

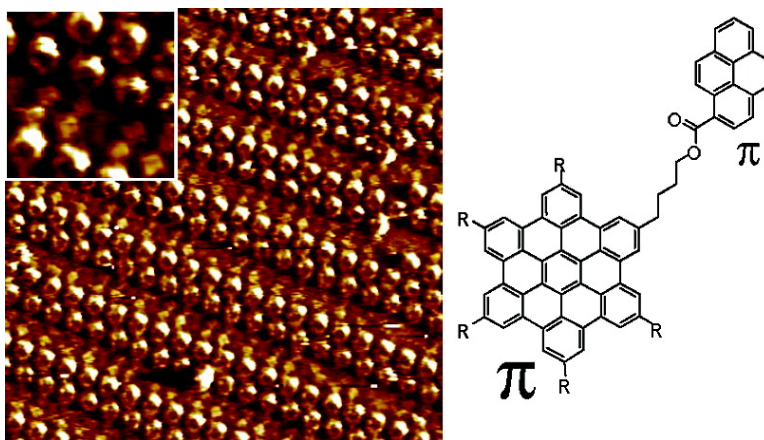
Article

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Ordered Architectures of a Soluble Hexa-*peri*-hexabenzocoronene–Pyrene Dyad: Thermotropic Bulk Properties and Nanoscale Phase Segregation at Surfaces

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Abstract: An alkylated hexa-*peri*-hexabenzocoronene with a covalently tethered pyrene unit serves as a model to study self-assembling discotic π -system dyads both in the bulk and at a surface. Wide-angle X-ray scattering, polarized light microscopy, and differential scanning calorimetry revealed bulk self-assembly into columnar structures. Relative to a control without a tethered pyrene, the new dyad exhibits a more ordered columnar phase at room temperature but with dramatically lowered isotropization temperature, facilitating homeotropic alignment. These two features are important for processing such materials into molecular electronic devices, e.g., photovoltaic diodes. Scanning tunneling microscopy at a solution–solid interface revealed uniform nanoscale segregation of the large from the small π -systems, leading to a well-defined two-dimensional crystalline monolayer, the likes of which may be employed in the future to study intramolecular electron transfer processes at surfaces, on the molecular scale.

Introduction

Understanding and controlling the self-assembly of complex π -conjugated molecular architectures with tailored functionalities into highly ordered nanostructures is important for tuning the physicochemical properties of the material, in particular in view of the fabrication of molecular electronic devices.¹ One class of organic molecular materials deserving particular attention is discotic liquid crystalline derivatives of hexa-*peri*-hexabenzocoronene (HBC),² a polycyclic aromatic hydrocarbon (PAH)³ with a large π -conjugated core consisting of 42 carbons. These discrete synthetic nanographenes self-assemble into highly ordered columnar structures in the bulk and crystalline monolayers at interfaces. The high order, together with the large functional electronic component (PAH core), endows excep-

tional one-dimensional transport properties,⁴ which so far have been exploited in the development of a solar cell.⁵ Moreover, HBCs can be easily functionalized asymmetrically in the peripheral positions,⁶ allowing surface patterning, modulation of electronic properties of the molecule, and modes of self-assembly.

Tethering of additional functional π -systems to self-organizing organic electronic components is an important approach in the frame of the fabrication of molecular electronics devices.⁷ During the course of designing more complex dyads with HBC linked to other functional π -systems, we chose to investigate first a system with a simple, small aromatic unit. In this way, we could delineate the effect of the presence of a smaller disklike block on the self-assembly before moving on to systems with more function, which demand consideration of other effects such as electron-transfer processes, charge-transfer complexes, etc. For this study, we prepared the novel HBC derivative (HBC-C₄-P, **1**) which has a pyrene unit attached to the HBC core

