Supramolecular chemistry

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Lateral Manipulation for the Positioning of Molecular Guests within the Confinements of a Highly Stable Self-Assembled Organic Surface Network**

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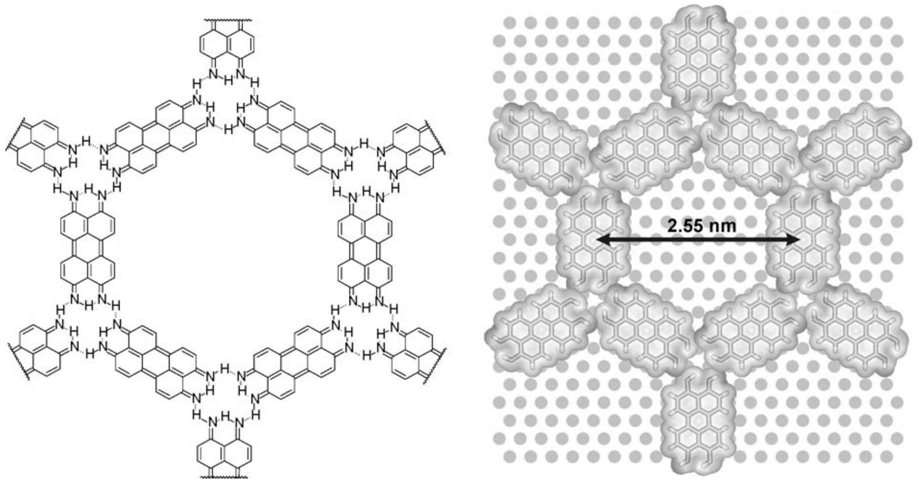
Structural hierarchies at the molecular level can be determined by the hierarchies of interaction energies; in other words, for the generation of complex structures in several steps, significant differences in the interaction energetics are required.[1] The assembly of the first structural level needs to involve strong interactions between the molecular building blocks, whereas its subsequent extension without modification of the scaffold is conveniently achieved on the basis of weaker bonding forces. This applies both to supramolecular assemblies in solution and in air/vacuum and to fixed or spatially confined structures.[2] Herein, we provide such an example based on a surface organic network structure of unprecedented thermal stability.

Crystal surfaces have served as initial scaffolds for the generation of such spatially addressable structures,[3] and the manipulation of single atoms and molecules has been achieved by scanning probe microscopy.[4,5] More recently, extensive investigations into the controlled lateral manipulation of large molecules[6] possessing multiple and even partially addressable degrees of freedom have been reported.[7] The scanning tunneling microscopy (STM) tip was even used to induce chemical reactions,[8] for example, the Ullman reaction.[9]



Scheme 1. Chemical structure and schematic drawing of the hexagonal network of thermally generated dehydro-DPDI on a Cu(111) surface.[12]

We recently reported the formation of a highly stable, hexagonal molecular network generated by thermal dehydrogenation of 4,9-diaminoperylene-quinone-3,10-diimine (DPDI)[10] on a Cu(111) surface (Scheme 1).[11] By thermal activation, these molecules form autocomplementary hydrogen-bond donors/acceptors, which preposition themselves in the formation of the surface network. The highly regular honeycomb structure[12] is commensurate with the Cu substrate (in the form of a p(10×10) superlattice with a lattice constant of 2.55 nm) and is thermally very stable (up to $>300\,^{\circ}\mathrm{C}$) as a consequence of a combination of strong π bonding between the organic molecules and the surface metal atoms and resonance-assisted H bonding between the molecules. Due to its structural regularity and stability, this surface structure provides the ideal starting point for the assembly of functional hierarchical aggregates. The hexagonal "holes" in the network provide the opportunity for the local deposition and fixation of other molecules (Scheme 1).

