Synthesis, Helical Organization, and Fibrous Formation of C_3 Symmetric Methoxy-Substituted Discotic Hexa-*peri*-hexabenzocoronene

Xinliang Feng, Wojciech Pisula,[†] Masayoshi Takase,
Xi Dou, Volker Enkelmann, Manfred Wagner, Ning Ding,
and Klaus Müllen*

Max Planck Institute for Polymer Research,
Ackermannweg 10, 55128 Mainz, Germany

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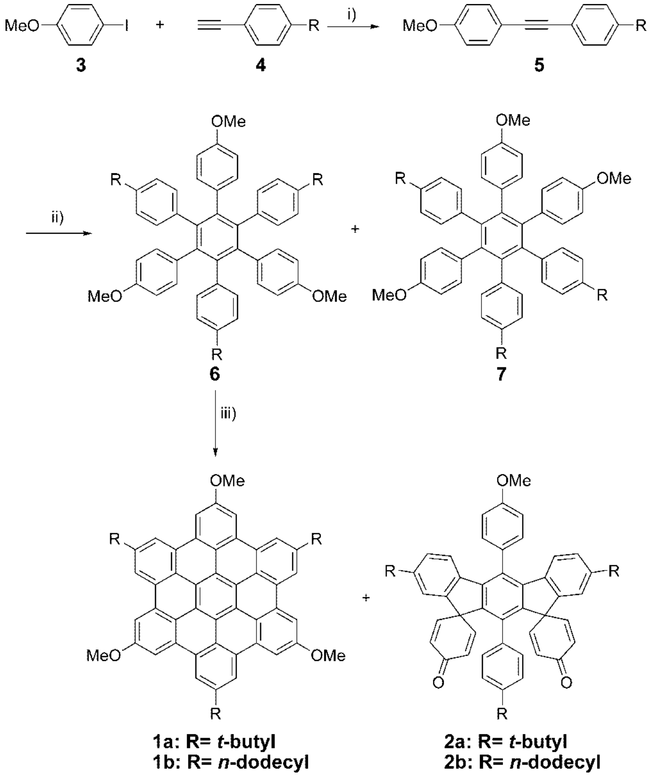
Hexa-*peri*-hexabenzocoronene (HBC) and its derivatives are attractive, not only due to their structural beauty but also because of their interesting electronic and optoelectronic properties.[1] Considerable attention has been paid to their self-assembly and the fabrication of long-range oriented discotic molecules in devices.[2] Supramolecular nanoscale objects such as nanowires and nanotubes on the nanometer up to the millimeter length scale are thereby of utmost importance for practical applications.[3] The synthetic approaches toward HBCs and their extended analogues have included the introduction of alkyl substituents and functional groups as well as the variation of topologies and molecular symmetries. Among them, C_3 symmetric discotics have exhibited unique self-assembly properties both in the solid-state and at the solid−liquid interface.[4] However, the incorporation of heteroatoms into the graphene core and the functionalization with heteroatom-containing substituents, which will significantly influence the electronic properties and thermal behavior, are still problematic.[5] So far, only few alkoxy-substituted[5c–e] HBCs have been successfully synthesized through the oxidative cyclodehydrogenations of proper hexaphenylbenzene precursors. Very recently, a *meta*-dimethoxy instead of a *para*-dimethoxy substitution of HBC has been achieved by a surprising rearrangement during the Scholl reaction of a *para*-dimethoxy substituted hexaphenylbenzene precursor.[5f] This indicated that *meta*-dimethoxy substituted HBC was a stable product and compatible with the conditions of the $FeCl_3$ mediated oxidative cyclodehydrogenation. Accordingly, we present here C_3 symmetric *meta*-trimethoxy substituted hexaphenylbenzene precursors which allow the construction of novel C_3 symmetric HBCs **1** with three alternating methoxy and alkyl substituents under the Scholl reaction. The strong tendency of **1b** toward self-assembly in solution was evaluated by NMR spectroscopy. Two-dimensional wide-angle X-ray scattering (2D-WAXS) demonstrated a helical organization with a large intracolumnar correlation in the solid state. Surprisingly enough, the self-assembly also led to fibrous nanostructures with several hundred micrometers in length upon simple drop-casting.

Scheme 1. Synthesis of C_3 Symmetric HBCs 1 and Bis-spirocyclic Dienones 2[a]



[a] (i) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, rt; (ii) $Co_2(CO)_8$, dioxane, reflux; (iii) $FeCl_3$, CH_3NO_2, CH_2Cl_2.

The synthetic protocol is outlined in Scheme 1. Asymmetric diphenylacetylenes **5** were first synthesized via Sonogashira coupling in high yields. Afterward $Co_2(CO)_8$ catalyzed cyclotrimerization gave two isomers (**6** and **7** in a ratio of roughly 1:2), which could be easily separated by column chromatography.[4c] The planarization of **6** was carried

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[†] Present address: Evonik Degussa GmbH, Process Technology & Engineering, Process Technology - New Processes, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany.

