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Expanded graphyne fragment: Trigonally expanded dehydrobenzo[12]annulenes (DBA; see figure) can be synthesized by three-fold alkyne metathesis reactions catalyzed by a Mo nitride complex. Tetrakis-DBAs show a large two-photon cross-section, enhanced aggregation properties in solution, the formation of columnar rectangular mesophases in the condensed state, and moderate charge-carrier mobility. These results indicate that large graphyne fragments may serve as promising organic semiconductors.



### **Graphyne Fragments** -

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Syntheses and Properties of Graphyne **Fragments: Trigonally Expanded** Dehydrobenzo[12]annulenes



### Syntheses and Properties of Graphyne Fragments: Trigonally Expanded Dehydrobenzo[12]annulenes

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Abstract: We present herein the synthesis and properties of the largest hitherto unknown graphyne fragment, namely trigonally expanded tetrakis-(dehydrobenzo[12]annulene)s (tetrakis-DBAs). Intramolecular three-fold alkyne metathesis reactions of hexakis(arylethynyl)DBAs 9a and 9b using Fürstner's Mo catalyst furnished tetrakis-DBAs 8a and 8b substituted with tert-butyl or branched alkyl ester groups in moderate and fair yields, respectively, demonstrating that the metathesis reaction of this protocol is a powerful tool for the construction of graphyne fragment backbones. For comparison, hexakis(arylethynyl)DBAs 9c-g have also been prepared. The one-photon absorption spectrum of tetrakis-DBA **8a** bearing *tert*-butyl groups revealed a remarkable bathochromic shift of the absorption cut-off ( $\lambda_{cutoff}$ ) compared with those of previously reported graphyne fragments due to extended  $\pi$ -conjugation. Moreover, in the two-photon absorption spectrum, **8a** showed a large cross-section for a pure hydrocarbon because of the planar *para*-phenylene-ethynylene conjugation pathways. Hexakis(arylethynyl)-DBAs **9c-e** and **9g** and tetrakis-DBA **8b** bearing electron-withdrawing groups aggregated in chloroform solutions.

**Keywords:** alkynes • dehydrobenzoannulenes • graphyne • metathesis • self-assembly Comparison between the free energies of 9e and 8b bearing the same substituents revealed the more favorable association of the latter due to stronger  $\pi$ - $\pi$  interactions between the extended  $\pi$ -cores. Polarized optical microscopy observations, DSC, and XRD measurements showed that 8b and 9e with branched alkyl ester groups displayed columnar rectangular mesophases. By the time-resolved microwave conductivity method, the columnar rectangular phase of 8b was shown to exhibit a moderate charge-carrier mobility of  $0.12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . These results indicate that large graphyne fragments can serve as good organic semiconductors.

#### Introduction

Highly conjugated carbon-rich molecules have attracted increased attention because of their potential utility in the field of organic materials science.<sup>[1]</sup> They show intriguing optical and electronic properties and are capable of building up highly organized supramolecular nanostructures in one, two, and three dimensions.<sup>[2]</sup> Among them, hexadehydrobenzo[12]annulene (DBA, 1, Figure 1),<sup>[3]</sup> which can be regarded as the smallest unit of a hitherto unknown carbon allotrope,  $\gamma$ -graphyne,<sup>[4,5]</sup> and its derivatives are currently the subject of intense interest. This is especially so in supramolecular chemistry, including the formation of one-dimensional columnar stacking<sup>[6]</sup> or rosette-shaped packing in three-dimensional crystals,<sup>[7]</sup> liquid crystals,<sup>[8]</sup> vesicles,<sup>[9]</sup> and two-dimensional (2D) molecular networks at the liquid-solid interface.<sup>[10]</sup> On the other hand, large  $\gamma$ -graphyne fragments, such as multiply fused DBAs 2-7, have been synthesized to investigate their optical and electronic properties as well as local aromaticity.<sup>[11,12]</sup> One of the largest known fragments is the trefoil-type triply-fused DBA 7, which exhibits a relatively large two-photon absorption cross-section among hydrocarbons of 1300 GM at 572 nm, due to the three para-phenyleneethynylene conjugation pathways locked in the planar

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Figure 1. Chemical structures of parent DBA 1 and multiply fused DBAs 2–7.

framework.<sup>[13]</sup> It is of further interest to develop viable synthetic approaches to even larger  $\gamma$ graphyne fragments and to gain insight into the issue of how many DBA units are needed to confer the graphyne-like character. Graphyne has been reported to exhibit nonlinear optical properties<sup>[14]</sup> and conductivity when doped with potassium metal.<sup>[15]</sup> Recently, graphyne and graphyne nanoribbons have become intriguing subjects of theoretical studies,<sup>[16]</sup> and FULL PAPER

as for the graphdiyne series a large fragment consisting of four [18]DBA units is known (Figure 2).<sup>[19d]</sup> Consequently, to design organic materials based on graphyne fragments, it is necessary to extend their structural size limit and to systematically study structure–property relationships using discrete molecular species.<sup>[20]</sup>

Recently, alkyne metathesis has become a powerful method for the construction of arylene-ethynylene macrocycles by virtue of a remarkable improvement in catalyst efficiency and stability.<sup>[21]</sup> The first synthesis of an arylene-ethynylene macrocycle by the use of alkyne metathesis was reported by Adams and Bunz et al., [22] whereby meta-cyclophenylene-ethynylene (m-CPE) hexamers were synthesized in up to 6% yield from *m*-dipropynylbenzene derivatives by an in situ generated molybdenum catalyst. Miljanić and Whitener et al. demonstrated the syntheses of DBAs and a bow-tie-shaped bis-DBA from the corresponding propynylbenzene precursors catalyzed by a tungsten carbyne complex.<sup>[12f]</sup> The maximum yields of the DBAs and bis-DBA were 55% and 6%, respectively. On the other hand, Moore et al. reported that a trialkoxymolybdenum alkylidyne complex showed high reactivity towards propynylbenzene deriv-



Figure 2. Structures of known multiply fused dehydrobenzoannulenes with trefoil shapes.

one of the interesting predictions is a remarkable hydrogenstorage capacity when they are decorated with Li or Ca.<sup>[17]</sup> As such, large graphyne fragments are intriguing synthetic targets.

