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Suppressing Aggregation in a Large Polycyclic Aromatic Hydrocarbon

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Abstract: With the approach presented herein, a large aromatic π-system is synthesized, which shows extraordinarily high solubility and an effective suppression of aggregation. This was due to a distortion of the aromatic core by bulky *tert*-butyl groups and the solubilizing effects of alkyl chains in the corona of the aromatic core. Therefore not only the processing and cleaning of the materials with standard laboratory techniques became possible, but moreover the first structure-rich UV/vis and a resolved ^{1}H NMR spectra for an aromatic system two times larger than hexa-*peri*-hexabenzocoronene were recorded. The bulk properties in an extruded fiber as well as on the surface showed a columnar self-assembly including a phase in which a homeotropic alignment on a substrate was observed, which turns the material into an interesting candidate for future applications in electronic devices.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) have proven their potential as active components in field-effect transistors,[1] photovoltaic devices,[2] and light-emitting diodes.[3] Alkyl substituted hexa-*peri*-hexabenzocoronenes (HBC) are known for their unique self-organization into columnar superstructures[4] and exhibit one of the highest charge-carrier mobilities for mesogens. As the charge-carrier mobility is in close relation to the size of the aromatic core, larger π-areas are expected to lead to improved mobilities.[5a] For photovoltaic applications a high extinction coefficient over a broad range of the spectrum is a prerequisite, which can also be achieved by enlarging the aromatic core component.[5] Moreover such disks are assumed to exhibit an improved self-ordering due to the extended π-area, which is another key feature to yield high performances in electronic devices.

The main problem with increasing the aromatic core size, however, is the much stronger π-stacking interaction, which reduces solubility and limits analytical methods such as NMR spectroscopy. Additionally, it has been shown for HBCs that a reduced solubility also hampers the processing of such materials into highly oriented films.[6] Until now large PAHs were synthesized by preparing oligophenylene precursors, which were directly converted to the planarized products by an oxidative cyclodehydrogenation step. By this method it is possible to establish a remarkable number of intramolecular aryl-aryl bonds.[7]

The solubilities of these compounds are based on the alkyl chains in the corona of the molecule. Even for HBCs with strongly solubilizing alkyl chains, concentrations of 10^{-4} mol/L

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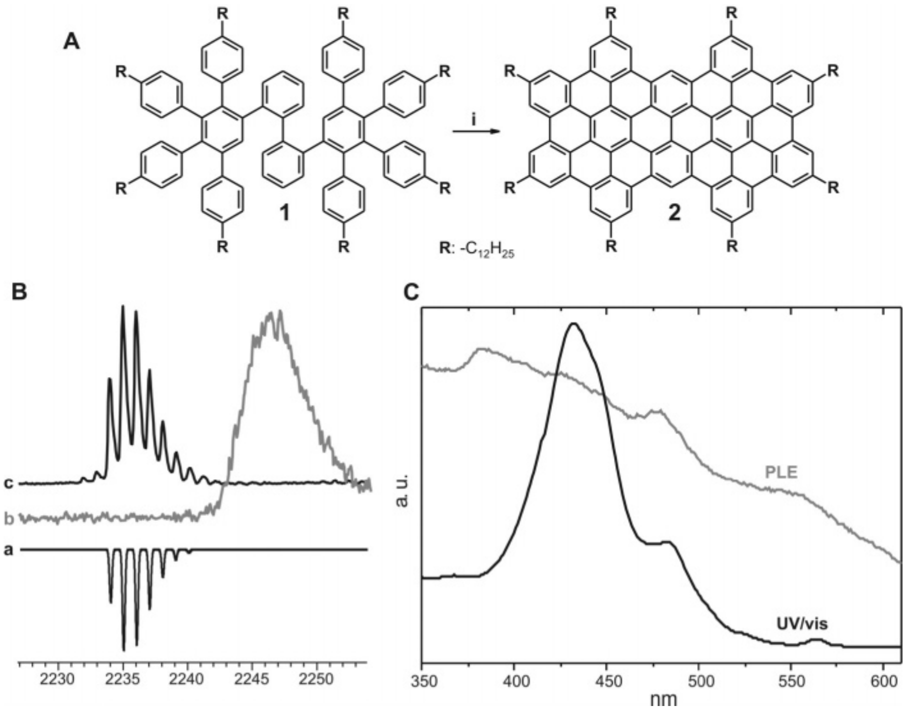

