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Partially stripped insulated nanowires: a lightly substituted hexa-*peri*-hexabenzocoronene-based columnar liquid crystal†

Zhaohui Wang, Mark D. Watson, Jishan Wu and Klaus Müllen*
Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany.
E-mail: muellen@mpip-mainz.mpg.de; Fax: +49 6131 379350; Tel: +49 6131 379150

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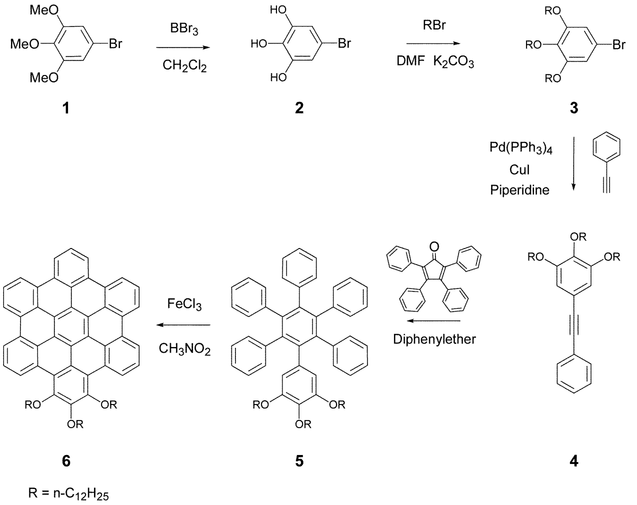
We present the facile preparation and characterization of the first "unwrapped" hexa-*peri*-hexabenzocoronene derivative, which forms a stable columnar liquid crystalline mesophase with a practically accessible isotropization temperature.

Discotic materials are receiving increasing attention in the search for organic materials which are technologically promising for electronic devices.[1] Disk-shaped molecules carrying multiple peripheral alkyl substituents spontaneously self-assemble into columnar structures of face-to-face stacked rigid cores, nanophase-separated from the side-chains, manifesting manifold unique superstructures.[2] The coaxial mantle of saturated hydrocarbon chains forms a barrier to charge transport between columnar cores, leading to their designation as one-dimensional nanowires.[3] Device performance[4] might be enhanced by some decrease in the one-dimensionality of charge-transport, *e.g.* to provide intercolumnar bypasses at defects and grain/domain boundaries. To this end, we propose to partially strip away the insulating wrapping of these nanowires, leaving residual flexible chains sufficient to ensure solution processability and phase-forming properties. With few exceptions, stable columnar phases require more than 3 alkyl substituents on the mesogenic core,[5] and exposure of edges can lead to other arrangements (*e.g.* edge-to-face).[6] Larger polycyclic aromatic hydrocarbons favour face-to-face stacking even when unsubstituted,[7] in particular hexa-*peri*-hexabenzocoronenes (HBC's) are especially insensitive in this regard.[8] Here we present the synthesis and characterization of the first "unwrapped" mesogenic HBC derivative, and report on its bulk self-assembly to a columnar mesophase which can be mechanically aligned.

The synthetic route towards 1,2,3-tris-dodecyloxy-hexa-*peri*-hexabenzocoronene (**6**) is shown in Scheme 1. Commercially available **1** was demethylated with BBr_3 to give 5-bromo-1,2,3-trihydroxybenzene followed by Williamson etherification with 1-bromododecane. Hagihara–Sonogashira coupling of **3** with phenylacetylene gave substituted diphenylacetylene **4** in 85% yield. Diels–Alder cycloaddition between **4** and commercially available 2,3,4,5-tetraphenylcyclopentadienone in refluxing diphenyl ether afforded the functionalized hexaphenylbenzene **5** in 90% yield. Despite strong dependence of its success on heteroatom substitution patterns,[9] the final cyclodehydrogenation step[10,11] to **6** was achieved in 70% yield. Given the vanishing solubility of unsubstituted HBC, "unwrapped" HBC **6** is surprisingly soluble in common organic solvents such as THF and chloroform.



Scheme 1 Synthesis of "unwrapped" HBC **6**.

UV–Vis absorption and fluorescence spectra ($CHCl_3$, $1.0*10^{-6}$ M) of HBC **6** are shown in Fig. 1. The absorption spectrum is essentially unchanged with reference to unsubstituted and alkylated HBCs,[12,13] in accord with the relatively weak donor effect of the alkoxy chains. The profile of the emission spectra is likewise similar, except that the band corresponding to the 0–0 transition (470 nm), which is otherwise very weak for the D_{6h}-symmetric unsubstituted HBC, is "more allowed" due to lower symmetry and some expected non-planarity caused by the alkoxy substituents in bay positions.

The thermotropic liquid crystalline behaviour of HBC **6** was studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and wide-angle X-ray diffraction (WAXD). The first DSC heating scan (supplementary information) shows two endothermic transitions, 2nd order and 1st order respectively, at 50 and 188 °C. Subsequent cooling and heating scans show two reversible 1st order transitions at 48 °C (Col_1–Col_2) ($\Delta H = -6.20$ kJ mol^{-1}) and 190 °C ($\Delta H = -18.49$ kJ mol^{-1}), the latter corresponding to the isotropization as confirmed by POM. We attribute the dramatic decrease of the isotropization temperature (~200 °C lower than alkyl substituted HBCs[8b,9]) to reduced symmetry and/or the expected slight nonplanarity of the HBC mesogenic core. The until recently[14] practically inaccessible isotropization temperatures of hexa-alkylated HBC's have limited their optimal processing by thermal means within certain devices or electrical characterization cell geometries.

