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Unusual Symmetry Effect on Hexa-*peri*-hexabenzocoronene

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Discotic columnar liquid crystal materials based on large polycyclic aromatic hydrocarbons (PAHs) have continuously attracted interest because of their high one-dimensional charge carrier mobility along their columnar superstructures.[1] Self-assembly of these disk-like molecules on surfaces provides the opportunity to build electronic devices at the nanoscale.[2] Many challenges have emerged in this area, such as the preparation of large PAHs, the control of molecular symmetry, and the peripheral substituents.[3] Hexa-*peri*-hexabenzocoronenes (HBCs) with hexagonal aromatic core symmetry and large π-conjugation are surely one of the prime concerns of large PAHs, such as the prominent D_6h symmetrically substituted **1**.[4] Substitution of the aromatic core allows the control over the solubility, thermotropic properties, and their self-assembly in the solid state and at the solid–liquid interface.[5] The material's properties can be modified through the architecture of the substituents, like, for example, the alkyl chain length and the substitution symmetry at the disk corona.[4] For instance, longer and more flexible side chains are expected to decrease the thermal phase transitions. On the other hand, reducing the number of substituents and maintaining a high substitution symmetry of the disk-shaped building blocks, for example, the D_3 symmetry, which are believed to influence significantly their thermal and self-assembly behaviors, are however restricted to their synthetic hitches.[6]

In this work, we present a surprising effect on the isotropization temperatures (T_i) of two HBC derivatives. The T_i values of a D_3 symmetric HBC (**2**) and a C_2 symmetric HBC (**3**) with three and two dodecyl chains, respectively, have been dramatically reduced by approximately 250 and 200 °C with respect to the D_{6h} symmetric hexadodecyl HBC

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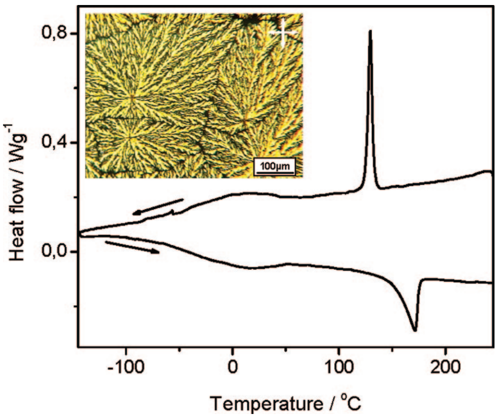
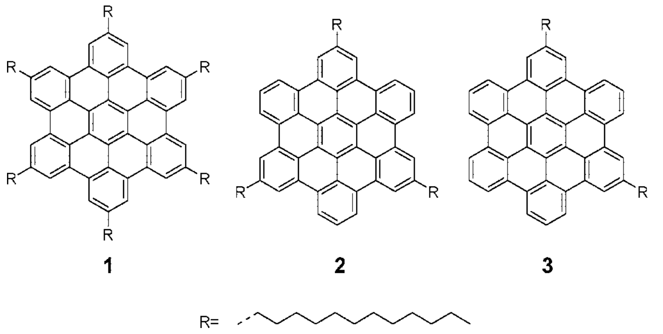


Figure 1. DSC traces of **2** during the first cooling and the second heating cycle at 10 °C/min; inset displays an image from polarized optical microscopy (POM) with cross-polarizers after cooling from the isotropic phase at 1 °C/min.

1 (Chart 1). This provides an attractive and novel strategy for the implementation of these materials in organic electronics as a result of the three following reasons: (I) the accessible phase transitions make thermal processing more facile, (II) the reduction of alkyl substituents results in a higher concentration of the active chromophore, and (III) the high substitution symmetry preserves a pronounced supramolecular order important for the charge carrier transport. Finally, scanning tunneling microscopy (STM) experiments reflected the significant effect of the substitution symmetry on the self-organized monolayer between highly oriented pyrolytic grahite (HOPG) and solution by displaying novel zigzag and flower-like patterns, which have never been observed for D_6h symmetrically substituted HBCs.

Chart 1



The detailed synthetic procedures of **2** and **3** are provided in the Supporting Information. Both compounds are soluble in hot toluene and were purified by columnar chromatography and precipitation from methanol. Further characterization by NMR, MALDI-TOF MS, and elemental analysis verified the purity of the compounds.

Differential scanning calorimetry (DSC) measurements of **2** revealed two phase transitions (Figure 1). During the second heating a broad first transition appeared at a temperature of 20 °C (maximum peak) which is attributed to the reorganization of the alkyl side chains, not affecting the supramolecular organization, as already reported for derivative **1**. Upon further heating, the second main transition at 171 °C (enthalpy 18.0 J/g) was observed. Two-dimensional wide-angle X-ray scattering (2D-WAXS) experiments of extruded samples[7] of **2** indicated a self-assembly into columnar superstructures, whereby the organization in the solid state did not change with temperature (cf. Supporting Information). The large number of distinct reflections in the 2D pattern and the highly birefringent optical textures observed by POM (inset in Figure 1) suggest, surprisingly, a crystalline phase of **2** over the whole solid-state phase up to the T_i of 171 °C.

