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Synthesis, Photophysical, and Device Properties of Novel Dendrimers Based on a Fluorene−Hexabenzocoronene (FHBC) Core

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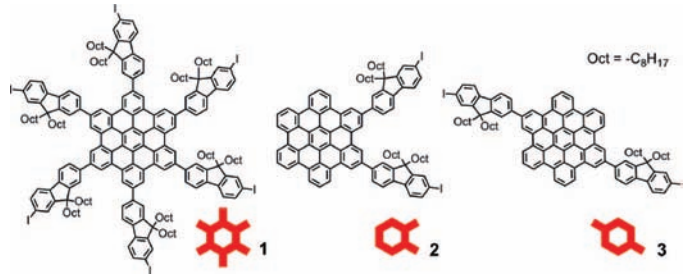
ABSTRACT



The synthesis of easily functionalized and highly soluble fluorene-containing hexabenzocoronenes (FHBC) has been achieved in high yield at a gram scale. Conjugated triarylamine oligomers were coupled to the FHBC cores via Buchwald−Hartwig coupling, and the photophysical properties of resulting dendritic materials were examined by ultrafast laser spectroscopic techniques. Efficient quenching of the triarylamine oligomer fluorescence was observed paving the way for the inclusion of these materials in bulk heterojunction solar cells. In preliminary studies, solar cell devices with external quantum efficiencies above 5% have been fabricated.

Hexabenzocoronene (HBC) is a planar aromatic molecule consisting of 13 fused six-membered rings (Figure 1).[1] It belongs to the family of polycyclic aromatic hydrocarbons consisting of flat disklike cores. HBC and its derivatives have been shown to self-assemble into columnar structures giving rise to ordered morphology in films.[2,3] This property is potentially very useful in bulk heterojunction solar cells where the active layer consists of an electron and a hole transport material usually blended together in a random fashion. The self-assembly of materials into ordered structures in a bulk heterojunction could increase the efficiency of the photovoltaic device by facilitating charge separation

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and transport. By using HBC as the core, the aim is to synthesize planar conjugated dendrimers with the option of incorporating electron and hole transport materials as well as dyes for use in organic bulk heterojunction photovoltaic devices (Figure 1).

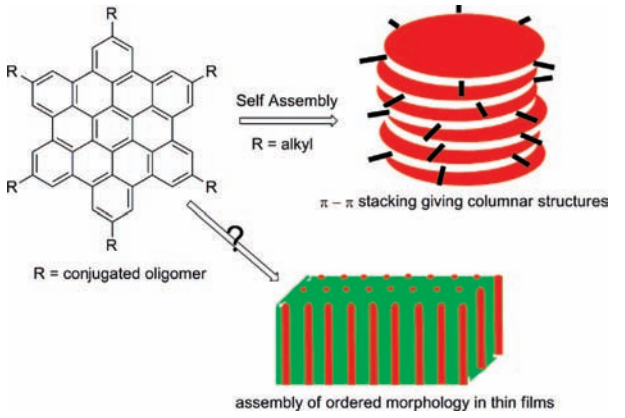
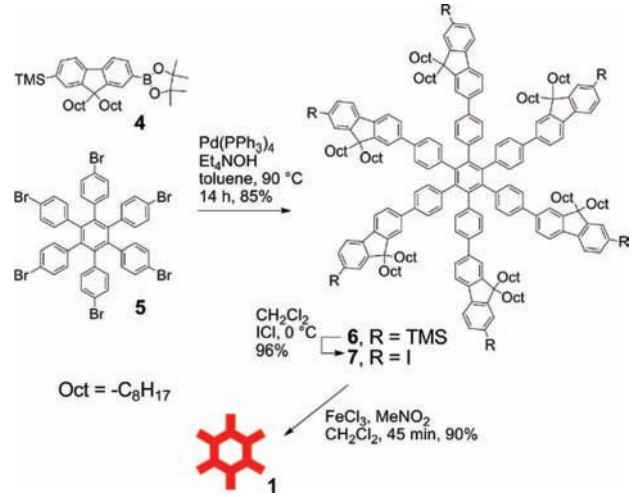


Figure 1. Self-assembly of HBC derivatives into columnar structures[3] and proposed assembly into thin films with ordered morphology.

