Host–Guest Systems

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Filling the Cavity of Conjugated Carbazole Macrocycles with Graphene Molecules: Monolayers Formed by Physisorption Serve as a Surface for Pulsed Laser Deposition**

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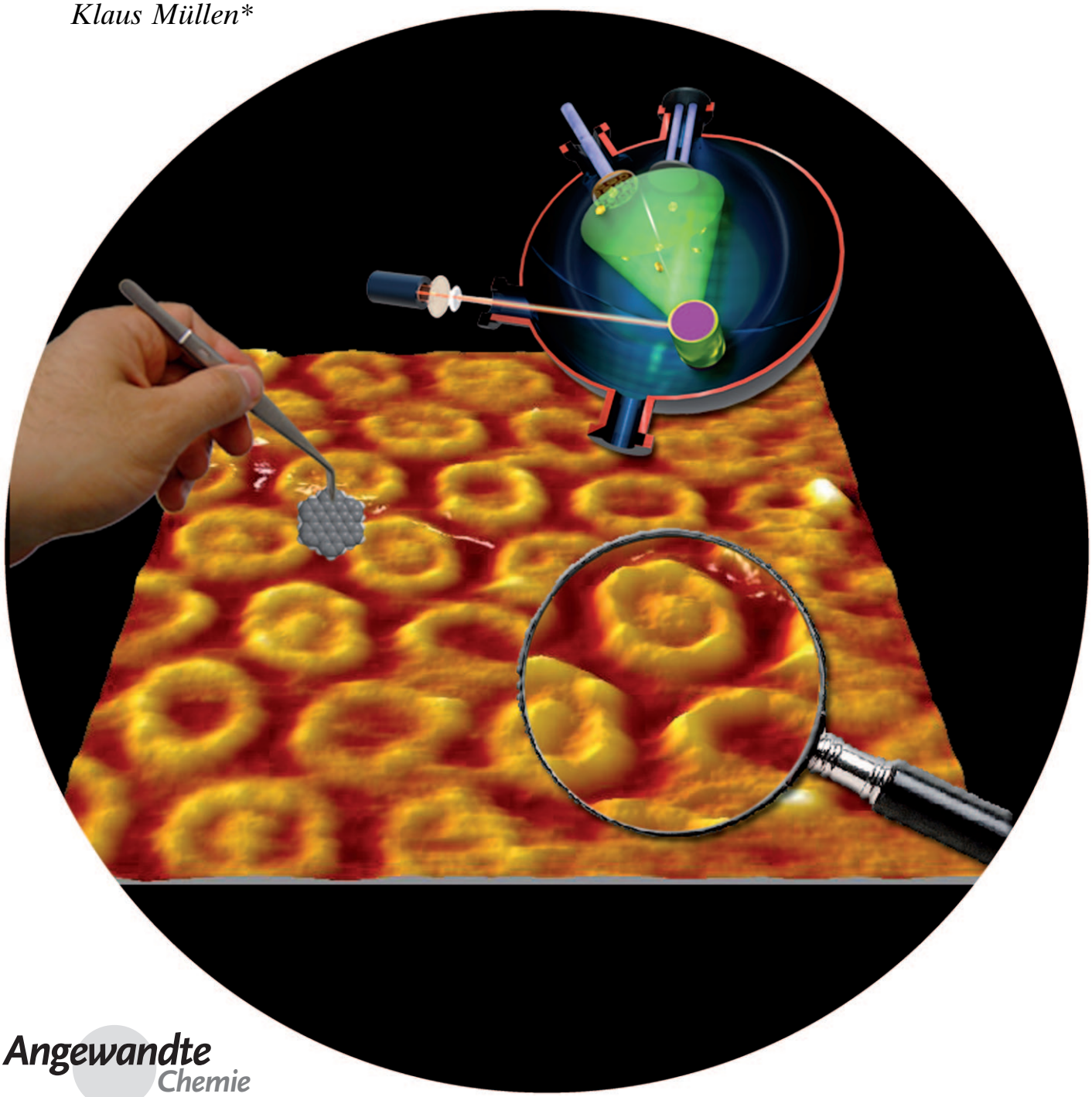