For the synthesis of multiply fused DBAs 2–7, the Sonogashira–Hagihara-type coupling reaction,<sup>[12a,d]</sup> the Stephens– Castro-type reaction,<sup>[12c]</sup> double-elimination following the formation of a single-bond linkage by intramolecular pinacol coupling reaction,<sup>[12e,g]</sup> and an alkyne metathesis reaction<sup>[12b,f]</sup> have been employed as pivotal steps for the construction of the DBA subunits. However, in view of the low efficiency in the construction of the twelve-membered ring, the syntheses of the graphyne fragments are generally difficult compared to those of multiply fused dehydrobenzo[18]annulene ([18]DBA) derivatives, graphdiyne fragments<sup>[18]</sup> that are constructed by oxidative coupling of terminal alkynes.<sup>[19]</sup> Indeed, large graphyne fragments composed of more than three DBA units have not been synthesized thus far, whereatives.<sup>[23]</sup> In this case, the reaction side-product 2-butyne had to be removed under reduced pressure in order to drive the reaction equilibrium toward the product and to prevent deactivation of the catalyst. An alternative method for removing the reaction side-product was developed by the same authors that utilized benzoylbiphenyl groups as the terminal groups of the alkyne in the precursors, which were converted into insoluble alkyne by-products. Multigram quantities of *m*-CPEs were obtained by the so-called precipitationdriven alkyne metathesis reactions.<sup>[24]</sup> Further modification of the Mo catalyst was achieved by changing the co-catalyst (Silanol-POSS)<sup>[25]</sup> or using a silica support.<sup>[26]</sup> Recently, Fürstner et al. reported that molybdenum nitride and alkylidyne complexes bearing triphenylsilyloxy ligands represented superior alkyne metathesis catalysts in terms of stability to both air and side-product (2-butyne), reaction efficiency, and functional group tolerance.<sup>[27]</sup> Such a catalyst can be used for the synthesis of m-CPEs.[28]

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We previously reported on theoretical studies based on DFT calculations on the graphyne fragments at the B3LYP/ 6-31G\* level of theory; the parent trigonally expanded tet-rakis(dehydrobenzo[12]annulene) (tetrakis-DBA, **8c**, Figure 3) was determined to have the smallest HOMO-LUMO gap (2.29 eV) among the multiply fused DBAs **2**–**7**.<sup>[11a]</sup> Though a structurally related trefoil dehydrobenzoan-nulene consisting of a central [12]DBA and peripheral dehy-



Figure 3. Chemical structures of trigonally expanded tetrakis-DBAs **8a–c** and reference compounds (AE)<sub>6</sub>-DBAs **9a–g**.

dro[14]annulene units has been reported by Haley and coworkers (Figure 2),<sup>[29]</sup> all-[12]DBA trefoil has hitherto remained unknown. In addition, tetrakis-DBA is expected to show a large two-photon absorption cross-section due to the planar tri(*para*-phenyleneethynylene) conjugation pathway.<sup>[13,30]</sup> Moreover, stacking interactions between the large planar  $\pi$ -conjugated cores are expected to enhance the selfassembly properties, not only in solution but also in the condensed phase, giving rise to columnar liquid-crystalline materials when appropriately decorated at the periphery. We therefore envisaged tetrakis-DBA derivatives as interesting target molecules for studies of their optoelectronic properties and self-assembly behavior.

Herein, we describe the syntheses and properties of tetrakis-DBA derivatives 8a,b. Hexakis(arylethynyl)dehydrobenzo[12]annulene ((AE)<sub>6</sub>-DBA) derivatives 9c-g have also been prepared as reference compounds. The alkyne linkages in tetrakis-DBAs 8a,b were introduced in moderate to fair yields by three-fold alkyne metathesis reactions of 9a and 9b catalyzed by an Mo nitride complex, demonstrating the power of alkyne metathesis for the construction of the multiple DBA units of graphyne fragments. Among the optical and physical properties of 8a and 8b, particularly noteworthy are the large two-photon cross-section of 8a due to the planarized *para*-phenyleneethynylene conjugation pathways, the enhanced aggregation properties of **8b** in solution due to strong  $\pi$ - $\pi$  interactions, the formation of columnar rectangular mesophases of **8b** in the condensed phase, and a moderate charge-carrier mobility of **8b**. These results indicate that large  $\gamma$ -graphyne fragments serve as promising organic semiconductors.

