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From Branched Hydrocarbon Propellers to C_3-Symmetric Graphite Disks

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Branched hydrocarbon propellers (**9** and **12**) were prepared by stepwise palladium-catalyzed Hagihara−Sonogashira coupling reactions and Diels−Alder cycloadditions and submitted to oxidative cyclodehydrogenation by $FeCl_3$ to afford two new giant graphite disks **2** and **3** with 3-fold symmetry in high yield. One of the precursors, the polyphenylene dendrimer **9** containing 150 carbon atoms, was crystallographically characterized. The poorly soluble graphite disks were characterized by isotope-resolved MALDI-TOF mass spectroscopy, and their electronic and vibrational properties were investigated by solid-state UV−vis and Raman spectroscopy. The effect of molecular size and geometry on their properties was discussed. The molecule **2** represents the largest, 3-fold-symmetric all-benzenoid graphite disk, and the five-membered rings in molecule **3** open the opportunity to synthesize large bowl-shaped PAHs.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent one of the most intensively investigated classes of carbon-rich compounds.[1] Their synthesis, characterization, and electronic properties have been widely studied since the beginning of the 20th century.[2] All-benzenoid PAHs such as triphenylene and hexa-*peri*-hexabenzocoronene (HBC) possess high thermal and chemical stability and thus are useful organic semiconductors in practical electronic and optoelectronic devices.[3] The synthesis of a series of graphite molecules with different size and periphery has been well developed in our group mainly based on oxidative cyclodehydrogenation of branched oligophenylene precursors.[4] Well-defined graphite disks carrying up to 222 carbons were prepared, and the synthetic concept was also used to prepare polydispersed graphite ribbons.[5] Attachment of flexible substituents onto the graphite disks improves the solubility and lowers the melting point. Melting leads to remarkably stable discotic mesophases with columnar superstructures.[4b] As a result, a high one-dimensional charge carrier mobility along the columns was observed, and this qualified the molecules as promising semiconductors for organic field effect transistors, light-emitting diodes, and photovoltaic devices.[6]

The molecular size, symmetry, and nature of the periphery have great influence on the electronic properties as well as the two- and three-dimensional superstructures of these graphite disks.[7] In our previous work, various graphite molecules with D_{2h} and D_{6h} symmetry have been prepared, and a D_{3h} symmetric disk **1** (Chart 1) with 96 carbons was synthesized by oxidative cyclodehydrogentation of a 1,3,5-tris(pentaphenylyl)benzene propeller molecule in nearly quantitative yield.[8] The hexadodecyl-substituted molecule **1** possesses a surprisingly high solubility in many organic solvents and gives rise to a highly ordered room-temperature columnar liquid crystalline phase.[9] The symmetry is thus expected to have an important influence on its packing in the bulk state. Herein, the synthesis and characterization of a new extended D_{3h}-symmetric graphite disk **2** (Chart 1) with 150 carbons and another C_3-symmetric disk **3** (Chart 1) with 90 carbons are presented. Their electronic and vibrational properties were studied by solid-state UV−vis and Raman spectroscopy as a function of size. Molecule **3**, containing three five-membered rings and

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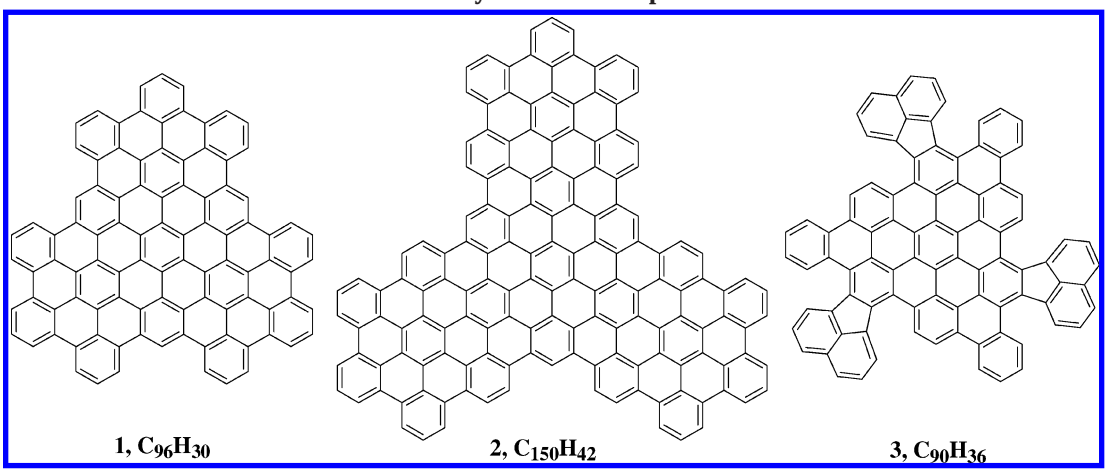
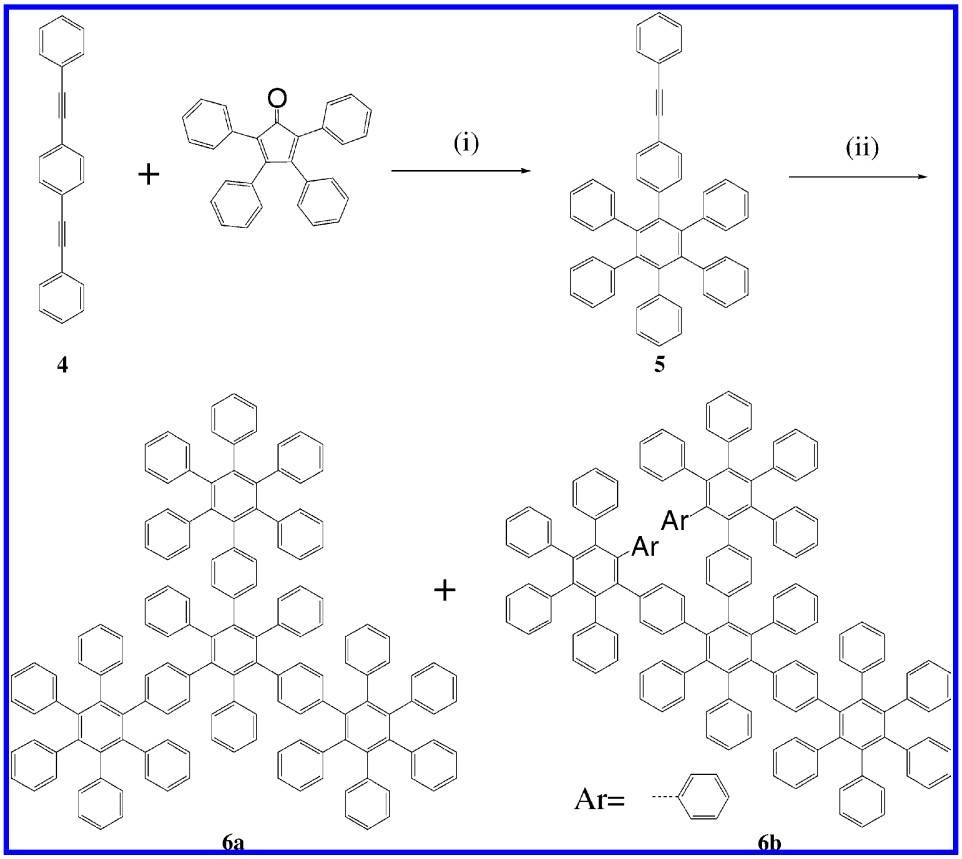
CHART 1. Molecular Structure of the 3-Fold Symmetric Graphite Disks