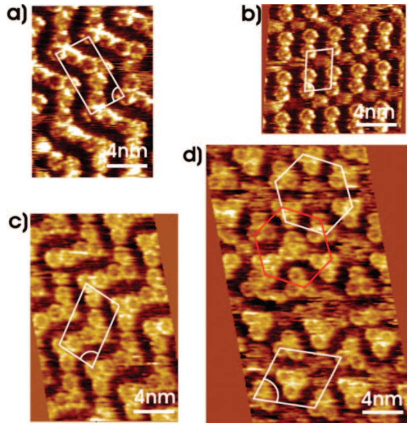


Figure 2. (a and b) STM current images of **2**; (c and d) STM height images of **3**.

This extraordinary low T_i is in strong contrast to the thermal behavior of **1**, which exhibits a transition to a liquid crystalline phase at 107 °C and an isotropic phase at approximately 420 °C. Despite fewer dodecyl substituents, the T_i of **2** was decreased by approximately 250 °C with respect to **1**. A similar trend for the thermal behavior was discerned for **3**. During the second heating **3** revealed a small first transition at 76 °C (1.6 J/g), which was also attributed to the side chain reorganization, and an isotropization point at 221 °C (4.9 J/g). Compound **3** exhibited an identical crystalline phase as **2** (see for 2D-WAXS and POM in Supporting Information). The dramatic T_i drop can only be explained in terms of a decrease of the molecular symmetry. In general, the aromatic cores approach each other via π-stacking interactions, while the alkyl side chains, bearing a certain steric demand, disturb these attractive noncovalent forces. This is usually reflected by enhanced solubility and decreased phase transition temperatures. Therefore, one might initially expect for the D_3 symmetric **2**, substituted by three alkyl substituents, a significant increase of T_i in comparison to **1**. The considerable impact of the lowered molecular symmetry from D_6h for **1** to D_3 of **2** on the thermal behavior, leading to the unexpectedly low isotropic phase transition, was confirmed by the lack of a mesophase. This phenomenon has so far only been observed for HBC derivatives carrying bulky 2-decyl-tetradecyl chains or asymmetrically substituted 1,2,3-tris-dodecyloxy HBC.[4a,8] In analogy, discotic alkyloxy

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substituted triphenylenes revealed also a lower T_i for derivatives with decreased number of aliphatic side chains and with high molecular symmetry, whereby the temperature decrease was relatively small.[9]

In the next step, the organization of **2** and **3** in a quasi-2D system at an interface has been investgated by STM in order to study the influence of the symmetry of the aromatic cores on molecular self-assembly at the solution-HOPG interface[6b] It is well-known that D_6h symmetric **1** self-assembles in oblique or dimer nanostructures on the basal plane of HOPG.[5] Here, for D_3 symmetric **2**, a significantly different packing besides dimer patterns (Figure 2b) was obtained, namely, a zigzag pattern, as shown in Figure 2a. The STM current image of **2** in the large scale revealed many domains (cf. Supporting Information). The zigzag pattern comprised six bright features (corresponding to high tunneling probability) in a unit cell, which were ascribed to the π-conjugated HBC discs.[10] The aliphatic side chains have not been resolved, probably due to their high conformational mobility on a time scale faster than the STM imaging. The C_2 symmetric **3** was also assembled into two different coexisting crystallographic phases (cf. Supporting Information). In addition to a zigzag structure (Figure 2c), which was similar to **2**, a flower-like pattern was found (Figure 2d). The flower-like pattern consisted of six triangle-shaped objects, each with three molecules of **3**. Noteworthy, the centers of the flowers were sometimes empty but in a few cases accommodated an object inside, marked by white and red hexagons correspondingly in Figure 2d. Fewer alkyl substituents and thus lower symmetry of **2** and **3** resulted in significantly distinguishable packings, that is, the zigzag and flower-like nanostructures, in comparison with the D_6h symmetric HBC derivatives.

In summary, we have synthesized D_3 symmetric (**2**) and C_2 symmetric (**3**) HBCs, which showed a surprisingly significant reduction of the isotropic temperatures with respect to their D_{6h} symmetric analogue. The accessible T_i should allow the fabrication of organic field-effect transistors by melt processing.[11] A better performance of the two compounds in devices is expected due to fewer insulating alkyl chains and an increase of the chromophore concentration, with a high degree of supermolecular order at the same time. STM revealed additionally a strong effect of symmetry and substituents on the self-assembly of both derivatives at the solid–liquid interface displaying novel zigzag and flower-like patterns with a lower symmetry than the D_6h symmetric analogue.

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Supporting Information Available: Experimental procedures, POM, thermal behavior, 2D-WAXS patterns, and STM pictures. This material is available free of charge via the Internet at http://pubs.acs.org.

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