Figure 1. (A) Published synthesis toward "supernaphthalene" (**2**)[9] where i = $FeCl_3$, CH_3NO_2, CH_2Cl_2; (B) (a) simulated mass distribution of **2**, MALDI-TOF spectra of same material with different matrixes; (b) dithranol; (c) TCNQ; (C) PL excitation and UV/vis spectrum of **2**.

are needed until they appear as monomers in solution,[6] and for larger PAHs, the aggregation is exceedingly stronger.[8] Only by a sufficient suppression of the π-stacking it can be expected to acquire resolved NMR spectra and a good processability of PAHs of that size. These issues and additional difficulties have been encountered while revisiting the synthesis of a PAH consisting of 72 aromatic carbon atoms with an enlarged naphthalene-like shape, called "supernaphthalene".[9]

Results and Discussion

The cyclodehydrogenation reaction of **1** toward **2** (Figure 1A) showed a poor reproducibility, and the prepared batches differed severely in their macroscopic behavior (phase transitions, solubility, UV/vis spectra). This can be explained by the presence of different amounts of side products, such as partially fused species, where not all of the bonds have been established. Furthermore, a methodological problem was determined for matrix-assisted laser desorption−ionization time-of-flight (MALDI-TOF), which has so far been used as the main characterization technique for such PAHs.[10] In the case of **2**, the choice of matrix proved to be crucial for the resulting spectra (Figure 1B). While for 7,7,8,8-tetracyanoquinodimethane (TCNQ) only the mass peak of the product was observed, dithranol provided solely the signals of the side products. Another indication for the presence of these partially fused byproducts was the strong discrepancy between the photoluminescence (PL) excitation and the UV/vis absorption spectra (Figure 1C).

All these arguments led on one hand to the necessity to develop a more reliable synthetic route and on the other to introduce effective solubilizing features into this type of PAH to extend the range of possible analytical methods and to additionally enhance the material properties such as columnar self-assembly, film formation, and thermal phase behavior.

Since it is known that a distortion of the aromatic skeletal structure will induce a higher solubility due to suppression of association,[11] two bulky *tert*-butyl group were introduced in the indentation (Scheme 1, red area) leading to the required distortion. They are also known to hinder the aromatic cores from approaching each other.[6] Second, dodecyl chains were introduced in the corona of the molecule together with four 2-decyl-tetradecyl chains to further increase the solubility due to the suppressed chain crystallization.[12]

The synthesis of **8** started with a 4-fold Knoevennagel-condensation from 2,7-di-*tert*-butyl-pyrene-4,5,9,10-tetraone (**3**)[13] and 1,3-bis(4-dodecylphenyl)-propan-2-one (**4**) to yield the thermally unstable biscyclopentadienone-derivative **5** (Scheme 1), which was directly converted in a microwave-assisted Diels−Alder cycloaddition with the alkylated diphenylacetylene (**6**) to yield the precursor **7**. Compound **7** was submitted to a highly reproducible oxidative cyclodehydrogenation using $FeCl_3$ to afford the strained PAH **8** in 85% yield. After removal of the *tert*-butyl groups using oleum (65%) and benzene, one obtained compound **9**. Interestingly the *tert*-butyl groups could not be removed from the precursor **7** although the same harsh conditions were applied. For the cyclodehydrogenated compound **8**, the relaxation of the twisted aromatic core into the planar product **9** seems to be a key driving force for the cleavage of the substituents. The resulting material **9** showed very limited