SCHEME 1 [a]



[a] Key: (i) diphenyl ether, 230 °C; (ii) $Co_2(CO)_8$, dioxane, 125 °C, 5 h.

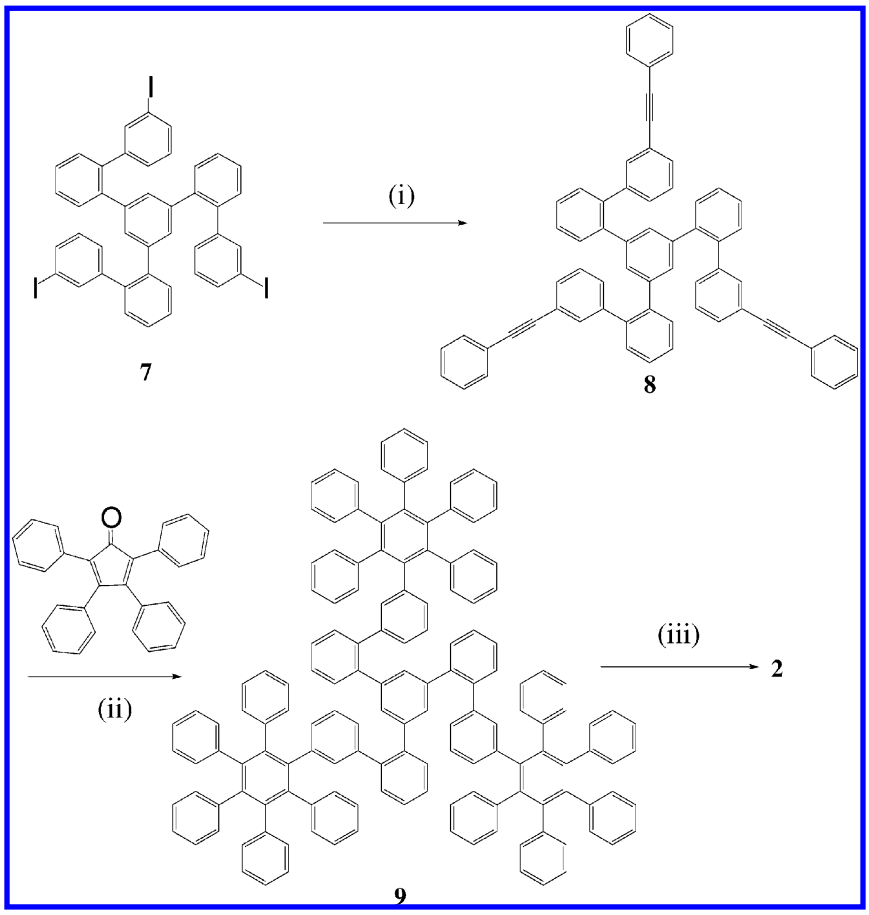
three naphthalene units, can serve as a reasonable precursor of larger bowl-shaped PAHs, which were widely studied by Scott et al.[10] The single-crystal structure of the precursor of **2**, a branched oligophenylene propeller molecule with 25 phenyl rings (**9**), was also analyzed to understand the oxidative cyclodehydrogenation process.

