Uniaxial Alignment of Polycyclic Aromatic Hydrocarbons by Solution Processing

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The self-organization of two polycyclic aromatic hydrocarbons with different aromatic core sizes, dodecylphenyl-substituted hexa-*peri*-hexabenzocoronene and an extended disk consisting of 96 carbon atoms 6-fold-alkyl-substituted, on the surface from solution has been investigated. Highly ordered surface layers of both materials could be obtained by the zone-casting technique, despite an apparently low self-organization in drop-cast films. The zone-cast films revealed high macroscopic uniaxial orientation of the columns with a molecular edge-on arrangement on the glass support as confirmed by polarized optical microscopy, UV−vis measurements in polarized light, high-resolution transmission electron microscopy, and X-ray diffraction. Electron diffraction indicated a high intracolumnar periodicity of the molecules, but a low intercolumnar correlation of the disks due to the increased molecular dynamics in the liquid crystalline phase.

Introduction

Processing is an essential step in the fabrication of electronic devices based on organic semiconductors due to the strong relationship between electronic performance and the degree of supramolecular order.[1] Therefore, the development of various processing techniques has advanced in the past decade together with the synthesis of new organic materials which are promising for the application.[2−4] Among various organic semiconductors, polycyclic aromatic hydrocarbons (PAHs) possessing a discotic liquid crystalline phase have attained great interest due to their particular characteristic supramolecular structure, which controls the electronic properties.[5−7] These PAHs consist of a rigid aromatic core, which can be substituted by different chemical units to control the solubility and thermal behavior. Due to strong π-stacking of the cores, the discotic molecules self-assemble into one-dimensional columnar supramolecular structures.[8−15] Moreover, the overlap of delocalized π-orbitals between two adjacent molecules allows a charge carrier transport along these columnar stacks. The charge carrier mobility is a key electronic property which determines device performance in applications such as field-effect transistors (FETs).[16] Hexa-*peri*-hexabenzocoronenes (HBC), as an example for a polycyclic aromatic hydrocarbon, revealed the highest intrinsic mobility for this kind of material and became the subject of many investigations.[17,18] However, the successful exploitation of organic semiconductors in devices depends on the degree of order of the active layer deposited between the electrodes. There are two characteristic supramolecular organizations on surfaces for discotics with high columnar orientation in the direction of the charge migration. Efficient photovoltaic devices necessitate homeotropical arrangement of the molecules, which is adopted spontaneously in some cases during cooling at controlled conditions from the isotropic phase.[7,19,20] The molecular edge-on order with

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uniaxially oriented columns is desired in FETs.[2,21] The uniaxial long-range order of the material deposited between electrodes reduces local defects which act as scattering sites for the charge carriers. However, the latter supramolecular orientation on a surface requires adequate processing techniques. The Langumir−Blodgett technique[22,23] and zone crystallization[24,25] were reported as suitable methods to gain highly ordered surface layers. Another important aspect in the device design is the fabrication of large areas, which is mainly possible by solution processing. The casting onto a preoriented PTFE layer was shown as an elegant way to highly orient discotic materials.[26,27] Field-effect experiments confirmed a significant anisotropy of the charge carrier mobility of the PTFE-oriented HBC layers with higher values in the columnar direction. Recently, using the zone-casting technique, which is also based on solution processing, highly ordered hexakisdodecylhexabenzocoronene (HBC−C_{12}) thin layers were prepared.[28] The optical properties in polarized light of these films could be switched reversibly from anisotropic in their crystalline state to highly birefringent in the mesophase.[29,30] This control of optical behavior was possible due to the highly ordered structure of the layers and the specific intracolumnar arrangement, which changed from the herringbone structure in the crystalline state to the cofacial π-stacking in the mesophase. Moreover, these HBC−C_{12} layers revealed a high field-effect mobility of 0.5 × 10^{-2} $cm^2/(V\ s)$.[31]

In general, the processing along a gradient acting within a defined zone requires pronounced nucleation and growth ability of the material. When the sample is moved along a gradient, the processing conditions such as temperature or sample motion can be varied to be in agreement with the optimal growth rate of the material. This was impressively shown for the zone crystallization of an HBC derivative 6-fold-substituted by long dove-tailed 2-decyltetradecyl ($C_{14,10}$) side chains which formed large spherulitic domains during cooling from the isotropic state. This pronounced directional growth from the isotropic phase opened the opportunity for the uniaxial alignment of this compound along a temperature gradient. Thereby, the optimized processing conditions were in agreement with the crystallization kinetics of the HBC derivative.[24] The relation between directed growth and processing within a defined zone is also valid for the solution processing along a concentration gradient. It was shown that the successful orientation of HBC−C_{12} by the solution-based zone-casting technique is based on the particularly strong aggregation tendency of the molecules in solution.[28]

