Self-Assembly

DOI: 10.1002/anie.200502142

Molecular Wires from Contorted Aromatic Compounds**

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Dedicated to Professor Thomas J. Katz

The use of planar molecules is one unifying design feature in essentially all the molecules that have been tested to date in organic field-effect transistors.[1–7] The concept explored herein is whether a nonplanar aromatic core could yield efficacious electronic materials. One significant aspect of using a nonplanar core is that the aromatic rings would be forced to adopt new and unusual intermolecular contacts that are typically unavailable to flat molecules. Moreover, these informationally rich subunits could form the basis for self-assembled and self-healing electronic materials if the core could be bent into a shape that was self-complementary.

Herein, we detail the first studies of the self-assembly and electrical properties of a new type of hexabenzocoronene (HBC) **1**, whose aromatic core is distorted away from planarity by steric congestion in its proximal carbon atoms. We became interested in this class of compound because it combines structural elements of linear acenes, which are well-

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[**] We acknowledge primary financial support from the Nanoscale Science and Engineering Initiative of the National Science Foundation (NSF Award Number CHE-0117752); the New York State Office of Science, Technology, and Academic Research (NYSTAR); and the Department of Energy, Nanoscience Initiative (NSET 04ER46118). C.N. thanks the US National Science Foundation (CAREER award DMR-02-37860), the American Chemical Society (PRF type G 39263-G7), the Camille Dreyfus Teacher Scholar Program (2004), and the Alfred P. Sloan Fellowship Program (2004). We thank the MRSEC Program of the National Science Foundation (Award Number DMR-0213574) and the New York State Office of Science, Technology, and Academic Research (NYSTAR) for financial support for M.L.S. and the shared instrument facility. S.S. acknowledges financial support from the Centre Microélectronique de Provence—Georges Charpak.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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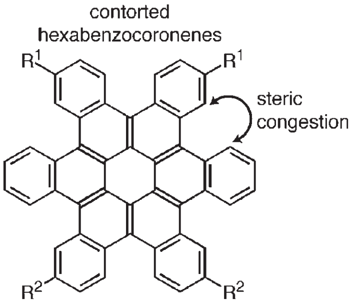
known electronic materials,[2,5,8–11] with a disk-shaped and potentially columnar liquid-crystalline core.[12–20] Methods for the synthesis and derivatization of **1** are essentially unknown.[21] Our important finding is that some derivatives of this new class of compound self-organize into liquid-crystalline phases composed of molecular stacks that orient themselves parallel to the surface. Field-effect transistors based on these materials show high charge-carrier mobilities, high on/off ratios, and low turn-on voltages.



1a: $R^1 = R^2 = H$
1b: $R^1 = H$, $R^2 = OC_{12}H_{25}$
1c: $R^1 = R^2 = OC_{12}H_{25}$

Compounds **1a–c**[22] are yellow-orange solids that are readily soluble in a number of common organic solvents; for example, more than 200 mg of **1c** can be dissolved in 1 mL of $CHCl_3$. Furthermore, these solutions have an intense optical emission in the visible region. The thermal and oxidative stabilities of these compounds are also remarkable, as no loss of color is observed when oxygen is bubbled through solutions of **1a–c** over a period of a few hours under ambient light. Under identical conditions, solutions of pentacene lose their color within a few minutes through photooxidation.[23] Differential scanning calorimetry (DSC) showed no decomposition of **1a–c** up to temperatures well above 320 °C. Uniform films (approximately 100-nm thick) could be formed by spin-casting **1c** from 1,2-dichloroethane or $CHCl_3$. In contrast, films formed from **1a** and **1b** were granular in appearance and of a low quality. The ability to form good films of **1c** is a harbinger of the electrical properties described below.

Field-effect transistors were fabricated on spin-cast films of **1a–c** (Figure 1a shows the structure of the resulting devices). Transistors fabricated from **1c** have good electrical characteristics, whereas those prepared from **1a** and **1b** showed no useful properties. We deposited Au source and drain electrodes by thermal evaporation onto the spin-cast films through a metal-shadow mask. The channel length was 75 μm and the electrode width was 2 mm, and the transconductance and transistor output are shown in Figure 1b,c. The mobility ($0.02\,cm^2V^{-1}s^{-1}$) shown is calculated from the linear portion of the data in Figure 1b[24] and uses a capacitance of $11.3\,nF\,cm^{-2}$ for the gate dielectric layer (300 nm of SiO_2 and a monolayer of octadecyltrichlorosilane).[11] The gate dielectric capacitance comes from measurements made over a range of frequencies[11] and is as expected for a 300-nm-thick layer of silicon oxide with few defects.[25] Other critical parameters, such as the threshold voltage for the device to turn on (as low as −3 V for some devices prepared from **1c**) and the on/off current ratios in the device (10^6:1), are also very good. These values are the best field-effect transistor properties achieved for a columnar discotic material[16,17,26,27] (see below) and are good for spin-cast films in general.[8,28–34] These results are even more impressive because it is likely that these properties could be improved by adjustment of critical parameters such as grain size, deposition conditions, and direction of column growth.