Results and Discussion

Synthesis of Compound 2. The two key steps toward the graphite disk **2** are the synthesis of the branched oligophenylene precursor and the subsequent oxidative cyclodehydrogenation. A possible precursor such as the C_3-symmetric molecule **6a** (Scheme 1) was pursued first. Diels−Alder cycloaddition between tetraphenylcyclopentadienone and excess 4,4-bis(phenylethynyl)benzene (**4**) gave the monophenylethynyl-substituted hexaphenylbenzene **5**, which was then submitted to $Co_2(CO)_8$-catalyzed cyclotrimerization reactions, however, affording two inseparable structural isomers **6a**, the desired precursor, and **6b**.

This obstacle was overcome by the design and synthesis of a novel C_3-symmetric precursor **9** as shown in Scheme 2. The synthesis started with a 3-fold Hagihara−Sonogashira coupling between 1,3,5-tris(3″-iodo-2′-bi-

SCHEME 2 [a]



[a] Key: (i) phenylacetylene, $Pd(PPh_3)_4$, CuI, piperidine, rt, 88%; (ii) diphenyl ether, reflux, 82%; (iii) $FeCl_3/CH_3NO_2$, dichloromethane, 19 h.

phenylyl)benzene (**7**)[11] and phenylacetylene to afford compound **8** in 88% yield and was followed by the 3-fold Diels−Alder cycloaddition between tetraphenylcyclopentadienone and compound **8** in refluxing diphenyl ether to give the branched oligophenylene **9** in 82% yield. The good solubility of **9** allows full structural characterization by NMR and mass spectroscopy (Figure 1a) as well as single-crystal analysis (see later). The key starting material **7** was synthesized from the corresponding 3-trimethylsilyl-substituted tris(1,3,5-biphenylbenzene), which was prepared by 3-fold Suzuki coupling reaction between the 1,3,5-tribromobenzene and a biphenylboronic acid.[11] The molecule **9** is expected to adopt a three-dimensional propeller-like conformation similar to other polyphenylene dendrimers,[12] raising the question of whether it can be fused to a planar graphite disk under oxidative cyclodehydrogenation conditions. Surprisingly, upon treatment with 180 equiv of $FeCl_3$, compound **9** lost exactly 60 hydrogen atoms to afford the desired disk **2** as an insoluble powder. Due to the very poor solubility of the graphite disk, NMR characterization failed. Elemental analysis of such kind of insoluble graphite disks cannot provide reliable information about the elemental composition because of the incomplete combustion during the measurements. Alternatively, isotope-resolved matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy using a solid-state sample preparation method with 7,7,8,8-tetracyanoquinodimethane (TCNQ) as matrix played a major role in the control of the reactions and the determination of the degree of cyclodehydrogenation.[13] It appeared that $FeCl_3$ (180 equiv) in dichloromethane was a more efficient oxidant than $Cu(OTf)_2-AlCl_3$ (180 equiv) in carbon disulfide but required a longer time for complete reaction. The MALDI-TOF mass spectrum of a sample of **2** synthesized by $FeCl_3$ in 19 h is shown in Figure 1b, and the molecular ion peak with good isotopic distribution (inset) indicates an exact loss of 60 hydrogen atoms during the reaction.

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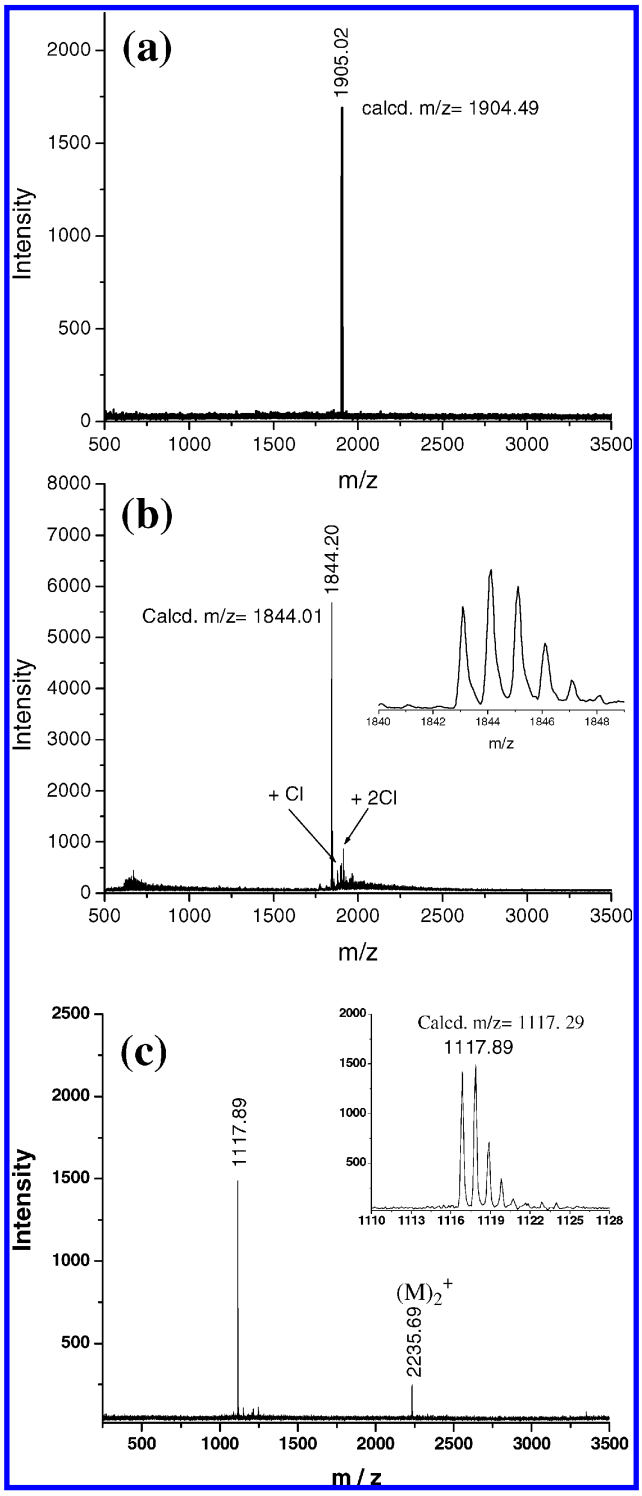

