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Supramolecular Chemistry

Bicomponent Supramolecular Packing in Flexible Phthalocyanine Networks**

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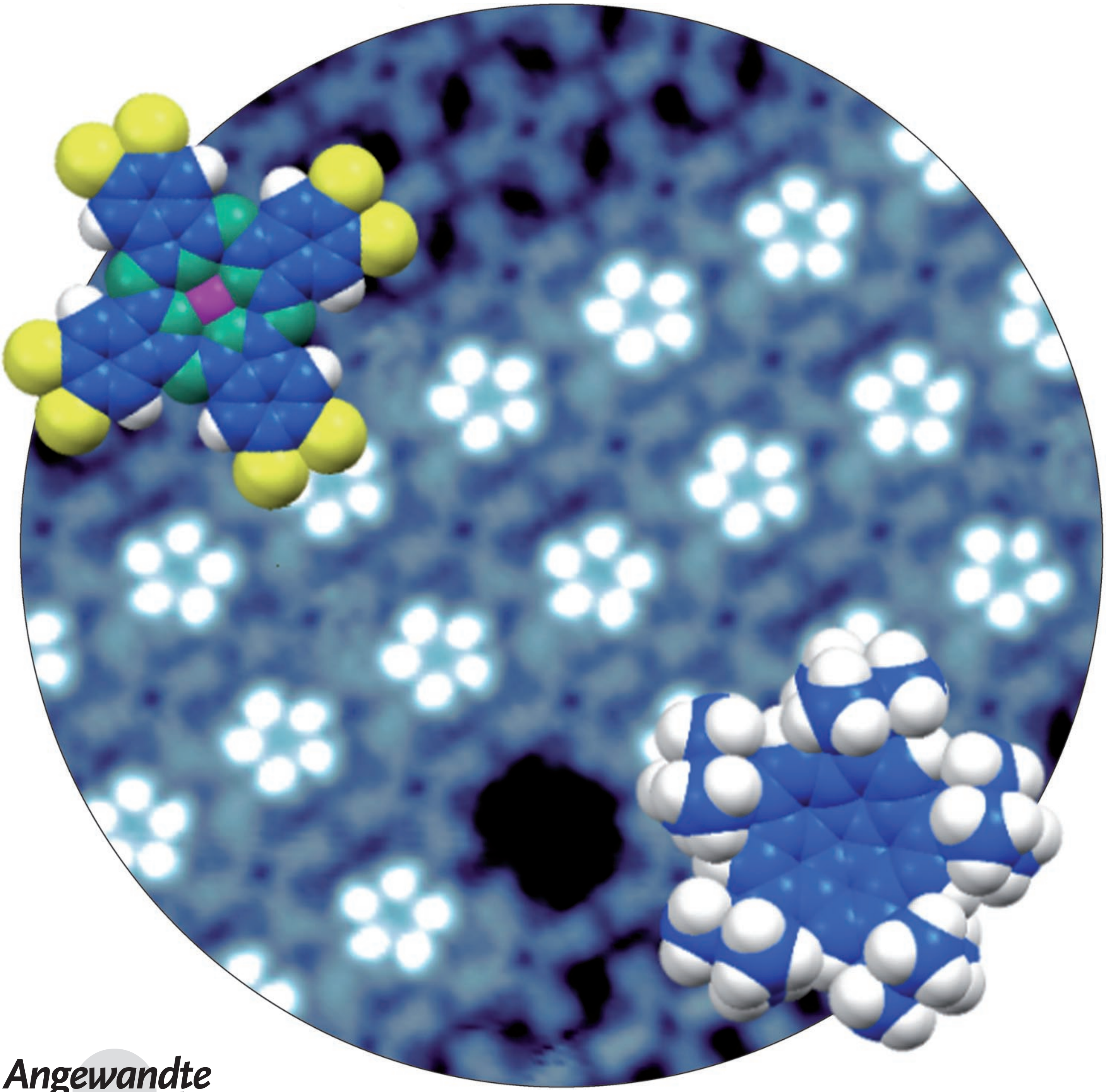

Functionalization of surfaces by adsorption and self-assembly of organic molecules is an increasingly popular field with potential applications in the fields of biosensors, molecular electronics, and heterogeneous catalysis.[1–5] So far, most studies have involved homomolecular interactions, but structures based on heteromolecular interactions have recently been described.[6–8] The preparation of these multicomponent nanostructures allows the formation of more complex patterns including, for example, alternating lines of molecules or honeycomb networks.[9–13] Thus, all these systems rely on relatively strong bonds such as heteromolecular hydrogen or coordination bonds. The characteristics of these interactions in terms of strength, specificity, and reversibility define a network with an overall geometry that is determined by the chemical structures of the two components.[14]

Herein, a different approach is presented that uses a metastable open 2D host-molecule packing motif that can accommodate a complementary guest molecule. By selection of the phase in which this guest molecule will be inserted, the final bimolecular 2D organization can be controlled.