#### **Results and Discussion**

#### Synthesis of trigonally expanded tetrakis-DBAs

Synthetic strategy: Our synthetic strategy for obtaining tetrakis-DBAs relies on stepwise construction of the DBA rings to circumvent obstacles in the construction of four DBA units, formation of the central DBA ring by Sonogashira– Hagihara coupling reaction, forming hexaethynyl-DBA **17**, and subsequent construction of the three peripheral DBA units. A double-elimination reaction after the intramolecular pinacol coupling of **9g** and subsequent chlorination were initially attempted. However, this reaction sequence resulted in the formation of a complex mixture of products. Therefore, we chose the alkyne metathesis reaction, which has proved to be successful for the construction of three peripheral DBA units.<sup>[12f]</sup>

Synthesis of arylene-ethynylene macrocycles by alkyne metathesis reactions: We tested the efficiency of alkyne metathesis catalysts for the construction of the DBA framework by using simple precursor 10. We first investigated a highly active trialkoxymolybdenum alkylidyne complex with Silanol-POSS as a co-catalyst.<sup>[25]</sup> One drawback of this catalyst system, in relation to our current studies, is that it has the potential to scramble the internal alkynes present in the pre-constructed central DBA ring of compounds 9.[31] Indeed, such a scrambling effect was observed when 10 was subjected to these conditions, giving rise to a complex mixture of tert-butyl-substituted DBAs. Thus, we chose an alternative catalyst, namely molybdenum nitride and an alkylidyne complex bearing triphenylsilyloxy ligands, which was superior in terms of stability to both air and side-product (2butyne), reaction efficiency, and functional group tolerance. Despite these advantageous properties, these catalytic systems have not been shown to react in a reversible way with "internal" diphenylacetylenes. In fact, by optimizing the reaction conditions (see the Supporting Information, Table S1), we found that DBA 11 could be obtained in excellent yield by the reaction of 10 in 1,2,4-trichlorobenzene (TCB) at 150°C (Scheme 1). Surprisingly, no detectable amounts of scrambled products were formed under these reaction conditions. Applying the optimized reaction conditions, we started the synthesis of tetrakis-DBA derivatives.

Syntheses of trigonally expanded tetrakis-DBAs: The synthesis of tetrakis-DBAs began with hexakis[(triisopropylsilyl)e-thynyl]DBA 16, which was prepared in 20% overall yield

#### Ph<sub>3</sub>SiO ···No···OSiPh<sub>3</sub> Ph<sub>3</sub>SiO ···No··OSiPh<sub>3</sub> (21 mol%) (21 mol%) 1,2,4-trichlorobenzene 150 °C, 24 h fBu fBu fBu 11, 87% fBu

Scheme 1. Synthesis of DBA  ${\bf 11}$  by alkyne metathesis catalyzed by a Mo nitride complex.

from 1,2-dibromo-3,4-diiodobenzene (Scheme 2; see also the Supporting Information). Desilvlation of 16 with tetrabutylammonium fluoride (TBAF) followed by a six-fold crosscoupling catalyzed by palladium with the corresponding aryl iodide (see the Supporting Information) gave the penultimate (AE)<sub>6</sub>-DBAs **9a** and **9b** in yields of 31% and 48% (from compound 16), respectively. As reference compounds, (AE)<sub>6</sub>-DBAs 9c-g were synthesized according to the same protocol. Next, a three-fold alkyne metathesis reaction was performed to construct the three peripheral DBA units. Specifically, treatment of 9a and 9b with 63 and 70 mol% of Fürstner's Mo nitride complex at 150°C in TCB afforded tetrakis-DBAs 8a and 8b as orange solids in yields of 19% and 56%, respectively (Scheme 3). The lower isolated yield of 8a was most probably due to physical loss during isolation owing to its low solubility in common organic solvents

(i.e., less than 0.1 mgmL<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>), in contrast to **8b**, which is reasonably soluble. Alternatively, it may also have been due to the different side-products of the metathesis because of the different alkyne terminal groups in **9a** (Me) and **9b** (Et); it has been reported that the deactivation rate of an Mo catalyst by 2-butyne (generated from **9a**) is faster than that by 3-hexyne (generated from **9b**).<sup>[23]</sup> Note that the

three-fold symmetries of the tetrakis-DBAs are evident from their NMR spectra, thus ruling out alternative prod-

#### **Photophysical properties**

ucts derived from metathesis scrambling.

One-photon absorption and emission spectra: The onephoton absorption (UV/Vis) spectrum of tetrakis-DBA provides useful insight into the electronic structure of the new  $\pi$ -system. Figure 4(a) displays the absorption spectrum of tetrakis-DBA 8a, together with those of  $(AE)_6$ -DBA 9c, tris-DBA 7, bis-DBA 2, and the parent DBA 1 for comparison. The spectrum of tetrakis-DBA 8a shows a strong band with its maximum at 360 nm ( $\lambda_{max}$ ) accompanied by a weak broadened band extending to 550 nm ( $\lambda_{cutoff}$ ). The former is attributable to the p-bis(phenylethynyl)benzene chromophore,<sup>[32]</sup> while the latter weak band is due to the forbidden  $S_0$ - $S_1$  transition of the  $D_{3h}$  symmetric structure of **8a**.<sup>[33]</sup> That is to say, TD-DFT calculations on the parent tetrakis-DBA at the B3LYP/6-31G\* level of theory under  $D_{3h}$  symmetric constraints indicated that the S<sub>0</sub>-S<sub>1</sub> transition is forbidden (Table S2 and Figure S1). Additionally, a significant bathochromic shift of the  $\lambda_{cutoff}$  value of tetrakis-DBA **8a** was observed compared with those of substituted tris-DBAs 6 and 7 ( $\lambda_{\text{cutoff}} = 525 \text{ nm for } 6$ ;  $\lambda_{\text{cutoff}} = 500 \text{ nm for } 7$ ), indicative of



Scheme 3. Synthesis of trigonally expanded tetrakis-DBAs 8a,b.