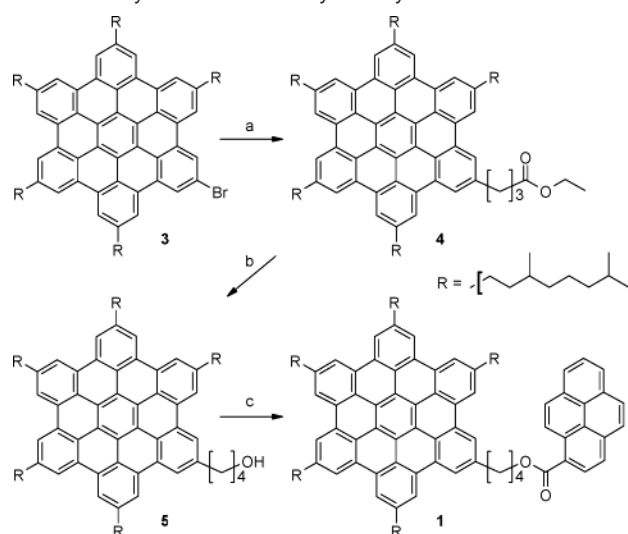
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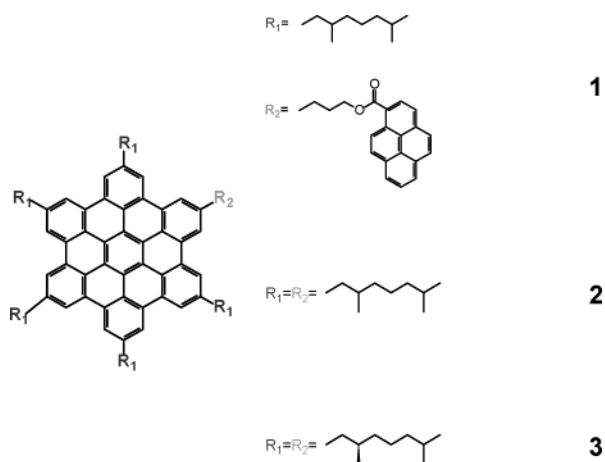
- (1) Lehn, J. M. *Science* **2002**, *29*, 2400–2403.
- (2) Watson, M. D.; Fechtenkotter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300.
- (3) (a) Clar, E. *The Aromatic Sextet*; John Wiley: London, 1972. (b) Diederich, F.; Rubin, Y. *Angew. Chem.* **1992**, *104*, 1123–1146; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101–1123. (c) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häußling, L.; Siemensmeyer, K.; Eitzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143. (d) Faust, R. *Angew. Chem.* **1995**, *107*, 1559–1562; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429–1432. (e) Hudgins, D. M.; Allamandola, L. J. *J. Phys. Chem.* **1995**, *99*, 3033–3046. (f) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963–10968. (g) Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 6000–6006. (h) Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476–2477. (i) Draper, S. M.; Gregg, D. J.; Madathil, R. *J. Am. Chem. Soc.* **2002**, *124*, 3486–3487.

- (4) (a) Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1609. (b) van de Craats, A. M.; Warman, J. M. *Adv. Mater.* **2001**, *13*, 130–133.
- (5) Schmidt-Mende, L.; Fechtenkotter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119–1123.
- (6) (a) Ito, S.; Wehmeier, M.; Brand, J. D.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 4327–4342. (b) Grimsdale, A. C.; Bauerr, R.; Weil, T.; Tchegotareva, N.; Wu, J.; Watson, M.; Müllen, K. *Synthesis-Stuttgart* **2002**, *9*, 1229–38.
- (7) (a) Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F.; Liu, S.-G.; Echegoyen, L.; Armaroli, N.; Barigelletti, F.; Ouali, L.; Krasnikov, V.; Hadziioannou, G. *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479. (b) Cravino, A.; Sariciftci, N. S. *J. Mater. Chem.* **2002**, *12*, 1931–1943. (c) Pourtois, G.; Beljonne, D.; Cornil, J.; Ratner, M. A.; Brédas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 4436–4447.

Scheme 1. Synthesis of HCB–Pyrene Dyad **1**^a

^a a, $\text{BrZn}(\text{CH}_2)_3\text{CO}_2\text{Et}$, $\text{Cl}_2\text{Pd}(\text{dppf})\cdot\text{MeCl}_2$, THF; b, LAH, THF; c, pyrene-1- CO_2H , EDC, DMAP, MeCl_2 .

through a flexible spacer. HCB compound **2**, which carries only



the solubilizing chains used in compound **1**, serves as a control. Herein we report the synthesis and structural characterization, over many length scales. While differential scanning calorimetry (DSC), X-ray diffraction, and polarized optical microscopy (POM) revealed the thermotropic behavior in the bulk, scanning tunneling microscopy (STM) was employed to study the self-assembly in crystalline nanoarchitectures at the graphite–solution interface.

Results and Discussion

Synthesis. The synthesis of HCB–pyrene dyad **1** is outlined in Scheme 1. Negishi type coupling of 2-bromo-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene **3**⁸ with commercially available 3-ethoxycarbonylpropyl-1-zinc bromide provided ester-functionalized HCB **4**, which was reduced to the alcohol **5** with LiAlH_4 . Finally, carbodiimide-promoted esterification of **5** with pyrene-1-carboxylic acid yielded the desired target **1**.

Bulk Properties. DSC traces for compounds **1** and **2** are shown in Figure 1, with relevant thermal data summarized in

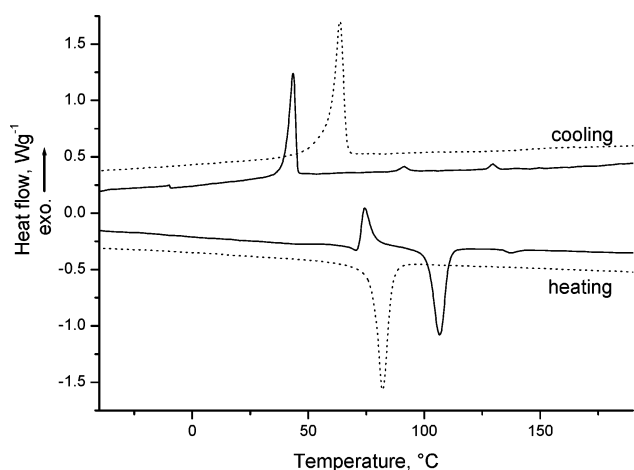


Figure 1. DSC thermograms of **1** (—) and **2** (···); heating and cooling rate 10 °C/min.

