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Amphiphilic Hairy Disks with Branched Hydrophilic Tails and a Hexa-*peri*-hexabenzocoronene Core

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Abstract: Amphiphilic discotic molecules with hydrophilic side branches consisting of hexaphenyl hexa-*peri*-hexabenzocoronene and hexabiphenyl hexa-*peri*-hexabiphenylcoronene as the aromatic core and hexa-substituted oligoethers as the branched peripheral chains have been synthesized, and their microstructure has been characterized. The discotic molecules based on dibranched oligoether side chains have been observed to self-organize into a well-ordered hexagonal columnar structure within liquid crystalline phases, which possessed an exceptionally high thermal stability and an unusually wide temperature range over >300 °C. We suggest that a combination of the large lateral dimensions of the rigid cores and disordered structure of the oxygen-containing branches tails is a driving force to the formation of a highly ordered columnar structure in the bulk state with enhanced molecular segregation. In contrast to the thermotropic phase behavior that favors the formation of highly ordered columnar aggregates through a strong stacking interaction, the hexabenzocoronene cores are packed in a face-on arrangement at the air/water interface and on solid surfaces with surface domains composed of an array of 7 × 7 molecules. We suggest a crablike molecular conformation and cluster-segregated monolayers with 6-fold symmetry and unusual face-on packing on a solid surface. Preliminary spectroscopic studies in the bulk state have shown that the molecules based on a hexaaromatic-substituted core may serve as functional supramolecular materials with high energy transfer characteristic within the columns due to near-perfect columnar ordering, which is unchanged over a wide temperature range. We believe that an absence of the crystallization phenomenon of side-branched oligoether chains is critical for the formation of long-range columnar ordering with strong intracolumnar correlation of conjugated disks important for high carrier mobility.

Introduction

The construction of disk-shaped molecules with rigid aromatic cores opens a way to novel supramolecular aggregates, which have attracted great interest in molecular and supramolecular materials. Rigid disk-shaped molecular architectures containing flexible chains on their periphery ("hairy disks") have proven to self-assemble into a large variety of organized supramolecular columns.[1−3] The individual columns can serve as nanowires in molecular electronic devices for one-dimensional transport processes such as energy migration, electric conductivity, and photoconductivity with exceptionally high transport properties along the columnar axes.[4−6] A typical example of disk-shaped molecules is provided by triphenylene and hexasubstituted hexa-*peri*-hexabenzocoronene derivatives. They have a propensity to form either hexagonal or rectangular columnar mesophases, with the flat aromatic core assisting in their formation.[7−9] The remarkable properties of the columnar mesophases of hexa-*peri*-hexabenzocoronene derivatives include a charge carrier mobility that is exhibited to be much higher than that of small discotic molecules such as triphenylene derivatives due to the formation of highly ordered columnar structures.[10] Increasing the size of the aromatic core can lead to highly ordered supramolecular columns because the molecular architecture imparts microphase separation of the rigid and flexible blocks into ordered periodic

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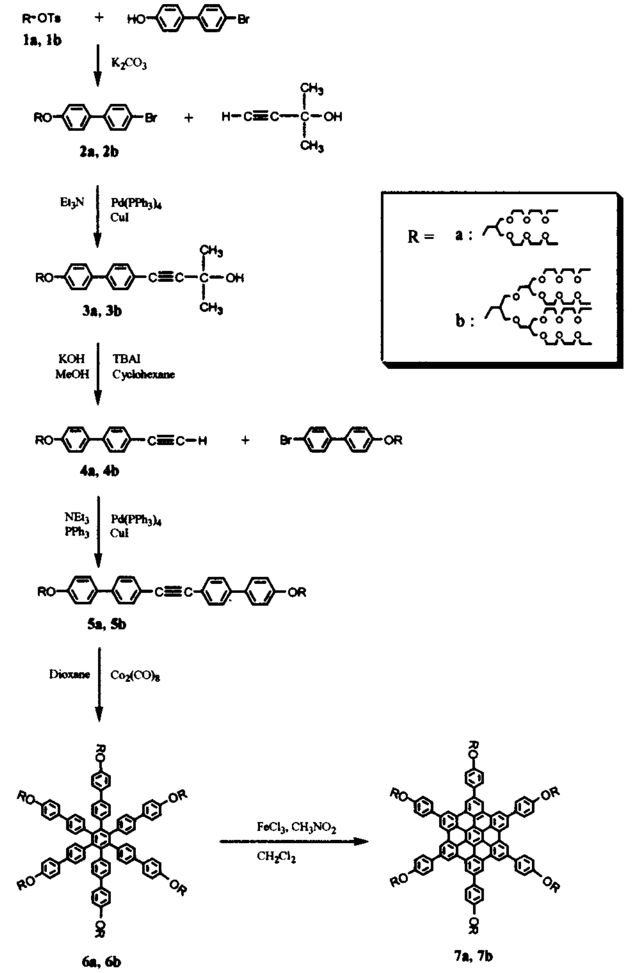
Scheme 1. Synthesis of the Discotic Molecules Based on Hexaphenyl Hexa-*peri*-hexabenzocoronene

