (30 mL) was placed in a pressure glass tube, purged by N<sub>2</sub> gas, and sealed. After stirred for 17 h at 100 °C, the solvent was removed in vacuo and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, and dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>), followed by rinsing with MeOH to give 5 (1.89 g, 67%) as a white solid.

5: mp: 144 °C. <sup>1</sup>H NMR (270 MHz, CDCl<sub>3</sub>):  $\delta$  7.63–7.60 (m, 4H), 7.45–7.37 (s, 8H), 0.14 (s, 18H). <sup>13</sup>C NMR (67.5 MHz, CDCl<sub>3</sub>):  $\delta$  144.0, 140.4, 129.7, 129.6, 128.1, 127.9, 125.2, 103.4, 103.0, 0.06. HR-MS(FAB): calcd for C<sub>28</sub>H<sub>30</sub>Si<sub>2</sub> [M]<sup>+</sup> 422.1886; found 422.1889.

Synthesis of [12]DBA 2. A mixture of 5 (802 mg, 1.90 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.25 g, 38.0 mmol) in THF (40 mL) and MeOH (40 mL) was stirred at room temperature for 2 h. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. The product was used in the following step without further purification.

To a solution of copper acetate monohydrate (8.20 g, 41.2 mmol) dissolved in pyridine (300 mL) and methanol (300 mL) was added dropwise the above product dissolved in pyridine (100 mL) over 1 h with stirring at 60 °C and stirred for 12 h at this temperature. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with 5% HCl and brine, and dried over anhydrous MgSO<sub>4</sub>. The product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) and preparative HPLC (CHCl<sub>3</sub>) to

give dimer 2 (267 mg, 51%) as a yellow solid and trimer 6 (149 mg, 28%) as a pale yellow solid.

**2**: mp (dec.) 296 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.50–7.48 (m, 8H), 7.42–7.36 (m, 12H), 7.18 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> 55 °C):  $\delta$  141.6, 139.5, 130.3, 129.9, 128.5, 128.4, 128.2, 91.6, 86.7. HR-MS(FAB): calcd for C<sub>44</sub>H<sub>24</sub> [M]<sup>+</sup> 552.1878; found 552.1884.

**6**: mp (dec.) 200 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> 25 °C): δ 7.59–7.56 (m, 12H), 7.49–7.46 (m, 12H), 7.41–7.38 (m, 12H). <sup>13</sup>C NMR (150 MHz, pyridine- $d_5$ , 80 °C): δ 145.6, 139.7, 130.7, 129.6, 129.0, 128.7, 124.6, 82.3, 82.1. HR-MS(MALDI-TOF): calcd for C<sub>66</sub>H<sub>36</sub>Na [M + Na]<sup>+</sup> 851.2709; found 851.2685. Crystal data for **6**: C<sub>66</sub>H<sub>36</sub>,  $M_r$  = 829.01, a = 27.5291(3) Å, b = 20.3658(2) Å, c = 15.8144(2) Å, V = 8866.38(18) Å<sup>3</sup>, T = 100 K, *orthorhombic*, space group *Pbca*, Z = 8,  $d_{calcd}$  = 1.242 g cm<sup>-3</sup>, 42030 collected, 8894 unique ( $R_{int}$  = 0.042) reflections, the final *R*1 and w*R*2 values 0.0450 (I > 2.0 $\sigma(I$ )) and 0.1249 (all data), respectively. CCDC-940777. Also see Figure S3 in the Supporting Information.

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#### **Supporting Information**

Spectral data, Crystallographic data of **6**, **IV**(AcOEt), and **IV**(DCE), and theoretical calculations. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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