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Supramolecular Chemistry

Controlling the Columnar Orientation of C_3-Symmetric "Superbenzenes" through Alternating Polar/Apolar Substitutents**

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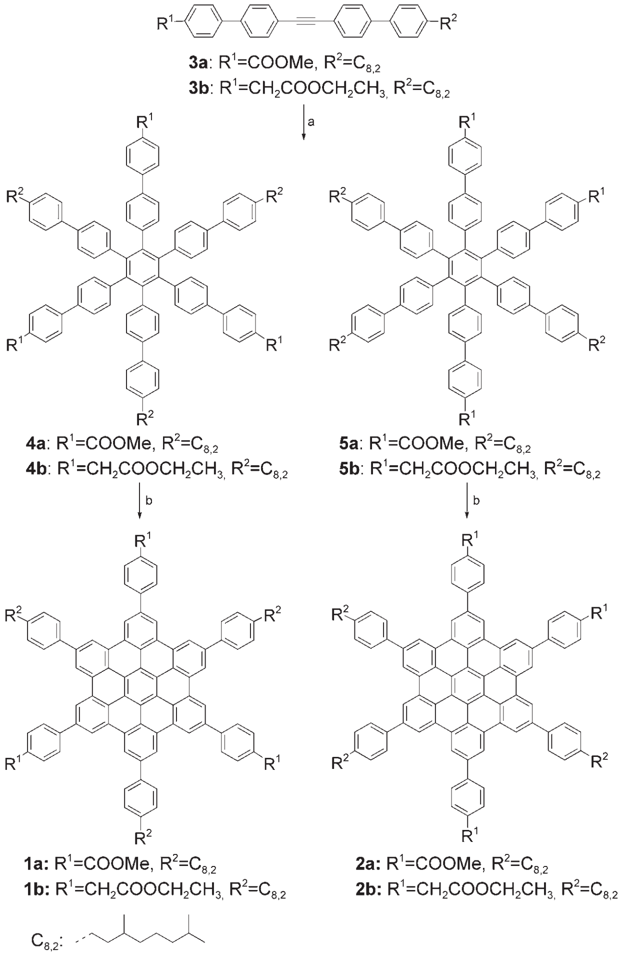
Dedicated to Professor Emanuel Vogel on the occasion of his 80th birthday

Hexa-*peri*-hexabenzocoronene (HBC, "superbenzene") and its hexaphenyl derivatives have continually attracted attention because of their large nanographene-type conjugated π systems,[1] which make for appealing applications in electronic devices.[2] Control over supramolecular organization in the solid state and of the interfaces between substrates and electrodes is thus essential. This approach utilizes the complex interplay between weak intermolecular forces such as π stacking, phase separation between aromatic cores and soft alkyl chain peripheries, as well as hydrogen bonding.[3] Another key factor is the competition between substrate–adsorbate and adsorbate–adsorbate interactions. To achieve an even higher level of control we introduce here HBCs such as **1** with an alternating array of apolar (alkyl) and polar (ester) substituents. The local dipole moments and the nanophase separation between polar and apolar sites are expected to profoundly change the packing modes in both 2D and 3D arrangements.[4] While hexasubstituted HBCs with D_{6h} symmetry have been widely studied, the necessary HBCs with C_3 symmetry are difficult to synthesize.[5] After the successful synthesis of the C_3-symmetric systems **1a** and **1b**, as well as of their asymmetric analogues **2a** and **2b**, solution NMR, UV/Vis, and fluorescence spectroscopy as well as X-ray scattering were applied to evaluate their self-assembly both in solution and in the solid state. Furthermore, the alternating attachment of polar ester and apolar alkyl chains together with the profound influence of even subtle structural changes allow a remarkably facile growth of fibrous structures from solution.

The synthetic approach is based on the asymmetrically substituted diphenylacetylenes **3**, in which one ester group and one alkyl group are introduced (Scheme 1). The different polarity of the substituents is important for the subsequent cyclotrimerization; two isomers (**4** and **5**, ratio ca. 1:2) are obtained which can be separated by column chromatography.



