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Polycyclic Hydrocarbons

Triangle-Shaped Polycyclic Aromatic Hydrocarbons[**]

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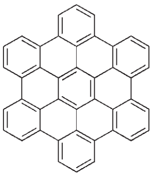
C_3-symmetric polycyclic aromatic hydrocarbons (PAHs) such as triphenylene and truxene derivatives have been studied as active materials in field-effect transistors and light-emitting diodes as well as for the construction of bowl-shaped subunits of fullerenes.[1] Hexa-*peri*-hexabenzocoronene (HBC, **1**) and its derivatives with D_{6h} symmetry have been synthesized by utilizing oxidative cyclodehydrogenation of hexaphenylbenzene precursors.[2] However, the synthesis of larger PAHs with C_3 symmetry, which are particularly interesting as supramolecular building blocks for deposition on surfaces,[3] has met with difficulties.[4] Herein, we report a versatile synthesis of a series of large triangle-shaped PAH molecules **2**–**10**) with different substituents and peripheral structures. The D_{3h}-symmetrical molecule **2** (benzo[o]bistriphenyleno[2,1,12,11-efghi:2′,1′,12′,11′-uvabc]ovalene; "trinaphthoHBC") is a simple triangle-shaped benzenoid PAH with the same number of carbon atoms as fullerene. Molecules **5**–**10** (derivatives of diphenanthro[3′,4′5,′6′-efghi:3,4,5,6-uvabc]-ovalene, "trizigzagHBC") have three "zigzag" peripheries and exhibit different optical and electronic properties from those of the PAHs with armchair peripheries.[5] As one example, the self-assembly of trizigzagHBC **10** is described. X-ray scattering experiments reveal an arrangement of **10** into helical superstructures in the solid state, and monolayers that consist of novel honeycomb patterns are observed by scanning tunneling microscopy (STM) at the liquid–solid interface.



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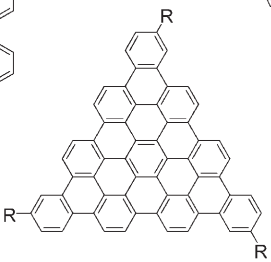
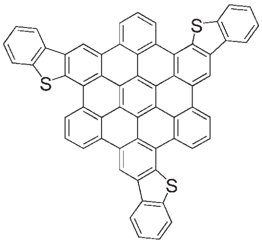


2 R= H
3 R = I



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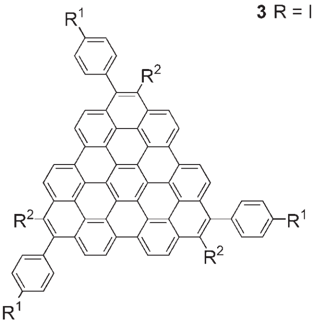
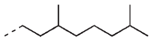


5 R^1 = H, R^2 = I
6 R^1 = H, R^2 = H
7 R^1 = H, R^2 = Ph
8 R^1 = $C_{8,2}$, R^2 = I
9 R^1 = $C_{8,2}$, R^2 = H
10 R^1 = $C_{8,2}$, R^2 = Ph$C_{8,2}$

$C_{8,2}$ =



The synthesis of the triangle molecules **2**–**10** was based on the same precursor, 1,3,5-tris-(2′-bromophenyl)benzene, which was obtained by condensation of 2-bromoacetophenone under strongly acidic conditions.[6] The synthetic protocol then comprised the following steps: 1) Suzuki coupling of 1,3,5-tris(2′-bromophenyl)benzene, 2) ICl-induced low-temperature ring cyclization,[7] and 3) proton–halogen exchange or further Suzuki coupling to afford the precursors with 1,3,5-tris(2′-biaryl)benzene (for **12**, **13**, and **16**; see Scheme 1) or 1,3,5-tris(2′-phenanthrenyl)benzene structure (for **18**, **19**, and **20**; see Scheme 2). Intramolecular oxidative cyclodehydrogenation reactions were then performed for the resulting precursors by using $FeCl_3$ as oxidant until the quantitative removal of 18 (for **12** and **16**) or 12 (for **13** and **18**–**20**) hydrogen atoms gave triangle discs **2**–**10** as red or yellow powders. No additional cyclization took place during the cyclodehydrogenation at the peripheral phenyl rings of **7** and **10** even under extended reaction time or UV irradiation.[8] TrinaphthoHBCs **2**–**3**, tribenzothiopheneHBC **4**, and trizigzagHBCs **5**–**7** are poorly soluble in common organic solvents and were thus purified by repeated washing with water and methanol (see below for characterization). TrizigzagHBCs **8**–**10** are well soluble in common organic solvents including THF, dichloromethane, and chloroform, and could thus be purified by column chromatography.