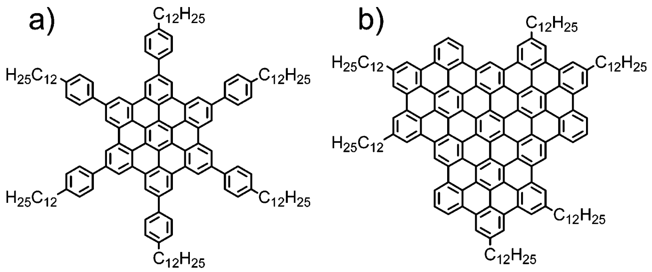

Figure 1. Chemical structures of (a) HBC−PhC_{12} and (b) C96−C_{12}.

In this work, we investigate the supramolecular organization of two polycyclic aromatic hydrocarbons after the zone-casting processing, dodecylphenyl-substituted hexa-*peri*-hexabenzocoronene (HBC−PhC_{12}) and an extended disk consisting of 96 carbon atoms 6-fold-alkyl-substituted (C96−C_{12}) (Figure 1), which both do not reveal a crystalline phase. Since the pulse-radiolysis time-resolved microwave conductivity technique revealed high charge carrier mobilities for both materials, HBC−PhC_{12} and C96−C_{12} are assumed as potential candidates for organic electronics.[17,32] HBC−PhC_{12} is particularly interesting due to the successful employment of this material as an active layer in photovoltaic cells,[18] which can be related to its particular intracolumnar packing.[33] On the other hand, the aromatic core of the second polycyclic aromatic hydrocarbon consists of 96 carbon atoms and is therefore significantly extended in comparison to the HBC core. Accordingly, the C96 core allows a considerably larger cofacial packing area, which might result in a higher charge transfer along the columnar stacks. Furthermore, the noncrystalline state at the application temperature enables self-healing of the already deposited active layer. One anticipates that the latter process is essential for the long-term application of discotics in electronic devices.

The important relationship between nucleation and processing from solution will be discussed in relation to the solution behavior of the compounds. Since both compounds do not show such pronounced nucleation ability in solution as was observed in the case of HBC−C_{12},[34] the importance of the degree of self-aggregation in solution for the alignment by the zone-casting technique will be clarified. The aggregation of the studied HBC derivative is significantly reduced by the substitution of phenyl rings directly to the HBC core.[34] Therefore, the solubility of the material increased signifi-

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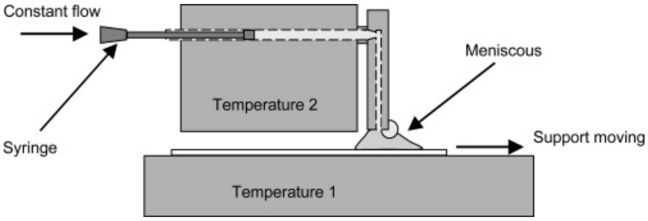

Figure 2. Schematic illustration of the zone-casting apparatus.

cantly in comparison to that of HBC−C_{12}. On the other hand, C96−C_{12} also revealed a considerably increased solubility in comparison to HBC−C_{12}, despite the extended aromatic core.[36]

Experimental Section

The synthesis of HBC−PhC_{12} and C96−C_{12} was described earlier.[35,36] Since the IUPAC nomenclature for the 6-fold-alkyl-substituted C96 is too complex, this compound is labeled by the number of carbon atoms in the aromatic core and the side chains. HBC−PhC_{12} was assigned as liquid crystalline (LC) at room temperature, with a phase transition at 80 °C to a second liquid crystalline state. During cooling, the material crystallized at 52 °C back to the first LC phase. Additionally, at −21 °C a further solid-state phase was detected. C96−C_{12} was determined as liquid crystalline even at room temperature. At 38 °C the material revealed a phase transition without any detectable structural change.

Both compounds were processed by a home-built zone-casting apparatus consisting of two heating blocks and two step motors. The schematic illustration of the setup is shown in Figure 2. Thereby, a syringe with the solution is placed into the upper heating block, whereas a glass support is placed on the lower block. Both blocks are thermally controlled. The solution flow is controlled by a step motor which is pressing out the solution at a constant flow rate. The support is moved under the nozzle at a controlled speed by the other motor. The solution is deposited onto the support by means of the nozzle. During this procedure, a meniscus is formed between the nozzle and the support. While the solvent evaporates, a concentration gradient is created within the meniscus. When the critical concentration is attained, the material nucleates onto the moving support, forming the aligned thin layer. Thereby, the film morphology is controlled by a number of processing parameters such as evaporation temperature and polarity of the solvent, solution concentration, temperature of the heating blocks, solution flow rate, substrate velocity, etc. which are related to the nucleation from solution of the corresponding material.

