DOI: 10.1002/anie.200705527

Hierarchically Self-Assembled Host–Guest Network at the Solid–Liquid Interface for Single-Molecule Manipulation**

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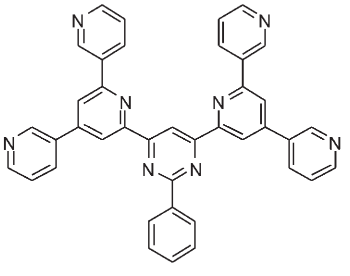
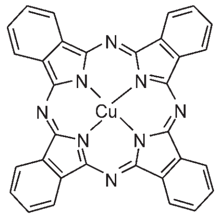
The manufacture of functional molecular devices is one of the key research topics in nanotechnology. For applications in molecular storage and quantum computing, molecules must be arranged in a repetitive structure and also be addressable and manipulable in a controlled fashion. The self-assembly of molecular building blocks with hydrogen-bonding capabilities is a suitable method for generating highly ordered and porous two-dimensional (2D) hydrogen-bonded networks (HBNs).[1,2] These porous 2D HBNs can be used to immobilize organic and inorganic guest molecules in a spatially well-ordered arrangement, predetermined by the host network structure.[3] The controlled manipulation of guest molecules was demonstrated for various functional guest molecules by means of scanning tunneling microscopy (STM) experiments but has been limited so far to the controlled desorption or the lateral manipulation of single molecules.[4–8] In contrast to ultrahigh-vacuum (UHV) conditions where the reservoir of manipulable molecules is restricted to the number of adsorbed species, the supernatant liquid phase at the solid–liquid interface in principle offers an almost unlimited depot of molecules (“ink”) and is therefore the perfect experimental environment for tip-controlled adsorption of guest molecules into the HBN. The “ink” attribute of a supernatant solution is used in scanning-probe-based lithographic techniques such as replacement lithography[9] and dip-pen lithography[10] to tailor the chemical composition and structure of a surface on the ≤ 100 nm scale. So far, these lithographic techniques are limited to a resolution of about 15 nm.[11]

For the spatially controlled adsorption of guest molecules in an HBN, the host–guest system must fulfill the following requirements: 1) the host network must be inert towards the manipulation process; 2) the dynamics of the manipulated components must be slow enough in order to follow the result of the manipulation with STM; and 3) the occupation of the cavities with guest molecules should be low such that unoccupied host cavities are available. All of these requirements need well-balanced adsorbate–adsorbate and substrate–adsorbate interactions.

Here we present a host–guest network that meets the demands for a spatially tip-controlled single-molecule manipulation. After describing the outstanding properties of our host–guest system, we demonstrate the spatially tip-controlled desorption of guest molecules from the cavities of the host network. Moreover, we show for the first time the tip-controlled adsorption of single solvated guest molecules at the solid–liquid interface. The C_{2v}-symmetric HBN building block 3,3′-BTP forms a polymorphic supramolecular HBN on highly ordered pyrolytic graphite (HOPG). The porous 2D network was used to generate a hierarchically self-assembled host–guest architecture with copper(II) phthalocyanine (CuPc) as guest molecule. The occupation of individual HBN cavities with CuPc can be altered with a voltage pulse applied to the tip (“erasing” and “writing”). As we recently reported, the deposition of 3,3′-BTP from a saturated 1,2,4-trichlorobenzene (TCB) solution ($1.5 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) onto HOPG leads to a densely packed linear structure, stabilized through weak hydrogen bonds between the terminal pyridyl rings.[2] Deposited from a diluted solution ($3 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$), the 3,3′-BTP molecules self-assemble into a 2D long-range-ordered porous nanostructure, further denoted as a gearwheel structure (see the Supporting Information).[12] The gearwheel structure exhibits cavities with an inner diameter of approximately 1.6 nm. After the addition of a solution of $1.7 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ CuPc in TCB to the preorganised 3,3′-BTP porous structure, bright spots with a diameter of about 1.4 nm appear in the network (Figure 1). The bright spots can be assigned to CuPc molecules randomly immobilized in the cavities of the 3,3′-BTP network. These features appear



3,3'-BTP



CuPc

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[**] We thank the Deutsche Forschungsgemeinschaft DFG for financial support within the SFB 569 and H. Hoster for the analysis of the short-range order.