The self-organization properties of 2,3,9,10,16,17,23,24-octachlorozinc phthalocyanine ($ZnPcCl_8$, Figure 1 a) have recently been studied by room-temperature scanning tunneling microscopy (STM) and density functional theory (DFT) calculations by Porte and co-workers.[15,16] 2D crystallization of this compound occurred from a low-density to a compact packing through two phase transitions. Similar results have been obtained by Samuely et al. with phenoxy-substituted phthalocyanines.[17] The presence of eight chlorine atoms in $ZnPcCl_8$, which are prone to relatively weak hydrogen bonds that compete with van der Waals H···H interactions, leads to kinetic control of the self-assembly process on the substrate. The choice of the guest molecule to be inserted into this adaptive network was governed by several considerations: a) its dimensions must match those of $ZnPcCl_8$ to easily form an ordered system, b) nonfunctionalized polyaromatic hydrocarbons are also more suitable for the prevention of strong directional bonding, and c) this molecule must exhibit a relatively weak interaction with the substrate so that the final packing is mainly driven by intermolecular interactions. With these criteria in mind, we selected 1,3,5,7,9-penta-*tert*-butylcorannulene (PTBC, Figure 1 b) as a potential candidate for insertion into the different crystalline phases of $ZnPcCl_8$ monolayers on Ag(111).

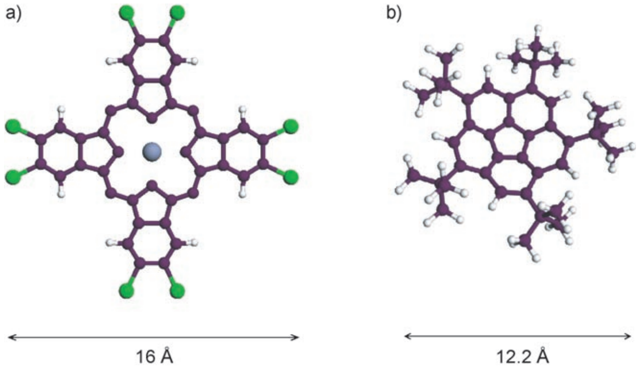

Figure 1. Structures of a) $ZnPcCl_8$ and b) PTBC.

Corannulene is a buckybowl with fivefold symmetry which can be considered as small fragment of C_{60}. Its symmetry prevents close-packed surface coverage. When unsubstituted corannulene is adsorbed onto Cu(110), a strong interaction with the surface leads to the formation of a quasi-hexagonal packing with weak direct intermolecular interactions.[18] This has prompted us to prepare the penta-*tert*-butyl derivative of corannulene that bears bulky groups on all five double bonds of the rim.[19] These groups raise the height of the central polyaromatic core and therefore reduce its interaction with Ag(111), which has a lower surface energy and shows a much weaker molecule–substrate interaction than Cu(110). Thus, the overall molecule–substrate interaction is lowered. After equilibration of the kinetic energy corresponding to the temperature of the source when the molecules are evaporated, formation of the 2D lattice structure is mainly driven by intermolecular interactions (van der Waals interactions and hydrogen bonds).