Table 1. Thermal Data for **1** and **2** and Unit Cells for the Hexagonally Packed Mesophases

compound	temp ($K-D_{ho}$) [°C]	LC phase		temp ($D_{ho}-I$) [°C]
		a [nm]	d [nm] (T [°C])	
HCB-C ₄ -P (1)	105	2.73	0.370 (125)	136
HCB (2)	82	2.64	0.368 (130)	420

Table 1. The control HCB, **2**, exhibits only one phase transition (first order, 82 °C, upon heating) separating the polycrystalline state (K)⁹ from the ordered discotic hexagonal mesophase (D_{ho}).⁸ Isotropization occurs upon heating to 420 °C, as observed by POM. This temperature is above the onset of thermal decomposition, but can be realized without a large change in the material's constitution when the thermal treatment is completed at fast rates in an inert atmosphere.

The DSC trace of HCB–pyrene dyad **1** has a significantly different profile. An apparent first-order exotherm (cold crystallization) immediately precedes a first-order endotherm corresponding to the transition from the polycrystalline (K) phase to the columnar hexagonal (D_h) phase (see below for phase assignments). The polycrystalline–mesophase transition temperature is increased by 23 °C relative to that of the control HCB **2**, indicating additional stabilizing interactions leading to a more thermally stable polycrystalline phase. Further, a substantially larger thermal hysteresis (64 °C) is observed on cooling relative to HCB **2** (18.5 °C). The thermal behavior suggests that the pyrene units are involved in the formation of the polycrystalline state, i.e., are not spectators randomly distributed within the liquidlike alkyl chain sheaths of the columns. Possibly a nanophase segregation, observed by STM at the solid–liquid interface (see below), occurs in the low-temperature bulk state as well. This would provide an additional stabilization to the crystal phase, similar to the already known case of triphenylene derivatives bearing one bulky aromatic substituent.¹⁰ The weak endotherm at 136 °C (heating scan) is confirmed by POM and wide-angle X-ray scattering (WAXS) as isotropization, ~280 °C lower than for control HCB **2**.

(8) Fechtenkötter, A.; Tchegobotava, N.; Watson, M. D.; Müllen, K. *Tetrahedron* **2001**, *57*, 3769–3783.

(9) (a) Bunk, O.; Nielsen, M. M.; Sölling, T. I.; van de Craats, A. M.; Stutzmann, N. *J. Am. Chem. Soc.* **2003**, *125*, 2252–2258. (b) van de Craats, A. M.; Stutzmann, N.; Bunk, O.; Nielsen, M. M.; Watson, M. D.; Müllen, K.; Chanzy, H. D.; Siringhaus, H.; Friend, R. H. *Adv. Mater.* **2003**, *15*, 495–99.

(10) Kettner, A.; Wendorff, J. H. *Liq. Cryst.* **1999**, *26*, 483–487.

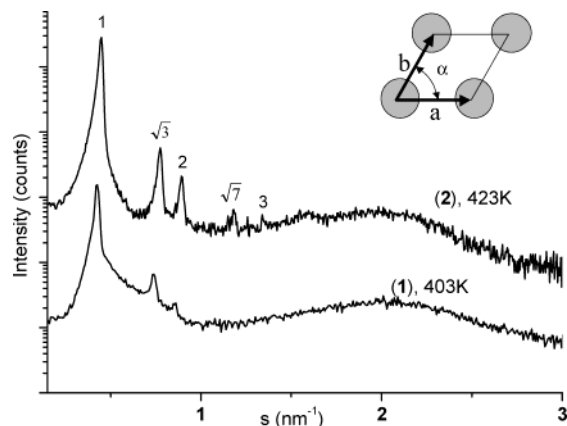


Figure 2. Equatorial integration of WAXS patterns obtained from oriented fibers of **1** and **2** illustrating hexagonal packing of columns in the high-temperature mesophase.

To gain further insight into the thermotropic behavior, temperature-dependent WAXS was performed on oriented samples. Good macroscopic orientation of the columnar structures along the axes of filaments was accomplished by extrusion of samples, heated to their mesophase, through a 0.7 mm circular die. Two-dimensional (2D) WAXS transmission measurements,^{11a} in concert with one-dimensional reflection measurements, collected with the beam perpendicular to the orientation direction, provided more detailed information.