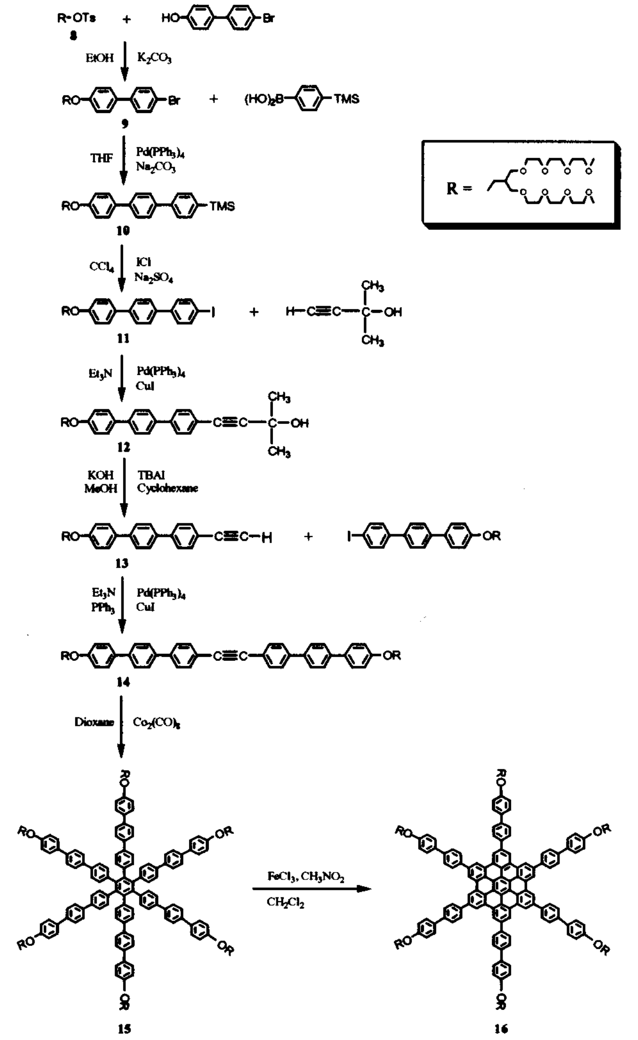


structures in combination with the parallel arrangement provided by rigid cores.[11] On the other hand, incorporation of hydrophilic chains into the periphery of an aromatic core can significantly enhance amphiphilic balance and result in reorganization of edge-on orientation of the columnar structures at the air/water interface and on solid substrates. Natural face-on orientation of discotic molecules is important for formation of molecular films with fast charge transfer across the film. Other complications in chemical architecture, such as branching of the peripheral tails, may induce amphiphilic behavior analogous to dendrimer compounds rather than conventional discotic phases.[12]

In this article, we report the self-assembling behavior of amphiphilic discotic molecules **7a**, **7b**, and **16**, consisting of a rigid coronene core and hydrophilic branched oligoethers (Schemes 1, 2). We focus on the bulk microstructure and UV adsorption properties of these compounds and their potentials to form organized molecular films on solid surfaces as determined by the length and degree of branching of the peripheral tails.

Experimental Section

Scheme 2. Synthesis of the Discotic Molecules Based on Hexabiphenyl Hexa-*peri*-hexabenzocoronene



Compounds **1a**, **1b**, **8**, and 4-trimethylsilylphenylboronic acid are synthesized using the procedures reported previously.[7b,12] Thin-layer chromatography is used to check the purity of the products. The chemical structure of all products is characterized by MALDI-TOF-MS, gel permeation chromatography (GPC), and ^{1}H NMR and ^{13}C NMR. Bulk properties are studied using differential scanning calorimetry and X-ray scattering measurements performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. Monomolecular films of the dendritic compounds are prepared by the Langmuir technique and are deposited on solid substrates following the usual Langmuir−Blodgett (LB) procedure.[13] Monolayer thickness is measured by ellipsometry, and imaging of monolayers is performed with scanning probe microscopes in the tapping mode according to an experimental procedure described in detail earlier.[14−16] X-ray reflectivity measurements from Langmuir monolayers at the air/water interface are conducted on an X-ray spectrometer at the 6ID beam line at the Advanced Photon Source synchrotron at Argonne National Laboratory.[17−19] Molecular models are created using Cerius^2 software. For technical detail, see the Supporting Information.

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Table 1. Characterization of Discotic Molecules **7a**, **7b**, and **16**

molecule	M_w/M_n[a]	state	d_{100} nm	intermolecular distance (d_{001}) nm
7a	1.03	columnar hexagonal phase[b]	3.29	0.349
7b	1.03	isotropic liquid		
16	1.06	columnar hexagonal phase[b]	3.84	0.346

[a] Determined from GPC. [b] Limited by decomposition for $T > 350$ °C. LC state exists at room temperature. Gellike state is characteristic of all compounds.

Results and Discussion

Chemical Microstructure. The synthesis of these molecules was performed in a stepwise fashion starting with a convergent route of oligoether dendron using etherification chemistry[7b,20] and continuing with Sonogashira reactions to generate tolane derivatives **5a**, **5b**, **14**.[7a,8−10] Subsequent cyclotrimerization of these molecules, catalyzed by [$Co_2(CO)_8$], in dioxane afforded the compounds **6a**, **6b**, **15**. The amphiphilic discotic molecules (**7a**, **7b**, **16**) were obtained by oxidative cyclodehydrogenation with a solution of $FeCl_3$ in nitromethane. The resulting compounds were purified by column chromatography (silica gel) using ethyl acetate as an eluent.