Figure 1 shows an STM image at 77 K of C_{60} and zinc octaethylporphyrin (ZnOEP) complexes subsequently deposited at ambient temperature on the previously prepared honeycomb network. Both C_{60} and ZnOEP are trapped and statistically distributed in the network. At this low tempera-

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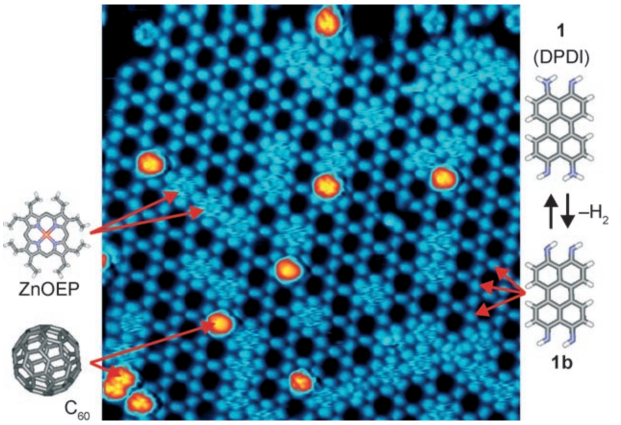

Figure 1. STM image (30 × 30 nm^2, 12 pA, −1.7 V, 77 K) of C_{60} and ZnOEP molecules trapped in the pores of the dehydro-DPDI honeycomb network. The chemical structures are assigned to the molecular units by arrows. The van der Waals diameters of C_{60} and ZnOEP are 0.7 and 1.6 nm, respectively.

ture, the C_{60} molecules do not show any mobility within the hexagonal pores, while the ZnOEP molecules still exhibit a thermally activated rotation libration.[13] However, STM images taken at room temperature display a translational mobility of some of the C_{60} molecules trapped within the pores.[14] This mobility is not purely tip-induced, since in the same STM image individual static and dynamic C_{60} molecules are found within the pores. We assume that the difference in mobility depends on the adsorption of the C_{60} on the Cu surface, that is, if the C_{60} is adsorbed via a five-membered ring, a six-membered ring, or a C=C double bond,[15] as well as the surrounding dehydro-DPDI network. Nevertheless, the C_{60} cannot move on its own from one pore to another. It is known that a charge transfer (about 0.8 eV) from the metal substrate to C_{60} takes place,[15] which leads to a strong interaction with the surface. Therefore, the probability of a C_{60} molecule jumping from one pore (energetic minimum) to another is low due to the high-energy barrier formed by the cavity walls of the dehydro-DPDI network. Outside the honeycomb network, again the behavior of C_{60} and ZnOEP differs at both low and room temperature. Even at room temperature, the C_{60} molecules arrange in close-packed hexagonal islands (Figure 2).[16]

This finding can be explained by highly attractive molecule–molecule interactions originating from the frontier π orbitals of C_{60}, which extend out of the carbon cage and lead to significant attractive van der Waals interactions due to polarization fluctuation waves on the molecule.[17] In contrast to C_{60}, no ordered arrangement of ZnOEP is found outside the honeycomb network. At room temperature, the ZnOEP molecules give rise to a mobile two-dimensional (2D) fluid phase[18] on the bare metal surface because their intermolecular interaction is rather weak. At 77 K, the diffusive motion on the free-metal area is close to frozen and single molecules appear immobile in STM. Again, their appearance indicates residual mobility; however, some ZnOEP molecules are pinned at the edges of the hexagonal DPDI islands and their eight "ethyl legs" are clearly visible.