Figure 2 shows UHV-STM (UHV = ultrahigh vacuum) images of the three phases of $ZnPcCl_8$ on Ag(111), which were observed at low temperature (4.6 K) in order to prevent the diffusion of the phthalocyanine molecules. The packing of $ZnPcCl_8$ by van der Waals interactions occurs immediately after deposition on the substrate at room temperature (Figure 2 a). This metastable phase (P1) presents an open oblique geometry with lattice parameters $a = b = 18$ Å and an angle $\gamma = 70°$. Two vectors are defined for this packing: $\vec{u} = \vec{a} + \vec{b}$ and $\vec{v} = \vec{a} - \vec{b}$. After a few hours at room temperature or 15 min annealing at $T = 320$ K, this packing motif evolves into a second, more compact 2D network (P2) characterized by the activation of four out of the eight possible intermolecular H···Cl hydrogen bonds (Figure 2 b).[20] Finally, after about ten hours at room temperature or annealing for one hour at 320 K, the network enters its final, stable phase (P3, Figure 2 c) with eight hydrogen bonds per molecule, shorter lattice parameters $a = b = 15$ Å, and an angle $\gamma = 90°$.[20] As clearly seen in Figure 2, the packing density upon this phase transition, from the metastable open network (P1, 0.33 mol nm^{-2}) to the more compact network (P2, 0.38 mol nm^{-2}) and finally to the thermally stable compact phase (P3, 0.44 mol nm^{-2}), progressively increases by more than 30 %. As discussed below, the low-density packing of the phases P1 and P2 allows the insertion of PTBC

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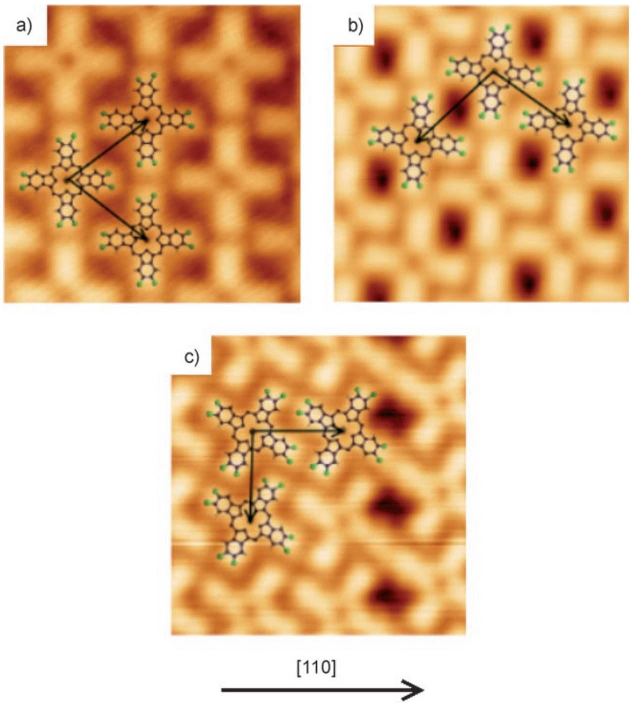

Figure 2. STM images (5×5 nm^2) at liquid-helium temperature ($T=4.6$ K) of the three 2D packings of ZnPcCl$_8$ on Ag(111): a) Phase 1 ($Vs=-1$ V, $I=200$ pA), observed immediately after molecule evaporation. z range: 0–0.8 Å. b) Phase 2, after 15 min annealing at 320 K (z range:0–1.25 Å, $Vs=0.4$ V, $I=250$ pA). c) Phase 3, after 1 h annealing (z range:0–1.2 Å, $Vs=-1.2$ V, $I=100$ pA). The horizontal arrow indicates the [110] direction of the Ag(111) surface.

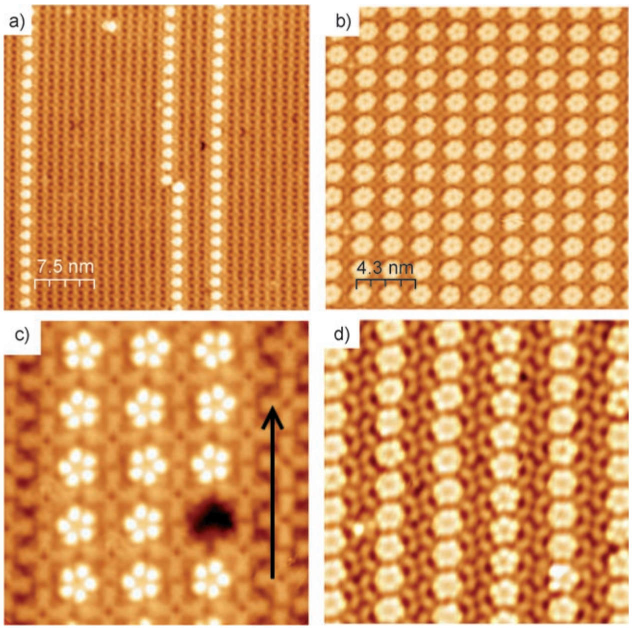

Figure 3. a) STM image of a P1 ZnPcCl$_8$ network observed at $T=77$ K after evaporation of PTBC molecules. Image obtained at low PTBC coverage ($Vs=1$ V, $I=100$ pA). b) STM image at higher PTBC coverage ($Vs=1$ V, $I=8$ pA). c) STM image (9×9 nm^2; $T=4.6$ K) of PTBC molecules in a ZnPcCl$_8$ network ($Vs=-1$ V, $I=200$ pA). The black arrow indicates the propagation direction of the PTBC lines. d) Bicomponent network obtained from the evaporation of PTBC molecules onto a P2 ZnPcCl$_8$ lattice ($Vs=1.2$ V, $I=10$ pA).