The following optimal processing parameters for HBC−PhC_{12} were determined: the concentration of 1 mg/mL in a mixture of tetrahydrofuran (THF) and toluene in a ratio of 4:1, the substrate velocity 60 μm/s, the solution temperature of 55 °C, and the substrate temperature of 46 °C. The C96−C_{12} was zone-cast-processed from toluene at a concentration of 1 mg/mL and a substrate velocity of 20 μm/s at temperatures of 55 and 45 °C for the solution and the substrate, respectively. Both compounds were zone-cast at ambient conditions directly onto an untreated glass substrate.

A Zeiss microscope equipped with polarizing filters equipped with a Hitachi KP-D50 color digital CCD camera was used to investigate the optical behavior of the films. Optical absorption studies were carried out using a Perkin-Elmer Lambda 800 spectrometer equipped with a Glan-Thomson polarizer.

The X-ray diffraction (XRD) measurements were performed at various temperatures to investigate the supramolecular structure of the zone-cast compounds at different phases. A $\theta\angle\theta$ Siemens D500 Kristalloflex with a graphite-monochromatized Cu Kα X-ray beam was used. The diffraction patterns were recorded in the 2θ range from 1° to 32° and are presented as functions of the scattering vector $\mathbf{s}$, with $\mathbf{s} = (2 \sin \theta)/\lambda$, where 2θ is the scattering angle.

High-resolution transmission electron microscopy (HR-TEM) was carried out on an FEI TECNAI F30 ST at 300 kV under liquid N_2 cryo conditions. Therefore, a 20 nm thick coal layer was evaporated onto the glass substrate onto which the material was deposited. The coal film together with the sample was floated off the substrate in a dilute HF aqueous solution and fished up by means of a TEM copper grid.

Results and Discussion

Our previous study revealed for HBC−C_{12} one of the highest self-aggregations in solution, $K_a = 898$ L mol^{-1} (in 1,1,2,2-tetrachloroethane-d_2 at 30 °C), in comparison to other molecules with π-stacking tendency, which is connected with a low solubility in solvents such as THF and toluene.[34] This strong aggregation tendency was in good agreement with the morphology obtained by drop-casting. Due to this pronounced aggregation behavior HBC−C_{12} forms several micrometer long ribbons with a thickness of 2−3 μm.[37] Therefore, this material was considered to be an adequate candidate for the processing from solution. Indeed, highly ordered “quasi-single-crystal” thin layers were obtained by zone-casting of HBC−C_{12}.

In this study, we have investigated the structure of zone-cast films based on two other discotic molecules, HBC−PhC_{12} and C96−C_{12}, which are liquid crystalline within the investigated temperature range. However, these two materials exhibit a behavior in solution considerably different from that found for HBC−C_{12}. When HBC−PhC_{12} was drop-cast from a 10^{-4} M toluene solution (Figure 3a), considerably shorter ribbons were formed than observed for HBC−C_{12}, indicating a smaller tendency for self-assembly. This is also in agreement with the enhanced solubility of the compound. The drop-casting of C96−C_{12} at room temperature resulted in the formation of an amorphous film, whereas the preparation of the surface layer above 45 °C led to the appearance of birefringence (Figure 3b). Bulk C96−C_{12} undergoes a thermal order−order transition at 38 °C, possibly related to an increased alkyl chain mobility, which could promote the formation of more ordered films under the utilization of a higher temperature. Upon inspection of the topography of the drop-cast C96−C_{12} layer by atomic force microscopy (AFM), one can observe several hundreds of nanometer long randomly distributed aggregates, which indicate some degree of self-organization on the surface.

Because of the different solubilities and probably different aggregation behavior in solution of the two compounds, the processing parameters such as the choice of the appropriate

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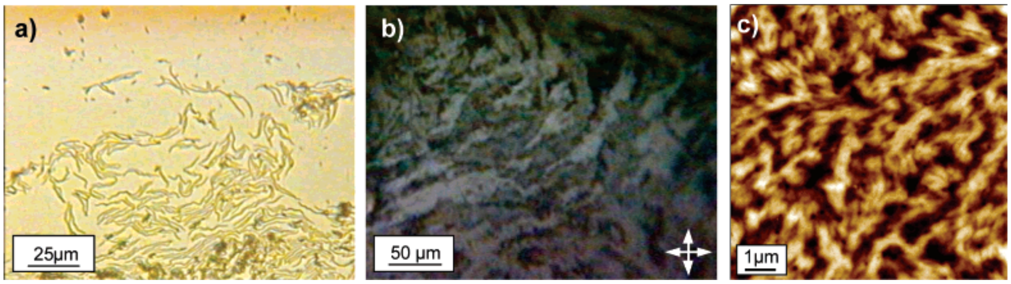