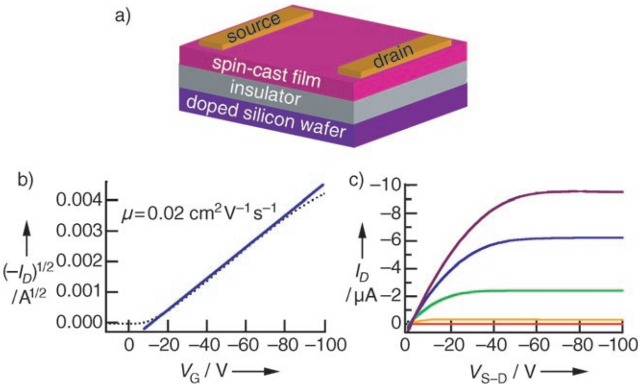


Figure 1. a) Schematic diagram of a field-effect transistor that was fabricated by evaporating source and drain electrodes onto a spin-cast film of **1c**. b) Transconductance: the blue line is a fit of the linear portion of the data points (the source–drain voltage V_{S-D} was held at −60 V). c) Transistor output for thin-film transistors from **1c**.

Encouraging electrical properties are only developed in the more substituted derivatives of **1**, thus indicating self-organization. One of the hallmarks of many self-assembled systems is the presence of liquid-crystalline phases. Each of these compounds were investigated by DSC, polarized light microscopy, and X-ray diffraction to determine whether mesophases are present (the DSC trace for **1c** is shown in Figure 2a). An extra transition that indicates the presence of an intermediate phase can be seen from both the heating and cooling cycles for **1c**. The microscopy and X-ray diffraction studies of **1c** (see below) indicate that it is a liquid-crystalline phase between 91 and 285 °C, whereas above these temperatures it melts to form an isotropic liquid. The enthalpy values, particularly going from the liquid-crystalline phase to the isotropic liquid phase, are larger than those typically observed for discotic liquid crystals.[12] This difference implies that **1c** associates strongly in this intermediate phase, possibly because it is not a flat disk.[35] DSC studies do not show any evidence for a liquid-crystalline phase for **1a** and **1b**; they simply melt, **1a** at 516 °C[21] and **1b** at 220 °C. The appearance of a mesophase correlates with **1c** having good electrical properties and indicates the potential of self-organized materials for electronic applications.

The structure of this phase was probed by powder X-ray diffraction studies and was found to be a hexagonally ordered columnar liquid-crystalline phase for **1c**. In the X-ray diffraction studies, **1c** was heated (in a Lindemann capillary tube) to an isotropic liquid (295 °C) and cooled into its mesophase. The data shown in Figure 2b were collected upon cooling to 120 °C. The diffractogram is dominated by an intense reflection characteristic of $d \approx 26$ Å. The only other discernible features of the diffractogram are two very weak,