Scheme 2. Synthesis of  $(AE)_6$ -DBAs **9a–g**. TIPSA = triisopropylsilylacetylene, TIPS = triisopropylsilyl, TMSA = trimethylsilylacetylene, TMS = trimethyl

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Figure 4. (a) Absorption and (b) emission spectra of DBA 1 (black), rhombic-shaped bis-DBA 2 (green), trefoil-shaped tris-DBA 7 (red), trigonally expanded tetrakis-DBA 8a (blue), and  $(AE)_6$ -DBA 9c (orange) measured in dichloromethane or chloroform at room temperature. (c) Two-photon cross-section of 8a in chloroform at room temperature.

extended  $\pi$ -conjugation. The HOMO–LUMO gap calculated for **8a** from the  $\lambda_{cutoff}$  value (2.25 eV) was also consistent with the value estimated by DFT simulation (2.29 eV).<sup>[11a]</sup> Attempts to determine the electrochemical HOMO/LUMO levels of **8b** and **9e** were not successful, because in cyclic voltammetry only irreversible and reversible reduction waves were observed ( $E_{pa} = -2.21$  V for **8a**;  $E_{1/2} = -1.68$  V for **9e** in THF,  $nBu_4NClO_4$  as electrolyte), and no oxidation waves were detected (Figures S2 and S3).

Figure 4(b) shows the emission spectra of tetrakis-DBA **8a**,  $(AE)_6$ -DBA **9c**, tris-DBA **7**, bis-DBA **2**, and the parent DBA **1**. The emission spectrum of **8a** is bathochromically shifted compared with those of the other multiply fused DBAs. In the emission profile of **8a**, the relative intensity of the 0–0 vibrational transition band is weak compared with the most intense 0–1 band. The same tendency is also observed in **9c**, but the other multiple DBA molecules, except for trapezoid-type tris-DBA **5**, exhibit a most intense 0–0 vibrational transition bard set of the tendence of tendence of the tendence of the tendence of the tendence of the tendence of tendence of the tendence of the tendence of the tendence of tendence o

brational transition band.<sup>[12g]</sup> These features are associated with the structural difference between the ground and excited states, which becomes more significant in larger  $\pi$ -conjugated cores. On the other hand, in spite of the large  $\pi$ -conjugated framework, the fluorescence quantum yields of **8a** and **9c** were determined as 0.20 and 0.22, respectively, which are comparable to those of the bow-tie-shaped bis-DBA (0.19–0.21) and tris-DBA **6** (0.27).

Two-photon absorption cross-section: Two-photon absorption measurements of tetrakis-DBA 8a were performed in chloroform at concentrations of 0.6-0.8 mm by using the open-aperture Z-scan method (see the Supporting Information). Tetrakis-DBA 8a was found to have a broad twophoton absorption spectrum with two peaks, centered at around 640 and 740 nm (Figure 4(c)). The peak at 640 nm showed a two-photon absorption cross-section of around 900 GM while that at 740 nm had a value of 500 GM, where  $1 \text{ GM} = 10^{-50} \text{ cm}^4 \text{ s-photon}^{-1} \cdot \text{molecule}^{-1}$ . This spectral shape is similar to that of  $\mathbf{7}^{[12e]}$  in terms of peak positions and relative peak intensities (the peaks are located at 610 and 750 nm for 7). In contrast, the magnitude of the spectrum of 8a is almost twice as large as that of 7 at all wavelengths. This larger two-photon absorption cross-section is considered to arise from the elongated  $\pi$ -conjugation path of 8a, with three "phenyleneethynylene" units, compared to that of 7 with only two such units. It is worth noting that the peak wavelengths of 8a do not show a significant bathochromic shift upon extension of the conjugation. Similar behavior of an increase in the two-photon absorption intensity without a spectral shift was observed for compounds having ethylene and butadiylene  $\pi$ -conjugation linkers.<sup>[34]</sup>

#### Self-assembling behavior of tetrakis-DBA and hexakis-(arylethynyl)-DBAs

Self-association behavior in solution: The self-association behavior of shape-persistent phenylene-ethynylene macrocyclic molecules in solution due to  $\pi$ - $\pi$  stacking as well as solvophobic interactions has been extensively studied in order to elucidate the structural and electronic factors in both the core  $\pi$ -systems and peripheral substituents that affect the self-assembling propensity. Systematic investigations on the self-association of m-CPEs have revealed the importance of structural planarity of the  $\pi$ -cores, as well as the presence of electron-withdrawing peripheral substituents such as ester groups attached to the  $\pi$ -cores and unbranched alkyl groups on the substituents, for achieving a strong tendency for selfassociation in apolar solvents.<sup>[35]</sup> When such compounds are solubilized in polar solvents, solvophobic interactions play a major role in the assembly of large aggregates. Presumably because of the low association propensity of small DBA derivatives, there seems to be no report on the self-association of ortho-phenyleneethynylene macrocycles such as DBA and its homologues, except for that on dehydrobenzo[14]annulene derivatives bearing strongly electron-withdrawing/ donating groups by Haley et al.<sup>[30f]</sup> Although DBA deriva-

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tives bearing tetrathiafulvalene (TTF) units rather than benzene rings have been shown to self-aggregate in solution,<sup>[36]</sup> we focus here on hydrocarbon backbones. In this context, we became interested in investigating the self-association behavior of tetrakis-DBAs and  $(AE)_6$ -DBAs in solution.