InterScience

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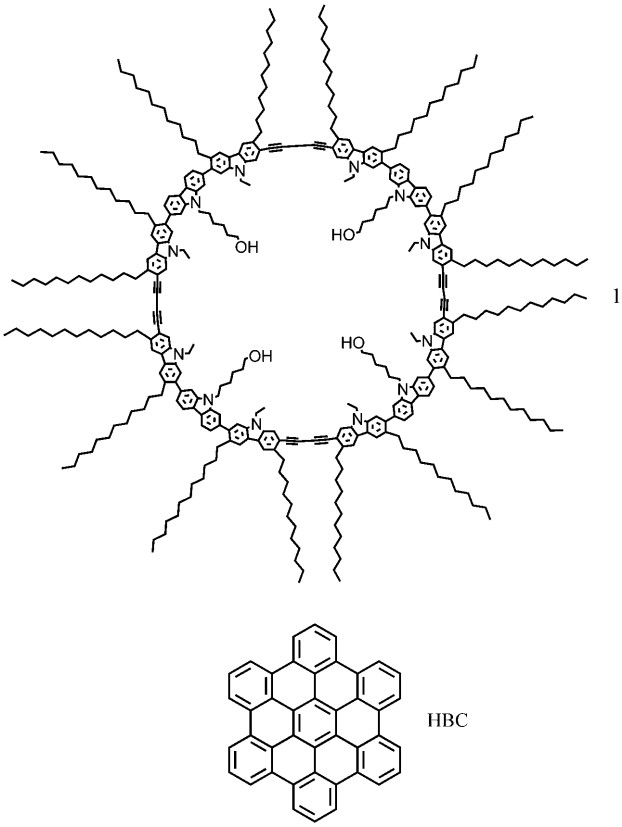
The formation of ordered monolayers of π-conjugated molecules on substrates by physisorption is fairly well understood.[1] Nevertheless, the construction of well defined host–guest complexes in which a π-conjugated macrocycle is used as a host to accommodate additional objects is still a challenge. Although metal insertion or ion complexation allow the possibility to fill the empty cavities,[2] they are too small for π-conjugated molecules. In general, depending on the solubility and stability of the deposited molecules, the formation of conjugated host–guest complexes requires either deposition by solution[3] or gas-phase[4] techniques. The utilization of both methods to form new host–guest systems and to allow the introduction of a disclike structure into the cavity of a conjugated macrocycle is unique. In addition, if both the discs and the macrocycles are able to self-organize into columnar structures, the application of such host–guest complexes in electronics, such as, for example, light amplification using cascade energy transfer, could become extremely interesting.[5]

Here, we present the direct observation of the first co-deposition of two-dimensional host–guest superstructures, including an organic semiconductor in the cavity of a fully π-conjugated macrocycle, on graphite by means of scanning tunneling microscopy (STM). Highly organized monolayers of nearly hexagonally packed ring-shaped carbazole macrocycles, spin-coated from a tetrahydrofuran (THF) solution, uniformly cover the surface. A hexa-*peri*-hexabenzocoronene (HBC) molecule was then preferentially deposited inside the cavities of the π-conjugated giant macrocycles by a solvent-free vacuum technique to form a 1:1 host–guest complex. Moreover, the supramolecular organization of the cyclic structures has been investigated by two-dimensional wide-angle X-ray scattering (2D-WAXS). In the bulk phase, the conjugated macrocycles self-assemble into columnar structures, driven by both π-stacking interactions and local phase separation between the rigid aromatic cycle and the flexible alkyl side chains.

The detailed synthesis and the characterizations of the new conjugated macrocycle will be described in a forthcoming report. The giant π-conjugated macrocycle **1**[6] was designed to be fully conjugated and to have an accessible cavity (Scheme 1). The first requirement has been fulfilled by the synthesis of a 2,7-carbazolediyl-derived macrocycle by using a template-assisted cyclization developed in our laboratory.[7] The target macrocycle contains additional acetylene functions in the backbone, thus allowing the increase in the size of the cavity that is necessary for the introduction of organic molecules. The second requirement has been achieved by the introduction of solubilizing groups to the outside of the carbazole macrocycle (Scheme 1). Unlike the previous conjugated macrocycle developed by us,[7] the design of this new ring, where the long alkyl chains point towards the exterior of the macrocycle and only the four hydroxy anchor groups turn towards the interior, allows a better access for the guest to the cavity.