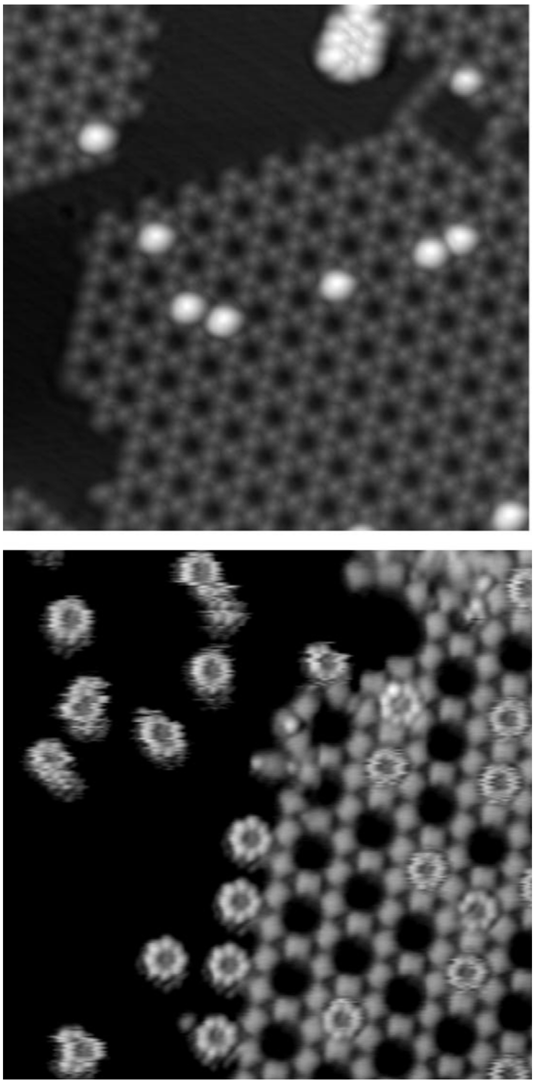

Figure 2. Top: STM image (30 × 30 nm^2, $I = 50$ pA, $U = -0.40$ V, 77 K) of C_{60} trapped in the honeycomb network of dehydro-DPDI on a Cu(111) surface. At the top of the image, outside the partially filled network, a C_{60} island consisting of about ten C_{60} molecules is formed due to the strong intermolecular interactions. Bottom: STM image (19 × 19 nm^2, $I = 25$ pA, $U = -1.55$ V, 77 K) of ZnOEP within and at the edges of the hexagonal network. The observed diffusive mobility is hindered for molecules adsorbed either within the network, where lateral mobility is blocked, or at the edges of the network, where the observable translational/vibrational libration is minimal due to site-specific interactions.

Upon increased C_{60} occupancy of the dehydro-DPDI honeycomb sublattice, up to three guest molecules may be inserted into each hexagonal pore (see Figure 3). Closer inspection of this array reveals that there appear to be preferential orientations of the C_{60} pairs and triplets, which are commensurate with the hexagonal symmetry of the organic "host" as well as the Cu(111) substrate.

Recently, a number of self-assembled porous networks on surfaces have been reported to which C_{60} molecules were added.[19] For a porous porphyrin network,[19a,b] a hopping behavior was found for the co-adsorbed C_{60} molecules that are not in contact with the metal surface. In a bicomponent

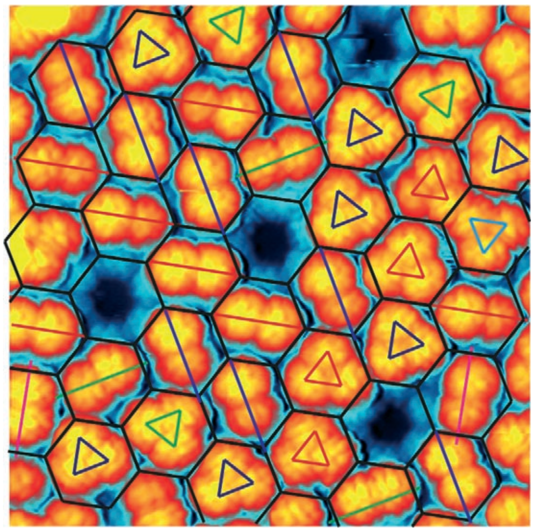

Figure 3. Higher-density deposition of C_{60} onto the dehydro-DPDI network (15 × 15 nm^2, 15 pA, 1.2 V, 77 K). Pores with zero to threefold C_{60} population are observed. Pairs and triplets of C_{60} appear predominantly centered within their host pore, and their preferential orientations are commensurate with the hexagonal symmetry of the organic "host" and the metal substrate.

system of C_{60} and a thiophene-containing macrocycle,[19c,d] the C_{60} molecules were found to interact with the thiophene units of the macrocycle, thus forming a donor–acceptor complex. In contrast, for our system, neither hopping behavior nor complex formation between C_{60} and perilene monomers was found. Instead, the extraordinarily high stability of our network is the principal advantage compared to all the other networks reported so far, which makes it the ideal candidate for hierarchical assembly.

