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From Helical to Staggered Stacking of Zigzag Nanographenes

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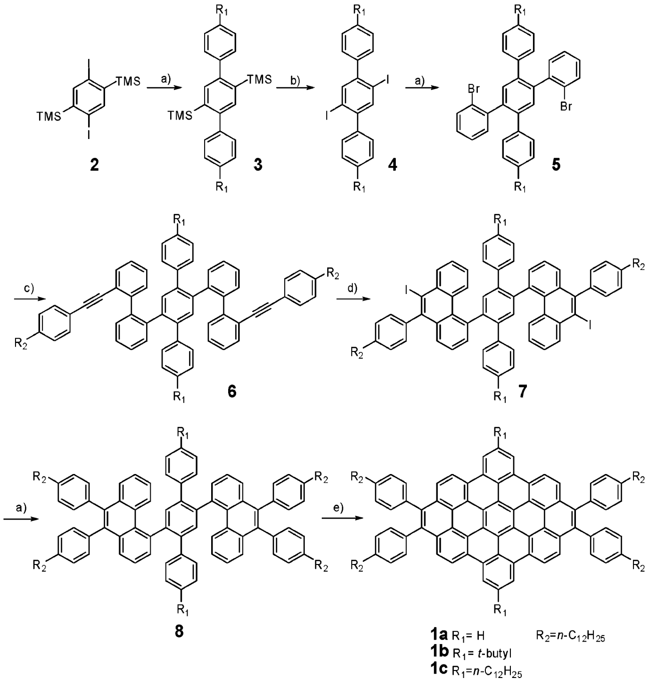
Discotic liquid crystalline materials with high one-dimensional charge carrier mobility along columnar superstructures show potential as active components in organic electronics,[1,2] whereby the control of their molecular packing and long-range organization through the design of the building block represents a prime concern for the performance in devices.[3] It has been shown for triphenylene derivatives that a helical arrangement of discotic molecules results in a significantly improved intracolumnar packing and in high mobility of charge carriers.[4]

Recently, we have described the introduction of alkyl-substituted phenyl groups on the periphery of hexa-*peri*-hexabenzocoronenes (HBCs) and C_3 symmetric zigzag nanographenes leading to the formation of helical self-assembly of the molecules accompanied with considerable mesophase stability over an extremely broad temperature range.[5] The intracolumnar arrangement of these extended PAHs could be related to the symmetry and substitution of the aromatic cores yielding a helical pitch with three building blocks. However, a strategy to control the helical packing within columnar structures by the substitution pattern of PAHs has not been reported so far. Herein, we introduce novel dodecylphenyl-substituted D_2 symmetric zigzag nanographenes (dibenzo[*hi*,*uv*]-phenanthro[3,4,5,6-*bcdef*]ovalene, **1**)[6] which open the opportunity to manipulate the packing of discs. For the first time, a modification of the supramolecular organization from helical stacking to a staggered superstructure has been observed simply upon changing the substitution pattern.

The synthetic route toward **1** is shown in Scheme 1. The key building blocks **5** were obtained in three steps from **2** by Suzuki coupling, trimethylsilyl-iodide exchange, and another selective Suzuki coupling in good yields, and allowed the synthesis of different 1,4-bis-2′-diaryl-2,5-diphenylbenzene precursors.[7] Subsequent reactions afforded **6** in good yields, whereby various substituents R_2 could be introduced in this step. ICl-induced ring cyclization under mild conditions provided precursors **7** with two phenanthrene units and iodo substituents in high yields.[8] Further coupling yielded precursors **8**. The final cyclodehydrogenation was performed with $FeCl_3$ under mild conditions to give **1** with two "zig/zag" edges. All compounds, **1a**, **1b**, and **1c**, are quite soluble in common organic solvents, including THF, dichloromethane, toluene, and can thus be purified by column chromatography. Further characterization by MALDI-TOF MS, UV−vis, photoluminescence, NMR, and elemental analysis confirmed the structures and purity of the new compounds.

Scheme 1. Synthetic Strategy toward **1**[a]



[a] Conditions: (a) aryl boronic acid, $Pd(PPh_3)_4$, THF, K_2CO_3, EtOH, H_2O, reflux, 84% for **3a**, 92% for **3b**, 79% for **3c**, 80% for **5a**, 81% for **5b**, 90% for **5c**, 89% for **8a**, 91% for **8b**, 76% for **8c**; (b) ICl, $CHCl_3$, 95% for **4a**, 92% for **4b**, 91% for **4c**; (c) aryl boronic acid, $Pd(PPh_3)_4$, toluene, K_2CO_3, EtOH, H_2O, reflux, 83% for **6a**, 85% for **6b**, 76% for **6c**; (d) ICl, CH_2Cl_2, −78 °C, 86% for **7a**, 91% for **7b**, 86% for **7c**; (e) $FeCl_3$, CH_3NO_2, CH_2Cl_2, 66% for **1a**, 87% for **1b**, 37% for **1c**.