MALDI-TOF mass spectrometry (TCNQ matrix) of **2**–**7** using a solid-state sample preparation method revealed single species with isotopic distributions, which were in accordance

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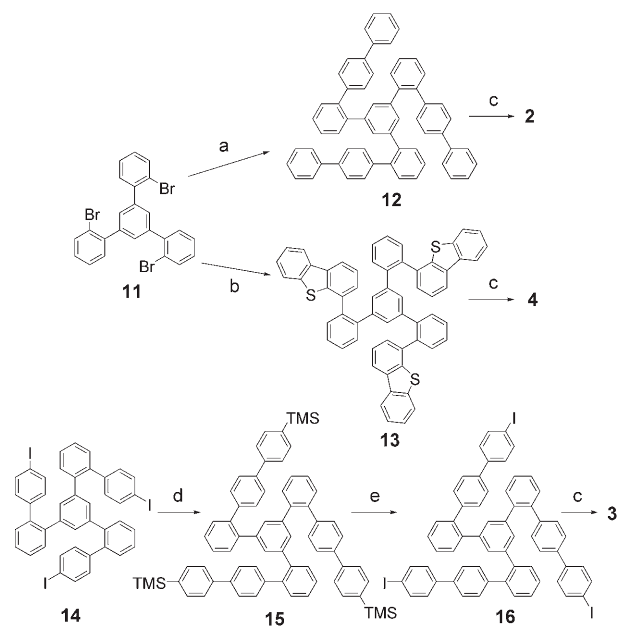
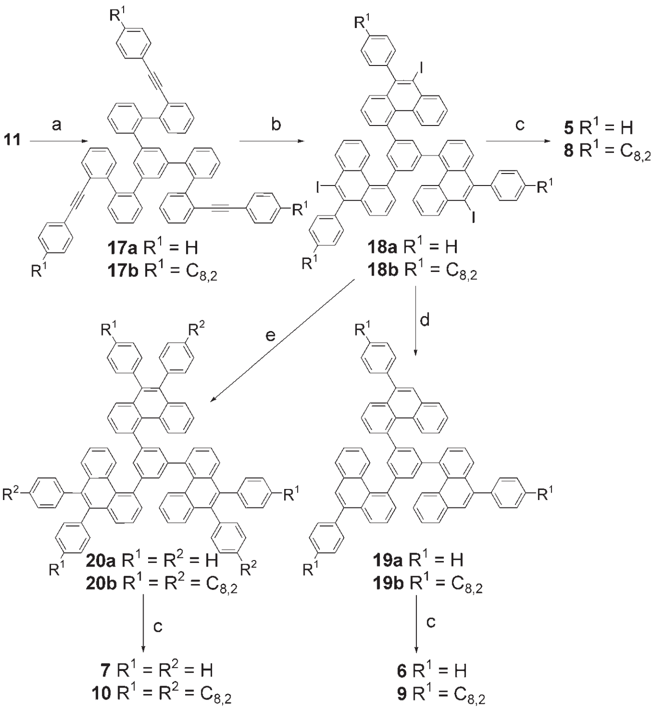
Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Versatile synthesis of **2**, **3**, and **4** based on **11**: a) 4-biphenylboronic acid, $[Pd(PPh_3)_4]$, toluene, K_2CO_3(aq), reflux, 83%; b) 4-dibenzothiopheneboronic acid, $[Pd(PPh_3)_4]$, toluene, K_2CO_3(aq), reflux, 87%; c) $FeCl_3$, CH_3NO_2/CH_2Cl_2, 71% for **2**, 83% for **3**, 81% for **4**; d) 4-trimethylsilylphenylboronic acid, $[Pd(PPh_3)_4]$, THF, K_2CO_3(aq), reflux, 70%; e) ICl, chloroform, 99%. TMS = trimethylsilyl.