FIGURE 1. MALDI-TOF mass spectra of compounds **9**, **2**, and **3**, TCNQ as matrix; inset is the isotope distribution which is in agreement with the simulated results.

Single-Crystal Structure of Compound 9. The successful synthesis of the fully closed graphite disk **2** from a branched precursor **9** is a surprise because its three hexaphenylbenzene units deviate more from the plane of the center benzene ring compared with the precursor **6a** and such a comformation requires more energy to compensate for the loss of entropy during the cyclodehydrogention. Thus, it is helpful to inspect the single-crystal structure of such branched oligophenylenes to understand the process of their planarization. Single-crystal growth and analysis of large hydrocarbons are a challenge, and recently, crystallographic structures of polyphenylene dendrimers containing up to 222 carbon atoms have been determined.[14] Herein, a single crystal was grown by slow evaporation of a saturated solution of **9** in dichloromethane. Projection of the single-crystal structure of **9** and its three-dimensional packing are shown in Figure 2.[15] Similar to the other polyphenylene dendrimers, the phenylene rings in molecular **9** remain planar and the dihedral angles between the neighboring covalently linked phenylene rings are in the range of 40−70°. Interestingly, the three hexaphenylbenzene arms are arranged on the same side of the plane of the center benzene ring instead of forming a C_3-symmetric three-bladed propeller. This unexpected structure can be related to the energy-favored three-dimensional packing. Molecule **9** possesses a triclinic unit cell with a *P*-1 space group; i.e., it contains two molecules in each unit cell. Cavities exist between the molecules which are filled with dichloromethane molecules. The molecular composition of the crystal is formulated as $C_{150}H_{102}\cdot 2CH_2Cl_2$.

The above crystallographic analysis clearly shows that the molecule **9** is branched with all the neighboring phenyl rings twisted to each other. While the detailed mechanism of the cyclodehydrogenation is not clear, the successful transformation of **9** to planar **2** reflects the magic of iron chloride as an oxidant in the planarization of branched polyphenylene dendrimers. It should be pointed out that a similar oxidative cyclodehydrogenation of **7** also gives a planar hexa-*peri*-hexabenzocoronene carrying three iodo functional groups, which allows versatile functionalization according to our new synthetic concept.[11,16]

Synthesis of Compound 3. The synthesis of **3** is similar to that of **1** (Scheme 3). Three-fold Diels−Alder cycloaddition of commercially available 1,3,5-triethynylbenzene (**10**) with excess (3.3 equiv) 7,9-diphenyl-8*H*-cyclopenta[l]acenaphthylen-8-one (**11**)[17] in refluxing *o*-xylene gave the propeller-like precursor **12** in 90% yield. Cyclodehydrogenation of **12** with 45 equiv of $FeCl_3$ afforded compound **3** as a dark-brown, fluorescent solid. The MALDI-TOF mass spectrum of **3** revealed a single species with good isotope distribution (Figure 1c). NMR characterization is impossible due to the poor solubility. Further attempts toward intramolecular cyclodehydro-

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(15) Crystal structure determination was carried out on a KCCD diffractometer with graphite-monochromated Mo Kα irradiation. The structure was solved by direct methods (SHELXS-97). 23 797 unique reflections ($\upsilon < 27.5°$) were measured of which 6124 were considered and used in the refinement. Refinement was done with anisotropic temperature factors for C and Cl, and the hydrogen atoms were refined with fixed isotropic temperature factors in the riding mode. Some of the solvent molecules are disordered. Refinement gave: $C_{150}H_{102}\cdot 2CH_2Cl_2$, a = 14.2289(7) Å, b = 18.0347(7) Å, c = 25.1367(9) Å, α = 72.471(1)°, β = 88.187(1)°, γ = 80.469(1)°, V = 7064.9 Å^3, Z = 2, D_x = 1.227 g cm^{-3}, μ = 0.242 mm^{-1}, R = 4.21%, R_w = 4.31%.