Figure 2 displays the equatorial intensity distributions integrated from the 2D WAXS diffractograms recorded in the mesophases of **1** and **2**. The sequence of reflections with relative positions 1, $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$ is characteristic for a hexagonal packing of the columns.¹² The lattice constants (a) for the hexagonal unit cells and the intracolumnar disk–disk distances (d , observed on the meridian of 2D diffractograms) are given in Table 1. While **1** and **2** may be indexed with approximately the same “ a ”, the profile in the low-angle region from **1** is markedly different. The broadness and asymmetric shape of the [100] peak and the following sloping baseline can be attributed to greater lateral fluctuation of the disks spinning about the columnar axes within the 2D lattice,¹⁰ which we attribute to steric perturbation by the bulky tethered pyrene. It is more reasonable then to designate this phase as D_{hd} rather than D_h (where “ d ” indicates disordered). This is one probable reason for the lower isotropization temperature via diminishing *inter-columnar* cohesiveness of the mesophase. However, we cannot exclude some contribution of the pyrene as a bound solvent, which might intercalate and disrupt the columns at the isotropization temperature.

At room temperature, compound **2** is known⁹ to exhibit a pseudohexagonal columnar packing with disks tilted 45–50° relative to the columnar axes. Likewise, equatorial intensity distributions¹¹ from 2D WAXS of an as-extruded fiber of **1** gave a similar pattern, but with very broad reflections that can be indexed to a pseudohexagonal cell with area 10% larger than for **2**. The broadness of the peaks and the larger unit cell can be attributed to random accommodation of the pyrene units

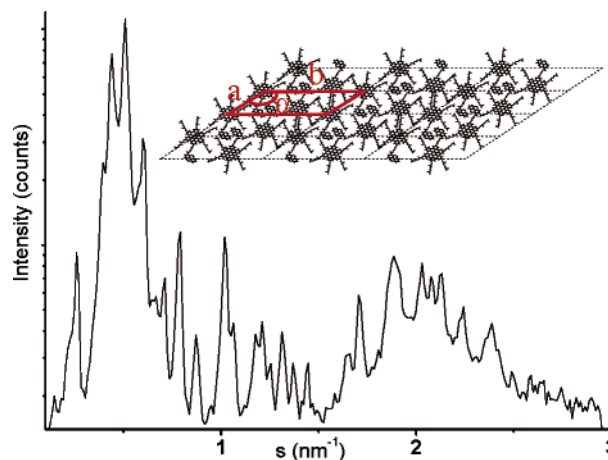


Figure 3. Equatorial integration of WAXS pattern obtained from an oriented fiber of **1** in the room temperature polycrystalline phase after slowly cooling from the melt and annealing just below the first-order endotherm. Inset shows proposed¹¹ 2D lateral packing in a 2D monoclinic cell with $a = 2.58$ nm, $b = 5.86$ nm, and $\alpha = 140^\circ$.

within the columnar packing. As for **2**, reflexes on the meridian of 2D WAXS diffractograms indicate a mean period of approximately 0.5 nm along the columns corresponding to a tilt angle between the disk planes and the columnar axes of $\arccos(3.5 \text{ \AA}/5 \text{ \AA}) = 45^\circ$.

After cooling from the melt and annealing at 85 °C, near the peak of the cold crystallization (DSC, Figure 1), the equatorial intensity distribution shown in Figure 3 was obtained. The large number and sharpness of higher order reflections clearly reflect longer range order than seen in **2**. The simplest assignment,¹¹ which matches 22 of the first 24 peaks, gives a monoclinic unit cell with $a = 2.58$ nm, $b = 5.86$ nm, and $\alpha = 140^\circ$. In light of the apparent increased order and concomitant higher thermal stability of the room temperature phase of **1** relative to **2**, any model where there is no organization of the pyrene units seems unlikely. The parent unsubstituted pyrene crystallizes in a sandwich–herringbone arrangement,¹³ and this tendency could prevail here where pyrene units from adjacent columns pair up to dimer “cross-links” or form stacks parallel to the HBC columns. A proposed 2D lateral packing arrangement is included in Figure 3. This model compares well with the self-assembled 2D crystalline structure from compound **1** at a solid–liquid interface (see below).

Molecular alignment plays an important role in organic electronic device performance. It is known that thermal annealing of column-forming materials after isotropization can provide homeotropic alignment,¹⁴ that is, columns aligned perpendicular to the substrate. Such an alignment of the one-dimensional conducting pathways would surely be beneficial for the optimization of solar cells, the target of future designs of HBC–acceptor dyads. Accordingly, slow cooling of a molten, isotropic thin film of **1** between two glass slides was shown by POM to give homeotropic alignment.¹¹ Lowering the isotropization to a practical processing temperature while increasing order at

(11) Supporting Information: (a) 2D WAXS diffractograms and their integrations; (b) tabulated reflexes and Miller indices; (c) optical micrograph of homeotropically aligned thin film of **1**; (d) survey (large-area) STM image of **1** at the graphite/solution interface.