The chemistry of hexabenzocoronenes has been well established by the group of Müllen in the past decade.[1,3,4] Many HBC derivatives with alkyl substituents have been reported. Some derivatives have been shown to $\pi-\pi$ stack in the solid state by X-ray crystallography,[5] while others were identified by AFM imaging and a variety of spectroscopic techniques to assemble into columnar structures.[3] Extended HBC derivatives have also been synthesized, and graphitic sheets of over 400 carbon atoms have been isolated and identified.[6] The group of Aida has reported an amphiphilic HBC system which has been shown to assemble into nanotube structures.[7] However, HBC derivatives with conjugated oligomeric substituents have not been reported. The primary challenge in the synthesis of these systems is the incorporation of the conjugated substituents as well as alkyl groups for solubility. As such, 9,9-dialkylfluorenes are ideal building blocks in conjugated oligomer−HBC hybrid systems. In this paper, the synthesis and photophysical properties of novel, planar, conjugated dendrimers based on a 9,9-dioctylfluorenyl hexabenzocoronene (FHBC) core are reported.

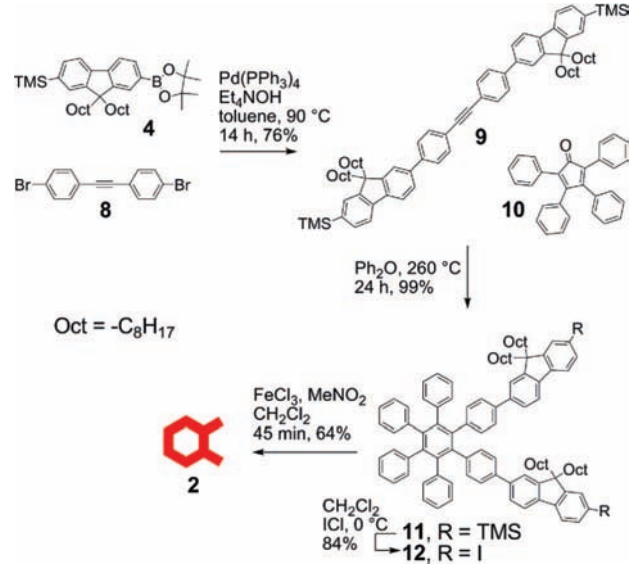
Three FHBC cores were synthesized in this study. The 6-fold symmetric hexakis-FHBC core **1** was obtained through the Suzuki−Miyaura coupling of the key asymmetric 9,9-dioctylfluorene synthon with hexabromophenylbenzene followed by iodination and oxidative cyclization with iron trichloride (Scheme 1).

Scheme 1. Synthesis of FHBC Core **1**



FHBC core **1** was highly soluble in most organic solvents and can be isolated in gram quantities in high yield. The 2-fold and 4-fold symmetric bis-FHBC cores **2** and **3** were also obtained in the gram scale in high yield through a series of Suzuki−Miyaura coupling and Diels−Alder reactions (Schemes 2 and 3). Cooling of warm dichloromethane solutions of FHBC cores **2** and **3** gave yellow crystalline solids which were collected by filtration.

Scheme 2. Synthesis of FHBC Core **2**



With the FHBC cores in hand, electron and hole transport materials as well as dyes can be attached through the iodo-

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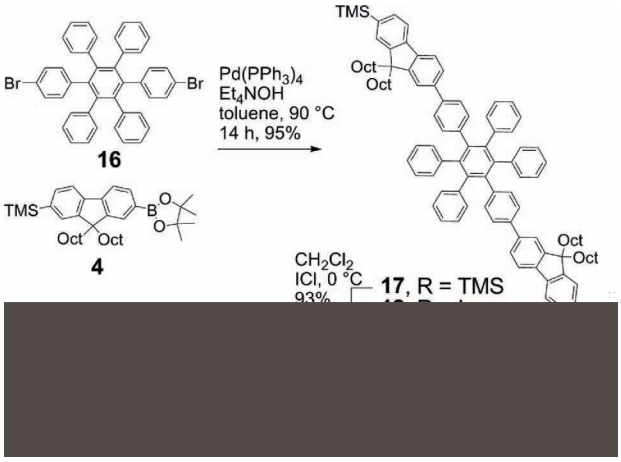
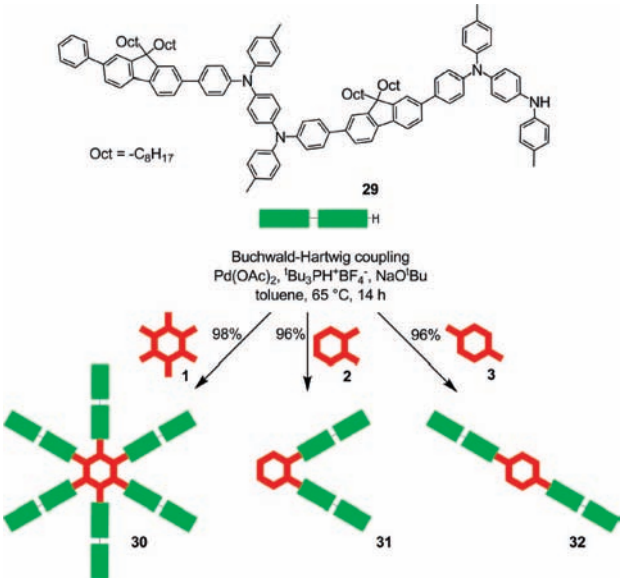
Scheme 3. Synthesis of FHBC Core **3**