The final products were characterized by ^1H and ^{13}C NMR spectroscopies elemental analysis, and were shown to be in a full agreement with the chemical structures presented in Schemes 1, 2 (see Supporting Information). In addition, GPC data showed a very narrow molecular weight distribution with the polydispersity index within 1.03−1.06, which indicated very uniform chemical composition and a minute presence of other fractions (Table 1).

Bulk Microstructure and Properties. The phase behavior of the discotic molecules in the bulk state was investigated by means of optical polarized microscopy and differential scanning calorimetry (DSC) in combination with powder X-ray scatterings (Table 1). The molecules based on dibranched oligoethers (**7a** and **16**) show a birefringent liquid crystalline (LC) phase at room temperature without any signs of crystallization. Both compounds are viscous gels at room temperature. This LC state is retained at elevated temperature up to decomposition temperatures at approximately 350 °C without significant changes of optical texture, as confirmed by optical microscopy and DSC.

The X-ray scattering study of **7a** in the bulk state using synchrotron radiation revealed a series of five well-resolved reflections, which could be indexed as two-dimensional hexagonal columnar order in a usual manner (Figure 1).[21−23] The center-to-center distances between neighboring columnar structures, *a*, determined from the (100) reflections according to a relationship for hexagonal lattice $a = 2d_{100}/\sqrt{3}$ are 3.81 and 4.43 nm for **7a** and **16**, respectively. These are lower than the lateral dimensions of the disks as estimated from molecular models for extended chains (5.0 and 6.1 nm, Figure 2), which indicates a certain level of interdigitation of the peripheral groups from neighboring columns. The number of reflections is relatively high and can be attributed to high level of ordering. All small-angle peaks are extremely sharp (close to the spatial resolution of the instrument), which indicates very well-defined long-range positional ordering in hexagonal lattice.

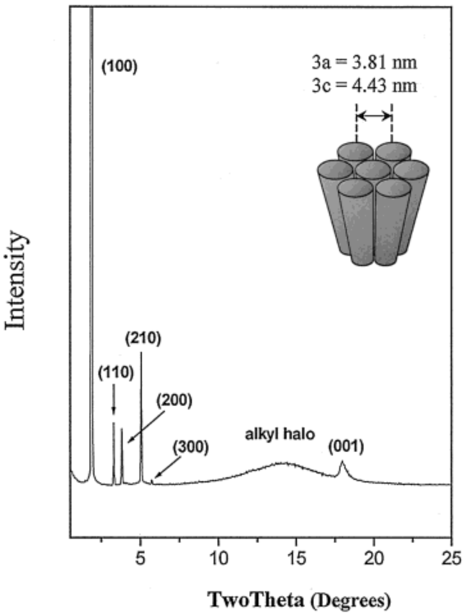

Figure 1. Representative X-ray diffraction data of molecule **7a** at room temperature.

In addition to these small-angle reflections, a broad halo centered at 0.47 nm was observed, which is associated with the liquidlike packing of flexible oligoether chains (Figure 1).[21] The sharp (001) reflections at 0.349 and 0.346 nm for **7a** and **16**, respectively, indicate the well-defined periodic stacking of the aromatic cores within the columns, usual for columnar phases of discotic compounds.[22,23] Compared to other similar molecules,[8,9] these intermolecular distances indicate an improved long-range ordering of the molecules with spatial correlations extending well beyond the short-range order and involving more than 20 molecules in the column as evaluated from the width of the (001) peaks according to the Sherrer equation.[22−26] These results indicate that the molecules **7a** and **16** exhibit an ordered hexagonal columnar mesophase. It should be noted that the incorporation of dibranched oligoethers on the periphery of the aromatic core suppresses a crystalline phase giving rise to a room-temperature columnar mesophase with high thermal stability, in contrast to the similar discotic molecules containing peripheral *n*-dodecyl chains.[8,9] Moreover, the discotic molecules based on tetrabranched oligoether (**7b**) show only an isotropic phase at room temperature. This is most likely because of the higher conformation entropy of bulkier peripheral chains and because of the fact that the volume fraction of rigid cores became small, preventing their effective segregation into ordered columns. We suggest that extra branching of the peripheral chains (four short tails per one site) plays a significant role, providing additional space constraints for the dense packing of the rigid cores forcing the chains out of the disk plane. Indeed, molecular modeling (Figure 2) shows that the effective thickness