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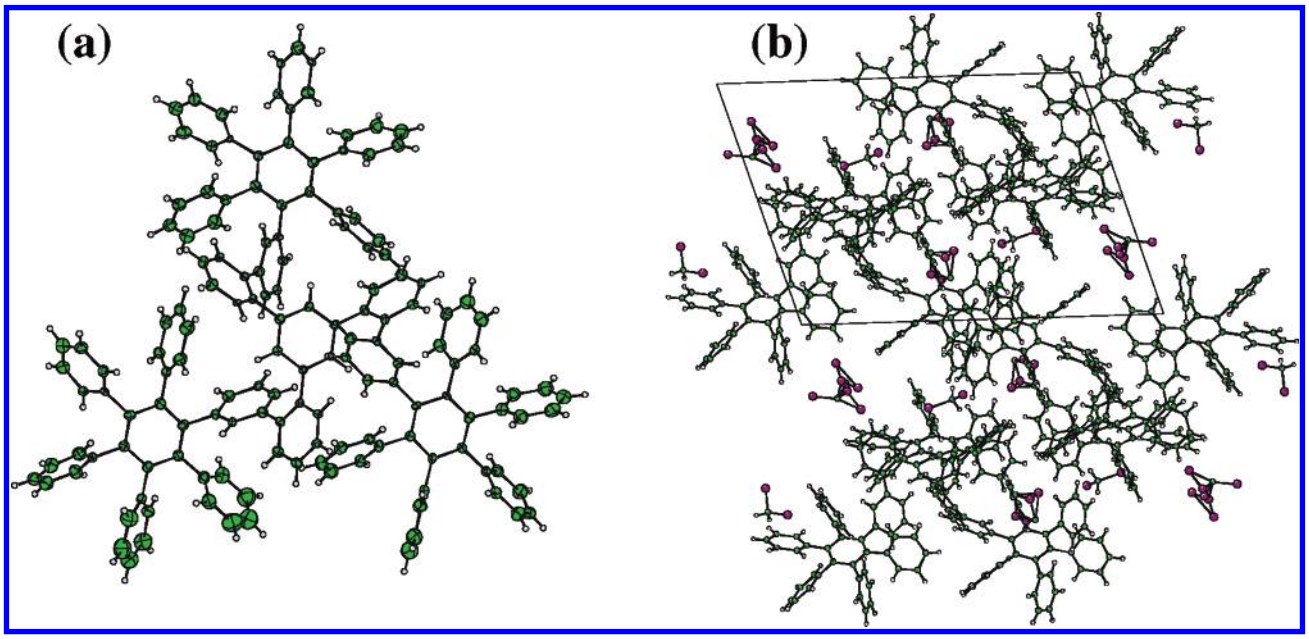
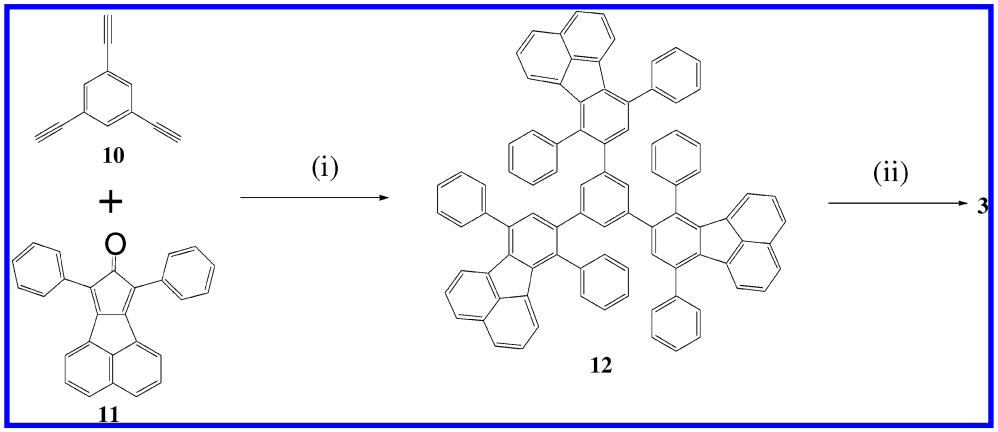


FIGURE 2. Single-crystal structure and packing of compound **9**.

SCHEME 3 [a]



[a] Key: (i) *o*-xylene, 170 °C, 90%; (ii) $FeCl_3/CH_3NO_2$, dichloromethane, 45 min.

genation at the peripheries by using large excesses of oxidant or by applying longer reaction times did not succeed, indicating a high energy requirement to make the bowl-shaped PAH. The molecule **3** has enough solubility in a normal organic solvent such as THF, allowing standard UV−vis and fluorescence spectroscopic characterization (see below). Molecule **3**, containing five-membered rings and naphthalene units, should display different electronic and optoelectronic properties compared with the all-benzenoid PAHs **1** and **2**.

UV−vis and Raman Spectroscopic Characterization of Compounds 1−3. The poor solubility of compounds **1** and **2** limits their conventional spectroscopic characterizations in solution. Alternatively, solid-state UV−vis and Raman spectroscopy are standard tools for the characterization of insoluble PAHs and nanosized graphite domains.[4,5,7] The UV−vis spectra of compounds **1** and **2** were recorded on mechanically "smeared" films on quartz and shown in Figure 3. Compound **1** possesses a broad absorption band centered at $\lambda_{max} = 491$ nm, red-shifted by about 10 nm with respect to its bands in dilute