Scheme 1. Conjugated carbazole macrocycle and hexa-*peri*-benzocoronene (HBC). For better comprehension, the molecules are not on the same scale.

To identify a suitable guest for the cavity of the π-conjugated system, we carried out simulations of the macrocycle with various species. Figure 1 shows the simulation[8] of molecule **1** with the HBC molecule located in the center of the cavity. The inner and outer diameters of the macrocycle are $\delta = 3.6$ and 4.2 nm, respectively. We also calculated the average distance between two opposite hydroxy groups (d_{o}-

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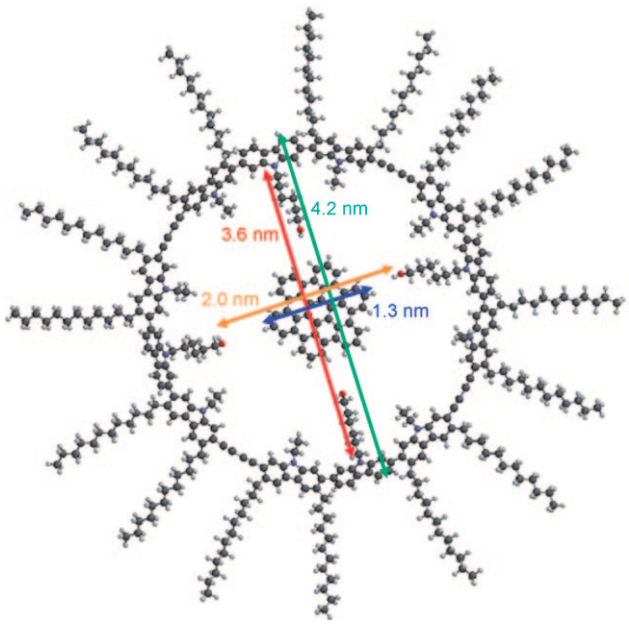

Figure 1. Energy minimization, calculated with Spartan 04V1.0.0, of the π-conjugated carbazole macrocycle containing an HBC molecule in its cavity. The inner and outer diameter of the ring system as well as the diameter of the HBC and the average distance between two opposite hydroxy groups are marked in green, red, blue, and orange, respectively.

$_{o}$ = 2 nm) to determine the average size of the possible guest molecule. The most promising candidate turned out to be the HBC molecule,[9] which has a diameter of 1.3 nm—thus matching with the size of the cavity.

We have studied the ordering of the giant conjugated macrocycle **1** in self-assembled monolayers spin-coated on highly oriented pyrolytic graphite (HOPG) by STM. Since the conjugated macrocycles cannot be vacuum deposited, a dilute solution (2×10^{-5} mol L^{-1}) of **1** in THF was spin-coated (5000 rpm) onto the (001) surface of HOPG. A representative STM image of a monolayer of carbazole macrocycles obtained at the solid/air interface is shown in Figure 2a. A long-range order of packed macrocycles facing the surface is typically found over areas larger than several hundred nm^2. The macrocycles are not closely packed, with an "empty" space of about 0.4 nm in each direction. This type of ordering is due to the presence of alkyl chains around the macrocycles which form a shield that prevents a close packing. The contrast of **1** in the STM picture is provided by the conjugated cyclic aromatic π system, as aromatic moieties show a higher tunneling efficiency than the aliphatic parts.[10] The monolayer of **1** reveals a chevron-like organization. Each macrocycle seems to be slightly distorted along one direction. This behavior is related to the chemical structure of the rings. The introduction of the acetylenic bridges in the rigid conjugated backbone tends to give more "flexibility" because the acetylene carbon atoms can be distorted away from the 180° strain-free geometry.[11] Furthermore, the macrocycles appear to be placed on a hexagonal lattice with a nearest neighbor distance of approximately d = 7.5 nm. The macrocycles are elliptical, with two different orientations of the ellipses long axes. Assuming that the centers of mass of the macrocycles still lie on a hexagonal lattice, we may describe this two-dimensional lattice by a unit cell comprising two macrocycles (Figure 2a). The two primitive grating vectors are $a_1 = d(1,0)$, $a_2 = 2d(\sin(60°),\cos(60°))$. Small deviations from a hexagonal ordering of the center of mass of the macrocycles should be considered since the structure does not have the full sixfold symmetry of the hexagonal lattice. Such deviations, if they exist, are beyond the accuracy of our experiment because of drift.

