Carbon-Rich Compounds

The Versatile Synthesis and Self-Assembly of Star-Type Hexabenzocoronenes**

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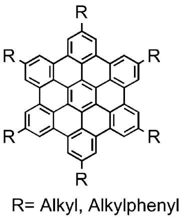
π-Stacking is a powerful motif for self-assembly that is ubiquitous in nature and utilized extensively by synthetic chemists to engineer complex supramolecular architectures—particularly in recent years, having been spurred on by the increasing technological promise of the π stacks as conducting pathways in organic-based electronics.[1] Hexa-*peri*-hexabenzocoronenes (HBCs) **1**[2] are larger than the widely studied triphenylenes,[3] porphyrins,[4] and phthalocyanines.[5] As a result, alkyl-substituted HBCs exhibit aggregation behavior in solution that persists to nanomolar concentrations, as well as bulk columnar mesophases with high order parameters, high charge-carrier mobilities, and exceptional thermal stability.[2] The bulk properties qualify them as active components in organic field-effect transistors (OFETs)[6] and as hole-conducting layers in photovoltaic devices or light-emitting diodes (LEDs).[7] Important targets include the understanding of the self-assembly of large disc molecules and improving device performance through 1) more specific assembly in solution, 2) further increasing the order in the columnar mesophases, and 3) modifying the electronic properties of the discs, in particular, for better hole stabilization.



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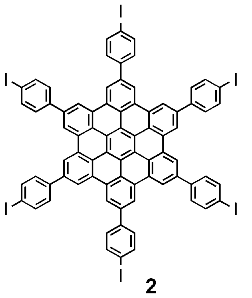

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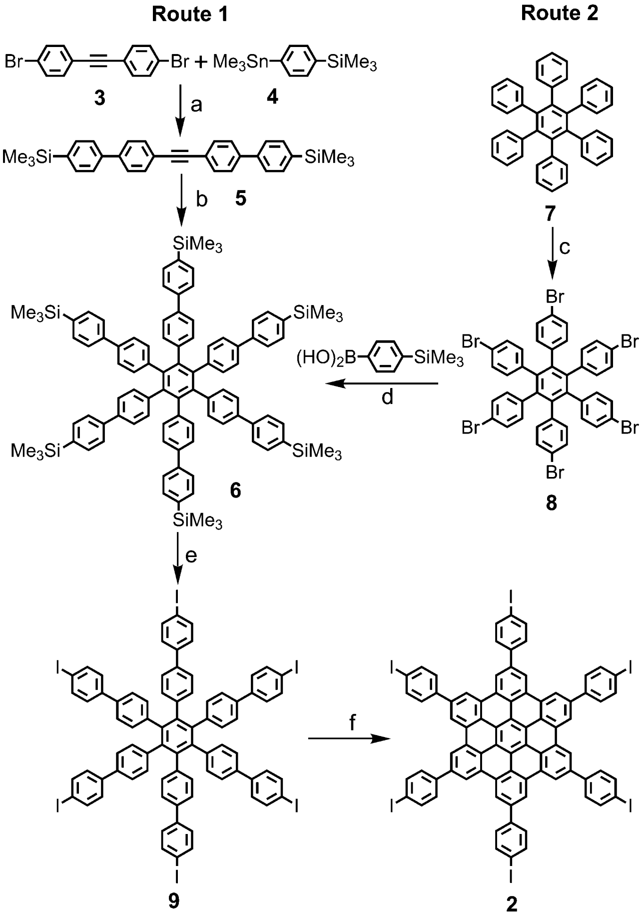
Herein, we address these functions by varying pendant substituents; thus hexa(4-iodophenyl)-*peri*-hexabenzocoronene (**2**) acts as an HBC building block with versatile reactive sites, which can be converted into a range of useful functionalities. Such an atom economy is important when enriching the library of HBCs, since their synthetic modification has so far involved variation of the diphenylacetylene starting compounds.[2c]

The synthesis of the key building block **2** is outlined in Scheme 1. The precursor hexa(4-iodophenyl)hexaphenylbenzene (**9**) was prepared in 92% yield by reaction of excess iodine monochloride with hexa(4-trimethylsilylphenyl)hexaphenylbenzene (**6**), which was synthesized by two different routes. The first so-called convergent route (Route 1) involves a Stille coupling[8] and a cobalt-catalyzed cyclotrimerization.[2c] To avoid the toxic organotin chemistry, as well as to simplify the synthesis, an alternate divergent route (Route 2) requiring one sixfold bromination[9] and one sixfold Suzuki coupling reaction[10] was developed. Final cyclodehydrogenation of **9** with iron(III) chloride gave the desired compound **2** as a yellow powder in quantitative yield. Notably, this divergent route involves four sixfold transformations, all



Scheme 1. Synthesis of compound **2**: a) $[Pd(PPh_3)_4]$, toluene, 125 °C, 75%; b) $[Co_2(CO)_8]$, dioxane, 125 °C, 92%; c) neat bromine, −20 °C→RT, 96%; d) $[Pd(PPh_3)_4]$, K_2CO_3(aq), 95 °C, 92%; e) ICl, chloroform, 92%; f) $FeCl_3$/nitromethane, CH_2Cl_2/CS_2 = 2:1.

