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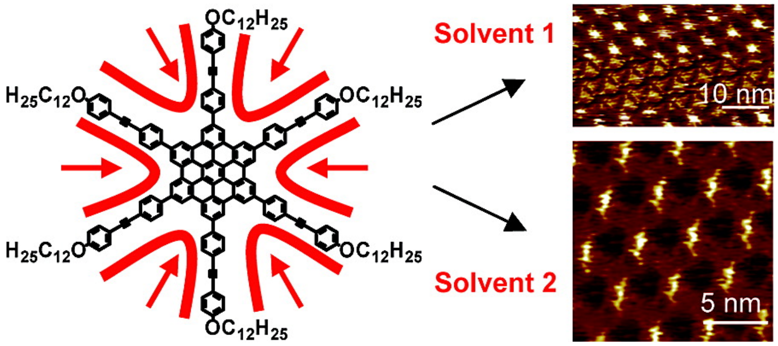

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Solvent Molecules in an Epitaxially Grown Scaffold of Star-Shaped Nanographenes

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Two- and three-dimensional architectures of well-defined molecular building blocks[1] are of major interest in the fields of microporous materials,[2] molecular electronics,[3] and molecular machines.[4] Their fabrication often relies on self-assembly processes using noncovalent intermolecular forces, such as metal−ligand complexation[2], hydrogen bonding,[5] π−π-stacking,[6] and interfacial forces.[7] At solid−solution interfaces, the resulting architectures have been extensively studied by means of scanning tunneling microscopy (STM).[7,8] However, little is known on the inclusion of solvents in these architectures.[9]

Polycyclic aromatic hydrocarbons, such as hexa-*peri*-hexabenzocoronenes (HBC), can be viewed as two-dimensional subsections of graphite ("nanographenes") that have been proven as versatile building blocks for organic[10] and molecular electronics.[11] They can be synthetically modified with respect to size, shape, and chemical functionalities in their periphery.[12]

In this contribution, we report an STM study at the graphite−solution interface of an HBC derivative (HBC-star, Figure 1a), whose star-shaped molecular design provides cavities at the disk's periphery, which can be filled by smaller molecules. These voids hamper a dense packing of the molecules at the interface, and they also allow for a fine-tuning of the supramolecular architectures' structure by applying solvents with different affinity to fill the voids.

Synthesis and self-assembly in the bulk of the HBC-star have been described previously.[13] The present STM investigations at the graphite−solution interface[7] were performed with a home-built STM interfaced with a commercial controller and software (Omicron).

Figure 1b displays an STM current image obtained from a solution of HBC-star in 1,2,4-trichlorobenzene at an average tunneling junction impedance of 0.8 GΩ. A regular pattern of triangles with large tunneling probability is visualized at both sample bias polarities. The dark (low tunneling probability) areas between the triangles reflect perfectly the size and shape of HBC-star molecules. The bright areas are attributed to solvent molecules filling the voids. The contrast implies that the current through the solvent-filled areas is larger than that through the nanographenes. The two-dimensional arrangement can be described by a unit cell ($a = 4.94 \pm 0.09$ nm, $b = 5.05 \pm 0.07$ nm, and $\alpha = 62 \pm 3°$) containing two triangles, with an angle between the short unit cell vector and a zigzag axis of the HOPG substrate of 6 ± 4°. Upon increasing the tip−sample separation (average impedance of 11.5 GΩ), a different structure is observed (Figure 1c). Now, the nanographenes cause larger tunneling currents than the surrounding areas, which can be attributed to the low HOMO−LUMO gap of HBC.[14] The parameters of the unit cell are identical to those determined for the structure observed at lower junction impedance.

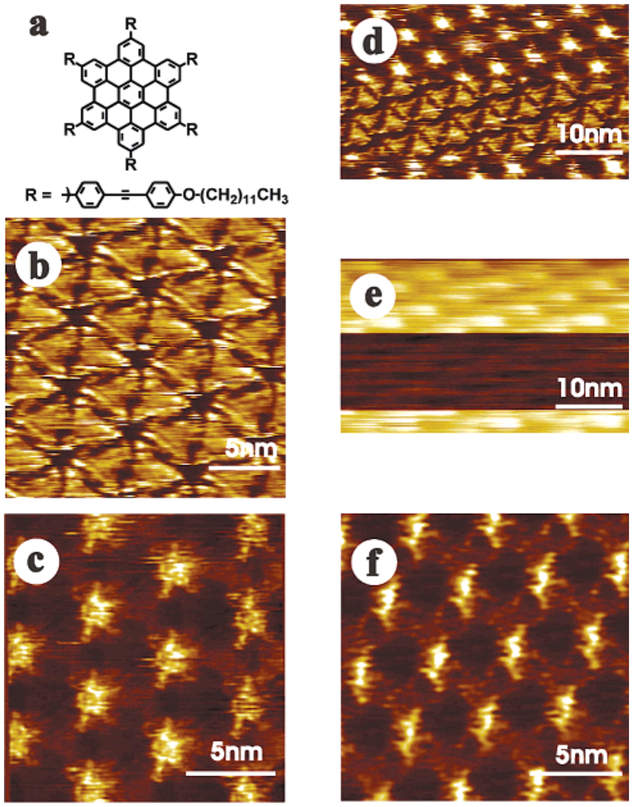

Figure 1. (a) Chemical structure of HBC-star, STM current images of HBC-star from a solution in 1,2,4-trichlorobenzene (b) in the first layer, (c) in the second layer, and (d) simultaneously imaged first and second layer. (e) STM height image simultaneously recorded with (d). (f) STM current image of a monolayer of HBC-star from a solution in 1-phenyloctane. Tunneling parameters were (b) sample bias $U_s = -0.4$ V and average tunneling current $I_t = 500$ pA; (c) $U_s = -1.15$ V, $I_t = 100$ pA, (d and e) $U_s = -1.0$ V, $I_t = 200$ pA and (f) $U_s = -1.0$ V, $I_t = 80$ pA.