inside two different networks which provide two different final stable 2D nanostructures.

In a first experiment, PTBC molecules were sublimed and deposited onto the phase P1 maintained at room temperature. Figure 3 shows two STM images taken at $T=77$ K immediately after PTBC evaporation for two different coverages. Figure 3a was obtained at low coverage and shows lines of PTBC along the $\vec{v}$ direction of the P1 lattice. Figure 3b shows a topography obtained for a 1:1 PTBC/phthalocyanine coverage. The molecules self-assemble into a chessboard structure. The distances between two PTBC lines are (24±0.2) Å along the $\vec{u}$ direction (originally $||\vec{u}||=(29\pm0.2)$ Å in P1), and (20±0.2) Å along the $\vec{v}$ direction (originally $||\vec{v}||=(21\pm0.2)$ Å).

A study of these PTBC lines has also been carried out at liquid-helium temperature (4.6 K). In the close-up view presented in Figure 3c, each PTBC molecule always appears as a fivefold symmetric structure and adopts only two possible positions, denoted "up" and "down". These positions are defined by the fact that one lobe points in the $\vec{u}$ or $-\vec{u}$ direction. 85 % of PTBC molecules appear as six-lobed structures at liquid-nitrogen temperature (Figure 3b). This arises from a time-averaged superposition of the two possible positions of the fivefold-symmetric PTBC in the lattice. These two positions are separated by a $\pi/5$ rad rotation angle. A small shift of about 100 pm in the position of some PTBC molecules in the lines is also observed. Because of the presence of both five- and six-lobed structures at this temperature, the rotation barriers of the PTBC in this heterogeneous network are estimated to be close to k_BT at 77 K, that is, about 7 meV. Such temperature effects in molecular imaging have already been observed by Diederich et al. in nanoporous packing.[21]

Similarly, PTBC evaporation at room temperature on ZnPcCl$_8$ layers in phase 2 also results in lines of PTBC (see Figure 3d). However, it results in a very different coassembly, in which the PTBC and phthalocyanine molecules align in separate lines. In comparison with the chessboard structure observed in phase P1, the phthalocyanines are now oriented along another main axis of the Ag(111) surface, that is, at 120° from the PTBC lines. The distance between these lines is (22±0.5) Å and the packing is extremely stable, with its 1:1 stoichiometry maintained over hundreds of nanometers. Evaporation of PTBC at room temperature on phthalocyanine monolayers in P3 has also been carried out. As expected, the dense phthalocyanine packing, which arises from the network of eight hydrogen bonds, prevents the insertion of PTBC into the 2D crystal.

At this stage, it is not clear from the topographic images whether the PTBC molecules are inserted into the ZnPcCl$_8$ network and physisorbed onto the silver substrate or alternatively lying on a phthalocyanine molecule. Experimental scan lines have been studied and are presented in Figure 4. Scan a was recorded for a single PTBC molecule lying on Ag(111) with an apparent height of about 2.2 Å (see Figure 4a). The corrugation of PTBC molecules deposited