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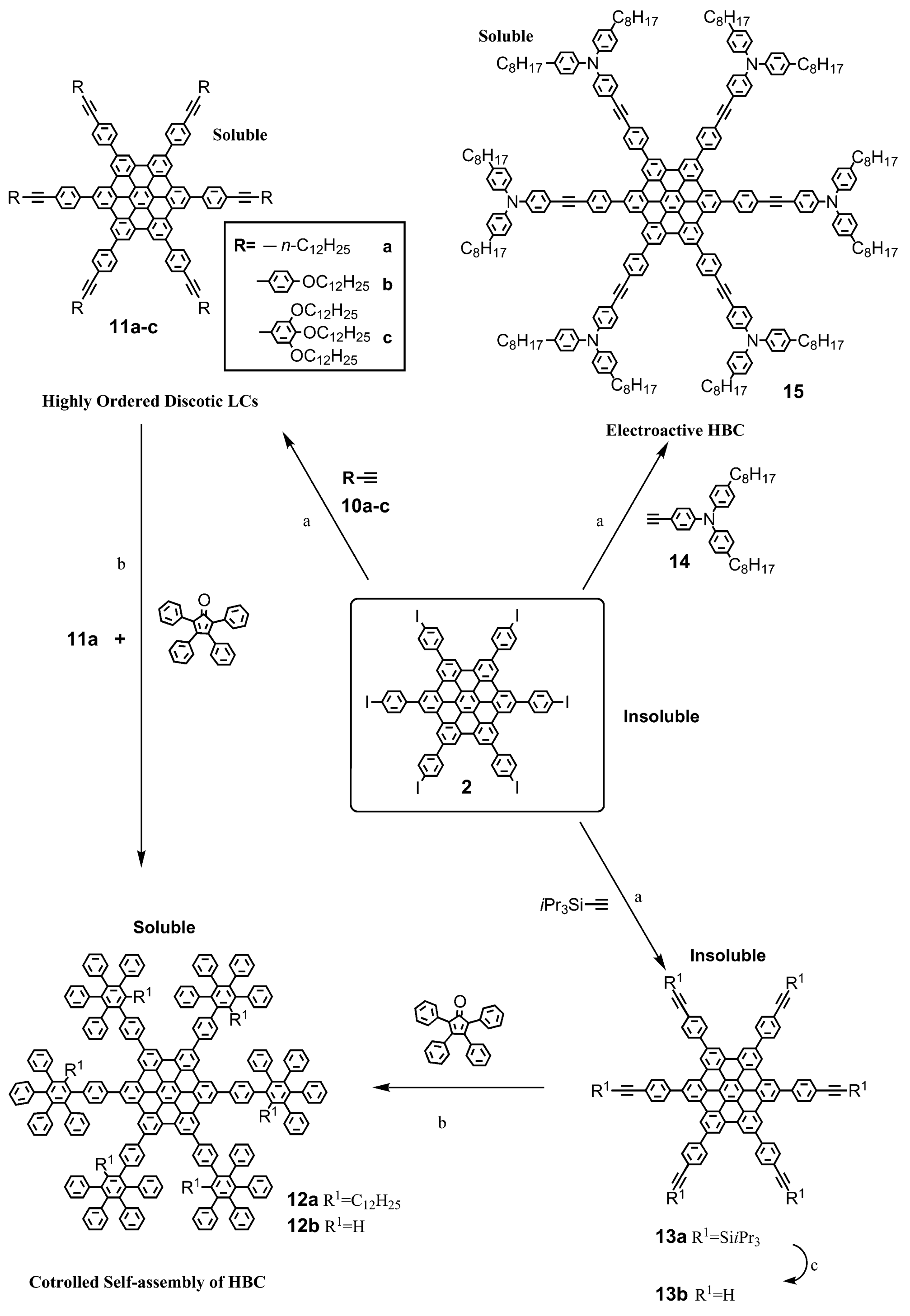
in excellent to near quantitative yields and provides compound **2** on a gram scale.[11]