Prior to studying tetrakis-DBA 8b, the self-association behavior of (AE)<sub>6</sub>-DBA derivatives was investigated by concentration-dependent <sup>1</sup>H NMR measurements. For example, the signals of the inner aromatic protons Ha and peripheral aromatic protons Hb (Figure 3) of butyl ester-substituted  $(AE)_6$ -DBA **9c** in CDCl<sub>3</sub> at 30 °C shifted from  $\delta = 7.57$  to 7.04 ppm and from  $\delta = 8.02$  to 7.55 ppm, respectively, on increasing the solute concentration from 0.15 to 19.1 mM (Figure S4), indicating face-to-face-type self-association. The chemical shift change was analyzed assuming a monomerdimer equilibrium, and from the least-squares curve-fitting (see the Supporting Information) the equilibrium constant (K) and the free energy  $(\Delta G)$  of dimerization were determined.<sup>[37]</sup> Table 1 lists the results, together with those similarly determined for (AE)<sub>6</sub>-DBAs **9d–g** and tetrakis-DBA 8b. Because the association constants determined by following the concentration-dependent shifts of Ha and Hb are not equal, average values are also included. The larger the K values, the greater the discrepancy becomes, most likely due to the formation of higher aggregates. The data in Table 1 nevertheless serve as a reasonable measure of the aggregation propensities of the DBA derivatives in solution. Similar observations have been reported previously.<sup>[30f, 35, 38]</sup>

The self-association propensity of dodecyl ester-substituted  $(AE)_6$ -DBA **9d** is similar to that of **9c**, indicating that the alkyl chain length does not influence the association behavior in a polar solvent (Figure S5). On the other hand, the branched alkyl chains in **9e** suppress the self-association of  $(AE)_6$ -DBA (Figure S6).<sup>[39]</sup> The largest association constant

Table 1. Association constants and the corresponding free energies for hexakis(arylethynyl)DBAs 9c-g and tetrakis-DBA 8b determined assuming a monomer-dimer model.<sup>[a]</sup>

Compound	Hydrogen atom <sup>[b]</sup>	$K_{ m assoc} \left[ { m M}^{-1}  ight]$	$\Delta G  [\mathrm{kJ}  \mathrm{mol}^{-1}]$
	На	$134\pm2$	$-12.3\pm0.1$
9c	Hb	$174\pm4$	$-13.0 \pm 0.1$
	average value	154	-12.7
9d	На	$93.3 \pm 1.5$	$-11.4 \pm 0.1$
	Hb	$126\pm2$	$-12.2 \pm 0.1$
	average value	110	-11.8
9e	На	$13.9\!\pm\!0.7$	$-6.6 \pm 0.1$
	Hb	$12.5\pm0.8$	$-6.4 \pm 0.1$
	average value	13.2	-6.5
9 f	_[c]	_[c]	_[c]
9g	На	$1800\pm130$	$-18.9 \pm 0.2$
8b	На	$247\pm\!15$	$-13.9 \pm 0.2$
	Hb	$594\pm34$	$-16.1 \pm 0.2$
	average value	421	-15.0

[a] In CDCl<sub>3</sub> at 30°C. [b] Ha and Hb correspond to the inner and peripheral aromatic protons, respectively (see Figure 3). [c] No association was observed.

was observed for the formyl derivative **9g**, presumably because of intermolecular hydrogen-bonding or dipole–dipole interactions between the formyl groups. A similar association-enhancing effect of formyl groups has been reported for a pyrene derivative (Figure S7).<sup>[40]</sup> Dodecyl-substituted (AE)<sub>6</sub>-DBA **9f** did not show a concentration-dependent change in its <sup>1</sup>H NMR spectrum, consistent with previous results.<sup>[35]</sup> Most importantly, tetrakis-DBA **8b** exhibited a larger association constant than that of (AE)<sub>6</sub>-DBA **9c** (Figure S8), clearly showing the role of the large planar  $\pi$ -core of the former, which enhances self-association by  $\pi$ - $\pi$  stacking interactions.

Self-assembly in the condensed phase: Disk-like planar conjugated molecules often show columnar liquid-crystalline behavior.<sup>[41]</sup> In general, the transition temperature, the thermal stability of the condensed phase, and the domain size are dependent on molecular features such as the size and shape of the  $\pi$ -conjugated core,<sup>[42]</sup> and the number, length, and branching of the peripheral alkyl chains.<sup>[43]</sup> For DBA derivatives, the formation of the liquid-crystalline phase is also influenced by the number and nature of the alkyl chains at the periphery.<sup>[8,44]</sup> For example, DBAs with three alkoxy groups displayed liquid-crystalline behavior while those with six alkoxy groups did not, in contrast to the triphenylene derivatives with smaller  $\pi$ -cores.<sup>[45]</sup> In the cases of tetrakis-DBA and  $(AE)_6$ -DBA, we expected the formation of stable liquid-crystalline phases because of their extended  $\pi$ -conjugated systems.[46]

First, we investigated the mesomorphism of (AE)<sub>6</sub>-DBA **9d** having C12 chains by TGA, DSC, and XRD measurements, as well as by polarized optical microscopy (POM) for optical texture observations of the mesophases. The TGA measurement indicated that **9d** showed gradual thermal decomposition above 150°C (Figure S9), and thus the isotropization temperature could not be determined. DSC measurement of **9d** revealed that a phase transition was observed at 53°C (Figure S10). Birefringence due to soft states of matter was clearly observed at 190°C, indicating a mesomorphism of **9d** (Figure S11 (a)). However, definitive assignment of the mesophase by XRD was hampered due to the presence of some unidentified diffractions.