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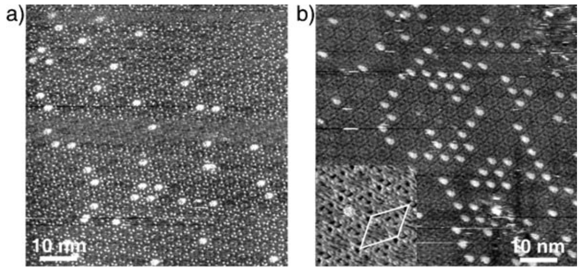

Figure 1. a) High-resolution STM image of the host–guest network recorded after addition of CuPc to the 3,3′-BTP network. The host network is imaged with inverse image contrast as a result of the applied tunneling conditions. b) Host–guest network after a second addition of CuPc solution to the network in (a). The inset (11 nm × 11 nm) shows one occupied cavity and the rhombic unit cell of the host network.

exclusively after addition of a CuPc solution to the gearwheel structure and appear selectively in the cavities of the network. Therefore, the host–guest interaction is associated exclusively with the supramolecularly assembled cavities of the gearwheel structure and is not a result of intermolecular donor–acceptor interactions as reported, for example, for cyclic thiophenes and C_{60}.[13]

The unit cell does not change within the experimental error upon incorporation of the CuPc molecules into the cavities. To our knowledge, CuPc does not form single-component monolayers at the solid–liquid interface; the HBN stabilizes the CuPc molecules in a templating fashion. The diffuse image contrast of unoccupied cavities is nearly identical in intensity to the surrounding molecules (Figure 1 b inset). As the STM measurements were performed at the solid–liquid interface, weakly bound solvent or 3,3′-BTP molecules present in the supernatant liquid are presumably coadsorbed in the comparatively large cavities (see below). The high mobility (rotation) of those weakly bound coadsorbed molecules results in the observed diffuse contrast. In the STM images of the CuPc/3,3′-BTP network, the D_{4h} symmetry of the incorporated CuPc molecules is not recognizable; the guest molecules are imaged as bright disks. The C_{6h} symmetry of the void and the D_{4h} symmetry of the CuPc guest molecules result in three energetically equivalent adsorption sites for CuPc in the cavity as indicated in Figure 2. At room temperature, the CuPc molecules are thermally activated and rotate in the cavity. Since most force fields (see the Supporting Information) do not permit Cu centers with square-planar coordination, the adsorption or stabilization energy of CuPc in the network could not be evaluated directly. Therefore we have computed the adsorption energy of phthalocyanine (H_2Pc), which will be very similar to the adsorption energy of CuPc as the binding occurs mainly through van der Waals forces and hydrogen bonds. An estimation of the rotation barrier of H_2Pc within the void using the different force fields indicates that it should be of the order of 40 kJ mol^{-1}. If one assumes a rather low prefactor of $k_0 = 1 \times 10^{10}\,\mathrm{s}^{-1}$ because of the large moment of inertia of the H_2Pc molecule, then a rate constant $k = k_0 \exp(-E_a/k_B T) \approx 2000\,\mathrm{s}^{-1}$ at room temperature results. This means that the H_2Pc molecules change their orientation about 2000 times per second. As the frequency of the rotation is higher than the scanning process, a CuPc molecule is imaged as a disk. Similar behavior was observed at RT and in UHV for CuPc on a hexagonal C_{60} phase[14] and for the fourfold symmetric zinc–octaethylporphyrin in a hexagonal molecular network.[15] In our calculations, the solvent is not included; however, this should have little influence on the determination of the rotation barrier since the effect of the solvent should be rather similar in the equilibrium configuration and at the barrier position. A schematic summary of the calculational results of the host–guest network on two graphite layers is shown in Figure 2. The 3,3′-BTP molecules are self-assembled into a C_{6h}-symmetric gearwheel-like structure, composed of six molecules in all three possible configurations (as a result of mirror symmetry along the lattice vectors) with respect to the lattice directions.