Differential scanning calorimetry (DSC) measurements of **1a**−**c** revealed phase transitions in the temperature range of −150 to 220 °C, and TGA proved a pronounced thermal stability up to 400 °C, which could be related to the enhanced supramolecular organization which will be discussed in the following. Two-dimensional wide-angle X-ray scattering (2D-WAXS) experiments on extruded fibers[9] of the three derivatives **1a**−**c** showed no significant changes of the organization at the phase transitions. However, strong differences in the supramolecular order among the three compounds were indicated by reflections of varying intensity and shape (Figure 1). It could be concluded that **1a** and **1c** self-assemble into hexagonal columnar structures over the whole temperature range and are well-aligned in the extrusion direction of the sample, characterized by distinct equatorial scattering intensities (Figure 1a,c). The hexagonal unit cell parameters are slightly dependent on the molecular design and the corresponding temperature (summarized in Supporting Information). In both cases, **1a** and **1c**, two meridional wide-angle high-intensity reflections were attributed to a face-to-face π-stacking distance of 0.35 nm between individual ovalenes, whereby their molecular planes are arranged perpendicularly to the columnar axis. Additional meridional and off-meridional reflections at different positions for **1a** and **1c** implied significant variations in the intracolumnar arrangement of the molecules. For **1a**, meridional reflections related to a further intracolumnar period of 1 nm and thus between every fourth unit suggested a helical packing with a molecular rotation of 60° (Figure 1a).[5c] A similar organization has already been experimentally

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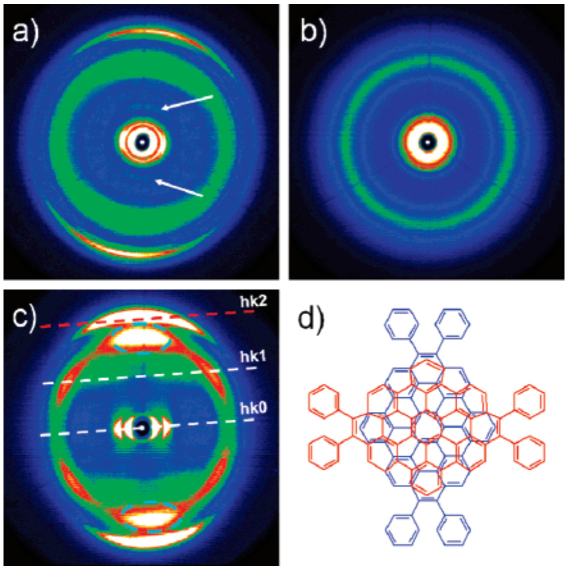

Figure 1. Two-dimensional WAXS patterns of (a) **1a** (arrows indicate intracolumnar periods of 1 nm), (b) **1b**, (c) **1c** (Miller's indices for the intracolumnar stacking and the higher order reflections are indicated), and (d) illustration of the rotation assigned for **1c**.

observed for hexaphenyl HBCs and C_3 symmetric zigzag nanographenes and confirmed by quantum-chemical calculations.[10] In sharp contrast, compound **1c** revealed a staggered packing characterized by off-meridional reflections corresponding to a period of 0.72 nm, being twice the stacking distance and leading to a correlation of every second molecule along the columns (Figure 1c). Figure 1d illustrates that this molecular packing is in good accordance with the ovalene architecture of **1c**. The lateral rotation of the ovalenes by 90° to each other is initiated not only by the hindrance of the phenyl rings at the aromatic core as for **1a** but also, intriguingly enough, by the introduction of alkyl side chains at the *para* position. The different lateral rotation angle of the molecules **1a** and **1c** is attributed to a different filling of the peripheral space by side chains. Since compound **1a** carries only four alkyl substituents in comparison to **1c** with six chains, the resulting rotation of **1a** is smaller to fill the peripheral space by the attached phenyls.

Cooling samples of **1c** to low temperatures (-100 °C) resulted in a higher supramolecular order as expressed by a higher intensity of the reflections and the appearance of new doublet reflections at a scattering vector $s = 2.32$ nm^{-1} (Figure 1c), which have been also observed for discotic triphenylenes with a similar staggered packing and a plastic crystalline phase.[11] We assigned **1a** and **1c** also as plastic crystalline over the whole temperature range attributable to their waxy/soft state and their above-described exceptional three-dimensional organization, which can be clearly distinguished from a typical crystalline and disordered liquid crystalline phase. On the other hand, poor order was observed only for **1b** caused by the *t*-butyl groups hindering a stacking of the molecules (Figure 1b). The weak interaction between the building blocks of **1b** was also reflected by the isotropization temperature (T_i) of 320 °C. This stood in contrast to **1a** and **1c**, which failed to show a T_i up to 500 °C, thus reflecting the strongly improved stability of the mesophase over a broad temperature range due to helical packing. It should be noted that birefringence in the polarized optical microscopy and the isotropic small-angle reflection implied columnar structures for **1b** which are, however, established only over short-range, whereby **1a** and **1c** exhibited self-assembly over long-range.

In conclusion, we have developed a synthetic protocol yielding the novel D_2 symmetric zigzag nanographenes, and allowing a specific substitution of the ovalene corona. The latter appeared as a key feature to modify the intracolumnar arrangement in a facile way. It thus became possible to modify the supramolecular organization of an extended PAH from helical to a unique staggered superstructure. It is expected that the variation of the molecular packing for one system is accompanied by a different performance in electronic devices.[12]

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Supporting Information Available: Experimental procedures, ^{1}H NMR, UV−vis, and photoluminescence spectra, POM, thermal behavior, and indexed 2D-WAXS patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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