Next, tetrakis-DBA **8b** and  $(AE)_6$ -DBA **9e** with branched alkyl chains were investigated, because it is known that the branched alkyl chains lower the isotropic temperature and increase the domain size.<sup>[43a,e]</sup> TGA measurements on **8b** and **9e** showed gradual thermal decomposition above 150 °C (Figures S12 and S13), similar to what was seen for **9d**; thus, the isotropization temperatures could not be determined. However, DSC measurements revealed that phase transitions occurred at lower temperatures, -2 °C for **8b** and 10 °C for **9e** (Figures S14 and S15), which corresponded to the melting points evidenced by POM observations (Figure S11 (b, c)). Consequently, three and two mesophases were detected for **8b** and **9e**, respectively. The phase-transition parameters are summarized in Table 2. In order to determine the molecular spatial orderings in the mesophases,

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Table 2. Phase-transition parameters of 8b, 9d, and 9e.

Phase-transition temperature [°C] ( $\Delta G [kJ mol^{-1}]$ )		
cryst. 53 (71) M1 <sup>[a]</sup> (decomp: >125 °C)		
cryst. 10 (16) M2 <sup>[b]</sup> 55 (4.9) M3 <sup>[b]</sup> (decomp: $>$ 150 °C)		
cryst. $-2$ (11) M4 <sup>[a]</sup> 4 (17) M5 <sup>[b]</sup> 178 (8.1) M6 <sup>[a]</sup> (decopm: >125 °C)		

[a] Unidentified phase. [b] Colr phase.

XRD analyses were performed. The XRD patterns observed from all mesophases for the non-aligned samples showed a broad halo at around 0.45 nm, originating from the molten alkyl chains (Figures S16 and S17). Moreover, it turned out that **8b** and **9e** adopted columnar mesophases with rectangular lattices ( $P2_1/a$  symmetry) (Table S8 and Figure S18). Note that, among them, only tetrakis-DBA **8b** exhibited a strong correlation of 0.34 nm, which corresponds to the stacking periodicity of molecules within a column. This is due to the planarity and rigidity of the  $\pi$ -conjugated core, which enhances the stacking order by the acetylene linkages connecting the peripheral phenyl groups in **8b**.

The observed mesophases exhibited relatively high thermal stability above 300 °C, though thermal decomposition gradually took place. Moreover, the introduction of branched alkyl chains at the periphery led to a lowering of the melting temperature.<sup>[43a,e]</sup> However, in all cases, no clearing points were observed before the thermal decomposition. The branched alkyl chains in **8b** and **9e** are presumably not large enough to reduce the clearing temperature to a value below the decomposition temperature, probably because of the large facial area generated by the trigonally expanded  $\pi$ -conjugated core.

Charge-carrier mobility in the liquid crystals: Disc-shaped  $\pi$ conjugated molecules, when assembled to form columnar ordering in 3D crystals and liquid-crystalline materials, often show semiconducting properties,<sup>[47]</sup> which are dependent on the intrinsic molecular features and molecular packing. Time-resolved microwave conductivity (TRMC) measurements can provide direct information on the local motion of charge carriers in these columnar stacks without using electrodes, which tend to localize the charge carriers at the electrode-semiconductor interfaces. The direct interaction between charge carriers and the probing microwave reveals the effective mass of the charge carriers along the conjugated columnar core stacks,<sup>[48]</sup> and hence the value of chargecarrier mobility reflecting the local oscillating motion of charge carriers in the potential induced by the alternating electric field of the probing microwave.

Upon excitation of **8b** and **9e** in the solid state, clear conductivity transients were observed at 296 K, at which both compounds adopted a columnar structure (*Colr* phase), as shown in Figure 5. The conductivity transient shows a rapid rise within the time constant of the present TRMC measurement apparatus (~50 ns) for **8b**, suggesting a predominant contribution from the singlet excited state to produce free charge carriers. Considerable evolution of the conductivity transient was, however, observed for **9e**, which may be due to photo-carrier generation through triplet excitedstate migration. A relatively high charge-carrier generation yield has often been observed for isolated columnar assemblies upon photo-excitation.<sup>[49]</sup> Clear kinetic traces of the transient absorption were observed for both compounds in the solid state. The transient absorption  $(S_1-S_n)$  of the



Figure 5. Kinetic traces of conductivity transients (blue lines) observed upon 355 nm excitation at 296 K with an excitation photon density of  $9.1 \times 10^{15}$  photons cm<sup>-2</sup> of **8b** (a) and **9e** (b) films cast on a quartz substrate. Transient absorption kinetic traces were also measured (a) for **8b** at 650 nm and (b) for **9e** at 600 nm, respectively, displayed in red.

singlet excited state of 8b decayed rapidly within 1 µs (Figure 5(a)), and largely overlapped kinetic traces were observed for both transient conductivity and optical absorption at 650 nm. After the decay processes of the singlet excited states, the transient absorption spectra for 8b indicated simultaneous bleaching of the steady-state S<sub>0</sub>-S<sub>1</sub> transition at 400 nm with an isosbestic point (Figure S19), suggesting that effective photo-ionization occurs in the present system. The photo-ionization yield was calculated based on the assumption of 100% conversion of the steady-state absorption bleaching into the radical cations monitored at 650 nm, with a molar extinction coefficient of 8b at 400 nm of 38500 m<sup>-1</sup> cm<sup>-1</sup>, leading to an initial photo-ionization yield ( $\phi$ ) of 2.1×10<sup>-4</sup>. An almost identical value of  $\phi$  was estimated for **9e** in the solid state upon excitation at 355 nm,  $\phi$  $\approx 1.9 \times 10^{-4}$  (Figure 5(b)). These values are an order of magnitude higher than the yields observed for conjugated molecular crystal systems,<sup>[50]</sup> reflecting suppression of inter-columnar charge recombination and/or isolation of positive charges in the columnar cores from the exposure of  $O_2^{-}$  superoxide anion produced by electron capture in the photoionization processes. The yield of photo-carrier generation was also determined by a photo-current integration method (Figure S20),<sup>[51]</sup> and the values of  $\phi$  derived were  $1.2 \times 10^{-4}$ 