Figure 3. (a) Optical image of an HBC−PhC$_{12}$ drop-cast film and (b) POM image of a C96−C$_{12}$ prepared by drop-casting at 45 °C (both were cast from a 10^{-4} M THF solution) and (c) AFM (tapping mode) image of the drop-cast C96−C$_{12}$ film in (b).

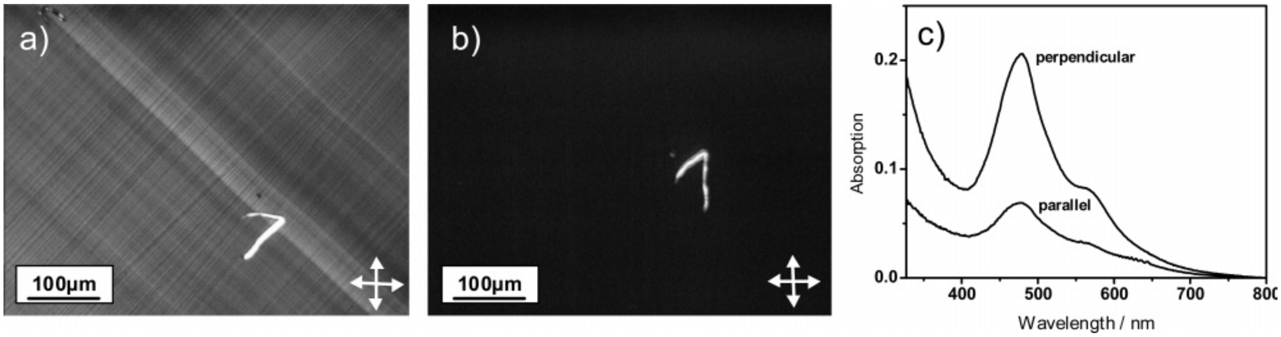

Figure 4. POM images of zone-cast C96−C$_{12}$ with (a) 45° and (b) 0° angles of the deposition direction with respect to the analyzer/polarizer axes. The number "1" confirms the same part of the sample and the same light intensity for both images (the white arrow in (a) indicates the zone-casting direction). (c) UV−vis absorption spectra in polarized light measured parallel and perpendicular to the casting direction.

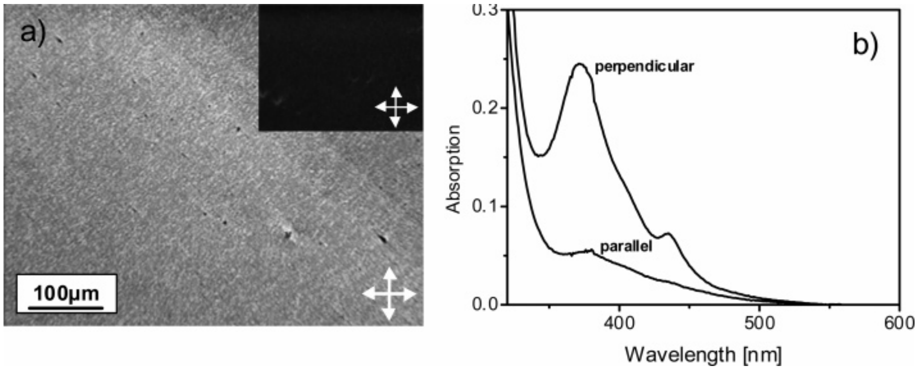

Figure 5. Optical anisotropy of the zone-cast HBC−PhC$_{12}$: (a) POM images with a 45° angle of the deposition direction related to the analyzer/polarizer axes (inset 0°) (the black arrow indicates the casting direction). (b) UV−vis absorption spectra in polarized light measured parallel and perpendicular to the casting direction.

solvent, concentration, and processing temperatures during zone-casting had to be optimized individually.