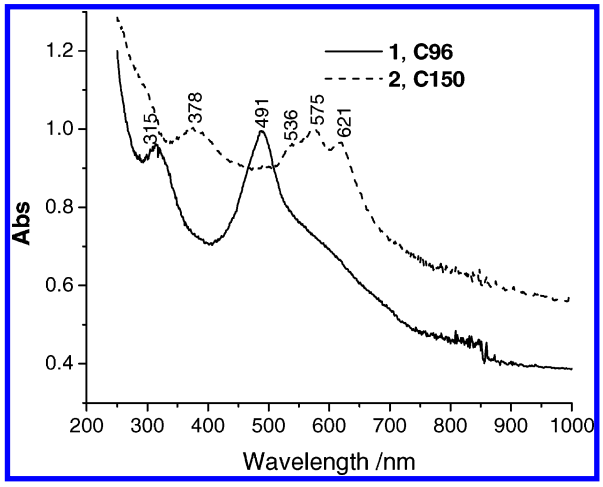


FIGURE 3. Solid-state UV−vis spectra of compounds **1** and **2**.

solution owing to solid aggregation. Compound **2**, however, displays well-resolved absorption bands with the

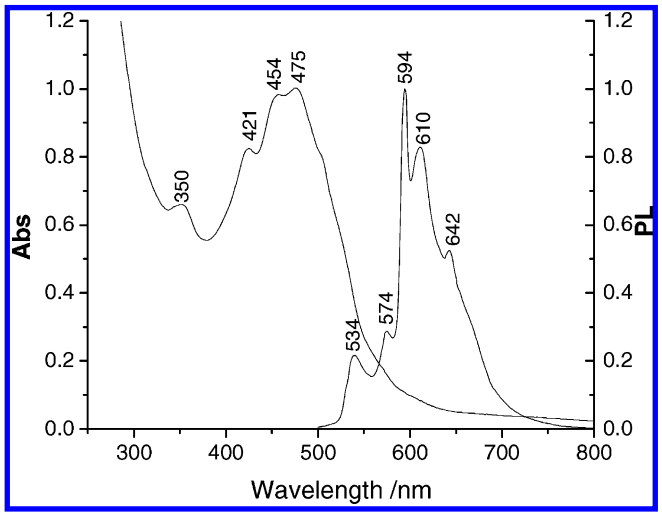


FIGURE 4. UV−vis and fluorescence spectra of compound **3** in THF (the spectra were normalized).

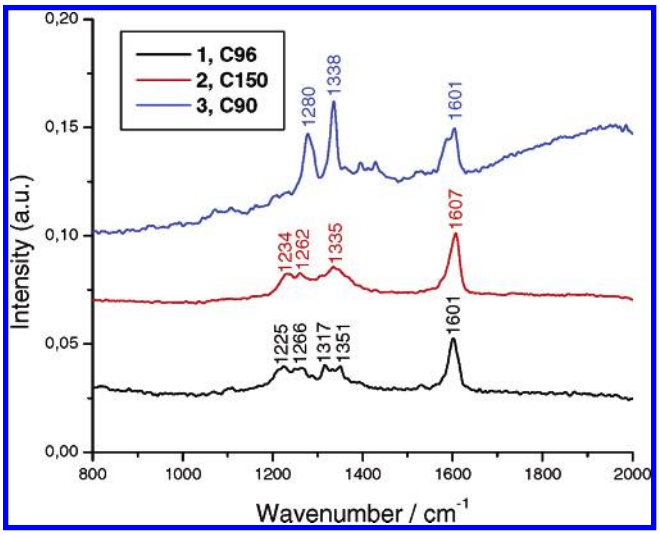


FIGURE 5. Raman spectra of compounds **1**−**3**.

λ_{max} = 575 nm (Figure 3). The bathochromic shift of 84 nm with respect to compound **1** can be explained by the extended π-conjugation upon going from **1** to **2**. The appearance of well-resolved peaks instead of a broad band is somewhat surprising since the increasing molecular size is supposed to also increase the face-to-face overlap between the disks. One explanation is that the overlap between molecules of **2**, after rotation some angle along the columnar axes, is less efficient than that of molecules **1**; i.e., the parts far from the center of **2** do not overlap and thus their electronic structures are less disturbed by the π-stacking. The UV−vis and fluorescence spectra of compound **3** were recorded in solution (Figure 4). Well-resolved absorption bands centered at 475 nm were observed, suggesting an extended conjugation. The appearance of well-resolved peaks instead of broad absorption bands as observed in compound **1** can be explained by the decreased symmetry in molecule **3** as well as possible distortion of the molecular plane owing to the steric hindrance between the naphthalene units and the center triangular graphite segment. An approximate mirror-imaged fluorescence spectrum ($\lambda_{em,max}$ = 594 nm) with a small Stokes shift was observed, in accordance with the highly fluorescent nature of compound **3** even in the solid state.