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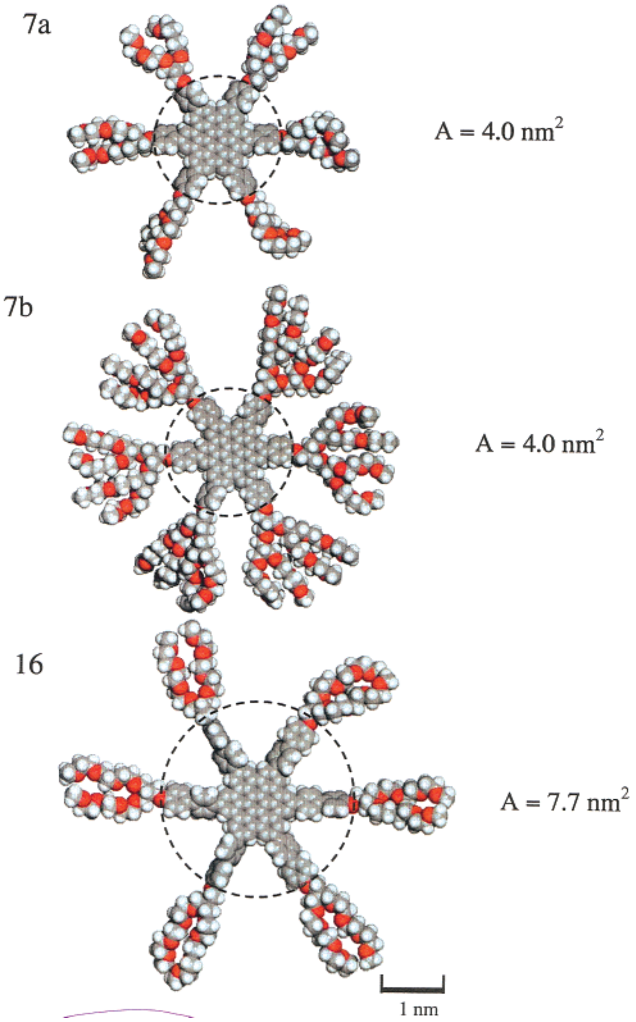

Figure 2. Molecular models of compounds studied in top-view (left) and side-view (right) projections. The dashed circles represent the surface area calculated to include the hexabenzocoronene and terminal phenyl rings.

of the shell area is higher for the tetrabranched compound as compared with the dibranched molecules, thus preventing dense packing of the thin (about 0.35 nm) central disks. Very short branches cannot be arranged within the disk plane and inevitably form loosely packed randomly oriented branches.

The microphase segregation between the hydrophilic flexible and hydrophobic rigid blocks of these molecules is likely to be the main driving force for the bulk microstructure and phase behavior. As known, this is a major mechanism of the LC phase formation in organic compounds with rigid rod-flexible tail architecture.[22] For these compounds, the effective dimension of the rigid disks and the flexible tails is crucial in defining the degree of segregation and molecular ordering. Obviously, the large lateral dimensions of the hexa-*peri*-hexabiphenylcoronene-based cores provide a much stronger trend for segregation and formation of strongly coupled columnar structures as compared with traditional LC discotics. On the other hand, branched oligoether peripheral tails are much less ordered than traditional alkyl tails that provide additional driving forces and promote segregated packing of the rigid cores. These two factors are important reasons for the formation of exceptionally ordered columnar phases in the bulk state with outstanding thermal stability. Moreover, a suppressed tendency to the crystallization of the peripheral groups prevents crystallization of the LC phase even at room temperature that, additionally, results in an exceptionally wide range of the LC columnar state in these compounds exceeding 300 °C.

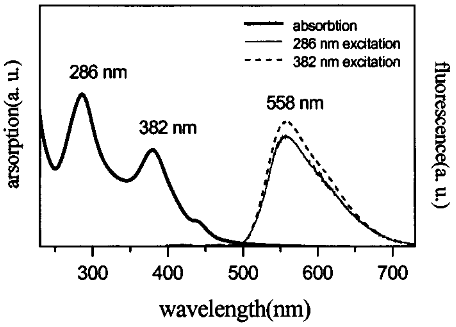

Figure 3. Absorption and emission spectra of **16** in bulk state. The thick solid line represents the UV absorption spectrum, the thin solid line presents the 286 nm excitation spectrum, and the dashed line represents the 382 nm excitation.

We tested preliminary optical properties of the molecules in LC state. All molecules possess similar UV spectra with strong adsorption in the ranges of 260−285 nm and 360−385 nm in the bulk state similar to that observed in solution. Figure 3 shows an example of absorption spectra for **16** in the bulk state. The absorption spectrum of this molecule exhibits two distinct bands at 286 and 382 nm, corresponding to the biphenyl unit and the hexa-*peri*-hexabenzocoronene core, respectively.[27] We observed that when the molecule was excited at 286 nm where most of the radiation is absorbed by the biphenyl unit, the fluorescence spectrum exhibits a strong increase with a maximum at 558 nm, corresponding to the hexa-*peri*-hexabenzocoronene core. Because the emission attributable to the biphenyl unit at 360 nm disappears almost completely, this change indicates that energy transfer takes place between the biphenyl and the hexabenzocoronene units of the molecule within the supramolecular columns.[27] Its appearance and peculiar properties are the subject of a future investigation.