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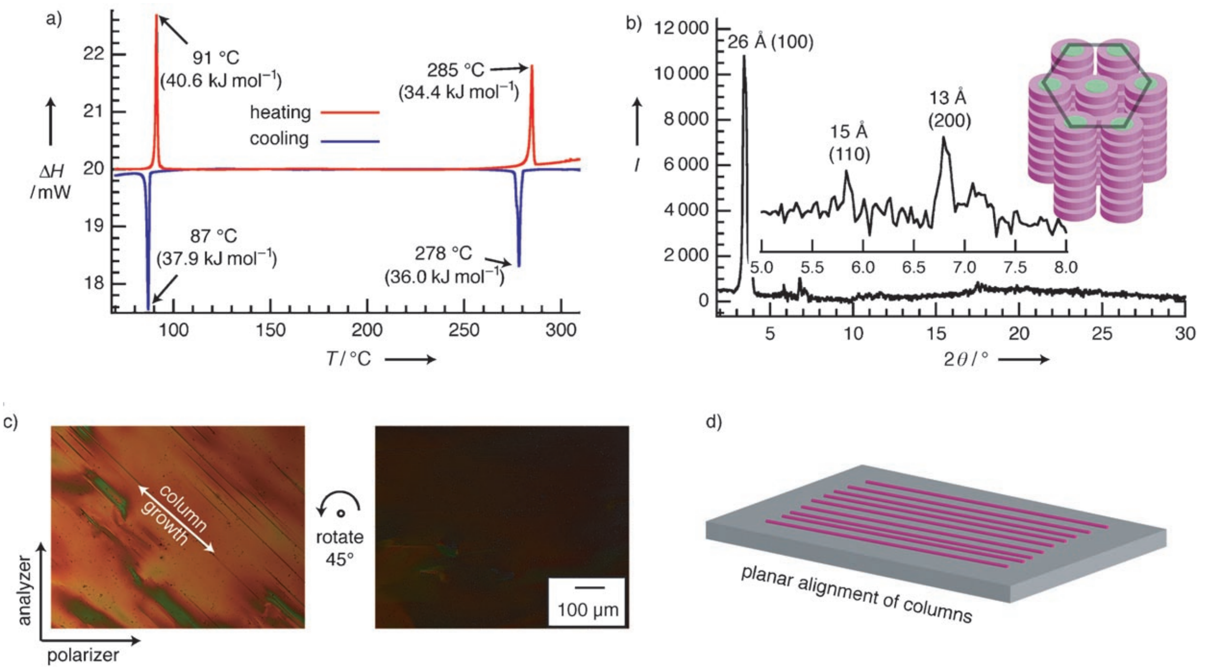


Figure 2. a) DSC trace of **1c** (scan rate = 5 °C min^{-1}) showing a mesophase. b) X-ray diffraction studies of **1c** cooled into its mesophase from 295 to 120 °C and a hexagonal lattice of columns. c) Polarized light micrograph of **1c** cooled into its mesophase which shows a planar alignment of columns that are extinguished when aligned with the polarizer or analyzer axes. The cooling rate was 5 °C min^{-1}, and the exposure time was the same for each picture. d) Schematic diagram of columns aligned parallel to the surface.

higher-order reflections ($d = 15$ and 13 Å) that allow the lattice to be indexed to a hexagonal arrangement of columns. The lack of intensity in these higher-order reflections indicates that the columns are not well correlated with each other, which is likely to be a result of the subunits not having a perfect disk shape, as is implied by the molecular model in Figure 3. The fourfold substitution would signal that at some level there is a competition between rectangular and hexagonal lattice formation.

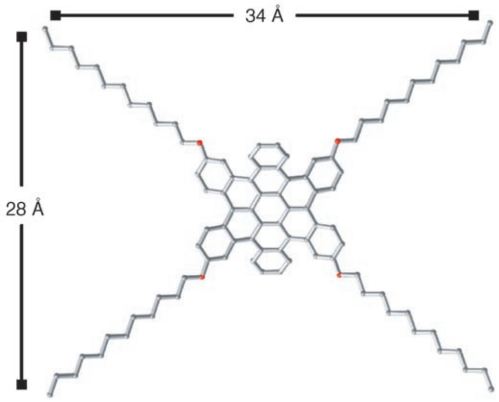


Figure 3. Molecular model of **1c** with its side chains fully extended.

Polarized light microscopy revealed that these materials tend to orient their columns parallel to the surface. The micrograph of a sample cooled to just below 278 °C and captured as the mesophase formed is shown in Figure 2c. The birefringence of the domains is extinguished when the column axes are aligned with the polarizer or analyzer (Figure 2c) and is maximally bright when the stage is rotated by 45°. The micrograph is characteristic of a planar arrangement[36] of columns in a discotic mesophase (shown schematically in Figure 2d). This arrangement of columns is important because the current flow in thin-film transistors is parallel to the surface and, in this case, runs along the column axis.