Scheme 1. General synthetic route toward **1** and **2**: a) $[Co_2(CO)_8]$, dioxane, reflux, 30% for **4a**, 63% for **5a**, 31% for **4b**, 63% for **5b**; b) $FeCl_3/CH_3NO_2$, CH_2Cl_2, 81% for **1a**, 84% for **2a**, 85% for **1b**, 87% for **2b**.

The key step of the oxidative planarization toward the HBCs is accomplished by treatment of these precursors with $FeCl_3$ under mild conditions to obtain the final C_3-symmetric HBCs **1** and asymmetric HBCs **2** in good yields after purification by column chromatography and reprecipitation from methanol.[6] Compounds **1a** and **2a**, in which the ester groups are directly attached to the hexaphenyl-substituted HBCs, show poor solubility in organic solvents including THF, dichloromethane, and chloroform, thus already indicating a high aggregation tendency in solution (see below). In contrast, **1b**

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and **2b** which have an additional methylene linkage are highly soluble in the above solvents.

Compound **1b** reveals a remarkably resolved ^{1}H NMR spectrum at 140 °C (see Figure S5 in the Supporting Information), whereas the signals of **1a** are still broadened at this temperature, and exhibit a significant upfield shift (HBC core at $\delta = 7.58$ ppm, peripheral phenyl protons at $\delta = 6.70$ ppm).[7] The solution UV/Vis and fluorescence spectra (5.0×10^{-6} M, see Figure S6 in the Supporting Information) show the absorption bands of **1a** (tailing to 490 nm) are broader than those of **1b**, and the emission band at 549 nm for **1a** is bathochromically shifted by 26 nm compared to that of **1b** (523 nm).[7] Thus, the self-assembly of **1a** and **1b** in solution is significantly different, thus emphasizing the role of the ester groups directly attached to the central aromatic system.

Two-dimensional wide-angle X-ray scattering (2D WAXS) experiments on mechanically oriented filaments reveal the self-assembly of all four investigated compounds (**1a**, **2a**, **1b**, and **2b**) into discotic columnar arrays.[8] Within the hexagonal columnar unit cells, the packing parameters (3.00 nm for **1a**, 2.90 nm for **2a**, 2.97 nm for **1b**, and 2.95 nm for **2b**) and the π-stacking distance of 0.35 nm are very close to those of hexaalkyl-substituted hexaphenyl HBCs.[9] However, **1a** shows a unique columnar alignment in the extruded filaments since its columns are arranged perpendicular to the alignment direction (Figure 1a). In general, columnar superstructures based on discotic molecules are aligned along the orientation direction, for example, along the shearing direction, and thus along the filament axis (Figure 1b).[10] The alignment of (macro)molecules usually depends strongly on their molecular aspect ratio.[11] The larger the aspect ratio of the building blocks, the higher the possibility for an orientation of the molecules with their molecular axis along the shearing direction, as is the case for conjugated polymers.[11] To our knowledge, this is the first case of low-molecular-weight discotic molecules aligned with their planes along the mechanical alignment direction.[12] This unusual orientation of the columns highlights not only (π-stacking) interactions between single building blocks leading to the columnar structures, but also intercolumnar interactions, as observed for **1a**. The unique property of **1a**, which has an alternating attachment of the polar ester groups and apolar alkyl chains, can be ascribed to a phase separation of the substituents in the disc periphery of **1a** as well as intermolecular dipole interactions induced by ester groups, which are responsible for the observed in-plane interaction and the orientation of the discs. Neither **1b** (see Figure S10a in the Supporting Information) nor **2a** (Figure 1b) reveal this unexpected orientation, thus indicating the crucial role of the substitution pattern and molecular symmetry. This special alignment under shearing has so far only been observed for high-molecular-weight main-chain discotic polymers consisting of covalently linked triphenylenes. In these systems the columns are aligned perpendicularly to the oriented polymer chains, as schematically illustrated in Figure 2a.[13] Our case utilizes a more complex supramolecular approach based on noncovalent forces between monomers. It can be assumed that the strong intermolecular dipole interactions between the ester groups of individual building blocks of **1a** lead first to a 2D in-plane hexagonal network possessing the necessary aspect ratio to be oriented in the above-described specific way (Figure 2b); during the further assembly steps under alignment, a 3D hexagonal columnar array is thus formed through π-stacking interactions.