Surface Microstructure. As a next step, we considered the molecular organization of the discotic molecules at solid surfaces transferred with the Langmuir−Blodgett (LB) technique as a first step in the formation of organized thin films with controlled molecular packing and transport properties. Initially, pressure−area isotherms were recorded for all compounds on a water subphase after residual solvent evaporation (Figure 4). The pressure−area isotherms for **7a** and **16** possess shapes common for amphiphilic molecules with large surface areas because of considerable cross-sectional areas of discotic cores.[13] They are characterized by two distinct phase regions as the surface pressure is increased. The areas per molecule at the two monolayer transformations of **7a**, obtained by extrapolation to a zero pressure, are 5.80 and 1.40 nm^2, respectively (Figure 4). Molecular models show the theoretical surface area of the aromatic core itself equals 1.02 nm^2. The surface area occupied by the molecule increases to 2.70 nm^2 if terminal phenyl rings are included (Figure 2). The dashed circles in Figure 2 represent the area of the total circle calculated with a diameter of phenyl ring to ring. This area would represent the cores packing with

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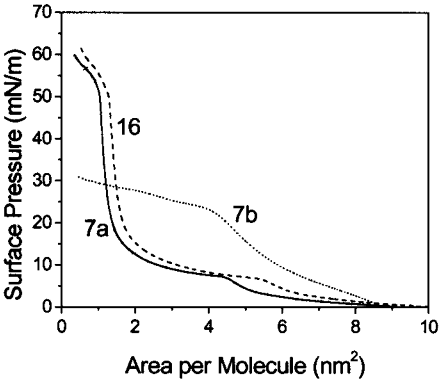

Figure 4. Pressure−area isotherms of Langmuir monolayers of compounds studied.

no interdigitation of the terminal phenyl rings. The theoretical cross-sectional area per molecule increases to 10.50 nm^2 if extended peripheral tails are located in the plane of the discotic core and no interdigitation occurs. This is only slightly lower than the cross-sectional area per column in the bulk LC state calculated from the center-to-center distance (11.4 nm^2). Therefore, the experimentally observed cross-sectional areas for first transformation (5.80 nm^2) immediately point to interdigitation of side chains in a condensed monolayer state. Moreover, in a solid monolayer state (region with a sharp rise of the surface pressure, Figure 4), significant bending of the hydrophilic tails should occur to accommodate a dense packing of hard disks with the cross-sectional area below 2 nm^2 per molecule. Therefore, we suggest that, at the first transformation, the molecules adopt an orientation in which the hydrophobic aromatic core lies flat on the water surface and the hydrophilic peripheral chains are partially interdigitated and bent toward the water surface, while at the second transformation they are completely bent and submerged in the water subphase. Indeed, X-ray reflectivity data confirm this suggestion and provide quantitative parameters of structural organization.

In fact, X-ray reflectivity data confirm flat-on orientation of the rigid cores at the air/water interface at low surface pressures. It shows one broad maximum with fast decreasing intensity for $Q > 3.0$ nm^{-1} (Figure 5). The best fit of the experimental data can be obtained with a two-box model with higher density of the flexible tails submerged in the water phase and lower density of the loosely packed aromatic cores. The higher electron density of terminal chains indicates significant presence of the water molecules at two pressures analyzed here (Table 2). On the other hand, the low electron density of aromatic core areas reflects their loose packing within the monolayer at very low surface pressures. The length of the terminal tails projected on the surface normal is equal to 1.0 nm for molecule **7a**, slightly lower than the contour length of 1.5 nm. Increasing surface pressure slightly above the first transformation resulted in thickening of the "tail layer" to 1.4 nm and a modest increase of the packing density of aromatic cores (Table 2). These parameters correspond to a crablike conformation of the discotic molecules with the oligoether terminal chains being completely submerged in water (Figure 6).

Table 2. Structural Parameters of Monolayers of **7a** and **16** Deduced from Fitting Reflectivity Data with the Two-Box Models for Different Pressures

	7a		16	
pressure (mN/m)	7	10	7	10
tail length (nm)	1.04	1.40	1.09	2.11
tail density (10^{-3} e/nm^3)	0.44	0.40	0.40	0.39
core length (nm)	0.69	0.59	0.36	0.62
core density (10^{-3} e/nm^3)	0.08	0.11	0.12	0.86
roughness (nm)	0.27	0.33	0.26	0.60

The thickness of the monolayers deposited on a solid substrate was measured by ellipsometry and represents "effective" thickness calculated assuming a uniform coverage and a value of refractive index close to known bulk values. The uniform coverage was confirmed by SPM, and possible variations of the refractive index could give an error margin of 20% at most. For monolayers deposited at pressures below the first transition, the effective thickness equals 0.6 nm, which confirms virtually flat orientation of the molecules. This demonstrates that the presence of branched, water-soluble peripheral chains instead of traditional hydrophobic single alkyl chains causes restructuring from traditional, edge-on orientation of discotic molecules[23−26] to flat, face-on orientation on both water and solid surfaces. Increasing the pressure to slightly above the transition to the condensed state results in a monolayer effective thickness of 1.2 nm corresponding to the molecular dimension of molecules in a crablike conformation (Figure 6).

Compression of the monolayer above 6 mN/m at the air/water interface resulted in a steady increase of the surface pressure over a wide range of areas followed by a sharp rise at very small cross-sectional areas as was discussed above (Figure 4). Considering that this increase happened at 1.40 nm^2, which is

