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A Fluorine-Substituted Hexakisdecyloxy-hexa-*peri*-hexabenzocoronene

Qing Zhang,[†] Paulette Prins,[‡] Simon C. Jones,[†] Stephen Barlow,[†] Takeshi Kondo,[†] Zesheng An,[†] Laurens D. A. Siebbeles,[‡] and Seth R. Marder*,[†]

*Center for Organic Photonics and Electronics and School of Chemistry and
Biochemistry, Georgia Institute of Technology, Atlanta 30332-0400, and
Opto-Electronic Materials Section, DelftChemTech, Delft University of Technology,
Mekelweg 15, 2629 JB Delft, The Netherlands*

seth.marder@chemistry.gatech.edu

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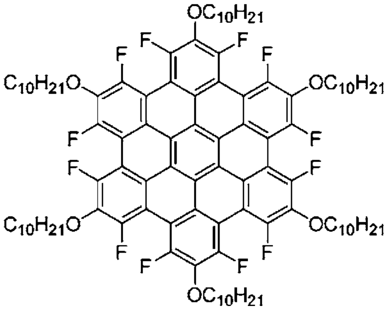
ABSTRACT



The first fluorine-substituted hexabenzocoronene has been synthesized and is much more readily reduced than its nonfluorinated analogues. Thin films of this material show columnar order at room temperature, and the charge-carrier mobility measured by the pulse-radiolysis time-resolved microwave conductivity technique is comparable to that of other hexabenzocoronene materials.

Hexa-*peri*-hexabenzocoronene (HBC) and its derivatives, often called “superbenzenes”, can be regarded as graphene fragments consisting of 13 fused benzene rings.[1a] These compounds often exhibit strong $\pi-\pi$ stacking interactions that promote self-assembly in solution and in films and have attracted increasing attention because of their electronic and optoelectronic properties. In measurements performed by van de Craats and co-workers, the sum of the hole and electron mobilities was determined to be as high as ca. 1 cm^2 V^{-1} s^{-1} in solid phases of certain hexakisalkyl derivatives by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC).[1c,d] There have been many studies on the supramolecular self-assembling properties of this family of compounds.[2a−d] It has been shown that substituted HBCs can be processed from solution to form films with uniaxially ordered columnar stacks, which lie parallel to the substrate.[2b,c] Aida reported that an amphiphilic HBC self-assembles to form graphite-like nanotubes.[2d]

Müllen’s group and others have functionalized HBC with extended conjugated structures and alkyl groups on the periphery.[3a−c] Alkyl- and aryl-substituted HBCs usually have very high isotropic clearing points, in some cases higher than 420 °C. To lower the clearing point of HBC compounds, thereby potentially simplifying processing of the materials into device structures, HBCs with multiply branched substituents have been synthesized.[3d] Recently, Draper reported

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[†] Georgia Institute of Technology.

[‡] Delft University of Technology.

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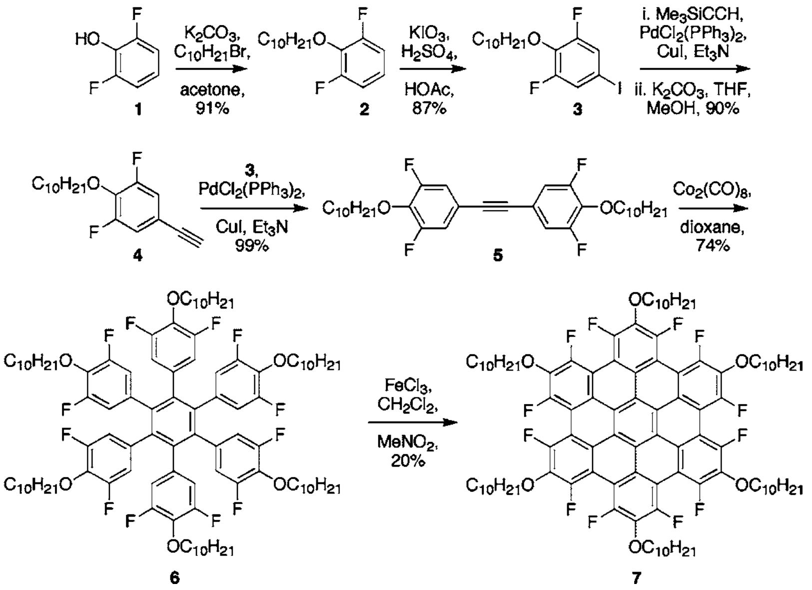
Scheme 1



a hetero-"superbenzene" by changing the chemical makeup of the core to form a new family of nitrogen-functionalized, graphene-like nanostructures.[3e] Direct attachment of heteratoms such as oxygen, nitrogen, and sulfur to the HBC core is expected to modify self-assembly and electronic properties.[3a] However, the attempted synthesis of hexakisalkoxy-substituted HBC resulted in an extended quinoidal compound in 96% yield through ether cleavage and oxidation.[4]

We were interested in the effects of different substituents on the morphological and electronic properties of HBCs. In particular, we reasoned that the undesirable oxidation reactions encountered in the synthesis of alkoxy HBCs could potentially be circumvented by using electron-withdrawing groups, such as fluorine, to counteract the electron-donating effects of the alkoxy groups. Here, we report the synthesis and thermotropic liquid-crystalline (LC) behavior of **7**, which is the first example both of a fluorine-substituted HBC and of a hexakisalkoxy HBC.