Scheme 2. Synthesis of trizigzagHBCs **5**–**10**: a) *o*-phenylethynylbenzeneboronic acid, $[Pd(PPh_3)_4]$, toluene, K_2CO_3(aq), reflux, 82% for **17a**, 86% for **17b**; b) ICl, CH_2Cl_2, −78 °C, 92% for **18a**, 95% for **18b**; c) $FeCl_3$, CH_3NO_2/CH_2Cl_2, 86% for **5**, 88% for **6**, 76% for **7**, 72% for **8**, 78% for **9**, 85% for **10**; d) sBuLi, THF, −78 °C, MeOH, 98% for **19a**, 97% for **19b**; e) phenylboronic acid, $[Pd(PPh_3)_4]$, toluene, K_2CO_3(aq), reflux, 81% for **20a**, 83% for **20b**.

with calculations.[9] UV/Vis absorption spectra of **4**–**7** were in good agreement with the excitation spectra. UV/Vis absorption spectra of tribenzoHBCs **2** and **3** were obtained from thin films. The spectrum of **2** (Figure S1 in the Supporting Information) showed three types of bands (α, β, p) that are characteristic of large polycyclic aromatic hydrocarbons.[10] In contrast to an elongated D_{2h}-symmetrical PAH molecule (D_{2h}-**C60**, inset in Figure S1 in the Supporting Information), which can be regarded as a structural isomer of molecule **2**, a blue shift of the absorption maximum by 10 nm was observed for **2**. This value is consistent with ZINDO/S calculations,[11] suggesting that the electronic properties of the molecules depend also on the symmetry of the PAHs.[12] The peaks of UV/Vis and fluorescence spectra of **4** in solution (Figure S4 in the Supporting Information) showed a blue shift of 10 nm and about 30 nm, respectively, as compared to HBC molecules.[13] Compound **4** represents the first example of large PAHs fused with electron-rich thiophene rings.

The UV/Vis and fluorescence spectra of **6** and **7** (recorded in 1,2,4-trichlorobenzene) exhibited three types of bands (α, β, p; Figure 1). The absorption maxima of **6** (401 nm, $\varepsilon = 2.50\times10^5\,\text{M}^{-1}\text{cm}^{-1}$) and **7** (405 nm, $\varepsilon = 3.58\times10^5\,\text{M}^{-1}\text{cm}^{-1}$) showed a significant bathochromic shift with respect to the corresponding band of parent HBC **1** ($\lambda_{max} = 359$ nm) and a HBC derivative with one C_2 unit as a "zigzag" periphery ($C_{44}H_{18}$, $\lambda_{max} = 380$ nm).[5b]

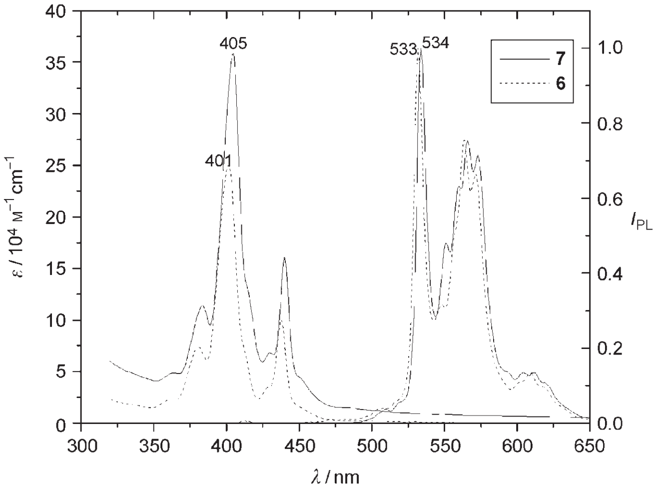


Figure 1. UV/Vis and photoluminescence spectra of **6** and **7** (1.0×10^{-6} M in 1,2,4-trichlorobenzene).