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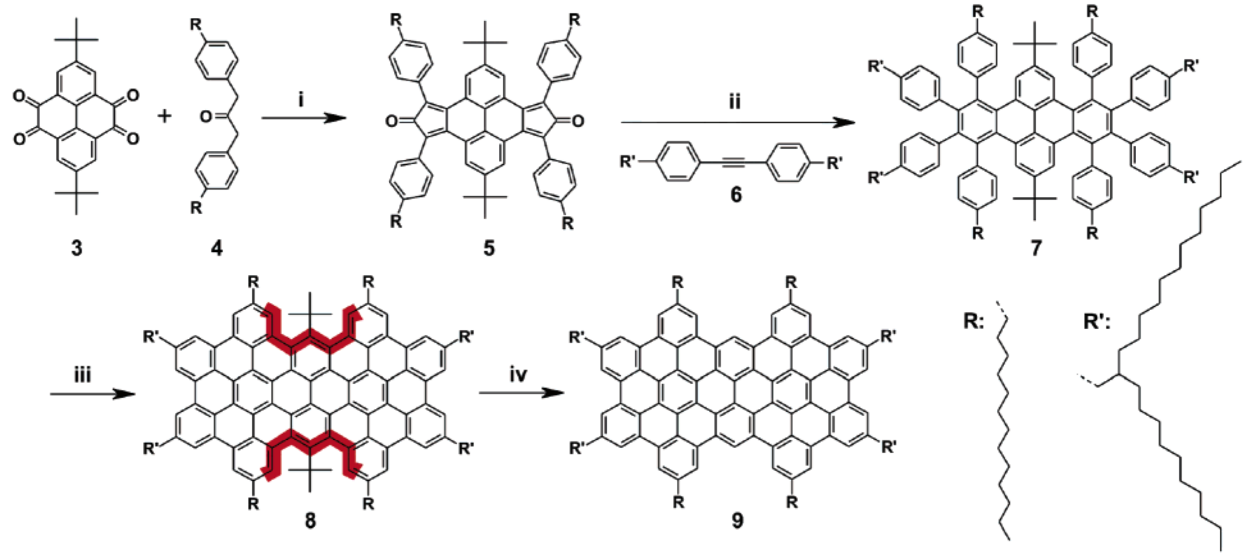
Scheme 1. Novel Synthesis of “Supernaphthalene”[a]



[a] Reagents and conditions: (i) KOH, MeOH, EtOH; 48%; (ii) Ph_2O, 21%; (iii) $FeCl_3$, CH_2Cl_2, CH_3NO_2, 85%; (iv) benzene, oleum (65%), 95%.