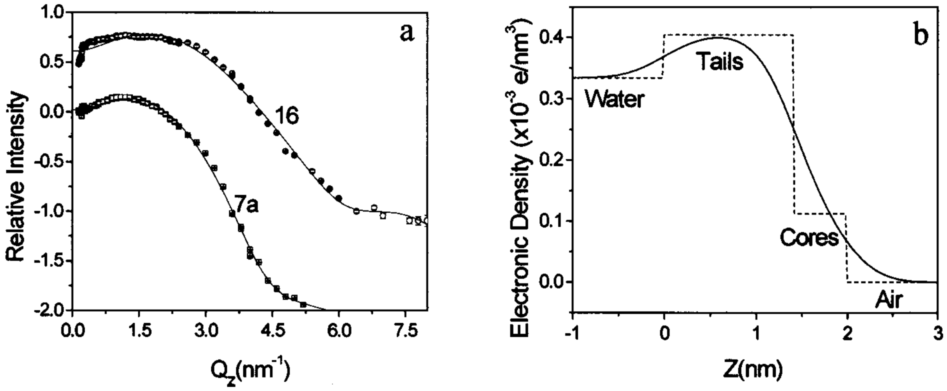

Figure 5. (a) X-ray reflectivity data at air/water interface for **7a** and **16** with the best fit; the symbols represent the data, while the solid lines represent the fits. (b) The two-box model with sharp interfaces and corresponding smeared electron density distribution along the normal to the surface plane for the highest pressure for **7a**.

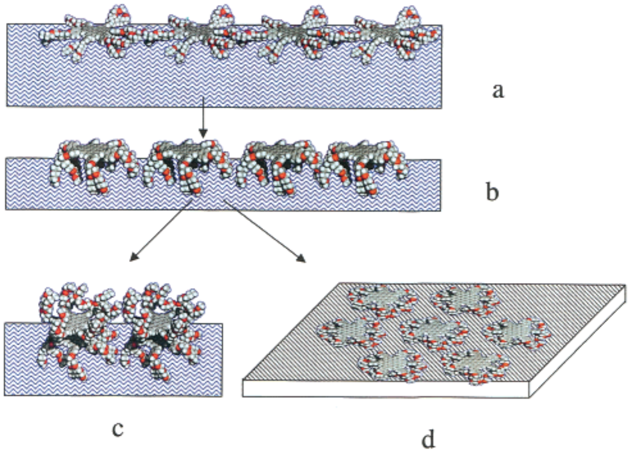

Figure 6. Schematic representations of **7a** at the air/water interface and deposited on solid substrate: (a) molecules are at low surface pressure, (b) oligoether chains submerged in subphase as surface pressure is increased, (c) formation of bilayer at the air/water interface, and (d) the formation of LB film on the solid surface.

smaller than the area required for flat-on orientation but larger than the area required for edge-on orientation of a single molecule, we can suggest that this transition corresponds to a collapse of a single monolayer and the gradual formation of the bilayer structure (Figure 6). Edge-on orientation is discounted also by the much smaller than expected thickness of the high surface pressure monolayer films. The molecular model estimates the height of edge-on oriented molecules to be in the range from 3.8 to 5.0 nm. The total effective layer thickness is much lower (2.7 nm), which confirms the bilayer film structure of crablike molecules (Figure 6).

Direct confirmation of the formation of the microstructure with 6-fold symmetry came from AFM imaging of the monolayers (Figure 7). At surface pressures below the first transformation, only uniform, featureless morphology was observed. Similarly, at pressures greater than 20 mN/m, we observed uniform surface morphology. However, at pressures in the beginning of the sharp pressure rise, characteristic domain texture was recorded with sizes of uniform domains of several micrometers across (Figure 7). Six-fold orientational symmetry clearly shows up. It manifests itself in needlelike islands preferably oriented along one of three axes, which are frequently intersected at ~60 and ~120° angles. Examples of the preferred orientation of the islands are demonstrated in Figure 8 with the desired axes labeled. The height of these islands determined by AFM is 1.5−1.7 nm, close to the estimated thickness of the molecules in the crablike conformation calculated by molecular models, and is about 50% of the total effective thickness of the films derived from ellipsometry.

Therefore, at intermediate surface pressures (6−10 mN/m), we observed the initial stages of the formation of the second layer through the initial growth of anisotropic islands. Symmetry of the island orientations allows one to conclude that, first, the underlying layer possesses 6-fold symmetry that is commensurate with face-on orientation of the molecules at the interface. Indeed, high-resolution imaging of the LB films displayed additional details of surface structure and confirmed its 6-fold character (Figure 8). First, all islands have a very uniform width of 30−40 nm and a length in the range from 100 to 200 nm as estimated after correction on the SPM tip dilation. They show clear grainy structures with, on average, the islands composed of two grains with a width of 20 nm across each (Figure 8a).