aryl functionality using a range of coupling reactions. As a proof of principle, a triarylamine oligomer **29** was coupled to the FHBC cores. Buchwald−Hartwig coupling of oligomer **29** with the FHBC cores gave the three dendritic products in high yield (Scheme 4). All novel compounds were

Scheme 4. Synthesis of the FHBC Dendrimers



characterized using ^{1}H and ^{13}C spectroscopy, mass spectrometry, and elemental analysis.

The compatibility of the FHBC cores and triarylamine hole transport material **29** was examined by fluorescence quenching studies. Thin films of FHBC cores and **29** and their 1:1 blends as well as the corresponding dendrimers were spincoated onto glass slides (20 mg/mL toluene solution at 2000 rpm). FHBC core **1** has an absorption maximum at 390 nm, while cores **2** and **3** have maxima at 368 and 366 nm, respectively (see Supporting Information). The dendrimers obtained from the FHBC cores all have similar absorption spectra with maxima at 375 nm. The fluorescence spectra of the films clearly showed the quenching of the triarylamine fluorescence in the blends and for the conjugated dendrimers. The hexakis(fluorenyl) HBC core **1** quenched the fluorescence of triarylamine **29** most efficiently (complete quenching for a 1:1 blend), while the fluorescence of **29** was partially quenched for FHBC cores **2** and **3**. Fluorescence decay data confirmed the steady state quenching results (see Supporting Information). No fluorescence attributed to the triarylamine was observed in all three dendrimers, but a weak exciplex emission at ~540 nm was identified. This is most prominent in dendrimer **32**.

The dendrimers were examined using laser spectroscopic techniques. Transient absorption data were collected using a highly sensitive microsecond absorption system under N_2 or air at room temperature. Figure 2 shows the decay of a

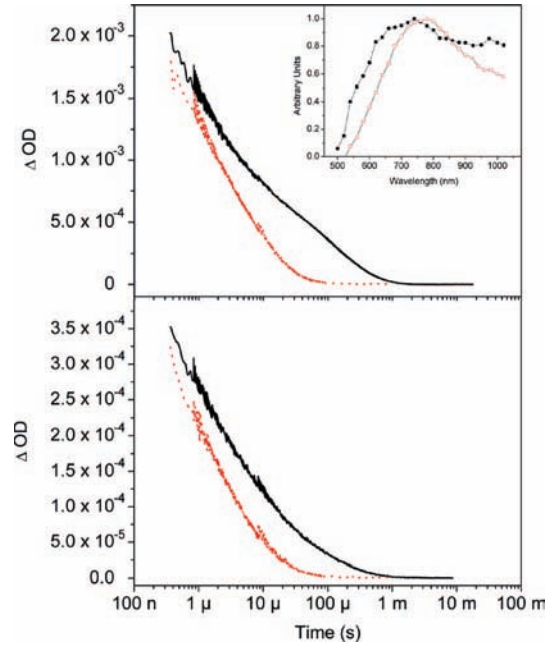


Figure 2. Transient spectroscopic kinetics of core **1** (upper graph) and FHBC dendrimer **30** (lower graph) recorded using a probe light of 750 nm wavelength. In both cases, the lifetime is reduced in the presence of air (dashed red trace) compared with a pure N_2 environment (solid black trace). The inset shows the transient spectral feature observed in core **1** (open red squares) and the FHBC dendrimer **30** (full black squares) at a time 90 μs after excitation for pure N_2 environments.

broad transient feature (see inset), whose peak is centered around 750 nm, observed in core **1** and the FHBC dendrimer **30**. The decrease in lifetime of this feature observed in an air atmosphere is indicative of quenching of triplet excited states due to a spin-allowed transition to the triplet ground state of molecular oxygen. As with HBCs studied elsewhere, there is no evidence of phosphorescence from these materials at room temperature by time-correlated single photon count-

ing.[8] Triplet state formation and, potentially, triplet energy migration may thus occur in the compact HBC core assemblies. If the triplet state energy is such that it precludes charge separation processes, then triplet state formation could be a limitation on the efficiency of photovoltaic devices since it would represent a potential loss of extracted current.