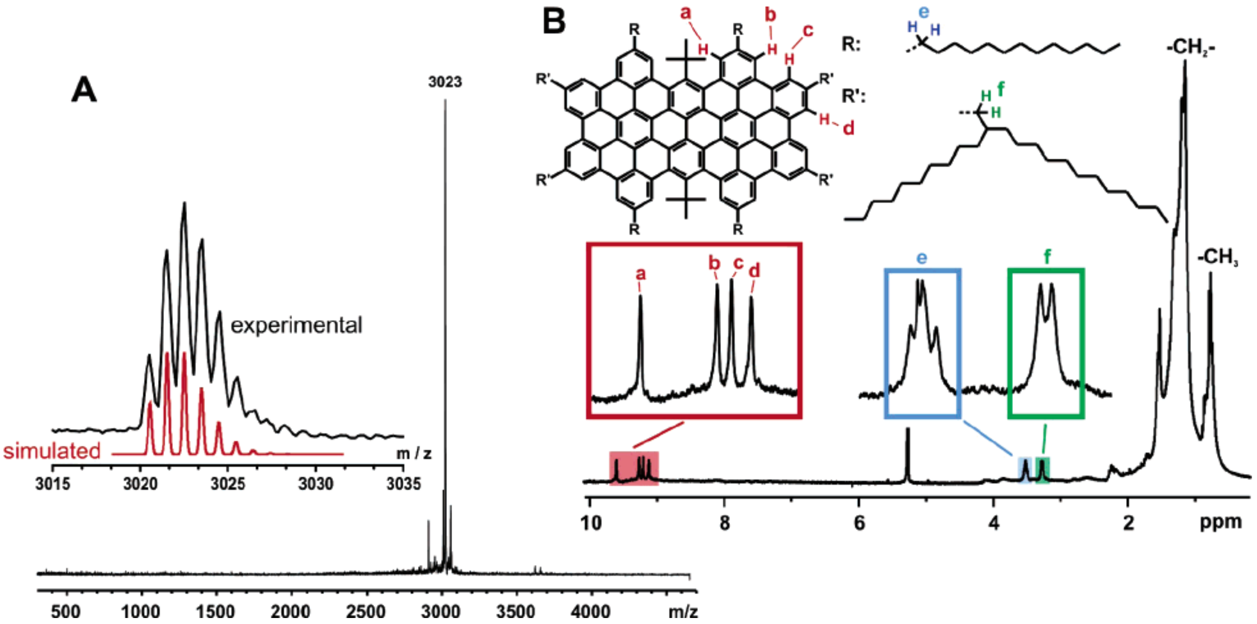


Figure 2. (A) MALDI-TOF of 8; (B) ^1H NMR of 8 in CD_2Cl_2/CS_2. Protons were assigned using HH correlation spectroscopy and nuclear Overhauser enhancement spectroscopy.

solubility and therefore contradicted the observations made for the good soluble compound **2**, supporting the possible existence of side products, which interfere with the π-interactions and induce the observed solubility for **2**.

In the MALDI-TOF spectrum (Figure 2A), the product was clearly identified, and the comparison with the simulation confirmed the successful cyclodehydrogenation. Depending on the laser attenuation, a fragmentation of the molecule could be observed, leading to the observed small peaks in the spectrum (Figure 2A). The ^1H NMR spectrum of **8** (Figure 2B) (CD_2Cl_2/CS_2) showed the resolved resonances of the four aromatic protons, which could be assigned by HH COSY and NOESY. Contrary to other PAHs, such as alkylated hexa-*peri*-hexabenzocoronenes, the chemical shifts of the aromatic resonances for **8** were independent of concentration and temperature, clearly indicating minimum or no aggregation in solution.[6] In contrast to the novel synthesis, the published route[9] did not yield a material that allowed the recording of a resolved NMR spectrum, indicating the enhanced purity of the new material **8**.

On the basis of theoretical calculations,[14] it was shown that the cis and the trans conformation exhibit almost the same heat of formation and therefore both conformers can be formed during the cyclodehydrogenation (Figure 3A). However, the observed four aromatic signals in the ^1H NMR implied that either only one conformer is present or a flipping of the *tert*-butyl groups occurs.

The possibility for the conformational change from cis to trans was investigated by density functional calculations of a section of the molecule (parts B and C of Figure 3).[15] Within this section the space coordinates of four carbon atoms were fixed in the simulations (Figure 3B, orange), whereby all other atoms were

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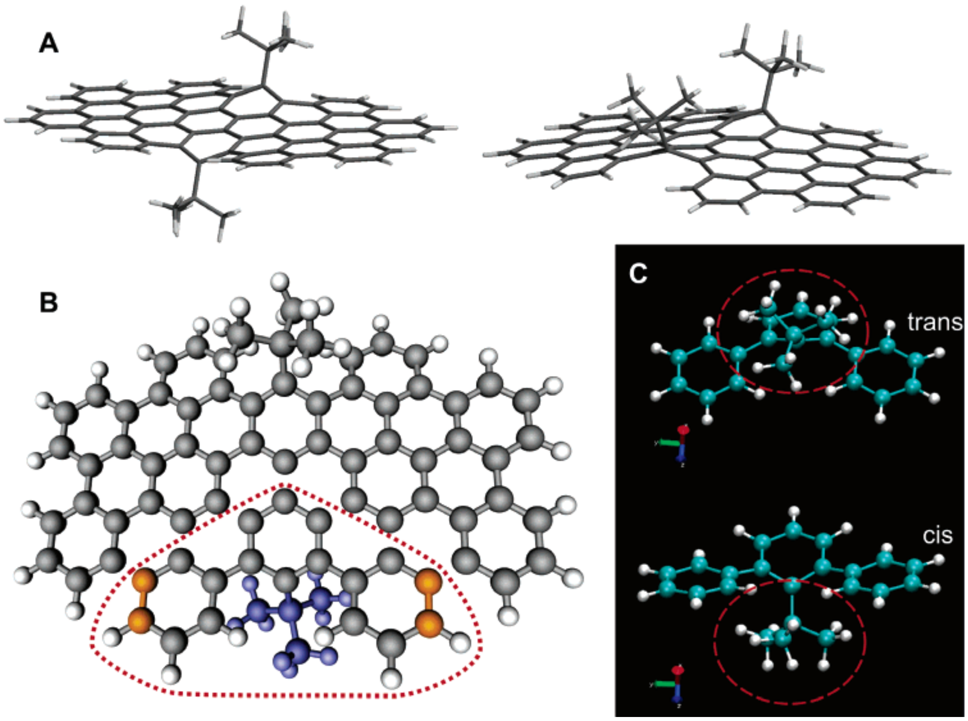

