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Synthesis of 2,5,8,11,14,17-Hexafluoro-hexa-*peri*-hexabenzocoronene for n-Type Organic Field-Effect Transistors

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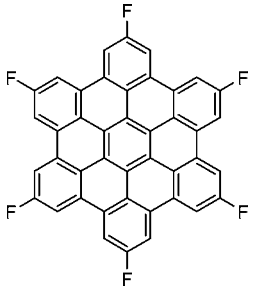
ABSTRACT



A fluorine-substituted hexa-*peri*-hexabenzocoronene was synthesized as a thermostable active material for n-type semiconductors. The LUMO and HOMO energy levels, estimated by UV–vis and photoelectron spectroscopy, were lower by 0.5 eV than those of hexa-*peri*-hexabenzocoronene. A field-effect transistor fabricated by vacuum sublimation showed n-type performance with a field-effect mobility of 1.6×10^{-2} cm²/Vs and an on/off ratio of 10^4. The electron-withdrawing effect of the fluorine substituents changed the polarity from p-type to n-type.

Over the past decade, organic field-effect transistors (OFETs)[1] have attracted much interest due to their possible applications as flexible displays, inexpensive sensors, and printable devices. Electron-transport (n-type) and hole-transport (p-type) organic materials are also essential for the fabrications of p-n junction devices and complementary logic circuits. Positive-type OFETs such as those based on acenes[2] and oligothiophenes[3] have been extensively studied and have excellent characteristics, whereas n-type OFETs are relatively rare, with unsatisfactory performance. It has recently been reported that p-type compounds with electronegative groups may be used as high-performance n-type materials.[4] For example, perfluoropentacene (pentacene substituted with

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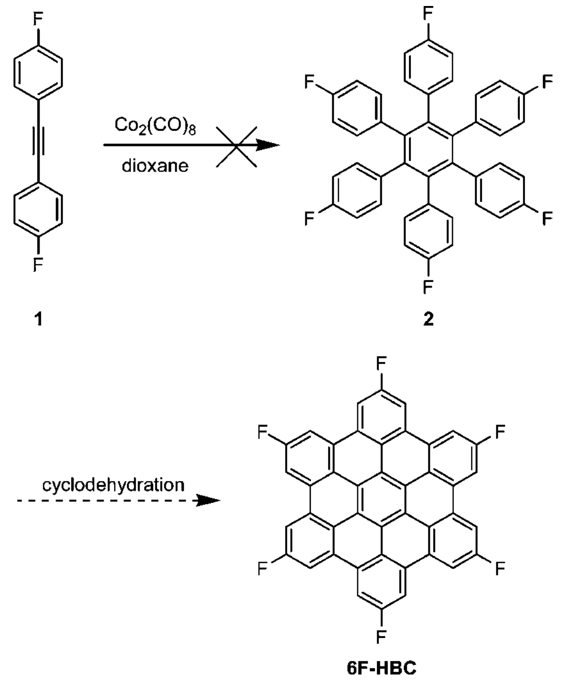
fluorines) was prepared with the aim of changing the polarity of pentacene to n-type;[4b] however, pentacene disproportionation occurred during sublimation for purification and fabrication.[5] The development of thermally and chemically stable organic materials is thus necessary.

Hexa-*peri*-hexabenzocoronene (HBC) derivatives,[6] pioneered by Müllen and co-workers,[7] show a very high chemical stability. The rigidity and planarity of their π-conjugated cores results in self-assembly of the molecules, leading to high carrier mobility. With the addition of functional groups around the periphery, HBCs have been shown to exhibit solubility, discotic liquid crystallinity, and additional intermolecular interactions that result in the formation of columnar stacks.[8] The formation of a decyloxy- and fluorine-substituted HBC (2,5,8,11,14,17-hexakis(decyloxy)-1,3,4,6,7,9,10,12,13,15,16,18-dodecafluoro-hexa-*peri*-hexabenzocoronene)[9] and perfluoroalkyl-substituted HBCs[10] has also been reported. HBC and alkyl-substituted HBCs exhibit p-type OFET activity,[11] whereas fluorine-substituted HBCs will be expected to show n-type performance. We are interested in the development of n-type HBCs and report herein the synthesis, thermostability, and n-type activity of a new fluorine-substituted HBC that possesses only hydro- and fluoro-substituents.