(12) Chandrasekhar, S.; Sadashiva, B. K.; Surish, K. A. *Pramana* **1977**, *9*, 471–480.

(13) Hazel, A. C.; Larsen, F. K.; Lehmann, M. S. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2977–2984.

(14) (a) Kroon, J. M.; Koehorst, R. B. M.; van Dijk, M.; Sanders, G. M.; Sudhölter, E. J. R. *J. Mater. Chem.* **1997**, *7*, 615–624. (b) Hatsusaka, K.; Ohto, K.; Yamamoto, I.; Shirai, H. *J. Mater. Chem.* **2001**, *11*, 423–433. (c) Jung, H. T.; Kim, S. O.; Ko, Y. K.; Yoon, D. K.; Hudson, S. D.; Percec, V.; Holerca, M. N.; Cho, W. D.; Mosier, P. E. *Macromolecules* **2002**, *35*, 3717–3721.

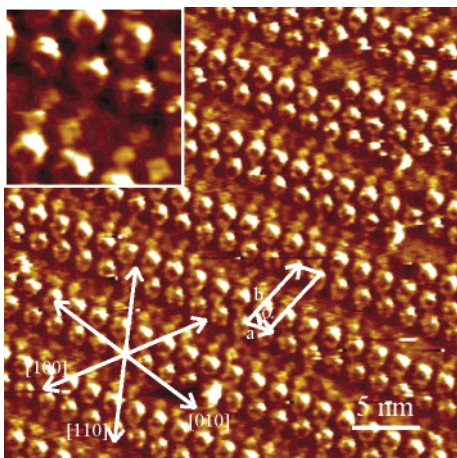


Figure 4. STM current image of **1** at the solid–liquid interface. Dimer row structures with smaller and darker bright spots between the dimer gaps. Inset: zoom-in image. Bias voltage = 1.2 V (tip positive); average tunneling current = 100 pA; scan rate = 30 line/s.

ambient temperature represents a serendipitous and hopefully general consequence of attaching functional π -systems, which could promote photovoltaic activity.

Solid–Liquid Interface. Scanning tunneling microscopy (STM) is an extremely valuable technique, which allows mapping, with a submolecular resolution, of the electronic states near the frontier orbitals of molecular adsorbates.¹⁵ In addition, its versatility enables the *in situ* exploration of the self-assembly of an organic molecule at the interface between its own solution in a low polarity solvent and a solid conductive substrate.¹⁶

A previous STM study has shown that the chiral version of **2**, namely, molecule **3**, can pack at the solution–graphite interface in a hexagonal arrangement.¹⁷ The measured area of the unit cell $A = (3.20 \pm 0.36) \text{ nm}^2$ is much smaller than the theoretical one $A = 4.57 \text{ nm}^2$ based on van der Waals contours. Maintaining the 3-fold symmetry of the molecular arrangement, one can roughly estimate that the HBC core plus three methylene units per side chain are packed on the substrate. This is in line with the theoretical calculation which indicates, from such a configuration, an occupied area of $\sim 3.1 \text{ nm}^2$. The methyl branch at the γ -carbon is likely to sterically inhibit the packing of the rest of the chain onto the surface, leaving it to extend upward into the solution.

A significantly different packing of the adlayer of the HCB–pyrene dyad **1** on the basal plane of the highly oriented pyrolytic graphite (HOPG) surface has been obtained, as shown in Figure 4. This STM current image clearly reveals a 2D crystalline dimer structure. The bright spots (corresponding to high tunneling current) can be attributed to the HBC π -conjugated cores, since the energy difference between their frontier orbital and the Fermi

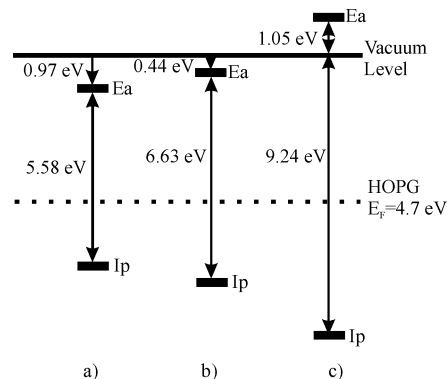


Figure 5. Scheme of the adiabatic electron affinities (E_a) and ionization potentials (I_p) for (a) HBC, (b) pyrene, and (c) aliphatic chain ($\text{C}_{10}\text{H}_{22}$) in vacuo, as calculated with full density functional optimizations. Since the experimental results have been obtained in condensed phases, for the interpretation of the STM contrasts they have to be considered only for the energy differences of the levels and not for their absolute values.

level of the substrate is relatively small.¹⁸ The aliphatic side chains have not been resolved, probably due to their high conformational mobility on a time scale faster than the STM imaging. The determined unit cell parameters are $a = (1.86 \pm 0.02) \text{ nm}$, $b = (5.69 \pm 0.11) \text{ nm}$, and $\alpha = (73.4 \pm 1.6)^\circ$. Consequently, the corresponding area of the cell, occupied by two molecules, amounts to $(10.1 \pm 0.2) \text{ nm}^2$, half of which is quite close to the theoretical van der Waals contour of a single molecule (5.2 nm^2). This latter has been computed taking into account that only the pyrene, the HBC core, and three methylene units of each of the alkyl side chains are lying flat on the graphite surface.