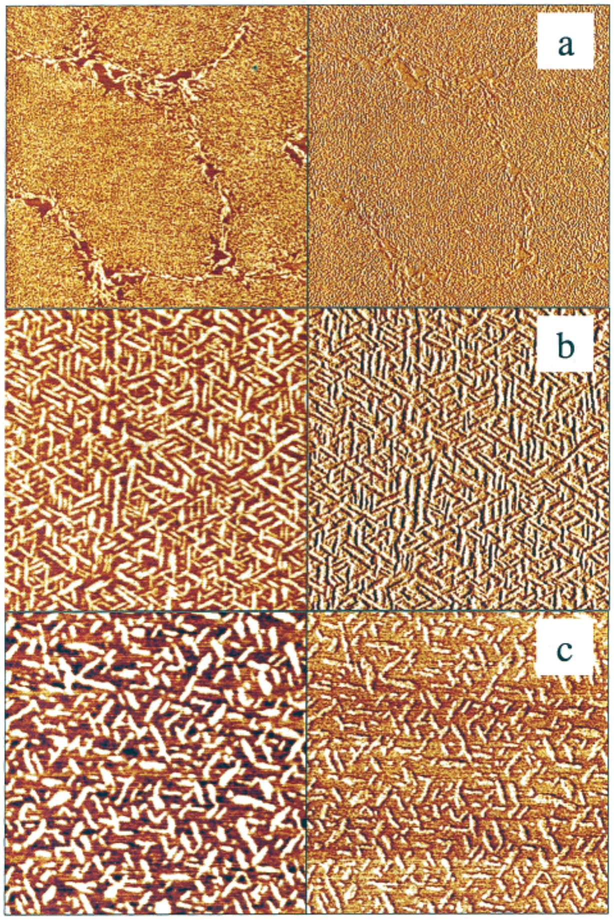

Figure 7. SPM images obtained in tapping mode: (a) 10 × 10 μm scan of **7a** at 12 mN/m surface pressure, (b) 2 × 2 μm scan of monolayer area, (c) 2 × 2 μm scan of **16** at 10 mN/m surface pressure. The left images are topography, and the right images are phase shift.

Scanning of the monolayer in the surface areas with scarce islands resolved an ordered lattice with periodicity of about 24 nm (Figure 8b). This lattice generates the 2-D Fourier pattern that confirms its 6-fold symmetry (inset of Figure 8b). Clusters, which compose this lattice, have lateral sizes close to 20 nm. Considering the average diameter of the **7a** molecules in the crablike conformation of about 3 nm, we can suggest that a single cluster is composed of an array of 7 × 7 molecules. The nature of such aggregation is not clear but, we suggest, is related to in-plane frustration during structural relaxation caused by transfer from water to solid surface. Indeed, as we suggested for the monolayer at the water surface, the oligoether tails are submerged in the water (Figure 6). In contact with a solid silicon oxide surface, they are in more confined conditions with a minor presence of water and must rearrange themselves to adapt a monolayer of 1−1.2 nm thickness by partially rearranging themselves beneath the aromatic cores. It can lead to contraction of the lateral packing and the formation of in-plane aggregates separated by regular defects.

Molecule **16**, based on a larger aromatic core, also shows a very similar phase behavior and monolayer microstructure to that of **7a**. Indeed, the pressure−area isotherm has the same shape except slightly larger cross-sectional areas per molecule at both transitions caused by the presence of additional phenyl

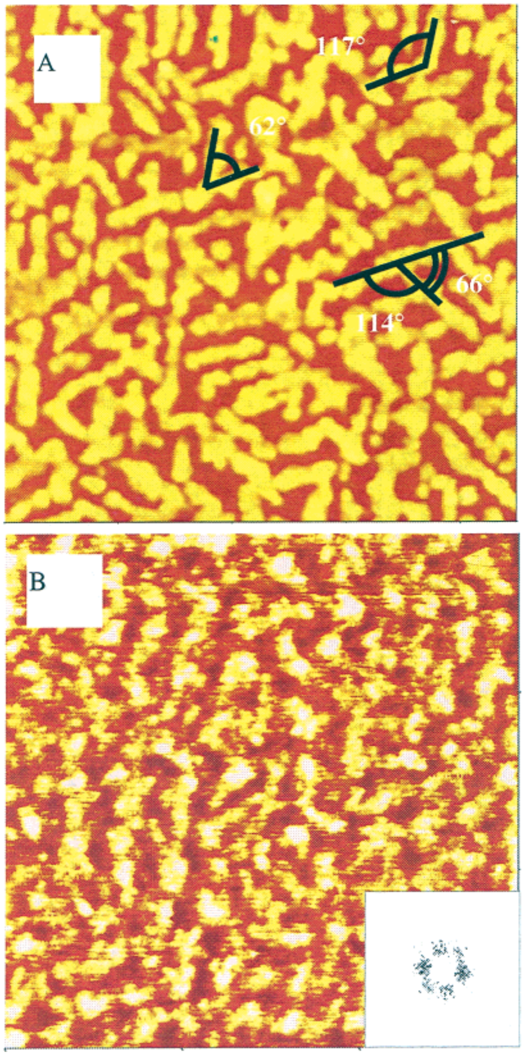

Figure 8. SPM images obtained in tapping mode: (a) 900 × 900 nm topography scan of **7a** at 12 mN/m surface pressure demonstrating selectively oriented anisodiametric islands of second layer formed on top of a monolayer, (b) 250 × 250 nm topography scan of a monolayer surface with corresponding 2-D Fourier transformation of the image (insert).

rings in the aromatic core and an additional monomeric unit in the oligoether tails (Figure 2). The first transition at 7.10 nm^2 corresponds to the calculated area of an aromatic core (circle with a diameter of 3.1 nm), indicative of face-on orientation to the water surface with bent side chains similar to the **7a** molecule (Figure 6). The thickness of the monolayer at the air/water interface, obtained from X-ray reflectivity data, is virtually indistinguishable from the effective thickness of the monolayer **7a** (Table 2). Also, very similar to that of **7a**, the second transition at 1.80 nm^2 corresponded to the formation of the second layer via needlelike island growth (Figure 7). The effective thickness of the film (0.56 nm at 5 N/m) and the parameters of the microstructural ordering of **16** are very similar to that observed for **7a** (Table 2). In contrast, molecule **7b** based on tetrabranched oligoethers shows steady increase of the surface pressure during gradual collapse of the monolayer and the formation of a disordered film.