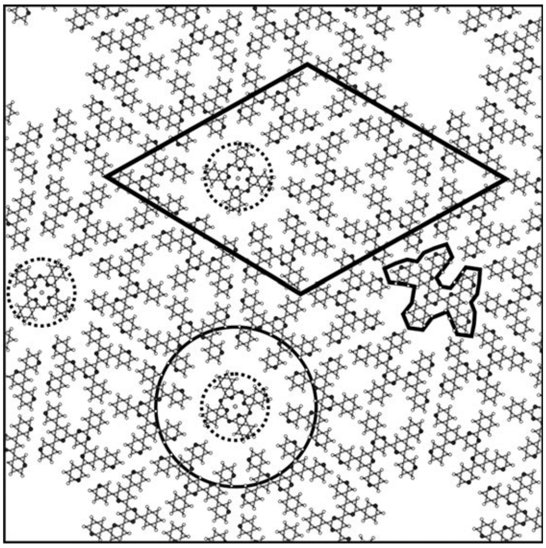

Figure 2. Molecular structure of the host–guest network and the rhombic unit cell. A single gearwheel is highlighted with a black circle. A 3,3′-BTP molecule incorporated as guest is outlined in black. CuPc in its three energetically equivalent adsorption configurations is highlighted by dashed circles. At the solid–liquid interface most of the cavities are occupied with coadsorbed 3,3′-BTP molecules.

The stabilization energy of a phthalocyanine molecule in the host network was calculated with the UFF force field to be 404.3 kJ mol^{-1}; the corresponding value of a 3,3′-BTP molecule was determined to 467.9 kJ mol^{-1}, which is only slightly less than the stabilization energy of 473.7 kJ mol^{-1} of 3,3′-BTP in the HBN. Similar results were obtained with other force fields. These stabilization energies were determined with respect to the free molecules in the gas phase; in other words, the influence of the solvent is entirely neglected although the solvation energies in principle enter the expression for the stabilization energy. Therefore the calculated energies are only meant to give qualitative trends. In additional coadsorption experiments we did not observe the immobilization of either C_{60} or coronene, both with significantly smaller stabilization energies, calculated with the Dreiding force field in a trimesic acid network.[6] With the qualitatively similar stabilization energies of CuPc and 3,3′-BTP taken into account and the supposition that there is an equilibrium between weakly adsorbed molecules and species dissolved in the supernatant liquid, we conclude that an equilibrium exists between the two components occupying the host cavities. Therefore the overall occupation with CuPc molecules should depend on the concentration of CuPc in the supernatant liquid.

The occupation of the host cavities in Figure 3 a, at a CuPc concentration of $1.7\times10^{-5}\,\mathrm{mol\,L^{-1}}$ and a 3,3′-BTP concentration of $3\times10^{-5}\,\mathrm{mol\,L^{-1}}$ (together in ca. 10 μL), is approximately 16 % and does not increase with time. A second addition (10 μL) of the same CuPc solution after (almost) complete evaporation of the solvent from the first CuPc addition doubles the occupation to roughly 31 % (Figure 1 b). An analysis of the short-range order of the adsorbed CuPc molecules revealed their random distribution in the cavities. This points to the fact that there are no significant interactions between guest molecules.[16] Thus, Langmuir-type adsorption isotherms are expected, from which the equilibrium constants for CuPc and 3,3′-BTP are determined to $K_{\mathrm{ads}}(\mathrm{CuPc}) = (21.2\pm0.6)\times10^4\,\mathrm{L\,mol^{-1}}$ and $K_{\mathrm{ads}}(\mathrm{BTP}) = (55.9\pm2.6)\times10^4\,\mathrm{L\,mol^{-1}}$, corresponding to adsorption enthalpies of $\Delta G_{\mathrm{ads}}(\mathrm{CuPc}) = (-30.4\pm0.1)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta G_{\mathrm{ads}}(\mathrm{BTP}) = (-32.8\pm0.1)\,\mathrm{kJ\,mol^{-1}}$, respectively (see the Supporting Information). As predicted qualitatively by theory, the stabilization energy of 3,3′-BTP molecules on HOPG is greater than that of the CuPc species (see above), but both are in the expected range of physisorption. According to these values, an (almost) complete occupation of the cavities with CuPc can be achieved only with a concentration of at least $8\times10^{-3}\,\mathrm{mol\,L^{-1}}$, which exceeds by far the solubility of CuPc in TCB.