A careful inspection of Figure 4 reveals some smaller bright spots tightly packed near the HBC cores. This feature becomes even more evident in the zoom-in image depicted in the top left corner.¹⁹ Compared to the HBC cores, these smaller bright spots exhibit a smaller current. This feature can be ascribed to the pyrene moieties, which possess an ionization potential energy slightly larger than that of the HBC core (Figure 5). The difference between the HOMO of the pyrene and the Fermi level of the substrate is roughly 0.5 eV larger than that of the HBC. Unlike the aliphatic side chains that have a HOMO which is energetically far from the Fermi level of the HOPG and thus cause a very small current in STM, the pyrene side groups can be resolved and exhibit a current which is between that of HBC and the aliphatic chains.

Strohmaier et al. carried out a series of STM studies on planar electron donor and acceptor PAHs.²⁰ A clear dependence of the tunneling current on the chemical nature of the functionalities of the adsorbates was suggested, where the image contrast is in accordance with the frontier orbitals. However, the measurements on each type of PAH were performed separately, and different tips can be the origin of artifacts. We have reported here the first simultaneous STM visualization of diverse moieties having various electronic properties. Such a system is highly important to discern the role of topography and local electronic properties on the contrast in current STM imaging of different

(15) (a) Gimzewski, J. K.; Joachim, C. *Science* **1999**, *283*, 1683–1688. (b) Yazdani, A.; Lieber, C. M. *Nature* **1999**, *401*, 227–230. (16) (a) McGonigal, G. C.; Bernhardt, R. H.; Thomson, D. J. *Appl. Phys. Lett.* **1990**, *57*, 28–30. (b) Rabe, J. P.; Buchholz, S. *Science* **1991**, *253*, 424–427. (c) Cyr, D. M.; Venkataraman, B.; Flynn, G. W. *Chem. Mater.* **1996**, *8*, 1600–1615. (d) Claypool, C. L.; Faglioni, F.; Goddard, W. A., III; Gray, H. B.; Lewis, N.; Marcus, R. A. *J. Phys. Chem. B* **1997**, *101*, 5978–5995. (e) Qiu, X.; Wang, C.; Zeng, Q.; Xu, B.; Yin, S.; Wang, H.; Xu, S.; Bai, C. *J. Am. Chem. Soc.* **2000**, *122*, 5550–5556. (f) Gesquière, A.; Abdel-Mottaleb, M. M. S.; De Feyter, S.; De Schryver, F. C.; Schoonbeek, F.; van Esch, J.; Kellogg, R. M.; Feringa, B. L.; Calderone, A.; Lazzaroni, R.; Brédas, J. L. *Langmuir* **2000**, *16*, 10385–10391. (g) Isoda, S.; Nemoto, T.; Fujiwara, E.; Adachi, Y.; Kobayashi, T. *J. Cryst. Growth* **2001**, *229*, 574–579. (17) Samorí, P.; Fechtenkötter, A.; Böhme, T.; Jäckel, F.; Müllen, K.; Rabe, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 11462–11467.

(18) Lazzaroni, R.; Calderone, A.; Brédas, J. L.; Rabe, J. P. *J. Chem. Phys.* **1997**, *107*, 99–105.

(19) By changing the STM tip and varying the scanning direction through imaging differently oriented domains, we could rule out imaging artifacts during the measurements.

(20) Strohmaier, R.; Petersen, J.; Gompf, B.; Eisenmenger, W. *Surf. Sci.* **1998**, *418*, 91–104.

molecular adsorbates. Covalently bonded, but nanophase-separated 2D aromatic moieties eliminates the first complication by keeping the topography quasi-constant, allowing a contrast image which is a true map of the electronic properties of the adlayer.

Concluding Remarks

The structural characterization of the bulk phase of a pyrene-substituted HBC revealed ordered architectures both in the room temperature polycrystalline state and in the higher temperature mesophase, the latter existing over a temperature range which reflects the nature of the substituents in the peripheral positions. The three-dimensional (3D) order indicates that the two aromatic units with different sizes do not tend to stack in hybrid HBC–pyrene columns. Increased order and thermal stability of the polycrystalline phase are explained by a proposed model involving interaction between nanophase-separated pyrene units. This postulation is in very good accordance with the nanoscale phase segregation monitored in monolayers by STM. The latter crystalline arrangement, which is stable on the time scale of several minutes, offers intriguing prospects for scanning tunneling spectroscopy (STS) studies on the two coplanar moieties, also upon photoexcitation. Furthermore, the possibility to grow highly ordered 2D and 3D structures of hybrid organic architectures containing pyrene moieties could open perspectives for the development of local scale polarity measurements characterized by higher resolution and better reproducibility. We continue to prepare other HBC– π -system dyads in which the tethered system is expected to contribute some electronic function, e.g., photoexcited charge separation and transport as is desirable in photovoltaic diodes. These could provide insight into the role of energy or electron transfer in such a system at surfaces.