Despite the virtual insolubility of compound **2**, palladium-catalyzed Hagihara–Sonagashira coupling reactions[12] with solubilizing acetylene groups work smoothly, thus paving the way to versatile functionalization. Compared to *n*-alkyl substituents, 4-alkylphenyl groups provide the following advantages to HBCs: good solubility, longer range order in the columnar mesophase, and the highest reported room-temperature charge-carrier mobility for a discotic liquid-crystalline material.[2d,e] Thus a functionalizable core such as **2** is expected to provide a new series of highly ordered liquid-crystalline materials. As shown in Scheme 2, cross-coupling between **2** and soluble monoacetylenes **10a–c** gave a series of extended, star-type HBC derivatives **11a–c** in high yield. Their good solubility facilitates their full structural characterization, despite their size. The bulk thermotropic liquid-crystalline properties of **11a–c** were investigated by differ-



Scheme 2. Versatile functionalization based on building block **2**. a) [Pd(PPh$_3$)$_4$]/CuI, piperidine, 50 °C; b) Ph$_2$O, 250 °C; c) tetrabutylammonium fluoride, THF, RT.

ential scanning calorimetry, polarized optical microscopy, and wide-angle X-ray diffraction (WAXD). As expected, highly ordered hexagonal columnar mesophases were observed at ambient temperature with compounds **11a–c**. Most interestingly, the 2D WAXD pattern of extruded fibers of **11b,c** revealed a helical stacking in the HBC column.[13] As a typical example, clear reflection peaks positioned in a first layer ($l=1$) above/below the equator corresponding to a repeating distance along the columns that is four times the π-π stacking distance of HBC disks are observed in the 2D X-ray pattern of **14b** (Figure 1). This pattern indicates the existence of superlattice periodicity in the direction of stacks of discs. Further analysis discloses that every 5th disc along the column axis is positionally/rotationally correlated to form a helical superstructure. As a consequence, reflection peaks appear at $l=2$ and 3 in addition to the reflection peaks at $l=4$, which is correlated to the normal π-π stacking distance. This packing could arise from additional π-π interactions between, and space-filling requirements introduced by, the rigid-rod side groups in the star-type molecules. A helical arrangement has rarely been observed experimentally by X-ray diffraction for discs without chiral substituents,[14] and to the best of our knowledge, this is the first case from a disc with sixfold symmetry. For example, such a helical D_{ho} mesophase was found in hexathioalkyltriphenylene and has exceptional one-dimensional charge-carrier mobilities.[14a]

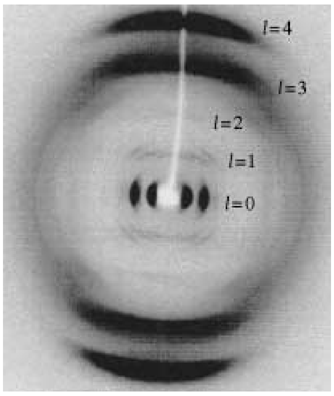


Figure 1. 2D X-ray pattern of **11b** showing a typical helical column stacking. The sample was oriented by extrusion from a mini-extruder to give a fiber with a diameter of about 0.7 mm, then 2-D X-ray diffractograms were collected in transmission mode with the beam perpendicular to the fiber(fiber/column axes vertical).

Disc molecules and structurally related shape-persistent macrocycles are known to exhibit dynamic aggregation in solution.[15] This process is relevant for the formation of films from solution and also serves as a model for phase formation from the melt. Attaching bulky substituents is expected to inhibit or even completely suppress face-to-face aggregation of the HBC discoid core. As shown in Scheme 2, a sixfold Diels–Alder cycloaddition between **11a** and tetraphenylcyclopentadienone proceeds smoothly in refluxing diphenyl ether to provide HBC **12a**, which is substituted with oligophenylene dendrons. ^{1}H NMR spectroscopic analysis reveals that molecule **12a** exhibits a unique monomer–dimer equilibrium in solution. The representative temperature-dependent ^{1}H NMR spetra of **12a** in [D$_4$]tetrachloroethane are shown in Figure 2. Two independent species, one expected monomer (labeled by star) and another dimer (labeled by a square), were identified. The monomer/dimer ratio increases with increasing temperature or decreasing concentration. Furthermore, only dimer exists in a relatively poor solvent such as cyclohexane, while only monomer can be observed in carbon disulfide (an excellent solvent for large aromatic compounds). Clearly, the bulky dendrons suppress the formation of higher aggregates and allow only a dimer aggregate to exist in solution. The appearance of separate ^{1}H NMR resonances, instead of averaged ones which shift with temperature/concentration/solvent, suggests that this self-assembly is slow on the NMR time scale. This could be ascribed to the bulky dendron structure as well as the steric hinderance produced by the dodecyl chains at the bay position. To further investigate the effect of the dodecyl group in **12a**, an analogous HBC molecule **12b**, in which the dodecyl groups are replaced by hydrogen atoms, was prepared (Scheme 2). Sixfold Hagihara–Sonogashira coupling between **2** and triisopropylacetylene gave the insoluble material **13a**, which was deprotected with tetrabutylammonium fluoride (TBAF) to provide insoluble material **13b**. Solid-state MALDI MS[11] of compounds **13a,b** indicated quantitative conversion even though both the starting materials and products are insoluble(!), further proving the high reactivity of the building block **2**. Diels–Alder cycloaddition between **13b** and tetraphenylcyclopentdienone proceeded smoothly to give the soluble **12b**. The ^{1}H NMR spectra of **12b** in [D$_4$]tetrachloroethane reveal only one aggregated species,[16] which does not show concentration dependence, which thus most probably pointing toward a dimeric structure.