To deposit the guest molecule onto the already-formed monolayer of macrocycles without disturbing it, we used an efficient method known to produce thin films,[12] and developed for graphitic molecules,[13] called pulsed laser deposition. This method allows the controlled intact deposition of HBC onto a specific substrate. The molecules are first vaporized through a pulsed nitrogen laser (337 nm) and then, under vacuum, deposited onto HOPG without destroying the molecules. We emphasize that HBC molecules are deposited from the gas phase onto the dry monolayer of macrocycles. Since we use a solvent-free technique, the already-existing supramolecular organization of **1** is not affected by the second deposition. The result of the deposition of HBC molecules by this method is shown in Figure 2b. In comparison to the pure monolayer of macrocycles, a new object could be detected, located in the cavities of the conjugated macrocycles. The lattice structure does not change upon insertion of the discotic species. The HBC molecules tend to appear larger than expected from simulations; this is presumably due to a limited

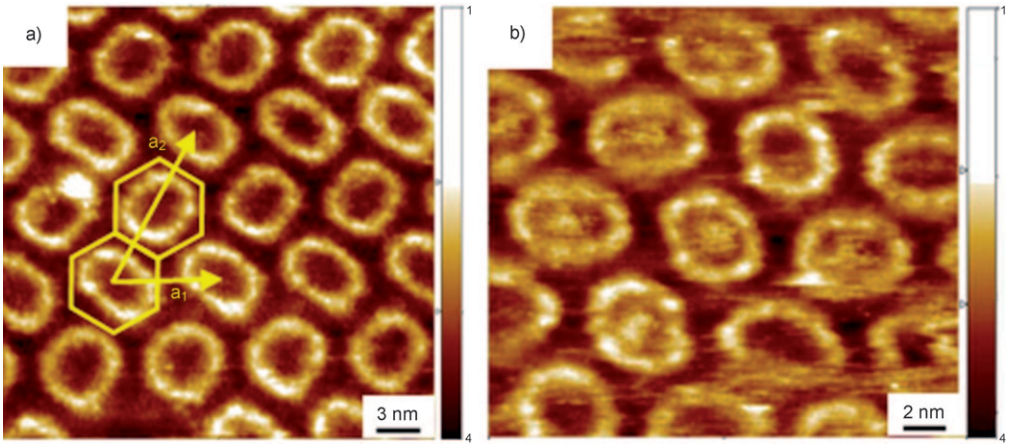

Figure 2. STM images of **1** and **1** + HBC on an HOPG surface at the solid/air interface (tunneling current: 1.6–2 pA, bias voltage: 750–900 mV). a) 2D view of a monolayer of **1** with hexagonal packing. b) 2D view of the same monolayer after deposition of HBC molecules.

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mobility of the HBC molecule inside the cavity of the macrocycle, which cause a diffuse HBC image with an apparent increased size. Nevertheless, a direct estimation of the size of the object inside the cavity (between 1.4 and 1.6 nm) from the STM pictures matches with the size of one HBC molecule (1.3 nm). Figure 2b shows that more than 50% of the cavities are filled with an HBC molecule, thus leading to the formation of 1:1 host–guest complexes. The driving force of such complexation seems to be the interaction of the HBC with the HOPG surface. It is not thermodynamically favorable for HBC molecules to be deposited between the macrocycles because of the presence of the alkyl chains. Nevertheless, they are small enough to fit inside the cavity and to interact with HOPG without being disturbed by the hydroxy chains present in the center of the ring. It is also interesting to note that the tunneling current flowing through the macrocycles and the HBC molecules is nearly identical, which suggests that both molecules are in the same plane and that the HBC is not located on top of the macrocycles, but effectively placed inside the cavity. Previously, Mena-Osteritz and Bäuerle[3a] reported a host–guest complex, based on donor–acceptor interactions, where the guest molecule (C_{60}) was stabilized on top of the backbone of the π-conjugated cyclo[12]thiophene macrocycle. Pan et al.[3b] subsequently presented 1:2 host–guest complexes where the C_{60} molecule was located on both sides of aromatic thiophene-based macrocycles. To the best of our knowledge, the complex presented in the current study is the first host–guest system where the π-conjugated guest molecule is trapped within the cavity of the π-conjugated macrocycle. The STM pictures give clear evidence for the cyclic structure and the visualization of the filling of the "electronic hole" of the macrocycle by a graphitic molecule.