Strong aggregation of **1c** occurs in solution, thus further indicating its tendency to self-associate. NMR, UV/Vis, and fluorescence spectroscopic techniques were used to monitor this aggregation in solution. All the resonances from the protons of the aromatic ring shifted upfield as the solutions of **1c** were concentrated. For example, the ring protons of **1c** shift upfield by approximately $\Delta\delta = 0.13$ ppm in $CDCl_3$ as the concentration is increased from 6.3 to 126 mg mL^{-1}. This shift is a result of shielding from the ring current of neighboring aromatic compounds within a cofacial stack.[37–39] This face-to-face association of molecules can be further probed by UV/Vis absorption and fluorescence emission spectroscopy. In both cases, the maxima are red-shifted as the solutions become more concentrated. This behavior is not unique as there are many discotic materials that also aggregate in solution to form isolated molecular columns which show similar shifts in their UV/Vis and fluorescence spectra.[40–43] The formation of the columns from the interlocking of gearlike molecular subunits is the model that develops from these spectroscopic data.

When films of these materials are spin-cast onto transparent substrates, birefringent domains form that have the same extinction as that described for the bulk films in

Figure 2c, thus indicating that the films also have their columns aligned parallel to the substrate. Aggregation in solution that causes the formation of columns, which can then be deposited by spin-casting, is likely to be responsible for the good electrical properties of **1c**.

Crystals of the parent HBC **1a** were grown to investigate the underlying molecular structure of the HBCs.[44] The crystals were grown from 1,2,4-trichlorobenzene and shown to include two disordered solvent molecules oriented over the coronene core. The molecular structure of this HBC moiety is shown in Figure 4a–d. The three intersecting pentacene subunits contort into a zigzag conformation. This bending of the acene core is visualized most clearly in Figure 4d, in which portions of the structure have been suppressed to show only one pentacene subunit of the HBC. Essentially all of the bending is concentrated in pairs of carbon atoms that act as pivot points (these are highlighted with magenta circles in Figure 4a). A comparison of some of the bond lengths in this HBC with those from the pentacene crystal structure[45] is given in Table 1. One of the most interesting features is that the C_a–C_b bond is short in the HBC relative to the pentacene, whereas the C_b–C_c bond is relatively long. A strong contribution from the radialene resonance would explain these unusual bond lengths.

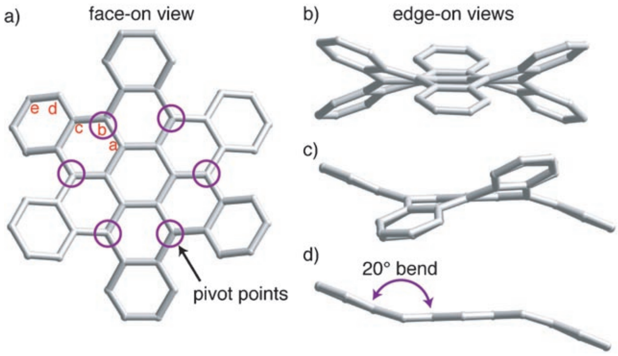
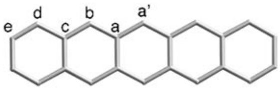


Figure 4. Crystal structure of **1a** grown from 1,2,4-trichlorobenzene. Hydrogen atoms have been removed for clarity. a) Face-on view with marked pivot points (magenta circles). The C_a–C_b bond is relatively short and the C_b–C_c bond is relatively long. Side views are given in (b) and (c). d) Side view of one of the acene segments extracted from the crystal structure. The other atoms of the HBC are hidden from view.

Table 1: Comparison of C–C bond lengths between **1a** and pentacene.

	C–C bond length [Å]	
	1a[a]	Pentacene[b]
C_a–$C_{a'}$	–	1.44
C_a–C_a	1.43	1.46
C_a–C_b	1.40	1.42
C_b–C_c	1.45	1.38
C_c–C_c	1.42	1.45
C_c–C_d	1.42	1.43
C_d–C_e	1.38	1.35
C_e–C_e	1.42	1.43

[a] The atom labeling scheme is shown in Figure 4a. [b] The atom labeling scheme of the pentacene skeleton is shown below.



In summary, this study puts forth a new design strategy for molecule-based electronic materials in which a nonplanar rigid core is used. We prepared a new class of hexabenzocoronene that is readily substituted to form columnar liquid-crystalline phases, and these columnar materials have good electrical properties in thin-film transistors. Structures with nonplanar aromatic units, such as **1**, may be able to achieve much higher mobilities than those available to flat hydrocarbons because the π surfaces of contorted molecules can approach each other and arrange themselves in very different ways. Moreover, these molecules make interesting starting materials for the synthesis of other topologically interesting hydrocarbons by oxidative closure of the proximal carbon atoms to form five-membered rings.

Received: June 20, 2005
Published online: September 20, 2005

Keywords: liquid crystals · molecular electronics · nanostructures · self-assembly

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