Compound **7** was synthesized in seven steps from commercially available 2,6-difluorophenol, **1**. Compound **1** was alkylated to form 2-decyloxy-1,3-difluoro-benzene, **2**;[5] this was then iodinated selectively to give 2-decyloxy-1,3-difluoro-5-iodo-benzene, **3**,[6] which was coupled with trimethylsilyacetylene using Hagihara−Sonogashira conditions. After removal of the solvent, the product was stirred with potassium carbonate in tetrahydrofuran to form 2-decyloxy-5-ethynyl-1,3-difluoro-benzene, **4**. Compound **4** was reacted with **3** under Hagihara−Sonogashira coupling conditions to make a substituted diphenylacetylene, **5**. Cobalt(0)-catalyzed cyclotrimerization was carried out on **5** to give compound **6**.[3b] This step was followed by intramolecular cyclodehydrogenation to yield the final product, **7**, in low yield.[3b,7] An analytically pure sample was obtained by passing the product through a silica gel column, eluting with hexane/dichloromethane. The product was soluble in most common organic solvents including hexane, acetone, THF, and dichloromethane. The UV−vis spectrum recorded in THF (Figure 1) shows a pattern of absorption bands characteristic of HBCs, but red-shifted ca. 600 to 1000 cm^{-1} nm relative to *n*-alkyl-substituted HBCs with λ_{max} (ϵ_{max}) = 365 (ϵ_{max} = 5.67×10^4), 408 nm (2.17×10^4) ($M^{-1}cm^{-1}$).[3a]

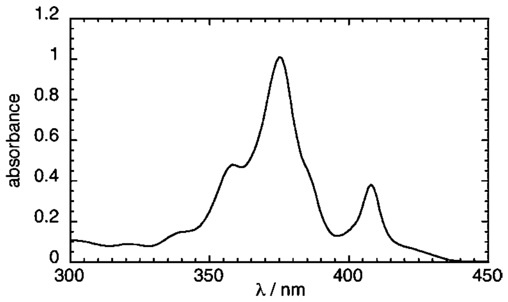


Figure 1. UV-vis spectrum of **7** in THF.

Previous electrochemical studies of hexa-*tert*-butyl HBC show two reversible reductions at $E_{1/2}$ = −2.66 and −2.96

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[7] We also obtained unreacted **6** and a yellow insoluble material from the reaction mixture, accounting for the low yield.

V vs $FeCp_2^{+/0}$ (THF, 0.1 M $^nBu_4NPF_6$) and two reversible oxidations at $E_{1/2} = +0.53$ and $+0.96$ V (CH_2Cl_2, 0.1 M $^nBu_4NPF_6$).[8] Compound **7** (Figure 2) shows two quasi-reversible reductions under the same conditions, but at considerably less reducing potential: $E_{1/2} = -1.96$ and -2.34 V vs $FeCp_2^{+/0}$. The oxidation is irreversible ($E_{ox} = +1.59$ V vs $FeCp_2^{+/0}$ at 250 mV s^{-1}), apparently due to absorption on the electrode, as previously observed for a hexakis-dodecyl HBC.[9] Evidentally the electron-withdrawing effect of the 12 fluorine substituents more than outweighs the electron-donating effect of the six alkoxy groups.

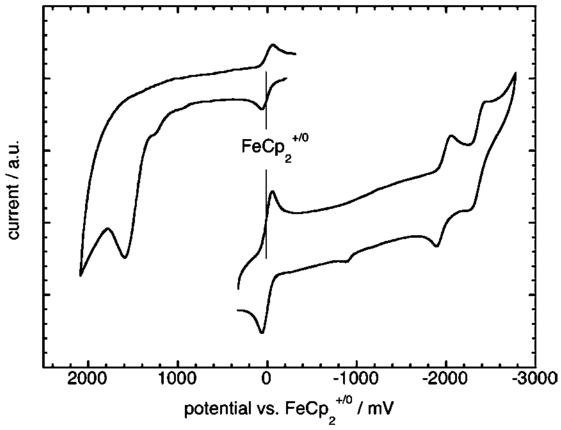

Figure 2. Cyclic voltammograms (250 mV s^{-1}, 0.1 M $^nBu_4NPF_6$, internal $FeCp_2$) of **7** in CH_2Cl_2 (left) and THF (right).