Concluding Discussion

In summary, we introduced a novel type of “hairy” disk molecule with branched peripheral chains and enhanced capability to form well-ordered columnar phases with exceptional thermal stability in the bulk state and nontrivial face-on molecular organization on solid surfaces. We have synthesized amiphiphilic discotic molecules based on a hexa-*peri*-hexabenzocoronene core and oligoether peripheral chains with different lengths and degrees of branching. The molecules based on dibranched oligoether chains have been observed to organize into hexagonal columnar LC structure at room temperature with suppressed crystallization of the side chains usually observed for alkyl tails. These mesophases are extremely thermally stable and possess an exceptionally wide temperature interval of columnar order extending over >300 °C. We suggest that a combination of the large lateral dimensions of the rigid cores and disordered structure of the oxygen-containing side branches is a driving force to the formation of the highly ordered columnar structure in the bulk state. Enhanced molecular segregation results in the exceptional thermal stability of the columnar ordering surpassing anything previously known for the discotic compounds.

We speculate that these molecules may provide access to prospective functional organic materials with characteristic high energy transfer due to near-perfect columnar ordering, which is unchanged over a wide temperature range. We believe that, for this purpose, an absence of the crystallization phenomenon of side-branched oligoether chains (unlike that usually observed for alkyl-based discotics) is critical for the formation of long-range columnar ordering with strong intracolumnar correlation of conjugated disks important for high carrier mobility. As known, cocrystallization of side alkyl chains is a dominant reason for disturbance of columnar ordering and disruption of the charge transfer along the columnar structures.[31] In fact, the hexa-*peri*-hexabenzocoronene cores with mainly alkyl side chains have been used before to synthesize hairy disks and fabricate organized films with promising high charge-transfer mobility.[10,32,33] However, cocrystallization phenomenon and, thus, coexistence of two crystalline phases resulted in distorted columnar ordering and highly skewed π-stacking reducing dramatically the transfer properties of these compounds.

The introduction of side chains with hydrophilic terminal groups has been used to induce sufficient amphiphilic balance required for the fabrication of organized molecular films with the LB technique.[32] As a result of such an asymmetric balance, a highly tilted packing of rigid cores and their edge-on orientation has been observed for molecular films deposited on solid surfaces. This ordering, along with additional crystallization of alkyl chains, is unfavorable for the high charge transport within surface films. Moreover, for such prospective applications as light-emitting devices, the necessary direction of charge transfer is *across* the film−substrate interface. This requires orientation of the columnar structures *perpendicular to the solid surface*.[21−26] The approach proposed in this work, in fact, promotes well-organized face-on orientation of the hairy disk molecules, which is critical for perpendicular orientation of the

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columnar structure and charge transfer across the film thickness (i.e., between two electrodes).[33,34] This dramatically distinguishes this class of molecules from all well-known hairy disks with orientation of columnar structures which overwhelmingly occurs in-plane of solid surfaces (edge-on orientation).

It is worth noting that this interfacial behavior is in contrast to that in other symmetrically substituted rigid discotic molecules with single side alkyl tails which favor an edge-on orientation at the air/water interface.[23−26,28−30] This interesting behavior is believed to originate from a strong hydrophilic character of the symmetrically substituted peripheral oligoether chains that have a tendency to dip into the water subphase. On the other hand, branching creates more challenging conditions for local ordering of the side chains and prevents edge-on orientation. These results demonstrate that the symmetrical incorporation of hydrophilic chains at the periphery of an extended aromatic core provides a powerful strategy to combine thermotropic liquid crystalline behavior and amphiphilic self-organization within one molecule. This approach is much more efficient than a common strategy adapted widely of fractional substitution of a selected terminal group with a hydrophilic group, which produces crystallizable films with edge-on orientation of poorly ordered columnar structures.

For dibranched molecules in the Langmuir monolayers, we proposed the crablike molecular conformation with the branched side chains submerged in water. This organization differs drastically from columnar packing in the bulk state where side chains are close to extended conformation and are, indeed, frequently crystallized as a separate phase. This also demonstrates that these branched compounds are very different from conventional discotic molecules with hydrophobic, single-tail side chains. After transfer to a solid substrate, the molecules with dibranched short peripheral chains formed an organized monolayer on solid supports with 6-fold symmetry of face-on molecular packing and cluster aggregation. We attributed aggregate formation to monolayer relaxation caused by peripheral chain restructuring during transfer from the water surface to the solid substrate. Formation of the second molecular layer on top of the surface layer showed well-defined 6-fold symmetry that indicates very strong stacking correlations among rigid cores, which overcomes usual poor ordering for the first surface layer due to the disturbing influence of the solid substrate. This is promising for further formation of perpendicularly oriented columnar structures with high charge transfer across the film thickness. On the other hand, a high level of flexibility of peripheral chains and their readiness to change conformation at different surface pressures may be a promising sign for controlled manipulation of columnar ordering and, thus, transfer properties.

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Supporting Information Available: Description of experimental instrumentation and synthetic details and characterization for **2−7** and **9−16** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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