The HOMO energy levels of the FHBC cores **1** and **2** and dendrimers **30** and **31** were measured using electrochemical techniques. Cyclic voltammograms of these compounds were recorded in toluene solution with 0.1 M $Bu_4N^+BF_4^-$ as electrolyte. Both onsets of oxidation for FHBC cores **1** and **2** are at 1.0 V vs ferrocene/ferrocenium, while the oxidation onsets for dendrimers **30** and **31** are at −0.1 V. This means the HOMO levels of the FHBC cores and the dendrimers are −5.8 and −4.7 eV, respectively. The optical band gaps of all three dendrimers obtained from their thin film UV−vis spectra are approximately 2.6 eV. These energy levels confirm that the FHBC dendrimers are an appropriate match with an electron acceptor, such as [6,6]-phenyl-C_{61}-butyric acid methyl ester (C_{60} PCBM) with LUMO at −3.7 eV and HOMO at −6.1 eV, for use in organic solar cells.[9]

In preliminary device studies, bulk heterojunction solar cells with a device structure of ITO/PEDOT:PSS (38 nm)/active layer (40−60 nm)/Ca (20 nm)/Al (100 nm) were fabricated. The devices were tested with an Oriel solar simulator fitted with a 1000 W Xe lamp filtered to give an output of 100 mW/cm^2 at AM 1.5. The active layer of the device consists of a blend of one of the dendrimers and C_{60} PCBM in ratios of 1:2 or 1:4. The performance of the devices with the three dendrimers is similar reaching $V_{oc} = 0.64$ V, $J_{sc} = 0.68$ mA/cm^2, fill factor = 0.30, and power conversion efficiency = 0.13% (see Supporting Information for all device data). It is worthy of note that no annealing was carried out on any of the devices, and this is the subject of ongoing studies. Devices consisting of the dendrimers and the C_{70} analogue of C_{60} PCBM were also fabricated. It has been shown that C_{70} can provide better device performance because of its superior optical absorption profile.[10] In a dendrimer−fullerene blend ratio of 1:2, devices with $V_{oc} = 0.66$ V, $J_{sc} = 1.0$ mA/cm^2, fill factor = 0.34, and power conversion efficiency = 0.22% were measured. A comparison of the IPCE spectra of the C_{60} and C_{70} devices clearly shows the contribution of C_{70} to the photocurrent (Figure 3). The performance of these solar cell devices are either better than or comparable to that reported in the literature for devices containing HBC derivatives.[11] In previous reports, the devices were typically tested using monochromatic light and under low power conditions (1 mW/cm^2) to prevent device degradation. All devices measured in this study are stable under a simulated solar spectrum of 100 mW/cm^2 at AM 1.5.

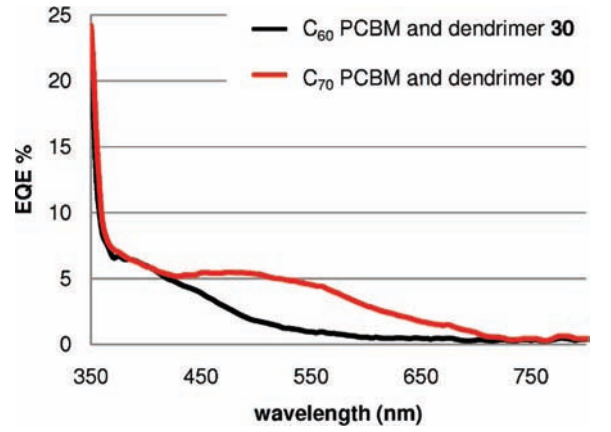


Figure 3. IPCE spectra of devices containing dendrimer **30** with C_{60} PCBM (black line) and C_{70} PCBM (red line). Device structure is ITO/PEDOT:PSS (38 nm)/dendrimer **30**:PCBM 1:2 (40−60 nm)/Ca (20 nm)/Al (100 nm).

In summary, a series of easily functionalized fluorenyl−hexabenzocoronene (FHBC) compounds have been synthesized in high yield at a gram scale. Triarylamine oligomers were attached to these FHBC moieties via Buchwald−Hartwig coupling leading to a series of electron-donating dendritic materials. In association with electron-accepting fullerene derivatives, bulk heterojunction solar cells were fabricated with external quantum efficiencies over 5%. The assembly of these FHBC compounds into columnar structures in thin films are currently under investigation. The effect of thermal or solvent annealing on solar cell performance is also under investigation. Further studies are underway to extend the series of FHBC compounds by attaching different organic electronic materials to their periphery.

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Supporting Information Available: Experimental procedures, full spectroscopic data for all new compounds, and device data. This material is available free of charge via the Internet at http://pubs.acs.org.

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