It was of interest to find out if and how trapped molecules could be moved from one pore in the dehydro-DPDI network to another. Figure 4 summarizes a series of controlled repositioning events. Molecular repositioning was carried out by switching off the feedback system and setting a negative tip-lift value of 0.40 nm. This means that once the feedback is switched off, the tip is approached 0.40 nm towards the sample surface. Herein, this distance is measured relative to the initial z height, which is defined by the combination of current setpoint and bias voltage, in our case 90 pA and −0.5 V. Therefore, the reproducibility of the manipulation sequence is assured by these tunneling parameters. Normally, the feedback system is switched off while the tip is placed above an empty pore and the C_{60} molecule to be repositioned is hosted in a neighboring pore. The repositioning of the C_{60} is thus performed in the so-called "constant-height manipulation mode".[4e]

The series of STM images in Figure 4 shows how such a C_{60} manipulation can be used to fabricate a model system of a ball bearing at the single-molecule level.[20] The sequence displays how a C_{60} molecule is moved on top of an individual ZnOEP molecule. This bimolecular system can be envisaged as a solid ball, which is placed onto the porphyrin ring system in a slightly off-center position and is suspended by the eight ethyl legs of ZnOEP (Figure 5). The preferred acentric position of the buckyball may be rationalized by the attractive π stacking with the heterocycle and the absence of any bonding interaction with the central zinc atom.[21]

However, this assembly is not very stable and rather difficult to prepare. It is evident that the greatest difficulty of

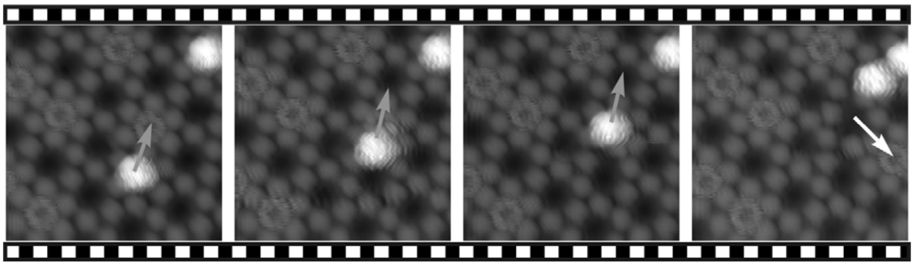

Figure 4. Sequence of STM images (10 × 10 nm^2, 90 pA, −0.5 V, 77 K) displaying the successful repositioning of an individual C_{60} molecule along the gray arrows. The C_{60} was first moved on top of an empty pore, as denoted in Figure 1, and from this position on top of a pore filled with a ZnOEP molecule. Thereby, a kind of molecular ball bearing is fabricated. On trying to move the C_{60}–ZnOEP complex into another pore, the two molecules separate again and are each found in distinct pores of the DPDI network. The white arrow points to the ZnOEP molecule, which changed its place after the attempted manipulation of the complex.