Figure 3. (A) Cis−trans conformation of 8 (alkyl chains are ommitted for clarity); (B) structure of trans conformation, selected section (red dotted line) for the density functional simulation and carbon atoms fixed in the simulations (orange), the *tert*-butyl group was colored blue for a better visualization; (C) ground-state conformation of cis and trans functional groups.

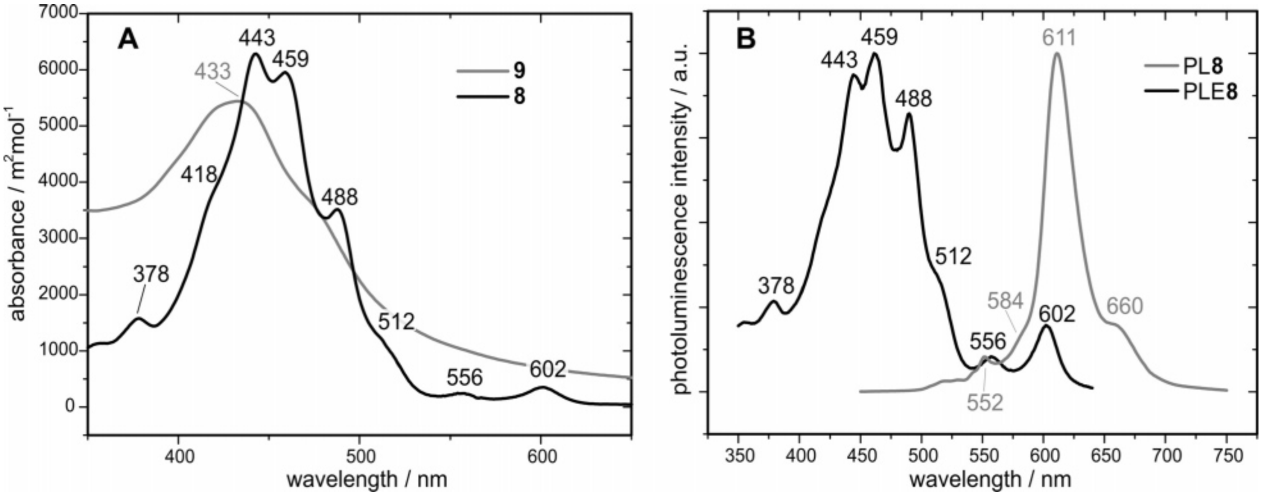

Figure 4. (A) UV/vis of **8** (black) compared to the fully planarized derivative 9 (grey); (B) PL excitation (black) and emission (gray) of **8** (4.52×10^{-6} mol/L) in THF.

fully relaxed. This fragment showed a similar flexibility with respect to the elasticity of the carbon−carbon bonds of the whole molecule, as the rigid entities were placed at the very end of the substructure. It also has to be considered that this part is usually connected to the rest of the molecule by seven covalent bonds, exerting further resistance to a conformational change. The energy barrier for transitions was calculated with the nudged elastic band method[16] and was found to exceed 1 eV/atom. This indicates that every bond of the segment would have to stabilize at least a strain energy of 450 kJ/mol; hence the molecule is more likely to fragment than changing its conformation. As a consequence the efficient aggregation suppression observed in the ^{1}H NMR was due to the bulky side chains and the fixed *tert*-butyl groups and was not partially enhanced by any disturbing effect of a dynamic conformational change.