Scheme 1. Attempted Synthesis of **6F-HBC** by Cyclotrimerization



We attempted to synthesize 2,5,8,11,14,17-hexafluoro-hexa-*peri*-hexabenzocoronene, **6F-HBC**, by a well-established method[7c] that involved cobalt-catalyzed cyclotrimerization of 4,4′-difluorodiphenylacetylenes **1**[12] to hexakis(4-fluorophenyl)benzene **2** (Scheme 1). Although cyclotrimerization of bis(4-trifluoromethylphenyl)acetylenes had previously been achieved by Jenny's group,[10b] in this case **1** did not react and was recovered. Consequently, another method via cyclopentadienone was used (Scheme 2).[7c] Tetrakis(4-fluorophenyl)cyclopentadienone **3**[13] was prepared by an Knoevenagel condensation with 1,3-bis(4-fluorophenyl)-2-propanone and 4,4′-difluorobenzil; Diels−Alder reaction with **1** and **3** gave **2** in 72% yield. Compound **6F-HBC** was obtained by cyclodehydrogenation with $FeCl_3$ (47% yield) and with $AlCl_3/Cu(OTf)_2$ (64%), in contrast to the reaction of hexakis(4-trifluoromethylphenyl)benzene, which showed no reaction with either $FeCl_3$ or $AlCl_3/Cu(OTf)_2$.[10b] It can be seen that, in contrast to the trifluoromethyl substituents, the fluorine substituents of **2** do not preclude this Scholl-type cyclodehydrogenation to extend the π-conjugated system.[10]

Because **6F-HBC** was insoluble in common organic solvents, it was purified by sublimation to give a yellow powder that was identified by elemental analysis. The product was also analyzed using MALDI-TOF MS. Signals at $m/z = 630$ were observed in both positive and negative mode; these were assigned as $M^{\bullet+}$ and $M^{\bullet-}$, respectively. These data indicate that highly pure **6F-HBC** was obtained and confirm the absence of insufficiently reacted byproducts.[14] The thermostability of **6F-HBC** was estimated by thermogravimetric analysis (TGA). The results were slightly inferior to those obtained for HBC, but the weight loss at 500 °C

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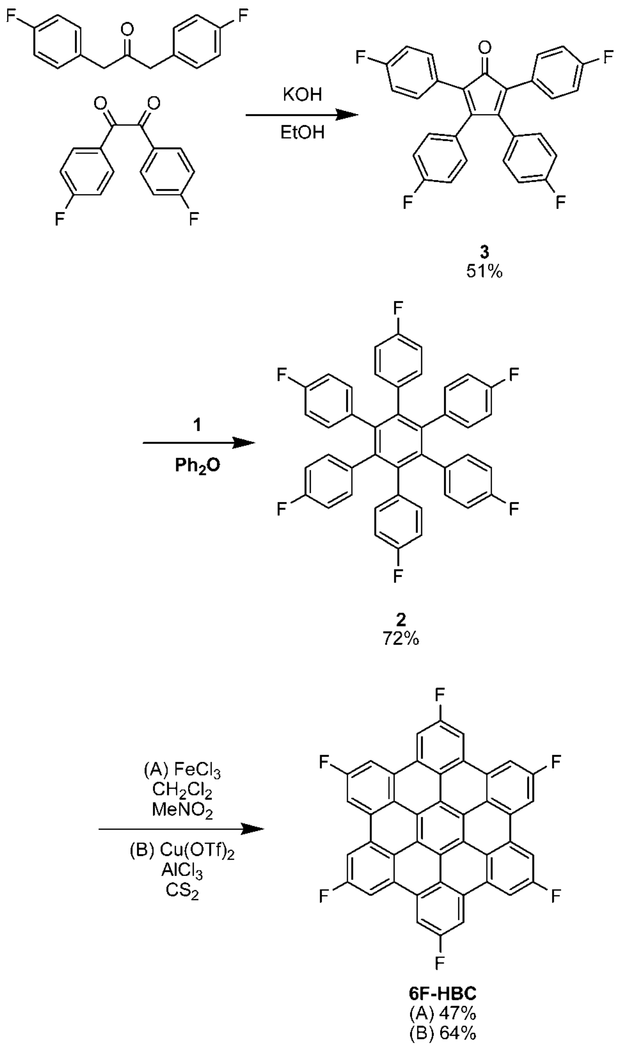
Scheme 2. Synthesis of **6F-HBC**



was less than 2%, which indicates that fluorine substituents have little effect on the thermostability of HBCs.