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out with $FeCl_3$ under mild conditions affording the desired HBCs **1**; purification was accomplished by reprecipitation and washing repeatedly with methanol. It is noteworthy that **1a** with *t*-butyl groups led to strong chlorination according to the MALDI-TOF MS spectrum (Supporting Information). In contrast, the *n*-dodecyl group for **1b** showed only minor chlorination probably due to the different electron-donating effect of *t*-butyl groups with respect to *n*-dodecyl groups.[6] Compound **1b** was soluble in organic solvents including THF, CH_2Cl_2, and toluene and thus could be further purified by column chromatography and characterized by UV−vis, photoluminescence, and NMR spectroscopy. The bis-spirocyclic dienones **2a** and **2b** were also separated, whereby their formation mechanisms were similar to discussions in recent reports.[5f,g] Their structures were confirmed additionally by single crystal X-ray diffraction (Supporting Information).

The UV−vis and photoluminescence spectra of **1b** (in chloroform, Supporting Information) showed similar types of bands as alkyl substituted HBCs, but with a bathochromic shift of the corresponding absorption maximum (λ_{max}= 367 nm compared to hexaalkyl-HBC at 362 nm), which could be ascribed to the electron donating effect of methoxy substitutents. ^{1}H NMR spectroscopy has been used as an efficient tool to evaluate the self-assembly of disk molecules in solution.[7] The ^{1}H NMR spectrum of **1b** in d^2-1,1,2,2-tetrachloroethane was recorded over a range of temperatures and concentrations as presented in the Supporting Information. Two kinds of core protons were recognized which were neighboring to the substitutions with methoxy or dodecyl substituents, respectively (Supporting Information). On heating from 30 to 140 °C, the aromatic signals assigned to the two types of HBC core protons experienced a downfield shift of 0.47 ppm and 0.49 ppm, respectively. Likewise, decreasing the concentration from 11.9×10^{-3} M to 2.38×10^{-4} M at 60 °C resulted in a downfield shift of 0.44 ppm for both core protons. It is clear that such shifts correspond to a stronger face-to-face stacking of the discs, resulting in shielding effects. We assume a similar high association constant for **1b** as recently reported for hexadodecyl substituted HBC, since identical chemical shifts were determined under the same experimental conditions.[7a,b]

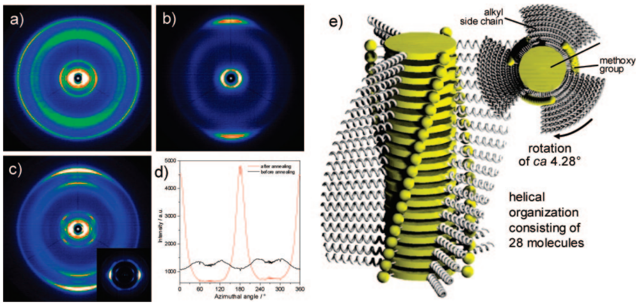

Figure 1. Structural characterization of **1b**; 2D-WAXS at 30 °C (a) before and (c) after annealing (inset: 2D-SAXS) and (b) at 170 °C; (d) comparison of the azimuthal integration of the scattering intensity corresponding to the π-stacking distance; and (e) schematic illustration of the intracolumnar arrangement of **1b** at 30 °C after annealing into a helical organization with a disk rotation of ca. 4.28°.

Differential scanning calorimetry (DSC) indicated thermotropic properties of **1b**. Two peaks appeared in the DSC scan during second heating: one minor peak at 80 °C (3 J/g) and a major peak at 145 °C (13 J/g). The minor transition was related to a reorganization of the alkyl side chains as already observed for other HBC derivatives by 2D-WAXS measurements on extruded fibers.[8] The second peak was assigned to a crystalline−liquid crystalline (LC) phase transition. Figure 1a shows a 2D-WAXS pattern for the crystalline phase before annealing. As a result of the poor macroscopic orientation, the typical disk tilting for this phase within the columnar structures was not well resolved by extremely broad off-meridional reflections in the pattern. Heating to the LC state improved the intracolumnar packing significantly as represented by the distinct meridional reflections related to a π-stacking distance of 0.36 nm (Figure 1b). Thereby, the molecular planes were arranged perpendicular to the columnar axis. The positions of equatorial reflections suggested a hexagonal arrangement of columnar structures with a packing parameter of a_{hex} = 2.51 nm. Remarkably, after cooling the sample, the 2D pattern revealed even a much more complex superstructure with a considerably enhanced order in comparison to the sample before thermal treatment (Figure 1c). For instance, the reflections corresponding to the π-stacking sharpened considerably, and their intensity increased drastically as evidenced by the azimuthal integration (Figure 1d). Furthermore, the intracolumnar packing mode changed from a tilted to a nontilted arrangement after annealing, implying the presence of additional interactions besides π-stacking.[9] The hexagonal unit cell at 30 °C showed a significantly larger intercolumnar distance of a_{hex} = 3.49 nm in comparison to the LC phase, while the π-stacking distance of 0.35 nm remained identical. Further X-ray measurements displayed scattering intensities also in the small-angle region (inset, Figure 1c). The reciprocal spacing of the first layer line formed by the off-meridional reflections in the small-angle region were related to a period of 9.8 nm along the stacking direction (Figure 1c).[10] We attribute this spacing to intermolecular correlations of discs possessing an identical lateral position within the columns.[11] This distance is surprisingly large including 28 molecules, if taking into account the π-stacking of 0.35 nm between individual building blocks. Thereby, the molecules were slightly laterally rotated by an angle of ca. 4.28° to each other resulting