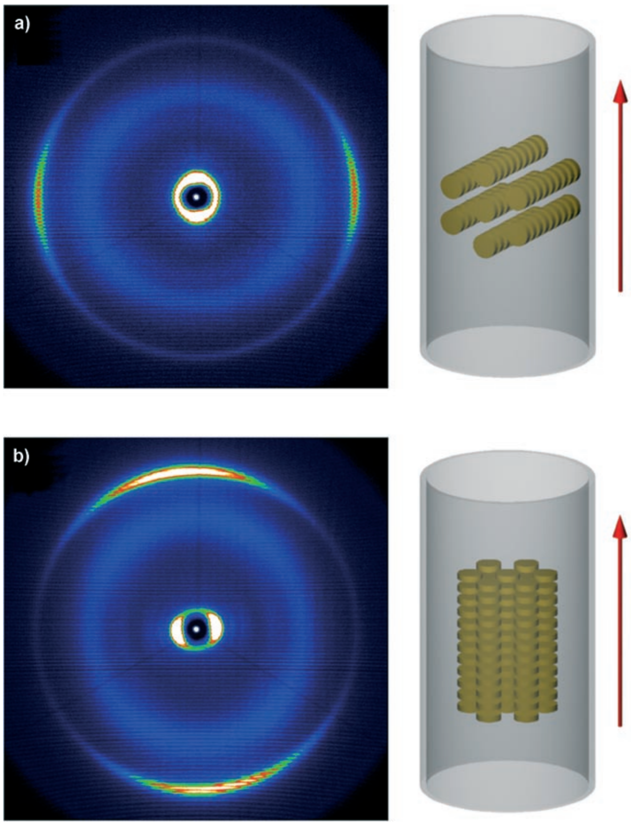

Figure 1. 2D WAXS patterns and schematic illustration of the corresponding alignment of the superstructures in the extruded filaments (the red arrow indicates the extrusion direction) for: a) **1a** and b) **2a**.

The self-assembly of suitably decorated disc-type molecules does not only lead to columnar arrangements in the bulk phase, but also to the growth of fibrous nanostructures from solution.[14] Thus, the polar solvent methanol was added to a solution of **1a** in THF (1.0×10^{-5} M). Although no gelation or precipitation were observed upon increasing the THF/MeOH ratio up to 1:1, the bands of the UV/Vis and fluorescence spectra show a significant broadening and tailing (see Figure S7a and S7b in the Supporting Information), which indicates pronounced formation of aggregates. Precipitated filaments were formed within several minutes, and then drop-cast at room temperature. Interestingly, fibrous structures were obtained with a diameter of around 100–200 nm and several micrometers in length (Figure 3a and see Figure S8a in the Supporting Information). Taking into account the molecular size, the submicrometer-sized fibers consist of 50–100 bundles of stacked molecular wires of **1a**. These results again confirm the strong aggregation and π-stacking tendency of **1a** to allow growth of the fibrous superstructures. The high-resolution transmission electron microscopy (HRTEM) images (Figure 3b) show individual columns along the fiber