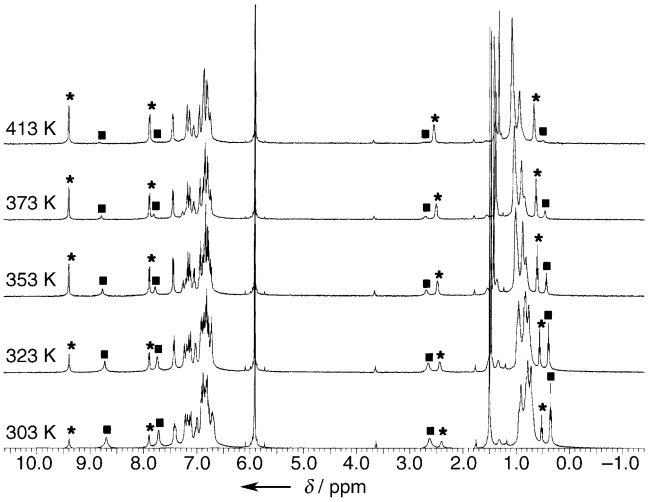
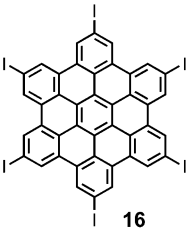


Figure 2. Temperature-dependent ^{1}H NMR (500 MHz) spectra of **12a** in [D$_4$]tetrachloroethane (3 mg mL^{-1}) which reveal two independent species, the ratio of which strongly depends on the temperature, concentration, and solvent. Resonances at about $\delta = 8.7$ ppm and 9.4 ppm are assigned to HBC core protons in the dimer and monomer, respectively.

Triarylamines are commonly used as hole-transport materials in organic LEDs.[17] Sixfold triarylamine-substituted HBC **15** can be prepared by similar Hagihara–Sonogashira coupling reaction between compound **2** and *N,N'*-di(4-octylphenyl)-*N''*-(4-ethynylphenyl)amine (**14**) as shown in Scheme 2. It should be pointed out that the triarylamine-substituted hexaphenylbenzenes are usually excluded from the standard $FeCl_3$ oxidative cyclodehydrogenation conditions as a result of preferential formation of charge-localized radical cations.[18] The successful synthesis of the electroactive materials **15** suggests that more electroactive materials could be made from building block **2**. Besides the hole-transfer channel of the HBC column, the triarylamine moieties in molecule **15** are expected to form an additional hole-transport channel. By adapting the term "double-cable" used for conjugated polymers with tethered electronic functional units the columnar structures formed from **15** could be described as coaxial cables. Scientific interest in this molecule also includes the study, after formation of a radical cation, of the electronic coupling of the electroactive triarylamines through the rigid π system including the "superbenzene" HBC core.

A large number of useful peripheral substituents can now be attached to the HBC core as a last synthetic step, which leads to three new types of materials: 1) more highly ordered discotic columnar mesogens **11b,c** which exhibit unique helical superstructures, 2) peripherally dendronized large π systems **12a,b** which provide for programmed self-assembly in solution, and 3) a novel electroactive material **15** containing seven positionally defined hole-transport units of two different types. Work is under way to prepare new mesogenic versions with six peripheral electron acceptor/transport units that would lead to core–shell columns (coaxial cables) in which each individual column is a self-contained photovoltaic element. As an extension of the above synthetic concept, another two functionalizable HBC building blocks (**16** and **17**) have been prepared by shorter synthetic routes and functionalized by palladium-catalyzed Hagihara–Sonogashira and Buchwald reactions.[19] The fact that substituents which may be incompatible with the normal synthetic build-up can be introduced to all three halo derivatives dramatically broadens the scope of HBC materials.



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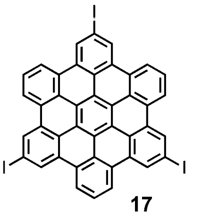

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[16] Only a single ^{1}H NMR resonance (ca. $\delta = 8.7$ ppm) is observed above 8 ppm. A single crystal of **12b** has been obtained and hopefully will disclose the atom positions of this supramolecular dimer. A more detailed analysis of this unique self-assembly process will be presented in a separate publication.

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