

Uniaxial Alignment of the Columnar Super-Structure of a Hexa (Alkyl) Hexa-*peri*-hexabenzocoronene on Untreated Glass by Simple Solution Processing

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Effective exploitation of the promise of semiconductive organic materials as active components in electronic devices rests on the development of facile means to produce thin films with directed order. A class of materials for which this is particularly relevant is columnar discotic liquid crystals, which form one-dimensional axially insulated nanowires. While charge-carrier mobilities more than sufficient for transistor applications have been reported,¹ utility will be realized only when the pathways for transport (the columns) can be uniaxially aligned parallel to surfaces in thin-film geometries over length scales of at least 100 nm. These requirements have been approached using Langmuir–Blodgett techniques² and capillary filling of microprinted channels on a surface³ to produce ordered films of phthalocyanine and helicene^{2c} derivatives. Processing onto alignment layers, which is effective for nematic liquid crystals including conjugated polymers, has also recently been demonstrated with columnar discotic liquid crystalline triphenylenes.^{4,5} An elegant and simple method, most similar in principle to the method described in this communication, simultaneously achieves alignment and higher purities by zone melting/recrystallization of thin films.⁶

Liquid crystalline hexa-*peri*-hexabenzocoronene (HBC) derivatives⁷ (**1** in Figure 1) have a shorter history than those column-forming materials mentioned above, but have already displayed a number of advantageous features such as ease of synthesis,⁸ desymmetrization,⁹ and functionalization¹⁰ as well as high intrinsic charge-carrier mobilities.¹¹ Highly ordered mono- and multilayers with columns running parallel to surfaces have been produced by Langmuir–Blodgett techniques.¹² Looking to another geometry where columns run perpendicular to surfaces, symmetric sandwich cells of the type ITO/ITO (**1**, R = 3,7,11,15-tetramethyl-1-hexadecanyl) were constructed, and short circuit photocurrents (I_{sc}) were measured in homeotropically aligned areas and compared to those in poorly oriented areas.¹³ The former gave I_{sc} values 5 times higher than the latter, illustrating the importance of alignment of the 1D-conducting pathways.

XRD studies of mechanically oriented samples¹⁴ of **1** (R = $nC_{12}H_{25}$) divulged a highly ordered “crystalline” columnar phase with a rectangular 2D lattice which, however, should be considered as one of a few possible room-temperature bulk states arising from different thermal histories. A “crystal” structure of **1** could not be assigned unambiguously due to disorder in the long alkyl side chains. Further, the average column length, an important parameter from the point of view of charge transport, remained unknown. We have shown¹⁵ that **1** solidifies from solution to form hundreds of micrometer-long fibrillar and ribbonlike structures (~10–20 nm thick) on various substrates and as a component in polymer

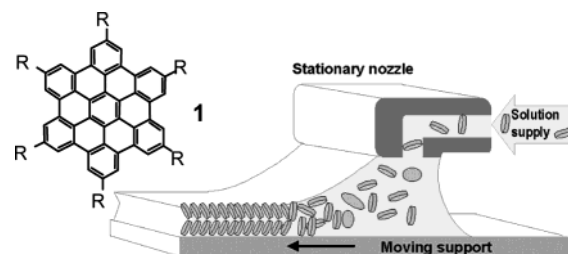


Figure 1. Schematic presentation of zone-casting process. The discs represent hexa-*peri*-hexabenzocoronene (**1**) molecules.

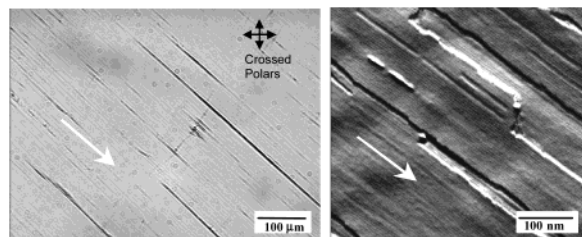


Figure 2. (Left) Optical micrograph of zone-cast layer of **1**. (Right) Large-scale AFM image. Arrows indicate casting direction.

composites. We now demonstrate that large-area, uniaxially aligned, thin films of **1** can be prepared in *one processing step on untreated glass by a simple solution casting method*.

Zone casting (see Figure 1) was performed by means of a specially constructed device analogous to that used earlier for other systems.¹⁶ A solution of **1** in tetrahydrofuran (0.6 mg/mL) was deposited through a flat nozzle (slit-like, width 3 cm) onto a moving glass support, both of which were thermally stabilized. The rates of support motion and solution deposition were optimized to obtain stationary film solidification conditions. This allows the molecules to naturally self-assemble to columns, uniaxially aligned parallel to the substrate, with only concentration/temperature gradients as guiding hands.