Experimental Section

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ on a Bruker 700 DRX using the solvent proton or carbon signal as internal standard. MALDI TOF mass spectra were obtained on Bruker Reflex MALDI TOF spectrometer using TCNQ as matrix. Elemental analyses were carried out on a Foss Heraeus Vario EL. Differential scanning calorimetry (DSC) was conducted with a Mettler DSC 30 with heating and cooling rate of $10\text{ }^\circ\text{C}/\text{min}$. A Zeiss Axioptot optical microscope with a nitrogen-flushed Linkam THM 600 hot stage was used to characterize the optical textures between crossed polars. Wide-angle X-ray diffraction (WAXD) experiments were performed on oriented filaments²¹ in two different geometries. One-dimensional (θ – 2θ , reflection) diffractograms were obtained using a Siemens D500 Kristalloflex with a graphite-monochromized $\text{Cu K}\alpha$ X-ray beam perpendicular to the fiber axis, emitted from a rotating Rigaku RV-300 anode. The temperature of the samples, which were positioned directly on a copper sample holder, was measured by a bimetal sensor and calibrated by reference measurements. 2D WAXD measurements of oriented filaments were conducted using a rotating anode (Rigaku 18 kW) X-ray beam ($\text{Cu K}\alpha$, pinhole collimation, double graphite monochromator) and CCD camera. The patterns were recorded with vertical orientation of the filament axis and with the beam perpendicular to the filament.

Materials. Unless otherwise noted, all starting materials and catalysts for chemical reactions were purchased from Aldrich and ABCR,

respectively, and used as received. THF was freshly distilled from Na metal. CH_2Cl_2 was distilled from CaH_2 .

2-(3-Ethoxycarbonylpropyl)-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (4). A 0.45 mL (0.9 mmol) sample of 3-ethoxycarbonylpropyl-1-zinc-bromide as a 2 M solution in THF was added via syringe to the solution of 0.4 g (0.3 mmol) of 2-bromo-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (**3**) and 10 mg of $\text{Cl}_2\text{Pd}[\text{dppf}]\cdot\text{CH}_2\text{Cl}_2$ in 1 mL of THF under argon, and heated to $55\text{ }^\circ\text{C}$ overnight. Methanol was added to quench the reaction and precipitate the product, which was purified by flash chromatography (petroleum ether/ CH_2Cl_2). Yellow solid, yield 95%, ^1H NMR (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, $T = 306\text{ K}$): $\delta = 8.21$ (s, 10H, Ar-H), 8.17 (s, 2H, Ar-H), 4.16 (q, 2H, $J = 6.84\text{ Hz}$, CH_2OCO), 3.00–2.92 (m, 12H, α - CH_2), 2.5 (t, 2H, $J = 7.89\text{ Hz}$, CH_2COO), 1.95 (m, 5H, CH), 1.78 (m, 12H, β - CH_2), 1.59–1.27 (m, 30H, CH_2), 1.16 (d, 15H, $J = 5.99\text{ Hz}$, CH_3), 0.91 (d, 30H, $J = 6.84\text{ Hz}$, CH_3). ^{13}C NMR (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, $T = 393\text{ K}$): 173.26 (CO), 140.85, 139.14, 130.37, 130.25, 130.14, 123.89, 123.68, 121.63, 119.92, 119.78, 60.36 (OCH_2), 39.83, 39.67, 39.63, 37.76, 36.63, 34.94, 34.45, 33.47, 33.43, 28.2, 27.25, 25.08, 25.05, 22.84, 22.77, 20.12, 14.55 (CH_3). MS (FD, 8 kV): m/z (%) = 1338.3 (100%) [M^+] (calcd for $\text{C}_{98}\text{H}_{128}\text{O}_2 = 1338.11$).