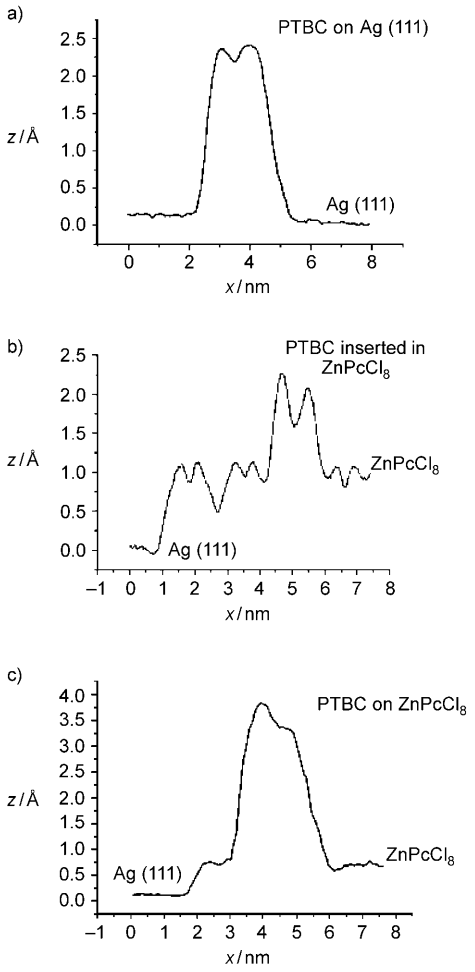

Figure 4. a) Experimental scan line of a single PTBC molecule on an Ag(111) substrate ($Vs = 1.5$ V, $I = 2$ pA). b) Profile corresponding to the relative height of PTBC in the P1 network ($V = -1$ V, $I = 200$ pA). c) Experimental profile obtained after evaporation of PTBC onto a P1 network at 4.6 K ($Vs = 1.5$ V, $I = 4$ pA). The origin is given by the Ag (111) substrate.

on the ZnPcCl$_8$ layer at room temperature is evident in Figure 4b; the relative apparent height is (1.0 ± 0.1) Å with a bias voltage of -1 V. Evaporation of PTBC onto a P1 lattice has been also conducted while the phthalocyanine layer was maintained at 4.6 K. Diffusion is impossible at this temperature and PTBC lies directly on the P1 lattice (Figure 4c). This shows that, neglecting the electronic structure effects, the measured corrugation of the PTBC molecule corresponds to the height of a phthalocyanine molecule lying on the metallic substrate plus the height of a single PTBC molecule (about $1.2 + 2.5$ Å).

These different results clearly indicate that PTBC is inserted into the phthalocyanine network when the substrate is maintained at room temperature during evaporation. The final packing is stabilized by the electronic attraction of the two molecules as well as the presence of chlorine atoms in ZnPcCl$_8$, which promotes the creation of hydrogen bonds between the two molecules.

The observation that phthalocyanine and penta-*tert*-butylcorannulenes molecules self-assemble demonstrates the existence of an original growth mechanism. The phthalocyanine molecules in the P1 phase are bound only by van der Waals interactions that are assumed to be weak.[20] Thus, the diffusion barriers of the phthalocyanine molecules remain low and an evaporated PTBC molecule can take advantage of this mobility at room temperature to enter the original P1 network.

The mechanism of formation of the PTBC lines is presented in Figure 5a,b. The open structure of packing type P1 results in the existence of favored PTBC adsorption sites (one is represented by a black circle surrounded by four ZnPcCl$_8$ molecules in Figure 5a). The surrounding phthalocyanine molecules are therefore moved by the adsorbed PTBC (black arrows) and the perturbation in the original pattern induces a stress. Because of the anisotropy of the P1 lattice ($||\vec{u}|| > ||\vec{v}||$), stress relaxation is essentially 1D and leads to a 1D opening in the original packing of the phthalocyanine (Figure 5b). Favored adsorption sites along the opened direction ($\vec{v}$) thus appear, which explains the formation of PTBC lines. In this bicomponent lattice, PTBC molecules adopt two positions ("up" and "down") which are stabilized by hydrogen bonds (see Figure 5b). This stabilization causes a contraction of approximately 15% of the original P1 lattice parameters. The same mechanism occurs in