Raman spectroscopy has been demonstrated to be a powerful tool in the determination of extended π-conjugation and ordering of cyclodehydrogenated products.[5b,18] The first-order Raman spectra of **1**−**3** were recorded from solid samples using 514 nm excitation laser wavelength (Figure 5). All spectra are characterized by two characteristic features, a first band situated around 1600 cm^{-1} and a second band with resolved peaks in the range of 1220 to 1350 cm^{-1}. The Raman spectra of various all-benzenoid PAHs with different but well-defined structure and size have been studied by Zerbi et al.[19] and revealed as a common feature a line near 1600 cm^{-1} and two or more lines near 1300 cm^{-1}. The number of the peaks in the region around 1300 cm^{-1}, their relative intensities, and their positions changed according to the size and the symmetry of the molecules. Two Raman peaks at 1580 and 1330 cm^{-1} appear in the spectrum of disordered graphite, usually referred to as the G and the D band, respectively. The first band (G) is the only feature observed in the first-order Raman spectrum of highly ordered, crystalline graphite. The D peak originates from imperfections and small conjugated domains with finite size.[20] From a structural point of view, molecules **1**−**3** can be regarded as nanosized, disorded graphitic islands. The line centered at 1600 cm^{-1} thus can be assigned to the G band and the lines located around 1220 and 1350 cm^{-1} to the D bands. For disordered graphite, the ratio of the intensities of the peaks at the D band and G band [I(D)/I(G)] varies inversely with the extension of the π-conjugation, i.e., the larger the conjugation, the smaller the value of I(D)/I(G).[21] This relationship was applied herein to qualitatively evaluate the size effect on the Raman spectra. The values of I(D)/I(G) for **1**, **2**, and **3** are about 0.76, 0.70, and 2.94, respectively, in accordance with the sequence of size **3** < **1** < **2**. The I(D)/I(G) relation of molecule **3** is much higher than that of **1** and **2**, indicating a less ordered packing in **3**.

Conclusion

The oxidative cyclodehydrogenation of two propeller-like hydrocarbons by iron chloride gave two giant graphite disks with 3-fold symmetry axis. The single-crystal structure of one of the hydrocarbon precursors (**9**) disclosed a highly branched conformation, which, however, did not forbid the subsequent cyclodehydrogenation

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process. Molecule **2** represents up to now the largest 3-fold symmetric graphite disk, and molecule **3** is one of the largest PAHs containing five-membered rings.[10] Their structure and the electronic and vibrational properties of the graphitic molecules had good correlations with the molecular size, geometry, and stacking. Self-assembly of these disks on the solid−liquid interface which can be studied by scanning tunneling microscopy (STM) and spectroscopy (STS) is a subject of future work.[22]

Experimental Section

Unless otherwise noted, all starting materials were commercially available and used as received. Compounds **11**[17] and **7**[11] were prepared according to the literature.

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents such as CD_2Cl_2 and $C_2D_2Cl_4$. Field desorption (FD) mass spectra were obtained under a working voltage of 8 kV. High-resolution MALDI mass spectra were recorded using a 337 nm nitrogen laser with TCNQ as matrix.[13] UV−vis spectra were recorded on a "smeared" thin film on quartz plate at room temperature. The fluorescence spectrum of compound **3** was recorded in a diluted solution in THF. Raman spectra were examined in KBr pellets and recorded by a liquid nitrogen cooled CCD detector and Raman microscopically unit. An excitation source Ar^+ laser has been used.

1,4-Bis(phenylethynyl)benzene (4). 1,4-Diiodobenzene (50 g, 0.15 mol), $Pd(PPh_3)_2Cl_2$ (5.33 g, 7.6 mmol), CuI (2.88 g, 15.2 mmol), and PPh_3 (3.97 g, 15.2 mmol) were mixed together with 500 mL of triethylamine and 200 mL of toluene. The mixture was degassed by bubbling argon for 15 min, and then 34 g (0.33 mol) phenylacetylene was added. After being stirred at room temperature overnight, the mixture was poured into saturated aqueous ammonium chloride solution and 150 mL of toluene was added. The organic layer was washed by water two times and dried over magnesium sulfate, and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, PE/dichloromethane (DCM) = 8:1) to give 37.5 g white powder (89%): FD-MS (8 kV) *m*/*z* 278.4 [M^+] (calcd for $C_{22}H_{14}$ 278.4); ^{1}H NMR (250 MHz, $C_2D_2Cl_4$) δ 7.54−7.24 (m); ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 100 °C) δ 131.9, 131.8, 128.6, 128.6, 123.6, 123.5, 91.8 (C≡C), 89.6 (C≡C). Anal. Calcd: C, 94.93; H, 5.07. Found: C, 95.01; H, 4.99.

1,2,3,4,5-Pentaphenyl-6-(4′phenylethynylphenyl)benzene (5). Compound **4** (10 g, 35.92 mmol), tetraphenylcyclopentadienone (6 g, 15.61 mmol), and diphenyl ether (11 mL) were heated at 230 °C under argon overnight. After cooling, the mixture was poured into methanol and the precipitate was purified by column chromatography (silical gel, PE/DCM = 7/3) to give 4.6 g of **5** as a light yellow powder (47%): FD-MS (8 kV) *m*/*z* 634.8 [M^+] (calcd for $C_{50}H_{34}$ 634.8); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 7.42−7.34 (br, 2H), 7.29−7.20 (br, 3H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.85−6.70 (m, 27H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 120 °C) δ 141.6, 140.9, 140.8, 140.75, 140.5, 139.8, 131.7, 130.1, 128.4, 128.2, 126.8, 126.6, 125.5, 125.3, 123.8, 120.1, 90.5 (C≡C), 89.3 (C≡C). Anal. Calcd: C, 94.60; H, 5.40. Found: C, 94.53; H, 5.47.