2-(4-Hydroxybutyl)-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (5). A 2 mL sample of a 1 M solution of LiAlH_4 in THF was added via syringe to 0.26 g (0.2 mmol) of 2-(3-ethoxycarbonylpropyl)-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (**4**) dissolved 120 mL of dry THF. The reaction mixture was stirred for 3 h at room temperature and quenched carefully with THF–water mixture. The product was extracted with toluene and then passed through a short pad of silica gel ($\text{CH}_2\text{Cl}_2/\text{THF}$). Yellow solid, yield = 94%, ^1H NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4/\text{CS}_2$, $T = 293\text{ K}$): $\delta = 8.31$ (s, 4H, Ar-H), 8.27 (s, 2H, Ar-H), 8.24 (s, 2H, Ar-H), 8.18 (s, 4H, Ar-H), 3.79 (t, 2H, $J = 6.49\text{ Hz}$, CH_2OH), 3.06–2.91 (m, 12H, α - CH_2), 1.97 (m, 5H, CH), 1.77 (m, 12H, β - CH_2), 1.59–1.27 (m, 32H, CH_2), 1.19 (d, 15H, $J = 5.99\text{ Hz}$, CH_3), 0.95 (d, 30H, $J = 6.84\text{ Hz}$, CH_3). ^{13}C NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_4/\text{CS}_2$, $T = 293\text{ K}$): $\delta = 140.14$, 139.3, 129.64, 123.11, 121.17, 119.44, 62.98 (CH_2OH), 40.22, 39.82, 37.82, 35.12, 33.59, 33.36, 28.42, 25.34, 23.1, 23, 20.14. MS (FD, 8 kV): m/z (%) = 1294.5 [M^+] (calcd for $\text{C}_{96}\text{H}_{126}\text{O} = 1295$).

2-[5,8,11,14,17-Penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene]butyl-1-pyrene Carboxylate (1). In a 25 mL Schlenk flask, 0.11 g (0.44 mmol) of pyrene-1-carboxylic acid, 0.08 g (0.44 mmol) of *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride, and a catalytic amount of 4-dimethylaminopyridine were stirred for 20 min in 1 mL of dry CH_2Cl_2 under argon, after which 0.1 g (0.07 mmol) of 2-(4-hydroxybutyl)-5,8,11,14,17-penta(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (**5**) in 1 mL of CH_2Cl_2 was added and stirred overnight. Methanol was added to quench the reaction and precipitate the product, which was purified by flash chromatography (petroleum ether/ CH_2Cl_2). Yellow solid, yield 70%, ^1H NMR (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4:\text{CS}_2$ 1:1): $\delta = 9.16$ (d, 1H, $J = 9.46\text{ Hz}$, pyrene-H), 8.5 (d, 1H, $J = 9.46\text{ Hz}$, pyrene-H), 8.45 (s, 12H, HBC-H), 8.13–7.9 (m, 7H, pyrene-H), 4.40 (t, 2H, $J = 5.8\text{ Hz}$, CH_2OCO), 3.06 (m, 12H, α - CH_2), 1.99 (m, 5H, CH), 1.74 (m, 12H, β - CH_2), 1.61–1.25 (m, 37H, CH_2), 1.21 (d, 15H, $J = 6.45\text{ Hz}$, CH_3), 0.91 (d, 30H, $J = 6.63\text{ Hz}$, CH_3). ^{13}C NMR (700 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, $T = 393\text{ K}$): 182.8 (CO), 182.5 (CO), 167.5 (CCOO), 140.49, 140.2, 134.19, 131.14, 130.99, 130.36, 129.87, 129.66, 129.39, 128.55, 127.27, 126.45, 126.38, 126.26, 125.2, 124.8, 124.19, 123.77, 123.33, 121.45, 119.66, 65.37, 40.22, 39.81, 37.79, 37.67, 35.15, 33.57, 32.83, 30.45, 30.29, 30.24, 30.15, 30.06, 29.82, 29.27, 28.42, 26.63, 25.34, 23.11, 23.01, 20.17 MS (MALDI TOF, TCNQ, 8 kV): m/z (%) = 1524 (100%) [M^+] (calcd for $\text{C}_{113}\text{H}_{134}\text{O}_2 = 1524.33$).

STM Investigation. Scanning tunneling microscopy imaging has been performed at room temperature employing a homemade setup²² at the interface between a freshly cleaved highly oriented pyrolytic

(21) Fischbach, I.; Pakula, T.; Minkin, P.; Fechtenkötter, A.; Müllen, K.; Spiess, H. W.; Saalwächter, K. *J. Phys. Chem. B* **2002**, *106*, 6408–18.

(22) Hillner, P. E.; Wolf, J. F.; Rabe, J. P. Humboldt University Berlin.

graphite (HOPG) crystal and an almost saturated solution in 1,2,4-trichlorobenzene (Aldrich). First the lattice of the HOPG surface was visualized for a few hours until the thermal equilibrium was reached. A drop of almost saturated solution was applied to the basal plane of the substrate. Measurements have been carried out with a scan rate of 10–50 lines/s. The correction of the images has been executed with respect to the hexagonal HOPG lattice underneath by means of SPIP software.²³ This allowed definition of the unit cell of the adsorbate crystal with a high degree of precision.

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(23) Scanning Probe Image Processor, version 1.72, Image Metrology ApS, Lyngby, Denmark.

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Supporting Information Available: 2D WAXS diffractograms and their integrations; tabulated reflexes and Miller indices; optical micrograph of homeotropically aligned thin film of **1**; survey (large-area) STM image of **1** at the graphite/solution interface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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