The bulk supramolecular organization of **1** was investigated by 2D-WAXS experiments on extruded fibers.[14] Figure 3a shows a typical two-dimensional pattern of **1** recorded at 30°C. For the analysis, the pattern can be separated into two planes. The reflections positioned in the equatorial plane are characteristic of a columnar superstructure, into which the macrocycles assemble (Figure 3b). The relatively large number of reflections with high intensity indicates a well-ordered columnar arrangement, with the stacks typically aligned along the fiber direction. The derived hexagonal unit cell parameter of 5.4 nm is in good agreement with the molecular size (Figure 3c) and of the monolayer array observed by STM (Figure 2a). Both the π-stacking interactions and a local phase separation between the rigid macrocycles and the flexible side chains lead to the assembly of the columnar phase, which can be assigned as a liquid-crystalline state. This classification of **1** is in line with other types of alkyl-substituted macrocycles.[15] The meridional reflections correspond to the intracolumnar spacing of 0.49 nm between individual building blocks. Thus, the molecules are oriented with their planes perpendicular to the columnar axis (Figure 3b). The broad meridional scattering intensities and the large spacing imply a decreased interaction between the molecules, which results most probably from the nonplanar and twisted shape of the macrocycle. A further effect might be induced by the oval shape of the macrocycle, as observed in the STM images, which generates additional disorder within the stacks.

In conclusion, 2D supramolecular structures of host–guest **1**/HBC complexes have been obtained on HOPG by two successive techniques: physisorption of macrocycles **1** and gas-phase deposition of HBC under high vacuum. The macrocycles, visible by STM, self-assembled in a hexagonal lattice on HOPG. The design of the giant π-conjugated 2,7-carbazole macrocycle and the utilization of both deposition methods led to the insertion of one HBC molecule inside the empty cavity of the ring, thereby forming a 1:1 complex. To the best of our knowledge, this complex is the first example of a host–guest system where an organic semiconductor is trapped inside the cavity of a π-conjugated macrocycle. This simple co-deposition method also allows the possibility to deposit larger polyaromatic hydrocarbons which could not be vaporized by traditional techniques. Additionally, the 2D-WAXS investigations show that these rings self-organize into columnar structures. Since HBC discs are also able to form columnar stacks,[14,16] this new type of self-organization allows the postulation of an identical organization in the bulk phase: columnar aggregates consisting of conjugated macrocycles with HBC pillars inside their channels. Such supramolecular structures could be attractive for electronic devices.

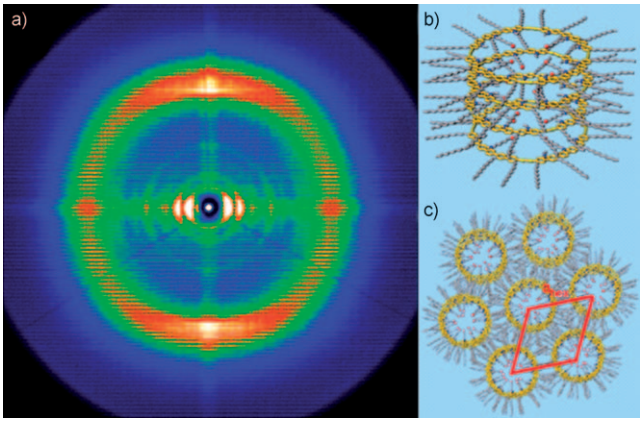

Figure 3. a) 2D WAXS image of **1** at 30°C; b) schematic illustration of the intracolumnar organization of **1**; c) hexagonal arrangement of the columnar structures with $a_{hex} = 5.4$ nm as the 2D lateral packing parameter.

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