Surface Chemistry

DOI: 10.1002/anie.200702531

Crossover Site-Selectivity in the Adsorption of the Fullerene Derivative PCBM on Au(111)**

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The adsorption and self-assembly of functional molecular systems on solid surfaces is a powerful tool to fabricate well-ordered structures suitable for potential applications in molecular electronics or nanomechanics.[1] In general, the 2D arrangement is the result of a combination of weak noncovalent intermolecular forces (such as van der Waals, or dispersive forces) with molecule–substrate interactions.[2] It is generally accepted that molecule–substrate interactions determine adsorption geometry and conformation in the first place, while intermolecular interactions only affect the subsequent self-assembly of the adsorbates.[2] Only when the molecules have the possibility of forming strong directional bonds, like hydrogen-type bonds,[3] and the corrugation of the potential energy for the adsorbed species is small compared to the energy gain from intermolecular interactions, are the supramolecular structures formed on surfaces mainly determined by intermolecular forces (although the substrate influence may still be important).[3] In contrast, there are also a few specific systems, involving vicinal or chemically heterogeneous surfaces,[4] for which there is a strong selectivity in the adsorption site of the adsorbates and where the substrate is thus the one that determines the final morphology. This is the case of the Au(111) surface, where preferential nucleation at the elbows of the "herringbone" reconstruction can give rise to an ordered network of nanodots of metals or organic materials.[5] A certain selectivity for nucleation at the fcc areas of this surface has also been reported for a number of systems,[6] but the interaction is not strong enough to create extended well-ordered structures.

Note that in the previously described cases the role of molecule–substrate interactions in controlling the self-assembled geometry is discussed at the single-molecule level; that is, the freedom of intermolecular interactions to dictate the geometry of the adsorbed molecules is determined by the interaction of one single molecule with the substrate. Strictly speaking, this is an approximation as the formation of intermolecular bonds might modify the adsorption geometry and, hence, molecule–substrate interactions. In particular, for surface/adsorbate systems showing site-selective adsorption, the modification of the adsorption geometry upon intermolecular bond formation might result in the removal of the site-selectivity. As intermolecular interactions become more important with increasing coverages, a coverage-dependent transition from site-specific to site-unspecific adsorption might be expected. This is particularly relevant for the technique of surface patterning—which holds great promise to control the morphology of organic overlayers on solid surfaces—with the last goal of providing the optimal conditions under which the surface-templating effect, arising from site-selective adsorption, can be maintained.

Here, by means of variable-temperature scanning tunneling microscopy (STM) experiments and density functional theory (DFT) calculations, we have investigated the crossover

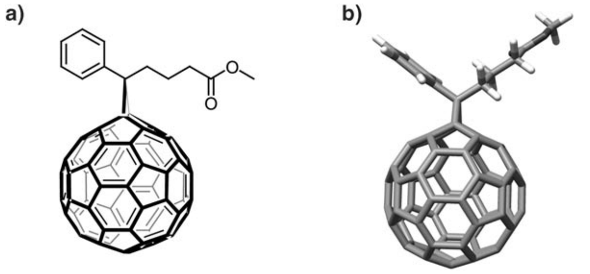

Figure 1. a) Chemical formula of PCMB and b) its optimized conformation according to DFT calculations (see text for details).

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[**] This work was supported by the MEC of Spain (MSR-FIS2004-0126, NAN-2004-08881-002-01, CTQ2004-00039/BQU, CTQ2005-02609/BTQ, CTQ2006-08558) and the Comunidad de Madrid (nanomagnet S-0505/MAT/0194, P-PPQ-000225-0505). R.O. thanks the Spanish Ministry for Education and Science for salary support. We thank Dr. E. M. Pérez for the helpful discussions. PCBM = phenyl-C_{61}-butyric acid methyl ester.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

of the site-selectivity in the adsorption and self-assembly of PCBM (phenyl-C_{61}-butyric acid methyl ester, Figure 1)[7] on the herringbone-reconstructed Au(111) surface as a function of the coverage (see Figure S1 in the Supporting Information). We show that whereas at low coverages PCBM self-assembles to create long, parallel, isolated 1D wires, or 2D extended networks, as dictated almost exclusively by the substrate-controlled preference for nucleating at the fcc sites of the reconstruction, at higher coverages intramolecular interactions take over, bypassing the substrate influence and giving rise to islands composed of laterally ordered parallel, 1D double rows of PCBM molecules. The identification of this structure by comparison with theoretical calculations offers a picture of this transition in good agreement with the above-mentioned scenario; at high-enough coverages, hydrogen bonds between double rows are formed that modify the adsorption geometry of PCBM molecules, which in turn removes site-selectivity. The phenomenon of intermolecular-interaction-driven modification of the adsorption geometry might thus be crucial to optimize the templating effect of surface nanoscale patterns on adsorbed organic overlayers.