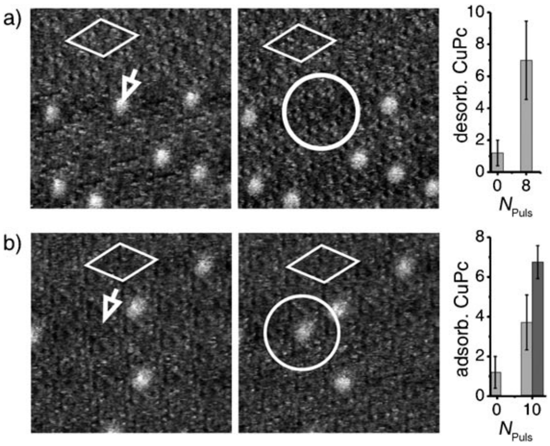

Figure 3. STM images and statistical analysis demonstrating the two manipulation experiments. The arrows indicate the tip position during the applied voltage pulse, the circles indicate the manipulated region. The rhombic unit cell of the host network is drawn for clarity. Image size is 21.8 nm × 21.8 nm. a) Sequence of STM images before and after the "erasing" of an incorporated CuPc molecule from the gearwheel structure. Plot of the number of CuPc molecules desorbing after zero (intrinsic dynamics) and eight voltage pulses (N_{Puls}). Pulse intensity +2 V, 10 μs. b) Sequence of STM images before and after the "writing" of a CuPc molecule into a cavity of the host network. Pulse intensity −2 V, 10 μs. Plot of the numbers of adsorbed CuPc molecules after zero and ten voltage pulses (N_{Puls}), comparing a CuPc concentration of $1.7\times10^{-5}\,\mathrm{mol\,L^{-1}}$ (light gray) and $3.5\times10^{-5}\,\mathrm{mol\,L^{-1}}$ (gray). Pulse intensity −2 V, 10 μs.

The low and adjustable occupation of the host network cavities already permits nonselective manipulation and also makes the CuPc/3,3′-BTP-system a perfect candidate for selective manipulation of individual guest molecules at the solid–liquid interface. The strong interaction of the large BTP π system with the substrate and the strong intermolecular hydrogen bonds between individual physisorbed BTP molecules (see the Supporting Information) results in a highly stable network. The mean resident time of a CuPc molecule in a host cavity was determined to be (435 ± 20) s, averaged over 97 CuPc molecules. While scanning with different imaging parameters (10 to 20 pA, −0.5 to −1 V), we detected no noticeable change in the resident time. Compared to other systems, the host–guest exchange in the CuPc/3,3′-BTP-network is very slow.[17]

The selective tip-controlled desorption of an individual CuPc molecule by a voltage pulse (+2 V, 10 μs) is shown in Figure 3 a. The process is selective for the CuPc molecule on which the tip is focused and successful for (76 ± 13) % of the manipulation events (see the Supporting Information). We did not observe the "refilling" of the emptied cavities with CuPc molecules in subsequent images, but we cannot exclude that the unsuccessful manipulation events arise from immediate reoccupation of the cavity with CuPc subsequent to the voltage pulse.

Besides the regioselective "erasing" of a single CuPc molecule, we were able to induce the CuPc adsorption into single HBN cavities with defined voltage pulses (−2 V, 10 μs). The "writing" process for a single CuPc molecule is shown in Figure 3 b). To induce the CuPc adsorption into the host network, a voltage pulse was applied to the tip focused on an individual cavity. The image recorded immediately after the voltage pulse shows an additional bright spot (Figure 3 b) in a surface region (cavity of the network) where no bright spot was previously present. Unfortunately, the tip-induced adsorption is not very selective for the aimed cavity presumably because of the large tip–sample separation (estimated to be more than 1 nm based on a 70 GΩ tunneling resistance according to $V_{\mathrm{Bias}} = -0.7$ V and $I_{\mathrm{T}} = 10$ pA). In principle, the lateral resolution of our method is restricted to the distance between HBN cavities of about 4.4 nm. We estimated the mean lateral error of the tip-induced deposition without correction for the intrinsic dynamic to be 10 nm (2.3 times the distance between HBN cavities).