At optimized conditions the zone-casting of both discotics HBC−PhC$_{12}$ and C$_{96}$−C$_{12}$ yielded thin homogeneous layers with a thickness of ca. 50 nm over large areas. The assignment of the optical anisotropy is one important tool in the structure characterization of the uniaxially oriented films.[38−42] The optical anisotropy is strongly dependent on the transition dipole moment of the molecules, which gives in turn essential information about the molecular organization. Polarized optical microscopy (POM) images presented in Figures 4a,b and 5a indicated a high optical anisotropy of the zone-cast films. The birefringence of the surface layers under cross-polarizers was strongly dependent on the relative position of the deposition direction with respect to the analyzer/polarizer axes. It is obvious that the maximum birefringence appears at angles of 45° with respect to the deposition axis of the layers and the analyzer/polarizer axes, whereas at the coincidence of both directions a nearly complete extinction occurs. This strong optical anisotropy of the films was verified by the absorption dichroism of polarized light measured parallel and perpendicular to the casting direction. The absorption spectra are shown in Figures 4c and 5b for C96−C$_{12}$ and HBC−PhC$_{12}$, respectively. The absorption spectra of zone-cast C96−C$_{12}$, recorded with polarization perpendicular and parallel with respect to the deposition direction, displayed a maximum absorption at 480 nm accompanied by a shoulder at 565 nm. A dichroic ratio of 3.04 was determined from the maximum absorption peaks, whereby the higher absorption was observed for the mea-

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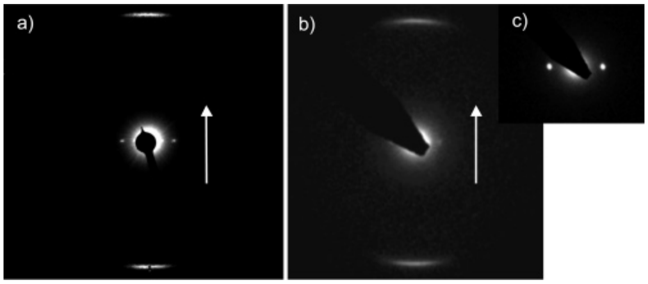

Figure 6. Electron diffraction of zone-cast films of (a) HBC−PhC$_{12}$ and (b) C96−C$_{12}$. (c) Equatorial reflections from the pattern in (b) (the arrows indicate the casting direction).

surements perpendicular to the casting direction. A similar optical behavior was found for zone-cast HBC−PhC$_{12}$ films for which the spectra revealed maximum absorption at 372 nm with a shoulder at 435 nm. A dichroic ratio of 4.52 was determined, which was considerably higher than for the C96−C$_{12}$ films.

The optical behavior of the zone-cast films is similar to that reported for thin HBC−PhC$_{12}$ films uniaxially oriented on friction-oriented PTFE.[43] The strong optical anisotropy of the zone-cast layers and on PTFE aligned films can be related to the transition dipole moments which are oriented in the aromatic core plane. Since the maximum absorption occurs perpendicular to the alignment direction, one can assume a uniaxial columnar orientation when the discotic molecules are arranged orthogonal to the columnar axes. Indeed, previous X-ray studies of extruded filaments revealed an orthogonal arrangement of the disks toward the columnar axis.[44] Therefore, the higher absorption of polarized light perpendicular to the casting direction indicates that the columnar axes are aligned with the processing direction.

To correlate the optical properties of the films with the supramolecular arrangement, the structure evaluation was performed by using electron diffraction, which enables the assignment of the intra- and intercolumnar in-plane structure within the zone-cast layers. Figure 6 presents typical electron diffraction patterns of zone-cast HBC−PhC$_{12}$ and C96−C$_{12}$. In both cases, distinct pointlike equatorial reflections indicate high uniaxial intercolumnar order with orientation of the columns in the casting direction. The appearance of only two equatorial reflections (the first and second orders) indicates the short-range intercolumnar correlation which is characteristic for the liquid crystalline phase with an increased molecular dynamics. The position of the first equatorial reflection in the electron diffraction pattern of zone-cast HBC−PhC$_{12}$ appeared at a position correlated to an intercolumnar distance of 3.02 nm within a cubic lattice, whereas the nearest hexagonal columnar distance of 3.26 nm for the zone-cast C96−C$_{12}$ was determined. Both observed intercolumnar periods were in good agreement with the lateral packing parameters obtained by X-ray diffraction for extruded filaments.