Figure 2 shows STM images (taken at 170 K) of the Au(111) surface after depositing increasing amounts of PCBM molecules in ultrahigh vacuum with the surface held at 300 K. After the first molecules decorate the atomic steps of the surface (which implies a high room-temperature diffusivity), the following molecules nucleate at the elbows of the herringbone reconstruction (Figure 2a and also Figure S2 in the Supporting Information). Unlike the preferential binding at the elbows observed for other systems,[5] PCBM shows a new selectivity for nucleating at only one type of these elbows (Figure 2a,b, and see also the Supporting Information).

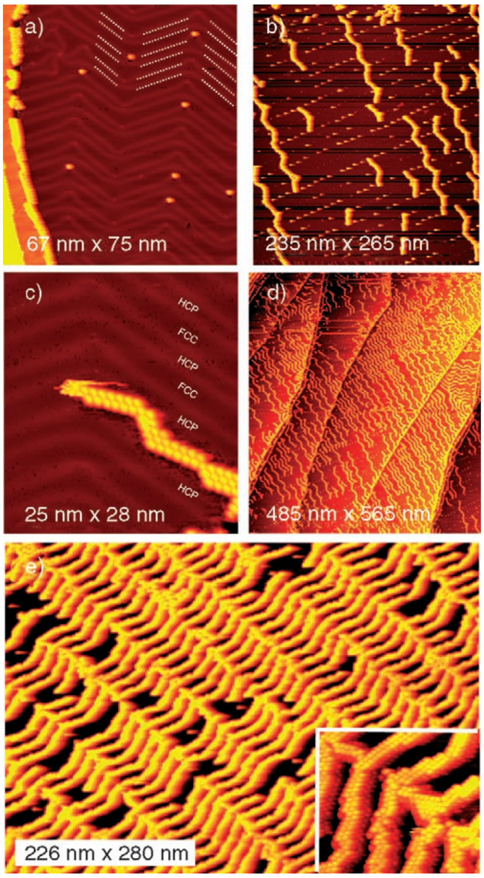

Figure 2. STM images of the Au(111) after depositing increasing amounts of PCBM (ML = monolayer). a) < 0.1 ML; b) 0.1 ML; d) 0.3 ML; e) 0.4 ML. The image in part (c) shows a close up of one of the zigzag structures. The dotted lines in part (a) mark the dislocation lines separating FCC and HCP areas. The place where two dislocation lines virtually meet is an "elbow" of the reconstruction.

When increasing the coverage, a number of fingerlike zigzag structures appear on the surface (Figure 2b). This involves the formation of one-dimensional molecular arrays starting from the molecules already nucleated at the elbows. A closer look (Figure 2c and also Figure S2 in the Supporting Information) reveals that these zigzag arrays appear exclusively on the fcc areas of the reconstruction and are actually double rows of PCBM molecules composed of shorter, linear fragments, each one containing a small number of molecules separated by around 10 Å. Note, however, that these short fragments do not run parallel to the fcc lines, but along (or close to) a close-packed direction of the surface, thus forming an angle of 30° with the fcc lines. Further deposition (Figure 2d and also Figure S2 in the Supporting Information) causes the formation of parallel molecular chains hundreds of nanometers long and separated only by a few nanometers (≈6 nm). These chains grow in length until they cover completely the fcc areas of the surface. Then, the growth proceeds along the lines joining the elbows of the reconstruction, giving rise to a highly organized 2D network of PCBM molecules resembling a nanosized "spiderweb" (Figure 2e and also Figure S4 in the Supporting Information).

For these coverages, the isolated double rows of PCBM seem not to be able to cross the dislocation lines separating the fcc from the hcp regions of the surface. Thus, when a double row reaches the dislocation lines of the reconstruction, it cannot grow further and another fragment starts from the opposite side of the chain (see Figure 2c and also Figure S4 in the Supporting Information). In this way, only the fcc regions of the reconstruction are decorated with PCBM molecules. This behavior contrasts with that previously observed for pristine C_{60} on the same surface which first nucleates at step edges and then produces compact hexagonal islands, disregarding the morphology of the Au(111) reconstruction.[8] As both the separation (≈10 Å) and the apparent height (between 4 and 6 Å depending on the bias voltage) of PCBM are very similar to those of C_{60}, we suppose that the "side tails" of the PCBM molecules must be pointing outwards the double rows. Moreover, the difference in site-selectivity between C_{60} and PCBM implies an important role of the organic addend of the latter in the mechanism of site-selective adsorption and, thus, suggest an adsorption geometry in which this addend is in close contact to the surface. Supporting this assumption, our calculations indicate that there is just not enough space for the tails to sit in between two adjacent molecules (see Figure S4 in the Supporting Information).

The data supports that the supramolecular ordering up to this stage is the result of two combined effects: first, the particular interaction between the molecular tail and the surface reconstruction, leading to the impossibility for adsorbed PCBM molecules to sit on the dislocation lines which results in an almost exclusive decoration of the fcc areas of the surface; and second, the π–π interactions among the C_{60} cages which causes the formation of double rows of molecules (further compact arrangement is impeded by the existence of the side tail and its attraction to the substrate surface). The reason for this preferential nucleation may be both steric (the fcc areas are wider than the hcp ones) and/or electronic (the charge density of the surface-state electrons is different in the fcc regions, the hcp regions, and the dislocation lines of the reconstruction).[9] Note that the corrugation of the Au(111) surface, that is, the height difference between the fcc areas and the dislocation lines is only 0.2 Å, which discards a simple geometric effect.