The UV/vis spectrum of **8**, recorded in THF, showed a large number of transition bands (Figure 4A) typical for PAHs and a more than three times higher molar extinction coefficient relative to the smaller HBC.[6] As already reported for [*n*]paracyclophanes,[17] the bathochromic shift seen for **8** with respect to **9** resulted from the distortion of the aromatic core caused by the *tert*-butyl groups, which induced a severe bending from planarity of the aromatic entities attached to them (Figure SI 1). The barely soluble material **9** could not be subjected to any solution-

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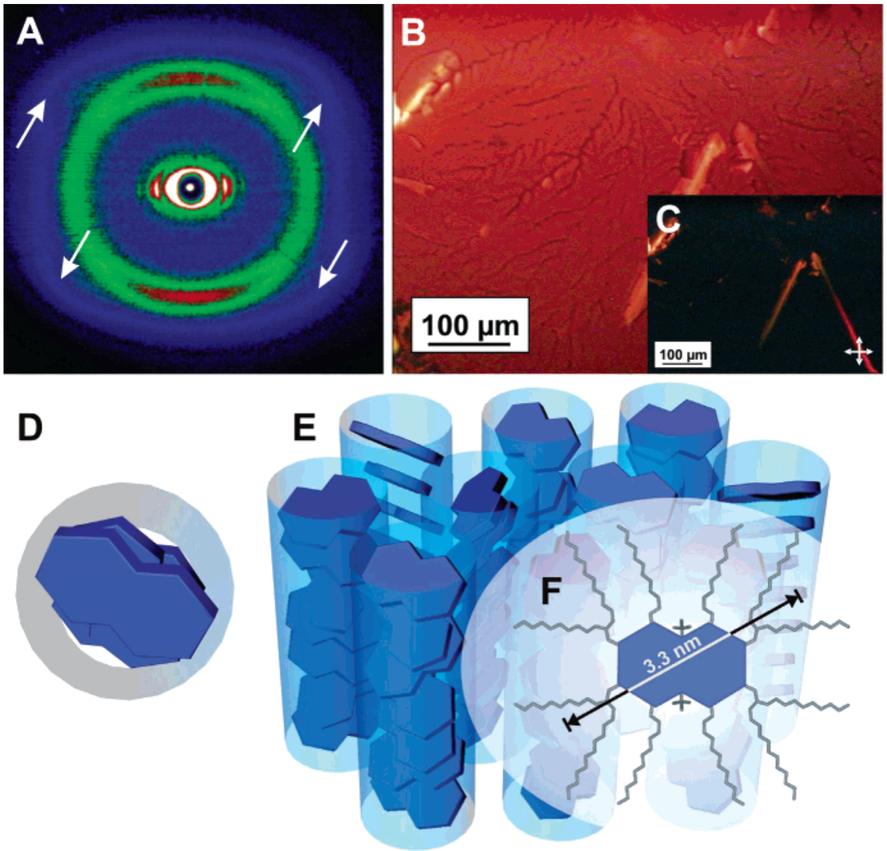

Figure 5. (A) 2D-WAXS of an extruded fiber of **8** at room temperature (arrows indicate tilted arrangement); (B) optical microsopy image of **8** at 370 °C; (C) cross-polarized optical microscopy image of **8** at 370 °C; (D) self-assembled column of **8** (top view); (E) hexagonal columnar arrangement of **8** in the bulk (alkyl chains are ommitted for clarity); (F) calculated dimensions of **8** with respect to hexagonal packing parameter (a = 3.3 nm).

based analytical techniques except UV/vis and PL. For the UV/vis measurements the compound had to be refluxed overnight in THF to dissolve sufficient material. The very pronounced association in even strongly diluted solutions led to a broadening of the absorption spectrum (Figure 4A) with a maximum absorption peak at 433 nm.

The PL emission spectrum (Figure 4B) of **8**, appeared simplified, which can be attributed to the low symmetry,[18] while the high aggregation of **9** led to a complete quenching of the fluorescence. For **8** quantum yields of 3% were determined, which correspond roughly to those of HBCs.[6] In contrast to compound **2** (parts A and C of Figure 1), the band structure of the PL excitation spectrum of **8** perfectly matched the one obtained in the UV/vis measurements (parts A and B of Figure 4), indicating the high purity of the material.