Occasionally, the two different contrasts can be observed in the same image (Figure 1d), and the simultaneously recorded height image (Figure 1e) reveals a decrease in tip−sample separation for the structure consisting of triangles. From solutions of HBC-star in 1,3-dichlorobenzene (no images shown), the same structures are observed within the experimental accuracy as those from 1,2,4-trichlorobenzene solutions. Figure 1f displays an STM current image of the arrangement obtained from solutions of HBC-star in 1-phenyloctane. Here, exclusively, one structure is found in which the star-shaped molecules can be recognized as bright features. The corresponding unit cell ($a = 4.27 \pm 0.14$ nm, $b = 4.23 \pm 0.24$ nm, and $\alpha = 60 \pm 3°$) is significantly smaller than the one observed from the solutions of HBC-star in the chlorinated benzenes.

In the chlorinated solvents, the observed structures depend on the junction impedance, indicating double layer formation since the two structures are visualized at different tip−sample-separations.[15] Given that at even smaller impedances of ~0.1 GΩ the substrate itself is visualized, we attribute the two different contrasts

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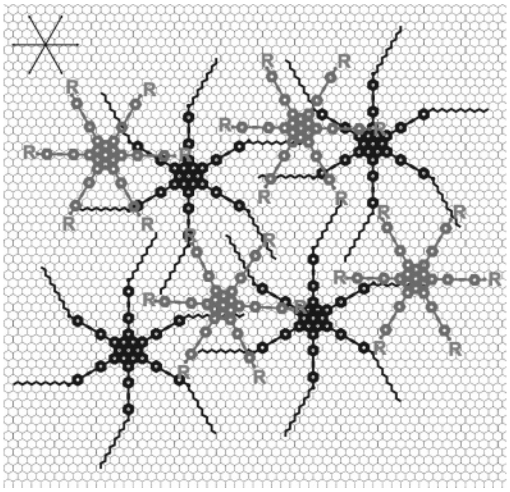

Figure 2. Packing model suggested for the double layer structure observed for HBC-star from solutions in 1,2,4-trichlorobenzene. The molecules in the first layer are depicted in black, those in the second in gray. The alkyl chains in the second layer have been replaced by R since their orientation is unknown.

to a first and second layer, respectively. The identical lattice constants (within the experimental accuracy) of the two layers underline the epitaxial nature of the self-assembly process. The interactions between the two layers are obviously strong enough to allow for the visualization of the second layer at larger junction impedance. The large size of the unit cell and its shrinkage upon replacing the chlorinated benzenes by 1-phenyloctane suggests that only the smaller solvent molecules readily fill the voids provided by the star-shape of the molecules. The larger current through the areas filled with chlorinated benzenes is surprising since an orientation of the polar molecules in the electrical field of the STM would actually increase the tunneling barrier. However, lowering of tunneling barriers due to polar molecules, such as water, has previously been observed and investigated theoretically.[16] Explanations being discussed differ from the usually applied resonant tunneling models;[14] they include effects of the solvent on electrode work functions and solvent-supported resonant structures which let the effective barrier depend on the detailed structure and order of the polar layers.[16]

Figure 2 displays a packing model for the observed double layer structure. It is constructed such that in the first layer the stars are placed at the sites of low tunneling current between the triangles, and that the unit cell is reproduced within the experimental accuracy ($a = 4.92$ nm, $b = 5.01$ nm, $\alpha = 64°$, and an angle of 7° with respect to HOPG in the model). If we assume an adsorption of the conjugated part onto the graphite in an A−B-type stacking, and an orientation of the alkyl chains along the zigzag axis of HOPG, a 30° angle between the “arms” of the star and the alkyl chains is found. Coadsorbed solvent molecules are not shown since no detailed information on their adsorption geometry is available. The precise positions of the molecules in the second layer with respect to the first can be determined from images, as shown in Figure 1d, or from images of the first layer on which a weak contrast modulation due to the second layer is observed (no images shown). The orientation of the arms in the second layer can be determined from high-resolution images, such as that displayed in Figure 1c.

In conclusion, we present an STM study of an epitaxially grown two-dimensional molecular scaffold of star-shaped nanographenes, stabilized by interfacial forces and liquid guests. The nature of the liquid allows tuning of the structure, which on the other hand may serve as a model system for studying, in the same experiment, the dependence of electron tunneling on order, mobility, and polarity of different molecular adsorbates.

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Supporting Information Available: Experimental procedure and packing model of HBC-star from 1-phenyloctane (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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