The meridional reflections, corresponding to the characteristic intracolumnar distance of 0.34 nm, confirm an orthogonal intracolumnar arrangement of the discotic molecules. Moreover, the shapes of the meridional reflections verify the high intracolumnar order. Meridional arcs imply a certain degree of columnar misalignment,[27] contrary to the reflections in the electron diffraction patterns in Figure 6 which are only laterally extended, confirming a high intracolumnar correlation, but indicating as well the absence of a pronounced intercolumnar correlation between the disks due to an increased lateral and longitudinal molecular mobility within the stacks in the liquid crystalline phase (see Figure 7).[44]

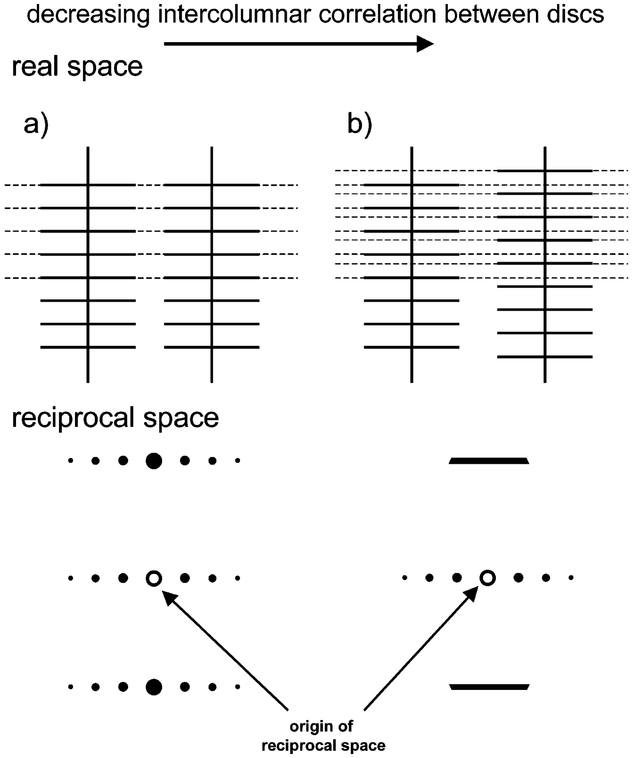

Figure 7. Effect of the structure factor on the scattering pattern of discotic molecules organized in columnar structures. Relationship between the intercolumnar correlation of the discotic molecules and the resulting scattering patterns for (a) a high intercolumnar correlation of the disks and (b) a poor correlation.

When the contrast of the electronic diffraction pattern of the zone-cast HBC−PhC$_{12}$ layer was increased, additional off-meridional reflections at an azimuthal angle of approximately 25° appeared at a correlation distance of 0.46 nm. These reflections can be related to the correlation between phenyl rings which are peripherally attached to the aromatic core. Previous quantum mechanical calculations confirmed the tilting angle of 25° of the phenyl rings with respect to the core plane, which leads to the appearance of the off-meridional reflections.[46]

Further insight into the supramolecular arrangement was obtained by HR-TEM. Figure 8 shows an HR-TEM image of a zone-cast HBC−PhC$_{12}$ film. The columns were highly uniaxially oriented in the deposition direction with a columnar length exceeding the investigated area. The fast Fourier transformation (FFT) image in Figure 8b revealed

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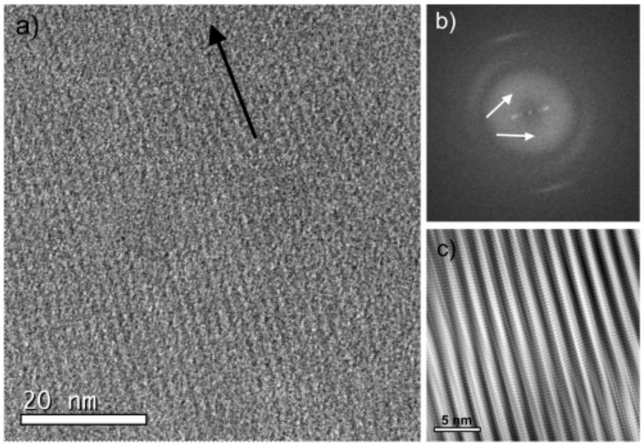

Figure 8. (a) HR-TEM image of zone-cast HBC−PhC$_{12}$ (the black arrow indicates the casting direction). (b) fast Fourier transformation (FFT) of (a) (the white arrows show higher order meridional peaks). (c) Inversed FFT image.