and  $9.5 \times 10^{-5}$  for **8b** and **9e**, respectively. The lower values of  $\phi$  compared to those derived from transient absorption spectroscopy were due to charge trapping in the long-range translational motion of charge carriers in the photo-current integration regime, leading to their underestimation. The minimum values of intracolumnar mobility were determined by the transient conductivity, with  $\phi$  values from transient absorption spectroscopy of  $\Sigma \mu = 0.12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for **8b** and  $\Sigma \mu = 0.058 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for **9e**, respectively. The value for **8b** is smaller than those of hexabenzocoronene derivatives,<sup>[52]</sup> but larger than those of triphenylene derivatives.<sup>[53]</sup> The 1D stacks of carboxylated DBA 1 in the 3D crystal were shown to exhibit comparable mobility.<sup>[6a]</sup> Taking into account the low ordering of 8b (non-aligned sample), the mobility of multiply fused DBAs is sufficiently large for potential applications as organic semiconductors.

#### Conclusion

In conclusion, the largest  $\gamma$ -graphyne fragments yet assembled, trigonally expanded tetrakis-DBAs, consisting of four DBA subunits, have been synthesized by intramolecular three-fold metathesis cyclization. The present results demonstrate the potential of alkyne metathesis for the construction of multiply fused DBA backbones. In the one-photon absorption spectrum of tetrakis-DBA 8a, a remarkable bathochromic shift of the absorption cut-off ( $\lambda_{cutoff}$ ) compared with those of previously reported graphyne fragments was observed because of the extended  $\pi$ -conjugation. Moreover, 8a displayed a large two-photon absorption cross-section among pure hydrocarbons due to the three planar paraphenyleneethynylene unit conjugation pathways. Hexakis(phenylene-ethynyl)-DBAs 9c-e and tetrakis-DBA 8b exhibited self-association behavior in chloroform: 8b showed a stronger tendency for association than the corresponding 9e due to stronger  $\pi$ - $\pi$  interactions between the extended  $\pi$ -cores. In the condensed state, **9e** and **8b** displayed liquid-crystalline phases. XRD analyses revealed the formation of columnar rectangular phases. The columnar rectangular phase of 8b showed moderate charge-carrier mobility, as determined by the TRMC method, suggesting that the graphyne fragments may be promising candidates as organic semiconductors. With this powerful method for the construction of graphyne fragments and the present knowledge on the structure-property relationship of tetrakis-DBAs, the rational design and synthesis of larger graphyne fragments of optoelectronic interest should be possible.

#### **Experimental Section**

General procedure for the synthesis of tetrakis-DBAs and hexakis(arylethynyl)-DBAs: All manipulations, except for the syntheses of 15, 18a, 18b, 20, and 23, were performed in an inert gas (nitrogen or argon) atmosphere. All solvents were distilled or passed through activated alumina and copper catalyst in a Glass Contour solvent purification system prior to use. All commercially available reagents were used as received. [Pd $(\mbox{PPh}_3)_4]$  and the Mo–alkylidyne complex were prepared according to literature procedures.  $^{[27a,54]}$ 

<sup>1</sup>H (400 MHz, 300 MHz, and 270 MHz) and <sup>13</sup>C (100 MHz, 75 MHz, and 67.5 MHz) NMR spectra were measured on JEOL JNM AL-400, Bruker AV400M, Varian Mercury 300, or JEOL JNM-GSX-270 spectrometers. Spectra measured in CDCl<sub>3</sub> were referenced to residual solvent protons for the <sup>1</sup>H NMR spectra ( $\delta$ =7.26 ppm) and to solvent carbons for the <sup>13</sup>C NMR spectra ( $\delta$ =77.0 ppm). Preparative HPLC was undertaken with a JAI LC-908 chromatograph using 600 mm ×20 mm JAIGEL-2H and 2.5H GPC columns with CHCl<sub>3</sub> as eluent. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer in EI or FAB ionization modes or an AXIMA-CFR in LD ionization mode. Elemental analyses were carried out on a Perkin–Elmer 2400 II analyzer.

UV/Vis–NIR absorption and fluorescence measurements: UV/Vis spectra were recorded on a Hitachi U-3310 spectrometer. Fluorescence spectra were measured on a JASCO FP750-DS/O spectrometer. All solutions for measurements were prepared in spectrophotometric grade dichloromethane or chloroform. The concentrations of each solution were as follows:  $1.00 \times 10^{-5}$  M for 8a and  $4.02 \times 10^{-6}$  M for 9c in UV/Vis absorption measurements and  $1.01 \times 10^{-6}$  M for 8a and  $2.01 \times 10^{-7}$  M for 9c in emission measurements. All measurements were performed at room temperature. Considering the relatively low association constants determined from the <sup>1</sup>H NMR spectra, the solute molecules are expected to exist as monomers at these concentrations.

**Computational details**: All theoretical calculations were performed with the Gaussian 09 package. The B3LYP functional with the  $6-31G^*$  basis set was used for geometry optimization of **8c**. Excited-state calculations (TD-DFT) were performed on the optimized structure (B3LYP/ $6-31G^*$  level of theory). The major electronic transitions and representative frontier molecular orbitals for **8c** are shown in Table S2 and Figure S1.