The ^{1}H NMR spectra of **10** at different temperatures together with the signal assignments are given in Figure 2. The spectral assignment is based on comparison with related compounds,[14] the dynamic behavior (see below), and NOESY measurements (data not shown). Although the signals are broad, the resolution of the spectra is already remarkable as the ^{1}H NMR signals of many larger but soluble analogues of **10** are broadened into the baseline as a result of pronounced aggregation effects.[14] The signals of the phenyl protons H_a and H_b, however, showed a temperature-dependent line broadening, which was more pronounced for the

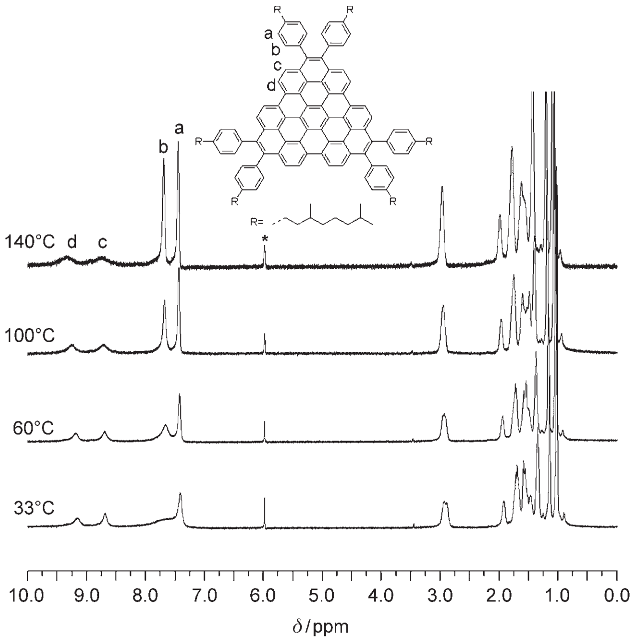


Figure 2. Temperature-dependent ^{1}H NMR (500 MHz) spectra of **10** in [D$_2$]tetrachloroethane (*).

signal of the *ortho* protons H$_b$. This observation suggested that an intramolecular rotation of the phenyl rings occurred around the neighboring single bond.

The bulk thermotropic properties of **10** were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and two-dimensional wide-angle X-ray scattering (2D-WAXS). DSC and POM analyses did not show any phase transition over the investigated temperature range between −150 °C and 250 °C. The 2D-WAXS pattern of filament-extruded[15] **10** in Figure 3 a indicated a supramolecular organization with helical discotic columnar structures characteristic for a 3D-ordered plastic crystalline phase. This kind of phase, reported also for other discotic PAHs,[16] could be clearly distinguished from the typical crystalline phase and disordered liquid-crystalline phase. The columns are arranged in a hexagonal unit cell with a packing parameter of $a_{\text{hex}} = 3.41$ nm, as determined from the positions of the equatorial reflections before thermal treatment. The positions of the reflections in the meridional axis of the X-ray pattern implied a correlation of 1.1 nm between every fourth triangle disc along the column, being a multiple distance of the π-stacking distance of 0.36 nm, which is usually not formed in the liquid-crystalline state.[17] The C_3 symmetry of the aromatic core is reflected in the molecular packing, as every disc is successively rotated by an angle of 30°. The helical stacking is induced by the sterically demanding out-of-plane arrangement of the attached phenyl rings, as schematically illustrated in Figure 3 b, whereby the molecular planes are oriented perpendicular to the columnar axis. Owing to the helical packing, an enhanced columnar and phase stability was observed over a remarkable temperature range. POM experiments showed an isotropization temperature far above 500 °C, which has not been reported for any discotics before. It is known that a helical organization improves the intracolumnar order and leads to high charge-carrier mobilities for discotic columnar systems, which was also expected for **10**.[1a]