When the density of deposited molecules exceeds that of the available fcc areas, the interactions between the organic addends of the fullerene molecules take over molecule–substrate interactions, removing the site-selectivity in the adsorption of PCBM and forcing the molecules to reorganize (Figure 3) into a compact arrangement of double-row chains, equally spaced, and running parallel to the close-packed directions of the Au(111) surface, with total disregard of the surface reconstruction. A higher resolution image of the compact double-row nanoscale network of PCBM is shown in Figure 3c. Again, the distance between molecules within a row is approximately 10 Å. In addition, the image reveals now some bright spots in the region separating adjacent double rows.

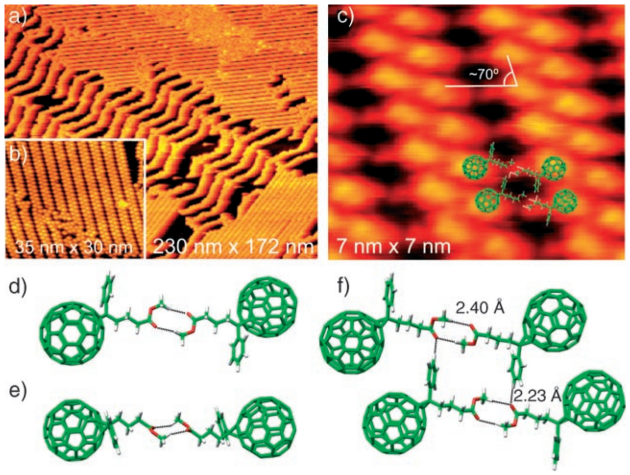

Figure 3. a) Large-scale STM image of the Au(111) surface after depositing approximately 0.6 ML of PCBM, showing the coexistence of two different phases: the nanoscale spiderweb (created by the templating effect of the substrate surface) and b) the sets of parallel double rows connected by an array of weak hydrogen bonds. c) STM image of the Au(111) surface after depositing approximately 0.6 ML of PCBM. d) Top and e) side views showing the optimized calculated structure for a PCBM dimer. f) Optimized structure for a PCBM tetramer. The dotted lines mark the weak hydrogen bonds responsible for this conformation.

To clarify the nature of the interaction between neighboring rows, we performed DFT calculations of the monomer, several possible dimers, and different tetrameric structures for freestanding PCBM. For these calculations, the optimized conformation of a single PCBM molecule was first determined (see Figure 1b). Thirteen dimer configurations, in which different separations and relative orientations of the PCBM molecules have been considered, were calculated, and the corresponding geometries were fully optimized. Top and side views of the resulting symmetric, minimum-energy dimer structure compatible with a 2D geometry on a solid surface are shown in Figure 3d and e. Under this configuration, two PCBM molecules are connected through two weak hydrogen bonds (calculated $H_{Me}\cdots O$ length is 2.40 Å) between the two tails, leading to an energy gain of 2.19 $kcal\,mol^{-1}$ with regards to two isolated molecules. The separation between the centers of the C_{60} cages is 23.7 Å, which is comparable to the experimental value of around 21 Å. Also, and now treating the PCBM dimer as a fixed unit, the optimized conformation for a tetramer was calculated as a function of the dimer separation and relative position. The final geometry (Figure 3 f) results from the formation of two additional hydrogen bonds between adjacent dimers (calculated $H_{Ar}\cdots O$ length is 2.23 Å). The comparison with the experimental data (see Figure S4a in the Supporting Information) is remarkable, including the separation between adjacent C_{60} cages (10.4 Å versus ≈10 Å) and the angle between three C_{60} cages of two different double rows (68° versus ≈70°; see inset in Figure 3c). Hydrogen bonds as those predicted by the calculations can only be formed if the hydrogen-donor and -acceptor groups at the PCBM tails face each other in the correct geometry. This implies that, as a result of the large size of the C_{60} cages, the tails cannot be in contact with the surface any more (see Figure 3e). Note that this model naturally explains the extra features found in the STM images as arising from the organic tails that hold the rows together.

The combination of the experimental findings and theoretical calculations reveal a general picture as follows: For low coverages, the interaction between the tails cannot keep the tails from touching the surface, which leads to site-selective adsorption on the fcc areas. Once the fcc areas are all occupied, new incoming molecules must sit on the energetically unfavorable dislocation lines. The molecular rows are now so close to each other that they must interact through the tails by hydrogen-bond formation, which implies a change in the adsorption geometry so that the PCBM tail does not touch the surface any longer, and the adsorption becomes site-unspecific. Further deposition of PCBM approaching one monolayer destroys the molecular order at the surface and produces an almost amorphous layer of molecules (see the central top part of Figure 3a).

The results reported here pave the way to the rational ordering of an outstanding type of functionalized carbon allotropes on gold surfaces, thus opening a new avenue in the quest for new properties and applications.

Received: June 11, 2007

Keywords: fullerenes · hydrogen bonds · scanning probe microscopy · self-assembly · surface chemistry

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