In the differential scanning calorimetry (DSC) of **8**, an endothermic transition was observed at 60 °C. As in the 2D-wide-angle X-ray scattering (2D-WAXS) diffractogram of an extruded fiber no change in the reflections appeared at this temperature, the transition was attributed to a reorganization of the alkyl chains. As expected, the fully planarized compound **9** did not show any thermal transition until degradation. In an extruded fiber[19] of **8**, the disks self-organized in columnar structures along the extrusion direction (Figure 5A). From the equatorial reflections, an intercolumnar hexagonal unit cell could be assigned with $a = 3.3$ nm as the packing parameter, which fits the calculated dimensions by taking into account an interdigitation of the alkyl chains (Figure 5F).[20] The meridional reflections combined with the weak offset signals (Figure 5A, arrows) implied that the disks adopted a tilted arrangement with respect to the columnar axis.[21] This stands in contrast to the old pathway, which only yielded materials[9] that could not be mechanically oriented.

Although the effective suppression of the π-stacking was expected to lead to a strong reduction of the supramolecular organization of the material in the bulk,[22] **8** featured a high degree of order in the 2D-WAXS experiment. Therefore the remaining π-interaction was sufficient for the self-assembly into the already known columnar superstructures. The found hexagonal arrangement is nevertheless contradictory to the D_{2h} symmetry of the molecule, which is explained by the intermolecular arrangement induced by the bulky *tert*-butyl groups. This forces the molecules to adopt an offset angle for gaining a higher π-contact area, leading to a round columnar structure (top view) and a hexagonal arrangement as seen for HBCs (parts D and E

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of Figure 5). The high transition temperature to the isotropic melt confirms the significant degree of intracolumnar π-stacking in the bulk, which is indispensable for the intrinsic charge-carrier migration in the bulk.

Polarization microscopy (POM) allowed the application of high heating rates to suppress thermal decomposition of the material, which was not possible with DSC, and was used to investigate the crystallization behavior from the isotropic phase. Compound **8** was sandwiched between two glass slides and heated under nitrogen flow at maximum heating rate. After reaching the isotropic phase, the sample was immediately cooled. At approximately 370 °C, a dendritic texture appeared, which did not reveal birefringence in polarized light, except for some defects. This indicated a homeotropic order (parts B and C of Figure 5), which is the preferred orientation on substrates for photovoltaic applications.[23]

As for **9**, no transitions were observed; any further thermal processing of this material is futile. Nevertheless it was possible to gain drop-casted films from THF (parts A and B of Figure SI 2), where small crystallinelike objects formed. It has been shown for HBCs[6] that a close correlation exists between the association constants of the disks in solution and their film-forming properties. Only compounds with already high association constants of the disks in solution provided films with a high degree of crystallinity. Therefore it becomes obvious that **9** exhibits a high association constant in solution pointing toward a pronounced degree of aggregation and cannot be used for any kind of application in electronic devices, as for these purposes a far better solubility and a thermal phase behavior are prerequisites.

In conclusion, the novel synthetic approach proved to be highly reproducible and no discrepancies between the batches, as for **2**, could be observed for **8** and **9**. It was verified that one can record well-resolved NMR and UV/vis data from large PAHs, as compound **1** is the largest reported PAH with a resolved ^{1}H NMR spectrum.[24] To achieve this goal, two main solubilizing features had to be introduced, whereby the induced distortion and the steric requirements of the bulky *tert*-butyl groups proved to be the main argument for the solubility, the effective aggregation suppression and the thermal properties of **8**. The compound kept, however, the necessary columnar self-assembly in the bulk, which is a prerequisite for a successful charge-carrier migration along the columnar axis. Also from drop casting the material already formed homogeneous films with low crystallinity, indicating good film forming properties. With the more than three times higher molar extinction coefficient of **8** and the bathochromically shifted absorption profile relative to HBCs the material becomes an interesting candidate for future photovoltaic applications.[2a]

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Supporting Information Available: Experimental Section, PL excitation and emission spectra of **8**, POM images of **9** and schematic arrangement of **8** in the bulk. This material is available free of charge via the Internet at http://pubs.acs.org.

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