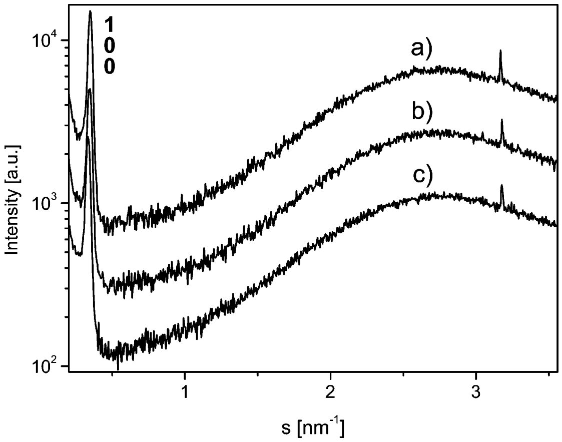

Figure 9. Temperature-dependent large-area X-ray diffraction in the reflection mode of zone-cast C96−C$_{12}$ (a) at 30 °C, (b) at 150 °C, and (c) at 30 °C after annealing (the reflection at s = 3.17 nm^{-1} is an artifact).

reflections corresponding to the intercolumnar as well as the intracolumnar periods found by the electron diffraction. Moreover, higher order meridional reflection peaks emerged, which indicated a higher intracolumnar periodicity of 1 nm. X-ray diffraction investigations of the extruded HBC−PhC$_{12}$ filaments exhibited the same superperiod along the columns, which was attributed to a helical arrangement of the discotic molecules.

The inverse FFT image not only displayed the uniaxial columnar alignment, but visualized additionally the intracolumnar periods of 0.34 nm, corresponding to the molecular stacking. This period is in good agreement with the results obtained from electron diffraction experiments. Since the electron diffraction results provide information only about the in-plane order in the zone-cast films, additional X-ray scattering experiments performed in the reflection mode reveal the out-of-plane arrangement.

The X-ray diffraction of zone-cast C96−C$_{12}$ presented in Figure 9 suggested a highly uniform out-of-plane structure with an intercolumnar period identical to that observed in-plane. During thermal treatment no changes in the supramolecular structure were determined. This is analogous to the behavior reported for the bulk material, which also did not show any temperature-dependent structural transitions.[36]

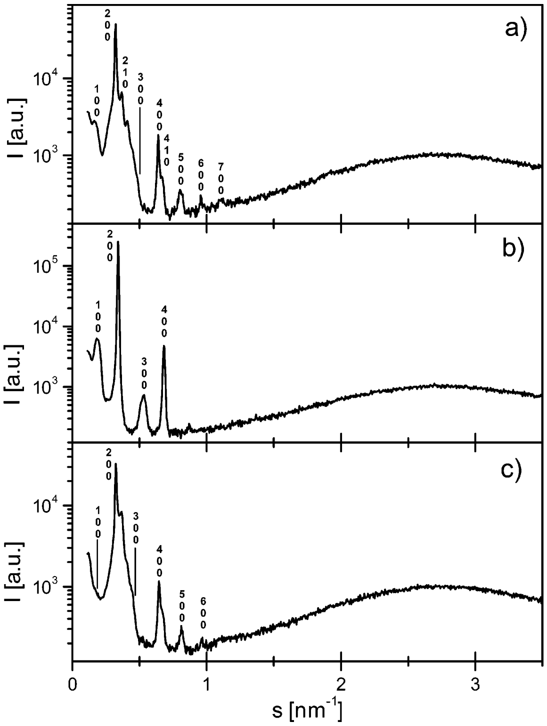

Figure 10. Temperature-dependent scattering intensity distribution as a function of the scattering vector acquired by large-area X-ray scattering measurements of zone-cast HBC−PhC$_{12}$ at (a) 30 °C, (b) 130 °C, and (c) 30 °C after annealing. Reflection peaks are assigned according to the Miller indexes (*hkl*).

In contrast, the X-ray diffraction pattern of zone-cast HBC−PhC$_{12}$ implied a more complex and temperature-dependent in-plane supramolecular arrangement. The XRD results in Figure 10 show a well-ordered HBC−PhC$_{12}$ zone-cast layer immediately after the zone-casting processing. The large number of higher order (*h*00) reflection peaks indicates a pronounced intercolumnar out-of-plane order in the investigated area. The peak positions were fitted according to a 2D lateral cubic unit cell which was in good agreement with the bulk lattice of HBC−PhC$_{12}$. The appearance of a distinctive small-angle reflection related to a periodicity of 6.25 nm, which was the double distance of a simple intercolumnar distance of 3.12 nm, confirmed a highly ordered superstructure. On the other hand, weak shoulders of the (200) and (400) reflection peaks suggested a slight degree of misalignment in the out-of-plane arrangement and were attributed to mixed lattice planes. It is assumed that not all columns in the successive layers lie on top of each other, giving rise to these additional (*hk*0) reflections. Despite these lattice displacements, the pronounced uniaxial columnar alignment was maintained as suggested by the distinct equatorial peaks in the electron diffraction and the HR-TEM image. When the zone-cast HBC−PhC$_{12}$ layer was heated above the bulk phase transition to 130 °C, two sharp reflections and two broad peaks appeared which were well fitted to a hexagonal lateral unit cell (Figure 10b). The packing parameter of a = 6.25 nm was calculated on the basis of the position of the (100) peak, implying a higher order supramolecular arrangement also at high temperatures. Interestingly, the odd and even Miller indexed reflections differed significantly in their shapes; the odd peaks were broad, whereas the even ones were sharp and distinct. An explanation might be a weaker correlation of the higher order structure than that of adjacent columns which possess the highest structural correlation, resulting in the strongest contrast during the X-ray scattering. After the material was cooled back to the room temperature phase, most of the reflections observed before annealing were recovered, except the first small-angle peak corresponding to 6.25 nm (Figure 10c), indicating that the higher order correlation disappeared after reorganization of molecules at the higher temperature phase.