Variable temperature 2D-WAXD data collected in transmission through an extruded fibre[15] of **6** clearly indicate a columnar mesophase, which is sufficiently cohesive that the columns are

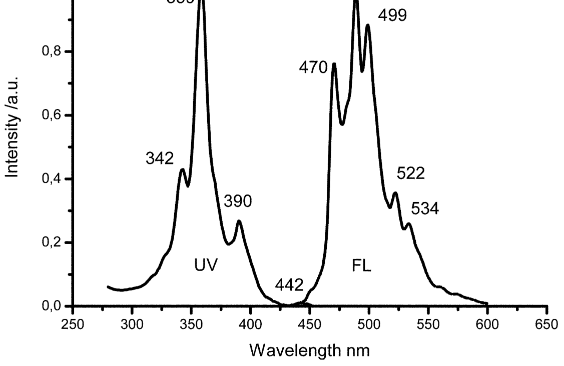


Fig. 1 UV-Vis absorption and fluorescence spectra of **6**.

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† Electronic supplementary information (ESI) available: full experimental details, differential scanning calorimetry (DSC) scans and MALDI-TOF spectrum of **6**. See http://www.rsc.org/suppdata/cc/b3/b311651d/

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aligned in the shear direction (inset Fig. 2). The number and relative intensity of reflexes are increased after annealing at 150 °C, in accord with the 2^{nd} order endothermic transition seen in the first DSC heating scan. A hyperbolic set of reflexes with vertices on the meridian ($d = 0.48$ nm) indicates columns of face-to-face disks with their molecular planes inclined 45° relative to the columnar axes. (Tilt angle calculated from $\theta = \arccos(d/d_0)$, $d_0 = 0.34$ nm – the typical π–π stacking distance).[16] The limited diffraction data do not allow determination of the relative direction of the tilt within adjacent columns.

Reflexes along the equator, which are better resolved in the reflection measurement (Fig. 2), arise from positional correlation in the lateral packing of columns. These are indexed as shown to fit a two-dimensional rectangular unit cell, the corners of which are formed by the columns. The large spacing of 4.01 nm could reasonably be explained by a lamellar arrangement of single rows of columns, with interstitial layers filled by nanophase-separated alkyloxy chains. Figure 3 shows a single column segment having approximately the width matching the lamellar spacing. The short side of the unit cell corresponds well to double the van der Waals cross-section of the HBC core, *i.e.* adjacent columns not separated by alkyl chains.

To the best of our knowledge, this is the first example of an "unwrapped" discotic mesogen with flexible chains attached at one focal point, which still preserves the ordered columnar stacking. Unlike the case of rod-like mesogens with substituents at one or both ends, for HBC **6** with an aspect ratio ~1 and the strong tendency[7] of large area π-systems to form columnar stacks, cohesive columns rather than molecule planes are aligned in the direction of shear.

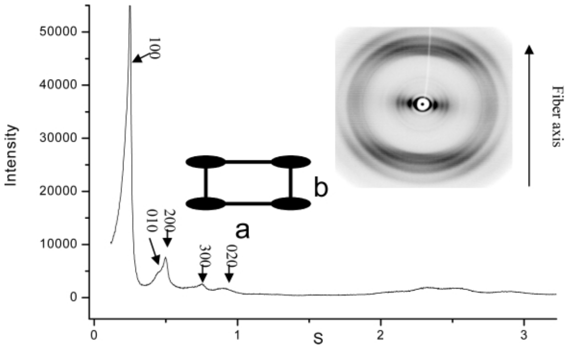

Fig. 2 Powder WAXD (reflection) of HBC **6**. Insets: proposed 2D rectangular unit cell describing lateral positional correlation of columns ($a = 4.01$ nm and $b = 2.23$ nm) and transmission WAXD pattern of extruded fibre. Measured at RT after annealing at 150 °C.

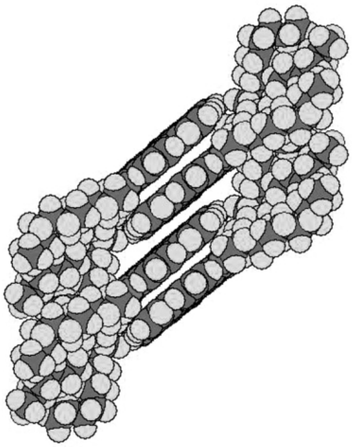

Fig. 3 Stacking model of HBC **6**.

To conclude, the combination of facile synthesis, low isotropization temperature, good solution processability, and long-range order make this new kind of "unwrapped" columnar material a potential active component in organic electronic devices. Charge-carrier mobilities and performance of devices prepared from **6** are the subject of future investigations.

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