1,3,5-Tris[(3″-phenylethynyl)biphenylyl-2′]benzene (8). Compound **7** (220 mg, 0.241 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol), CuI (7 mg, 0.037 mmol), and piperidine (5 mL) were mixed together in a 25 mL Schlenck tube. The mixture was degassed by two "freeze−pump−thaw" cycles, and then 150 mg (1.47 mmol) of phenylacetylene was added. The reaction was quenched by 15 mL of 2 M saturated aqueous NH_4Cl solution after being stirred at room temperature for 3.5 h under argon atmosphere. The crude product was extracted by dichloromethane, and the organic layer was washed with water three times and dried over magnesium sulfate. After solvent was removed, the residue was purified by column chromatography (silica gel, peltroleum ether/dichloromethane = 5:1) to afford 177 mg of **8** as a white powder (88%): FD-MS (8 kV) *m*/*z* 834.7 [M^+] (calcd for $C_{66}H_{42}$ 835.0); ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.0−7.8 (broad); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 142.3, 141.0, 140.5, 139.9, 133.1, 131.9, 131.0, 130.9, 130.6, 130.4, 130.1, 128.8, 128.7, 128.3, 128.1, 89.72 (C≡C), 89.7 (C≡C). Anal. Calcd: C, 94.93; H, 5.07. Found: C, 94.53; H, 5.33.

Compound 9. Compound **8** (140 mg, 0.168 mmol), tetraphenylcyclopentadienones (443 mg, 1.15 mmol), and diphenyl ether (2 mL) were heated to reflux under argon for 19 h. After cooling, the mixture was poured into 30 mL of methanol and the precipitate was purified by column chromatography (silica gel, PE/DCM = 4:1 then 2:1 and finally pure dichloromethane) to afford 260 mg of compound **9** as a white powder (82%): MALDI-TOF MS *m*/*z* 1905.02 (100) [M^+] (calcd for $C_{150}H_{102}$ 1904.49); ^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.7−6.5 (m). Anal. Calcd: C, 94.60; H, 5.40. Found: C, 94.49; H, 5.46.

Graphite Disk $C_{150}H_{42}$ (2). A solution of 50 mg (0.0263 mmol) of compound **9** in 50 mL of dichloromethane was degassed by bubbling argon for 15 min, and then 765 mg (4.72 mmol) of iron(III) chloride dissolved in 3 mL of nitromethane was added dropwise via a syringe. A constant argon stream was carried out during the entire reaction, and the reaction was quenched by adding methanol after 19 h. The dark precipitate was collected and washed repetitively with methanol and dried under vacuum to give 42 mg **2** as a black powder: MALDI-TOF MS *m*/*z* 1844.12 (100) [M^+] (calcd for $C_{150}H_{42}$ 1844.01); isotopic distribution calcd *m*/*z* 1842.33 (59.71), 1843.33 (100.00), 1844.33 (83.18), 1845.34 (45.82), 1846.34 (18.80), 1847.35 (6.13); found *m*/*z* 1843.12 (73.71), 1844.12 (100.00), 1845.12 (87.96), 1846.12 (47.43), 1847.11 (21.39), 1848.05 (10.45).

Compound 12. 1,3,5-Triethynylbenzene (**10**; 192 mg, 1.28 mmol) and 7,9-diphenyl-8*H*-cyclopenta[l]acenaphthylen-8-one (**11**; 1.50 g, 4.21 mmol) were dissolved in *o*-xylene (10 mL) under an argon atmosphere, and the resultant mixture was heated for 18 h at 170 °C (oil bath temperature). After the mixture was cooled to room temperature, ethanol (20 mL) was added. The precipitate was filtered, washed with ethanol (300 mL), and dried in a vacuum to afford **12** as a slightly yellow, strongly fluorescent solid (1.30 g, 90%): FD MS (8 kV) *m*/*z* 1135.6 (100) [M^+] (calcd for $C_{90}H_{54}$ 1135.4); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 100 °C) δ 7.70−7.50 (m, 21H), 7.33 (t, *J* = 7.6 Hz, 3H), 7.27−7.16 (m, 18H), 7.10 (t, *J* = 7.3 Hz, 3H), 6.86 (s, 3H), 6.75 (s, 3H), 6.71 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100 °C) δ 141.2, 141.0, 139.8, 139.6, 138.1, 138.1, 137.2, 136.5, 136.4, 135.8, 133.4, 131.5, 130.8, 130.2, 130.1, 129.6, 128.7, 128.6, 128.0, 127.9, 127.8, 127.5, 126.7, 123.5, 123.0. Anal. Calcd: C, 95.21; H, 4.79. Found: C, 95.10; H, 5.01.

Graphite Disk $C_{90}H_{36}$ (3). Compound **12** (150 mg, 0.13 mmol) was dissolved in dichloromethane (100 mL) in a 250 mL two-necked round-bottom flask. A constant stream of argon was bubbled into the solution through a glass capillary. A solution of $FeCl_3$ (0.96 g, 5.92 mmol) in CH_3NO_2 (5 mL) was then added dropwise via syringe. Throughout the whole reaction, a constant stream of argon was bubbled through the mixture to remove HCl formed in situ. The reaction was stirred for 45 min and then quenched by adding methanol (120 mL). The precipitate was collected by filtration, washed with methanol (300 mL), and dried in a vacuum to afford 138 mg of **3** as a dark brown solid: mp > 300 °C; MALDI-TOF MS: *m*/*z* 1117.89 (100) [M^+] (calcd for $C_{90}H_{36}$:1117.29); isotopic distribution calcd *m*/*z* 1116.28 (99.36), 1117.29 (100.00), 1118.29 (49.77), 1119.29 (16.33), 1120.30 (3.97), found 1116.90 (95.10), 1117.89 (100.00), 1118.89 (47.75), 1119.84 (22.90), 1120.75 (9.34).

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