In general, the X-ray diffractograms of both aligned compounds did not reveal the π-stacking correlation of the discotic molecules, being in good structural agreement with the supramolecular arrangement on the support.

In comparison to the supramolecular organization observed for bulk HBC−PhC$_{12}$ samples, the zone-cast layers revealed a remarkably higher ordered superstructure due to a significantly more efficient alignment, whereas the packing parameters were not influenced by the alignment techniques. Both investigated planes of the zone-cast films, in-plane and out-of-plane with respect to the substrate, exhibited the same value for the nearest intercolumnar packing of 3.12 nm, fitting a cubic arrangement. The large number of (h00) reflection peaks in the X-ray diffractogram for the HBC−PhC$_{12}$ zone-cast layer at room temperature indicated a higher order supramolecular correlation. Since it is known that the HBC−PhC$_{12}$ molecules are arranged in a helical manner within the columnar stacks, the appearance of the (100) reflection at 0.16 nm^{-1} before annealing might be correlated with every second column consisting of disks with the same rotation sense.[33] Interestingly, this small-angle reflection was also observed for the high-temperature phase. The appearance of such a high columnar organization in the high-temperature liquid crystalline phase of discotics has not yet been reported and is quite untypical, since the degree of order decreases usually with an increase of lateral and longitudinal dynamics of the molecules.

The structure evaluation of the zone-cast C96−C$_{12}$ layers revealed only one reflection peak related to the intercolumnar arrangement at an identical position in both planes. When the same hexagonal columnar organization in the bulk and in the zone-cast surface layers exists, then the appearance of the same unit cell parameter in both investigated planes suggests displacements of the columnar lattice along the casting direction. A uniform hexagonal columnar order on the surface would allow the observation of the characteristic (h00) scattering intensities only in-plane or out-of-plane. Nevertheless, the results from electron diffraction proved that the C96−C$_{12}$ columns were also highly oriented in the deposition direction. The packing parameters suggested that the discotic molecules HBC−PhC$_{12}$ and C96−C$_{12}$ were in an edge-on orientation with respect to the support and orthogonally arranged in the columnar stacks.

The successful fabrication of highly ordered HBC−C$_{12}$ surface layers by the zone-casting technique is based on the extraordinarily high self-aggregation of the molecules in solution and is in a close correlation to the morphology formation in drop-cast or spin-coated films. This study shows that discotic molecules with a significantly higher solubility, which is closely related to a lower self-aggregation in solution, reveal less organized films prepared by drop-casting, but form highly ordered surface layers as well when processed by the zone-casting technique. Despite the greater difficulties to determine the optimized processing conditions for compounds with a lower self-aggregation, this study confirms the great advantages of the zone-casting as an efficient alignment technique. These conclusions are essential for the film fabrication of other soluble organic semiconductors for the application in electronic devices.

Conclusions

The supramolecular order of the zone-cast films is strongly related to the nucleation and growth ability of the material. In this study, we have proven the successful fabrication of highly ordered and long-range, uniaxially aligned surface layers based on two different liquid crystalline discotics, HBC−PhC$_{12}$ and C96−C$_{12}$, by using the solution-based zone-casting technique. A high columnar orientation in the casting direction with an edge-on arrangement of the molecules was obtained, despite the great solubility of the processed compounds and their relatively weak self-organization propensity in drop-cast surface layers. Therefore, the zone-casting method is not necessarily restricted to the alignment of materials possessing a strong self-aggregation and a high nucleation, but it can also be applied to many other organic self-assembling semiconductors, making this technique more versatile. It should however be noted that the optimal processing parameters for discotic materials with poorer directional growth related to a weaker interaction between the single molecules in solution are more difficult to determine.

Finally, the successful alignment of HBC−PhC$_{12}$ and C96−C$_{12}$ as thin films opens the opportunity to employ both compounds as active layers in field-effect transistors and investigate of their bulk electronic properties.

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