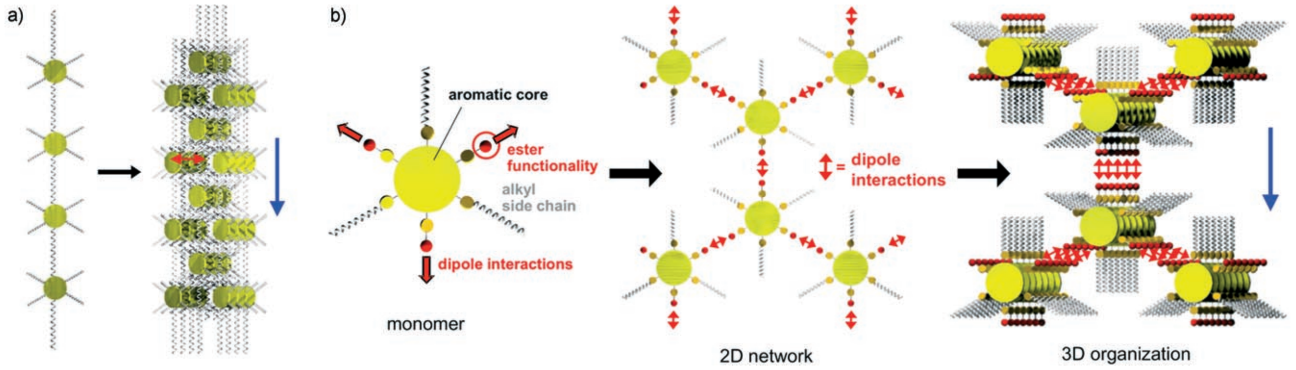

Figure 2. Schematic illustration of self-assembly and orientation during mechanical processing of: a) main-chain discotic polymers (the red arrow indicates π-stacking interactions), and b) **1a**, which assembles first through dipole interactions into a 2D network and in a further step through π stacking into a 3D hexagonal columnar organization. In both cases, the blue arrow indicates the alignment direction to which the columns are arranged perpendicularly.

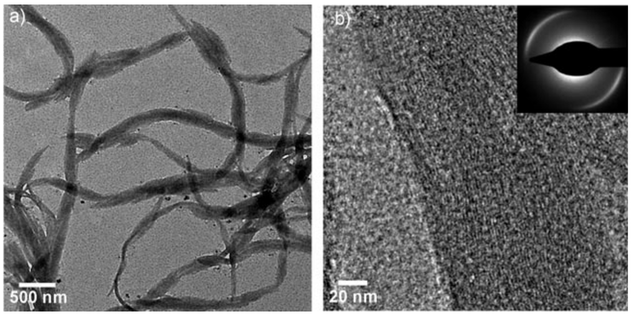

Figure 3. a) Electron microscopy of **1a** fibers grown from THF/MeOH (1:1) solution, and b) HRTEM image of a fiber displaying columnar structures of **1a**, with the electron diffraction pattern with reflections assigned to the π-stacking distance of 0.35 nm shown as an inset.

direction. Sharp and distinct reflections in the small area-selected electron diffraction pattern indicate well-oriented columnar structures (inset of Figure 3b). An intercolumnar distance of 2.5 nm was calculated, which is slightly smaller than that observed for the extruded samples.

Similarly, when the THF/MeOH ratio is increased up to 1:1 (see Figure S7c and S7d in the Supporting Information), the bathochromic shift in the fluorescence spectra of **1b** is even more remarkable, which again suggests the formation of aggregates. Filaments precipitate after several minutes, but in this case only large structures on the substrate are observed by SEM (see Figure S8b in the Supporting Information). Interestingly, when the solution was allowed to stand for a further two days at room temperature large bundles of fibrous structures (300–600 nm) were formed (see Figure S9 in the Supporting Information). This behavior might be explained by the lower tendency for phase separation between polar ester groups and apolar alkyl chains in **1b** that lead to a longer time necessary to self-assemble into ordered one-dimensional nanostructures.

In conclusion, we have developed a synthetic route toward novel C_3-symmetric HBCs with alternating polar and apolar substituents that are attached to the hexaphenyl-HBCs either directly or through a spacer group. Spectroscopic studies reveal the stronger aggregation ability in solution of **1a** with respect to **1b**, This observation can be ascribed to the strong intermolecular dipole interactions. These pronounced non-covalent forces lead to a perpendicular orientation of the columnar superstructures of the discotic molecules to the applied alignment direction, which has not been reported so far. The substitution symmetry of the functional groups plays a key role in the self-assembly, and thus indicates an opportunity to strongly enhance supramolecular assembly by introducing appropriate functional groups. Clearly, the corresponding C_3-symmetric HBCs with three acid functional groups open up new opportunities for the formation of fibers from basic solution and for the epitaxial growth of mono- and multilayers on surfaces.[15]

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[7] The ^{1}H NMR spectra of **1a** and **1b** at room temperature exhibit significant line broadening and differ from those of hexaalkylphenyl-substituted HBCs. The broad and less-structured emission spectra of **1a** and **1b** were also different from hexaalkylphenyl-substituted HBCs with more resolved bands.

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