The UV−vis absorption spectrum of a thin film of **6F-HBC**, prepared by vacuum sublimation onto a quartz substrate, is shown in Figure 1, along with a spectrum of HBC. There is little difference in shape between the two spectra, and the HOMO−LUMO energy gap of both materials, obtained from the end absorptions, is 2.7 eV. Based on photoelectron spectra (Figure 2), the HOMO energy levels of HBC and **6F-HBC** were found to be 5.4 and 5.9 eV, respectively; thus, the LUMO levels were estimated at 2.7

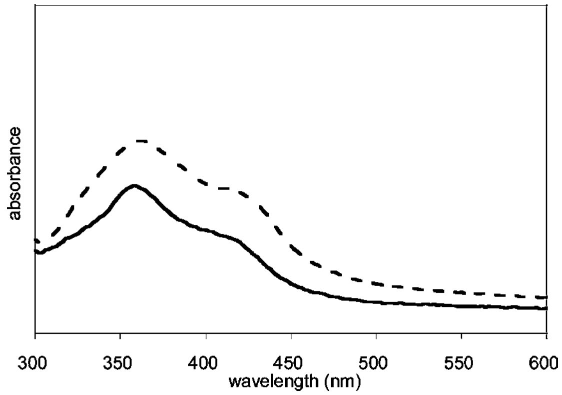


Figure 1. UV−vis spectra of HBC (- - -) and **6F-HBC** (—).

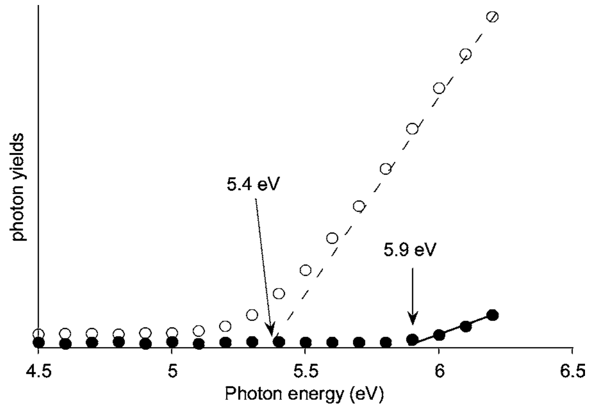


Figure 2. Photoelectron spectra of HBC (○) and **6F-HBC** (●).

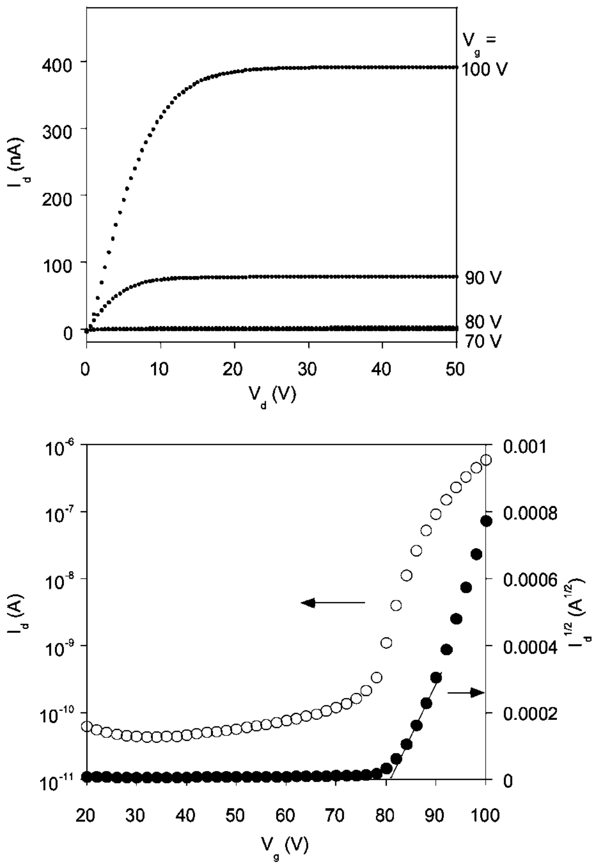


Figure 3. Output (upper) and transfer (lower) characteristics of an OFET with **6F-HBC** as an active layer.

and 3.2 eV, respectively. It was concluded that the introduction of fluorine substituents lowered the LUMO energy level, facilitating electron injection.

An OFET device with top contact configuration was fabricated.[15] As shown in Figure 3, **6F-HBC** shows n-type performance, in that the drain current (I_d) increases with positive gate voltage (V_g). The electron field-effect mobility and on/off ratio were estimated from the saturated regime; values of 1.6×10^{-2} cm^2/Vs and 10^4, respectively, were obtained.

In conclusion, we synthesized a hexafluoro-hexa-*peri*-hexabenzocoronene with thermostability equal to that of hexa-*peri*-hexabenzocoronene. Both the HOMO and LUMO energy levels of the new fluorine-substituted HBC, measured by UV−vis and photoelectron spectroscopy, were lower than those of HBC. A FET device based on this material showed good n-type performance with high carrier mobility. The introduction of six fluorine substituents as electron-withdrawing groups resulted in n-type behavior of this HBC derivative.

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Supporting Information Available: Full experimental details, synthesis, and characterization of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] See Supporting Information for the details of the device fabrication.