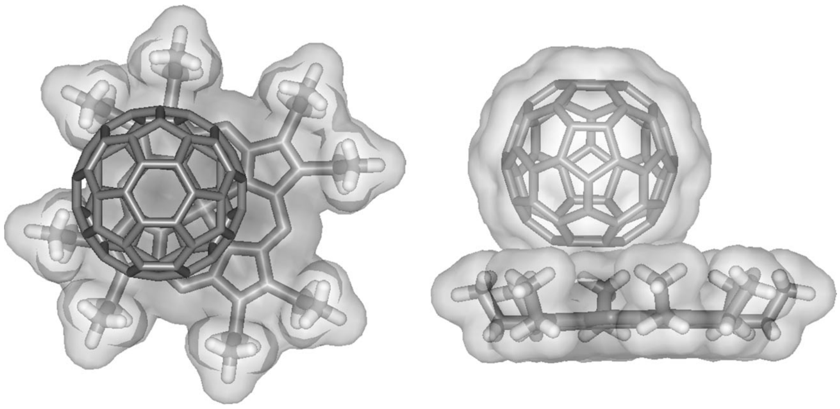

Figure 5. Model of the C_{60} molecule placed on top of a ZnOEP molecule: a molecular "ball bearing" trapped in a dehydro-DPDI cavity. The spherical C_{60} molecule occupies a slightly off-center position and is suspended by the eight "ethyl legs" of ZnOEP.

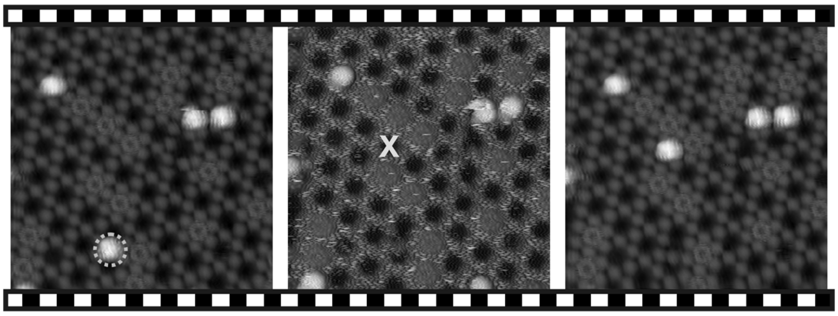

Figure 6. Sequence of STM images (20 × 20 nm^2, 90 pA, −0.5 V, 77 K) displaying the vertical manipulation of an individual C_{60} molecule. The C_{60} molecule marked with a dashed circle was picked up with the tip (left image). The middle image was then scanned with the C_{60} attached to the tip apex. The image on the right was recorded after putting the C_{60} back onto the surface at the position marked with the X.

such positioning experiments is the fact that it is not possible to position and image at the same time, and thus no real-time feedback about the status of the surface exists while performing manipulations.

For vertical manipulation, the tip is placed directly above a C_{60} molecule. The feedback loop is turned off and the tip is approached 0.4 nm towards the surface, to pick up the molecule with the tip. This vertical manipulation of a molecule can be followed in the current and height signals, because they change their characteristic noise when the molecule is picked up. The image sequence in Figure 6 shows such a vertical manipulation for an individual C_{60} molecule. The C_{60} sphere, which is marked by a yellow circle in the left-hand image, was transferred to the tip apex via the aforementioned procedure. The successful transfer of the C_{60} from the surface to the tip was proven by imaging the same area but this time with the C_{60}-modified tip. The molecule that was picked up is no longer visible and the change of the image contrast is due to the C_{60}-modified tip.[22] By positioning the tip above an empty pore, turning off the feedback loop, and approaching the tip 0.4 nm towards the surface, the C_{60} was placed back onto the position marked with an X in Figure 6 (center).

In summary, we have demonstrated how a highly stable porous organic network, which was generated on a Cu(111) substrate by an irreversible chemical transformation, may provide a spatial grid for the manipulation and positioning of single molecules. This has been shown, in particular, through the piece-by-piece assembly of the weakly aggregated ZnOEP–C_{60} complex, which may be viewed as a "supramolecular bearing".[20] To what degree the shallow pores of the dehydro-DPDI network may serve as confinements for chemical reactions is the object of ongoing research activity.

Supporting Information: The experimental procedure, STM images of C_{60} deposited onto dehydro-DPDI on Cu(111) recorded at ambient temperature and at 77 K, and STM images of C_{60} deposited at high density onto dehydro-DPDI on Cu(111) are given in the Supporting Information.

Keywords:
carbon · complexes · networks · porphyrins · supramolecular chemistry

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