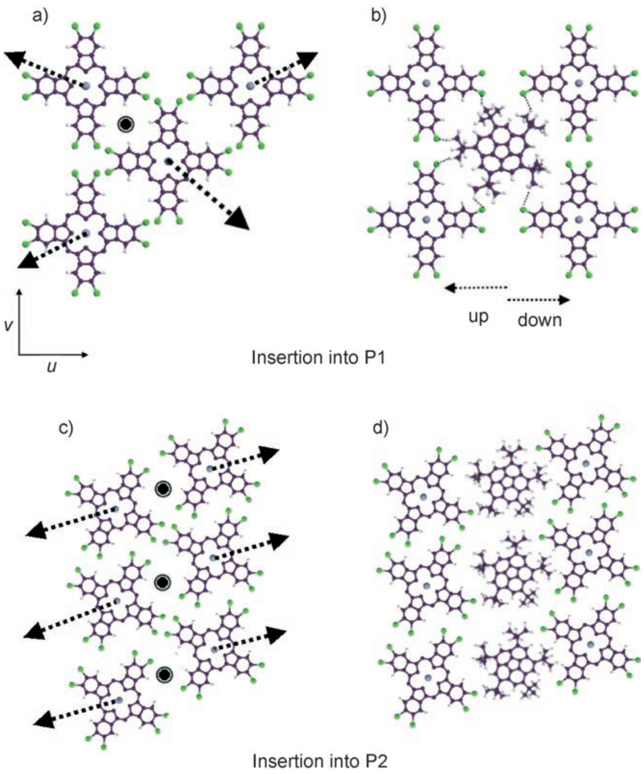

Figure 5. a) Scheme representing the original phthalocyanine positions in P1. The circle indicates one of the favored adsorption sites for an incoming PTBC molecule. The arrow shows the direction of motion of the phthalocyanine molecules when PTBC is adsorbed. b) Schematic representation of PTBC inserted into the phthalocyanine network stabilized by H-bonding. c) Schematic representation of the P2 phase with adsorption sites in the packing. d) Schematic representation of the creation of PTBC lines in the original P2 network.

the P2 lattice and PTBC molecules can use the opening to insert into the P2 network (see Figure 5c,d).

The bicomponent layers may also be modified by using the STM tip. This is illustrated in Figure 6, where "holes" in the packing have been created. Indeed, a PTBC molecule could be removed by a vertical manipulation when the STM tip was positioned over it. This process was found to be reproducible. Because of a strong interaction with the substrate (charge transfer of 0.65 electrons),[20] the same operation cannot be achieved with the phthalocyanine network. A single $ZnPcCl_8$ molecule has been isolated by repeating the process three more times (Figure 6c). The energy from the tip induces the motion of the $ZnPcCl_8$ molecule in the small cavity created by removal of the PTBC molecules. The final position of the molecule results from the lateral interactions of its nearest neighbors. This suggests that PTBC molecules can be used as a mask to generate artificial patterns and these unique structures highlight a particularly interesting aspect of these flexible bicomponent assemblies.

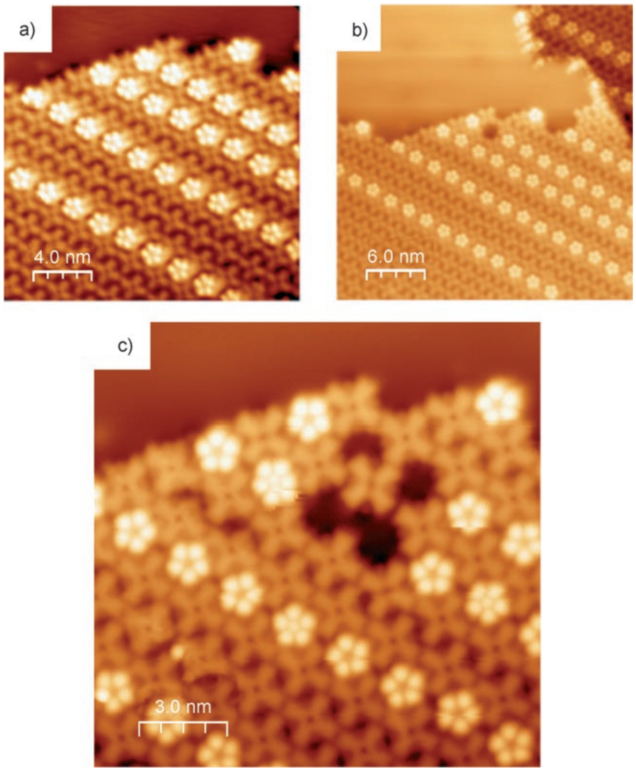

Figure 6. a) STM image at $T = 4.6$ K of PTBC molecules in a $ZnPcCl_8$ network originally in P1 ($Vs = 1$ V, $I = 200$ pA). b) A hole in the packing has been created by positioning the STM tip over a PTBC molecule. c) Isolation of a phthalocyanine molecule after repetition of this operation three more times.

In conclusion, our results support the view that the various structures of weakly bonded networks, such as the metastable phases of $ZnPcCl_8$, can be used as deformable flexible templates for the controlled insertion of a second molecule. This insertion results in the formation of either stable lines or chessboard arrays which bear resemblance to the original packing.

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