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in a helical packing with pronounced order (Figure 1e).[12] As a consequence, the small rotational angle resulted in a higher side chain density in the outer alkyl mantle and thus to a larger hexagonal unit cell after annealing in comparison to the LC phase. Typically, the helical arrangement of discotics can be induced by additional intra- and intermolecular hydrogen bonds[4e,f] or peripheral bulky substituents.[12] The presented case differs from these examples. We attribute the helical organization of **1b** to local dipole moments between the C−O bonds.[13] Both π-stacking and dipole interactions are known to play an important role for the self-assembly leading to complex superstructures.[14] In contrast, hexa-alkyl substituted HBCs without local dipole moment do not reveal such pronounced intracolumnar packing.

Toward solution processing of organic semiconductors in electronic devices, the control of the morphology formation on surfaces is an essential step which determines in many cases the performance.[15] The relation between solution and bulk behavior is quite apparent in the case of **1b**. The self-assembly of **1b** on a glass substrate upon simple drop-casting was studied by optical microscopy. Surprisingly, the thin film (1.0×10^{-4} M in *o*-dichlorobenzene) was homogeneously composed of several hundred micrometer long fibers (Figure 2a), indicating a strong one-dimensional self-assembly of **1b**. The birefringence of the fibers suggested a high supramolecular order within these structures, and the optical anisotropy was characteristic for macroscopic orientation of the columnar structures along the fiber direction. The fibers revealed only birefringence at a relative arrangement of 45° toward the analyzer/polarizer (Figure 2a). Drop-casting from different solvents, including toluene, THF, and $CHCl_3$, displayed in all cases a similar morphology within the films but different lengths of the fibrous assemblies (Supporting Information). The transmission electron microscope (TEM) allowed a deeper inspection of this fibrous network as obtained from THF (Figure 2b). The fibers revealed an average diameter of 500 nm and a length up to few hundred micrometers. The high-resolution TEM image (Figure 2c) displayed individual columns well oriented along the fiber direction suggesting a high supramolecular order which was in agreement with the POM image. The electron diffraction (ED) of such a fiber shown in Figure 2d exhibited a pattern characterisistic for a crystalline state confirming the high degree of order in the fibrous structures. This was in accordance with the bulk organization observed by X-ray before annealing (Figure 1a). The ED pattern indicated a tilting of ca. 45° of the disk molecules toward the columnar axis with the corresponding intracolumnar period of 0.48 nm and π-stacking distance of 0.34 nm. After annealing the fiber morphology and columnar structures in the fibers were maintained, while ED showed a change to a nontilted packing as also oberved for the bulk (Supporting Information).

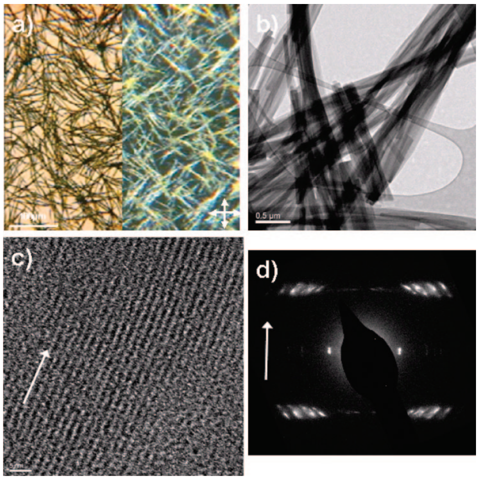

Figure 2. (a) Optical images of the morphology of **1b** drop-cast from *o*-dichlorobenzene (1.0×10^{-4} M) without (left) and with cross-polarizers (right), (b) TEM image of **1b** drop-cast from THF (1.0×10^{-4} M), (c) high resolution TEM of a fiber displaying columnar structures, and (d) electron diffraction pattern of **1b** fiber (white arrows indicate the fiber direction).

In conclusion, a novel C_3 symmetric HBC with three alternating dodecyl and methoxy substituents was successfully synthesized via the Scholl reaction from its hexaphenylbenzene precursor. It showed pronounced aggregation in solution as characterized by concentration and temperature dependent ^{1}H NMR measurements. Additionally, the influence of methoxy units at the meta positions and the distinct intermolecular interactions were manifested in the formation of a complex helical superstructure in the solid state as derived from X-ray scattering results. The solution processing onto a substrate resulted in the formation of exceptionally long fibrous microstructures. The facile transformation of methoxy units into hydroxyl groups is expected to afford new alkoxy-substituted HBC discotics.

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Supporting Information Available: Full experiment details and the MALDI-TOF mass spectra of compound **1a** and **1b** (PDF) and crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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