**Characterization of the liquid-crystalline phase**: Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments DSC2920. The characteristics of the liquid-crystalline materials were observed by polarization microscopy on an Olympus BH2 microscope equipped with a Mettler FP90 hot stage. X-ray diffraction analysis of liquid-crystalline materials was performed using a Rigaku RINT2000 (Cu<sub>*k*a</sub> radiation) diffractometer.

Two-photon absorption cross-section: The two-photon absorption spectrum of 8a in chloroform was measured using the open-aperture Z-scan method. A femtosecond optical parametric amplifier (typically 120 fs) operating at a repetition rate of 1 kHz was used as the light source to scan the excitation wavelength range from 590 to 820 nm. Details of this set-up have been reported previously.[55] The Rayleigh range of this optical set-up was 6-7 mm for the wavelengths employed and much larger than the optical pathlength of the sample solution held in a quartz cuvette (2 mm), which satisfied the "optically thin" condition needed for quantitative analysis. The recorded data were analyzed by the curve-fitting procedure with the theoretical model of the transmittance of a spatially and temporally resolved Gaussian pulse through two-photon absorptive media. From the curve-fitting, the two-photon absorbance of the sample  $q_0 = \alpha^{(2)} I_0 L_{\text{eff}}$  was obtained, where  $\alpha^{(2)}$  is the two-photon absorption coefficient,  $I_0$  is the peak optical intensity at the focal point, and  $L_{\rm eff}$ is the effective pathlength of the sample. The proportionality relationship between  $q_0$  and  $I_0$  was confirmed by varying the incident power over the range 0.1-0.8 mW for each measurement, which verified that the observed signal was indeed due to the two-photon absorption process. Conditions of  $I_0 \leq 250 \ {\rm GW \, cm^{-2}}$  at the focal point of the set-up were maintained to avoid higher-order nonlinear optical processes. Finally, the twophoton absorption cross-section was calculated using the convention  $\sigma^{(2)} = E_{\rm ph} \alpha^{(2)} / N$ , where N is the number density of the molecules in the sample and  $E_{\rm ph}$  is the photon energy. The obtained  $\sigma^{(2)}$  was calibrated with our in-house standard compound, MPPBT,<sup>[33]</sup> measured at the same time.

**Time-resolved microwave conductivity (TRMC) measurements**: Besides the symmetry-forbidden S0-S1 transitions of tetrakis-DBA **8b** and  $(AE)_6$ -DBA **9e** at around 400–500 nm depending on the intramolecular conjugation, excitation light pulses at 355 nm from a Spectra Physics INDI-

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HG nanosecond Nd:YAG laser were used to induce photo-carrier generation, whereby the extinction coefficients of the molecules per number of DBA moieties were almost identical. The power density of the excitation light source was set at  $5.1-10.2 \text{ mJ cm}^{-2} (9.1-18 \times 10^{15} \text{ photons cm}^{-2})$ . The probing microwave frequency and power were set at ~9.1 GHz and 3 mW, respectively. Tetrakis-DBA **8b** and (AE)<sub>6</sub>-DBA **9e** were cast on a quartz substrate of thickness 2.5 µm from solutions in chloroform, and the TRMC signals were monitored upon excitation and averaged over 256 shots. Transmittance of excitation light pulses at 355 nm through the film was calculated based on the electronic absorption spectra of the compounds. All of the above experiments were carried out at 296 K. Transient photoconductivity ( $\Delta \sigma$ ) of the samples was derived directly from the transient traces of reflected microwave power change ( $\Delta P_t$ ) relative to steady-reflected microwave power ( $P_t$ ), and converted into the sum of the mobilities of charge carriers according to:

$$\frac{1}{A}\frac{\Delta P_{\rm r}}{P_{\rm r}} = \Delta \sigma = e\phi N\Sigma\mu$$

in which A, e,  $\phi$ , N, and  $\Sigma\mu$  are the sensitivity factor, the elementary charge of the electron, the quantum efficiency of photo-carrier generation, the number of absorbed photons per unit volume, and the sum of the mobilities for negative and positive carriers, respectively. Details of the apparatus have been described elsewhere.<sup>[48,56]</sup>

**Determination of quantum efficiency of photo-carrier generation**: Transient absorption spectroscopy was performed under ambient conditions at 296 K. Films of tetrakis-DBA **8b** and (AE)<sub>6</sub>-DBA **9e** were cast on a quartz substrate of thickness 2.2 µm from solutions in chloroform. Time-dependent absorption spectral changes were monitored by means of a Hamamatsu C7700 streak camera in conjunction with a Hamamatsu C5094 spectrometer upon excitation with pulses from an Nd:YAG laser (Spectra Physics, INDI-HG). The excitation density was tuned to  $9.5 \times 10^{16}$  cm<sup>-2</sup> photons per pulse. To collect two-dimensional time–wavelength correlation data of the transient absorption, the streak scope images were averaged over 400 shots of excitation.<sup>[57]</sup>

Photo-current accumulation was carried out for solid films of **8b** and **9e** cast on an Au interdigitated electrode with a gap of 5 µm. Excitation was carried out at 355 nm with a photon density of  $1.8 \times 10^{16}$  photons cm<sup>-2</sup> from a Spectra Physics, Quanta-Ray, GCR-130, and under a variety of applied bias voltages. Photo-current transients were accumulated directly by means of a Keithley 6514 electrometer, and by monitoring with a Tektronix 3052B digital oscilloscope equipped with 10 k $\Omega$  termination resistance.<sup>[51a]</sup>

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