A powerful method to investigate the two-dimensional organization of functionalized organic molecules on surfaces is STM at a solid–liquid interface, which provides access to molecular and supramolecular structure and dynamics on the single-molecule level.[18] To date, the largest C_3-symmetrical discs investigated are derivatized triphenylenes.[19] We expected that the larger novel triangle-shaped discs provided might be exploited to form new 2D superstructures at interfaces. Consequently, the 2D self-assembly of **4** (Figure 4 a) was investigated at the interface between a concentrated solution of 1,2,4-trichlorobenzene and the basal plane of highly oriented pyrolytic graphite (HOPG), a two-dimensional polycrystal, where the single crystallites were oriented epitaxially along one of the three graphite axes. In each grain, the two-dimensional crystal exhibited a hexagonal unit cell with one triangular molecule. The unit cell[20] was about twice as large as a footprint of the molecule (≈2.85 nm^2), indicating that the self-assembled molecules lay completely flat on the substrate, all oriented in the same direction with the interstices filled by solvent molecules. On the other hand, Figure 4 b reveals that **10** packed highly regular within a honeycomb lattice, with the determined unit cell[20] being smaller than

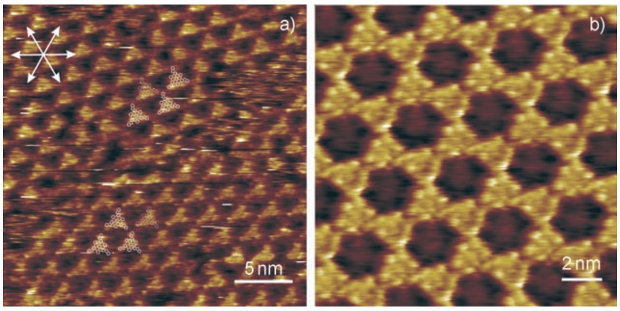


Figure 4. STM current images of a) **4** and b) **10** at the HOPG–solution interface.

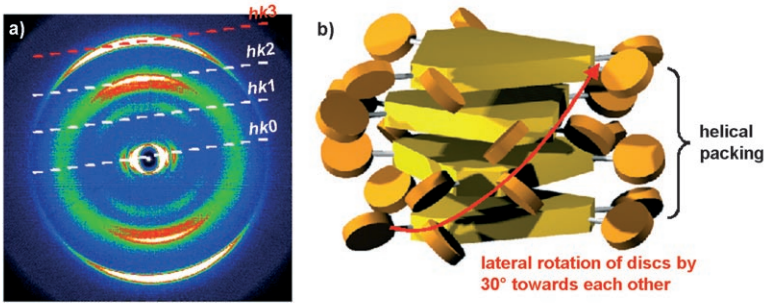


Figure 3. a) 2D-WAXS of an extruded fiber of **10** including the Miller indices for the intracolumnar packing, and b) schematic illustration of a helical pitch (the alkyl side chains are omitted for clarity). Note that there is a correlation of 1.1 nm between each fourth triangle disc in the helical packing.

required for two molecules lying totally flat on the graphite surface (6.95 nm^2 per molecule). This observation indicated that the alkyl chains dissolved partially in the supernatant organic solution. The honeycomb pattern, which was only observed for molecules **8–10** and formed by weak intermolecular and interfacial forces, represents the first visualization in a series of substituted PAHs by STM.[21] Thereby, substituted trizigzagHBCs give rise to a new superstructure, which may be employed for the design of molecular electronic devices based on PAHs as a host and a second molecular species as a guest.

In summary, we have established a novel synthetic method towards large PAHs with C_3-symmetrical triangular shape and multiple "zigzag" peripheries. The title compounds serve as models for describing the relationship between the molecular structure and the electronic absorption and photoluminescence properties. Further, they reveal a unique self-assembly behavior in solution, in the solid state, and at the solution–substrate interface. Mesophase stability over an extremely large temperature range was obtained as a result of the helical supramolecular arrangement of the discs, reflecting the C_3 symmetry. The honeycomb pattern with "holes" observed for monolayers of **10** suggests a molecular engineering with host–guest interaction and surface patterning. Attachment of long alkyl chains onto molecules **3**, **5**, and **8** by transition-metal-catalyzed coupling reaction was feasible and should provide a new series of discotic liquid-crystalline materials with novel self-assembling behaviors and promising applications in organic electronics.[22]

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[11] More details of calculations can be found in the Supporting Information.

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