In both cases, "writing" and "erasing", the host network remains unaffected. To verify the tip-induced desorption and adsorption, we separated the intrinsic dynamics of the host–guest network from the manipulation process. We compared the numbers of CuPc molecules adsorbing and desorbing with and without the application of several voltage pulses. The results show a significant difference between the intrinsic dynamics and the tip-induced adsorption and desorption (see Figure 3 and the Supporting Information). Note that as the bimolecular system is in the thermodynamic equilibrium, the overall CuPc occupation remains constant before and after the manipulation process.

Regarding the mechanism of the tip-induced desorption of single molecules at the solid–liquid interface, we refer to an increased tip–molecule interaction at constant tip height, controlled with a voltage pulse.[5] Increasing the tip–molecule interaction with a smaller tip–sample separation[6,8] results in an uncontrolled perturbation of the host–guest network. However, the tip-induced selective adsorption of a guest molecule in a host network cavity has not been reported before. We exclude the possibility that a CuPc molecule attached to the tip apex is placed in the cavity with the voltage pulse. For this, the electronic and therefore imaging difference between a bare tip and a tip with a molecule adsorbed to the apex was not observed.[7] It is more likely that the molecule that gets adsorbed was previously in the solution. We consider that either a CuPc molecule is trapped in the dielectric between the two electrodes or that the equilibrium between immobilized 3,3′-BTP and solvated CuPc molecules is disturbed. Thus, an increase of concentration of CuPc in the supernatant should increase the number of successful tip-induced adsorption experiments, which indeed could be shown (see Figure 3 and the Supporting Information).

In summary, we have reported on the reversible host–guest interaction of CuPc molecules with a hydrogen-bonded network of the oligopyridine 3,3′-BTP at the liquid–solid interface. Equilibrium constants of adsorption and corresponding adsorption enthalpies were determined. Furthermore, we described the tip-induced adsorption and desorption of CuPc molecules. The specific host–guest chemistry of the CuPc/3,3′-BTP HBN, referred to well-balanced intermolecular interactions, and the controlled "writing" and "erasing" of individual guest molecules creates an opportunity to develop new functional nanomaterials. In ongoing experiments we are fine-tuning the binary system for the controlled formation of defined molecular structures by method described here. Besides its own relevance as a catalytic and electronic material, CuPc has served in the present contribution as a model compound within the huge class of phthalocyanines as further potential guest molecules in the 3,3′-BTP network.

Experimental Section

The investigated oligopyridine derivative 3,3′-BTP was synthesized as previously described.[2] Copper(II) phthalocyanine (CuPc) and 1,2,4-trichlorobenzene (TCB) were used as received from commercial sources. The scanning tunneling microscopy (STM) experiments were performed at ambient conditions at the solid–liquid interface with a commercially available low-current RHK SPM1000 STM with a resolution of 1024 × 1024 data points per image and a scan speed between 0.6 $\mu m\,s^{-1}$ for the host and host–guest network and 512 × 512 data points and 3 $\mu m\,s^{-1}$ for the manipulation experiments. Generally, after the highly ordered pyrolytic graphite (HOPG) surface had been cleaned with adhesive tape, the quality of the mechanically cut Pt/Ir(80/20) tip was examined through atomic resolution of the graphite surface. The atomically resolved graphite images were used for calibration. After the scanning process had been stopped, a drop (10 μL) of a solution of 3,3′-BTP in TCB was applied to the surface with the tip in tunnel contact. After successful imaging of the 3,3′-BTP network, a drop (10 μL) of a saturated solution of CuPc in TCB was applied to the surface. For the manipulation experiments, the scanning process was interrupted and the tip was located above the desired surface area. After application of the voltage pulses of preset intensity and duration, the scanning process was immediately resumed. The tunneling current setpoint was between 10 and 20 pA, the bias voltage between −0.5 and −1.0 V. For the tip-controlled desorption and adsorption, the feedback loop was deactivated. The presented STM images of the host–guest network were filtered to reduce noise and to enhance image contrast. The STM images of the host network were not subjected to image processing except slope subtraction.

Received: December 3, 2007
Revised: January 31, 2008

Keywords: host–guest systems · porous networks · scanning probe microscopy · self-assembly · single-molecule studies

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