As-cast films exhibit negligible birefringence and optical anisotropy between crossed polars (Figure 2), which at first seems inconsistent with oriented columns lying parallel to the surface. High anisotropy was observed when the same layer was heated above the mesophase transition. XRD of bulk samples shows that at room temperature, the disks are tilted by approximately 45° with respect to the columnar axes and this tilt alternates within adjacent columns (herringbone-like). This arrangement of diametrically opposed optical elements, if highly ordered, can appear optically isotropic. When heated to the columnar mesophase, the disk planes become parallel, thus constructively contributing to the optical anisotropy. Repeated heating/cooling imparts progressively more birefringent defects at room temperature, interpreted as conversion

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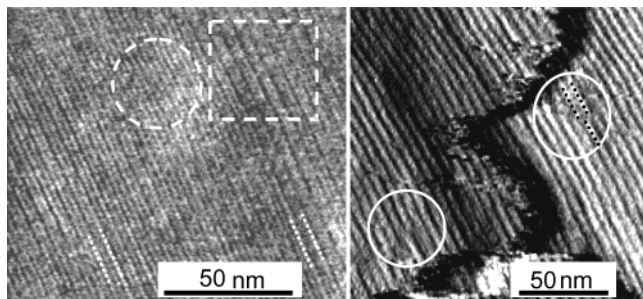


Figure 3. AFM images of zone cast films of **1**. (Left) Contact mode showing details of columnar structure. (Right) Tapping mode, amplitude image. Circles indicate columnar defects. Stripes are pairs of columns.

of the as-cast single-crystalline-like film to a polycrystalline one through random nucleation events.

Closer inspection by AFM (Nanoscope IIIa MultiMode scanning probe microscope; Digital Instruments, Santa Barbara, CA) discloses a layered morphology (Figure 2, right), with step heights which are multiples of ca. 2.1 nm (monomolecular or multimolecular steps). Further examination (not shown) revealed that the somewhat regularly spaced parallel dislocations in Figure 2 (left) are not cracks but rather folds protruding from the flat thin layer by ~ 100 nm; that is, several times greater than the layer thickness (10–20 nm determined by AFM after removing the layer in some places). We propose that these are formed via a contraction of the films (perpendicular to the columnar axes), occurring during final evaporation of the solvent.

Nonoptimal casting conditions produced highly oriented whiskerlike microfibers, instead of continuous films. Likewise, random solidification of **1** from solution below 45 °C gives thin whiskers, but “wide” ribbonlike structures above this temperature.¹⁵ Bulk **1** undergoes a thermal order–order transition at 42 °C, possibly related to an increased alkyl chain mobility, which could promote the formation of continuous films under the optimized conditions utilized here.

Higher magnifications shown in Figure 3 reveal columnar structure on the molecular level. The columns are typically coherent over distances on the order of 200–500 nm, corresponding to more than 400 molecules (intracolumnar spacing ≈ 0.5 nm). One can see more than one contrast pattern: (a) the contrast is the same for adjacent columns (circle, Figure 3, left), (b) paired columns form rows (square, Figure 3, left), or (c) every second column gives stronger contrast (dotted lines, Figure 3, left), leading to apparent spacing of ca. 5.2 nm. This effect is probably due to different local packing of aliphatic chains which, however, does not influence considerably the average lateral column spacing of ca. 2.6 nm. One can also see some defects of the columnar packing, for example adding or removing one column at some places (circles, Figure 3, right). The columnar structure accommodates these defects by column tilting and reorganization over distances of a dozen nanometers. Scan-induced etching exposed the underlying layer of columns (Figure 3, right). The pairs of columns in successive layers lie one on the top of the other correlating to rectangular columnar packing observed in bulk samples by XRD.

The step height was determined to be 2.1 nm, which gives a rectangular unit cell with dimensions considerably smaller (2.1 nm \times 2.6 nm) than those determined from XRD of bulk samples (2.38 nm \times 3.05 nm). Unit cell dimensions are highly dependent on alkyl chain packing, and it should not necessarily be expected that this would be the same in the bulk and at the solid–

air interface of these films. Regarding the apparent existence of differing domains at the surface, three immediate possible explanations exist. The most simple is that there is a unique unit cell and the variability results from one or the other plane of the rectangular column packing, (100) or (010), being parallel to the film surface. Another possibility is surface reconstruction which, although not commonly reported for organic materials, has been observed in phase-separated block copolymers.¹⁷ A third possibility is the coexistence of more than one unit cell (polymorphism) with sides parallel to the surface corresponding to the different lateral spacings seen in Figure 3. Large-area XRD in reflection mode revealed only one sharp reflex (and its second order) corresponding to the step height observed by AFM. This indicates that there is little variability in the layer spacing normal to the surface.

In conclusion zone solidification of a hexa (alkyl) hexa-*peri*-hexabenzocoronene from solution produces thin (ca. 15 nm) films composed of uniaxially aligned, exceptionally long columns with single-crystalline-like order over several square centimeters. The exceptionally high column length and coherence, reported here for solution-processed films, is highly promising in regards to production of molecular electronic devices.

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