Thermogravimetric analysis (TGA) shows the onset of weight loss (attributed to decomposition) at 392 °C. Using differential scanning calorimetry (DSC), the sample shows two endothermic peaks. The peak at 39 °C is assigned to a crystalline-to-mesophase transition. Compound **7** exhibits a texture consistent with a columnar discotic LC mesophase over temperature range from 39 to 220 °C (the highest temperature accessible with our microscope); moreover, a sample cooled from the mesophase to room temperature shows a similar texture (Figure 3), suggesting that the columnar structure is retained in the solid phase. The transition at 310 °C presumably represents the clearing point, since the compound appears to be a free-flowing liquid above this temperature. This clearing point is lower than that for many alkyl- and phenyl-substituted HBC compounds (ca. 420 °C for hexakis-*n*-alkyl derivatives[3d]); however, clearing points as low as 46 °C can be obtained by using branched alkyl chains in hexa-alkyl HBCs.[1b]

X-ray diffraction patterns of both the bulk LC phase of **7** (prepared by heating the sample past the crystalline-LC transition) and of a thin film of **7** (prepared by drop casting a THF solution onto a quartz substrate at room temperature, Figure 4) were characteristic of a discotic columnar assembly.[10] These patterns can each be indexed to a hexagonal unit cell, indicating an ordered 2D-hexagonal arrangement of columns in the lateral direction. The unit cell parameters calculated from the (100) reflections are $a_{hex} = 26.8$ Å (bulk LC) and $a_{hex} = 26.6$ Å (thin film), and represent the intercolumn core−core distances, which are slightly smaller than that determined for the Col_{hd} mesophase of dodecyl-substituted HBC (28.6 Å).[11] These core−core distances are smaller than the diameter of **7** with fully extended alkyl chains (calculated by molecular modeling to be ca. 38 Å), indicating some chain interdigitation or folding between columns.

Figure 3. Polarized optical micrograph of **7** cooled to room temperature from the mesophase (250 μm × 190 μm).

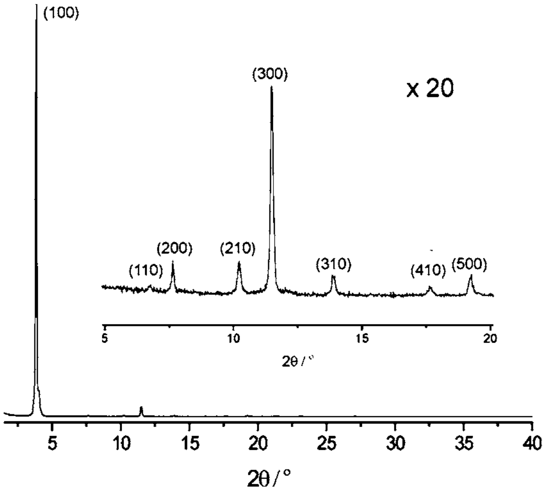

Figure 4. X-ray diffraction pattern of a thin film sample of **7** prepared on quartz; indexing is to a hexagonal unit cell.

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The charge-carrier mobility of **7** was studied with the PR-TRMC technique,[12] at an electromagnetic field frequency of 30 GHz. Pressed pellets (10 mg) of the material were irradiated with 10 nanosecond pulses of 3 MeV electrons from a Van de Graaff accelerator, which results in the creation of a uniform micromolar concentration of electron–hole pairs. The resulting change in conductivity was monitored through the microwave power absorbed by the mobile charge carriers in the material. If one assumes that no charge recombination occurs during the 3 MeV electron pulse, a value of 0.028 $cm^2\ V^{-1}\ s^{-1}$ is obtained as a lower limit for the sum of the charge-carrier mobilities. However, the charge-carrier concentration is overestimated in this experiment by the assumption of no charge recombination; if one takes into account that only a fraction of the charges survives the recombination during the electron pulse[13] one can estimate the one-dimensional mobility along the stacks of molecules as 0.50 $cm^2\ V^{-1}\ s^{-1}$, very similar to the 0.55 $cm^2\ V^{-1}\ s^{-1}$ reported for hexakis-decyl-HBC.[1c]

The PR-TRMC measurements do not enable us to distinguish between hole and electron mobilities. HBCs have previous been found to act as hole-transport agents in photovoltaics[2a] and field-effect transistors;[2b] however, the changes in energy levels revealed by the electrochemical data suggest that, at least relative to a hexakisalkyl HBC, electron injection might be facilitated in **7** and hole injection might be diminished. Indeed **7** is more readily reduced than the well-known electron-transport material, Alq_3 ($E_{1/2} = -2.30$ V vs $FeCp_2^{+/0}$).[14] There are several literature reports of fluorinated derivatives of well-known hole-transport materials that function as electron-transport materials.[15]

In conclusion, a fluorine-substituted hexakis-decyloxy-hexa-*peri*-hexabenzocoronene has been synthesized and shown to form columnar assemblies in its LC phase and in thin films. Its solubility in many common organic solvents suggests facile processibility. The new fluorine-substituted HBC shows similar mobility characteristics to a nonfluorinated analogue, but electrochemical data suggests electron injection may be possible into this material.

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Supporting Information Available: Experimental details and characterizing data; X-ray data for thin film and bulk LC samples of **7**; NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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