UNDERSTANDING THE SUPRAMOLECULAR SELF-ASSEMBLY OF THE FULLERENE DERIVATIVE PCBM ON Au(111) SURFACE

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Recent variable-temperature STM experiments[1] have observed a crossover of the site-selectivity in the adsorption and self-assembly of PCBM (Phenyl-C_{61}-Butyric acid Methyl ester), a C_{60} derivative, on the herringbone-reconstructed Au(111) surface as a function of the coverage. 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. However, at higher coverages, intermolecular interactions take over, bypassing the substrate influence, giving islands composed of laterally ordered parallel, 1D double rows of PCBM molecules (Fig. 1a). In order to understand this last step in the self-assembly of PCBM molecules on the gold surface, theoretical calculations were performed based on density functional theory (DFT).

The geometries of the PCBM monomer and 10 possible dimers were fully optimized at the B3LYP/3-21G and B3LYP/6-31G(d) levels. The calculations show that the binding of the two PCBM molecules is due mainly to the formation of weak hydrogen bonds (C–H···O) between the two PCBM tails (Fig. 1b and c). Then, four low-energy dimers with reasonable C_{60}–C_{60} distances were considered to form PCBM tetramers. By treating the PCBM dimer as a fixed unit, the conformation for a tetramer was optimized as a function of their separation and relative position at the B3LYP/3-21G level. The final geometry is due to the formation of two additional hydrogen bonds between adjacent dimers (Fig. 1d). The comparison with the experimental data is quite good (Fig. 1a), since the estimated values of distances (23.7 and 10.4 Å) and angle (68^o) for the arrangement of the C_{60} balls are in good agreement with experiment (21 and 10 Å and 70^o, respectively). These hydrogen bonds lie well above the surface due to the large size of the C_{60} cages, thus implying that the surface has little influence on them. This is why calculated arrangements of PCBM in the gas phase are in good agreement with the STM images at high coverage. Additionally, the lack of interaction between the tails and the surface also explains the site-insensitive adsorption of PCBM.

At low coverage, the PCBM molecules must approach each other by putting their “bald” sides face to face. This is due to the relatively strong van der Waals interaction between C60 cages. In this arrangement, the tails point in opposite directions (see Figure 2). This should be the dominant mechanism until the fcc areas of the Au(111) reconstruction are completely filled.

To study possible effects due to the surface, we carry out model calculations in which the tails of two interacting PCBM molecules are placed as in the dimer, but replacing the C60 cages and phenyl rings by hydrogen atoms. This simplified structure is placed over two layers of gold atoms representing the Au(111) surface (figure 3) Even though all the atoms are allowed to move from their initial positions, the tails do not approach the surface after geometry optimization. This is because the tails are so far away from the surface that the gold–oxygen interaction barely affects the weak hydrogen bonds formed between the two tails. Thus, our model calculations support the fact that the surface plays a very minor role in the self-assembly of PCBM at high coverage

References:

[1] D. Écija, R. Otero, L. Sánchez, J. M. Gallego, Y. Wang, M. Alcamí. F.Martín, N. Martín, R. Miranda, Angew. Chem., **119** (2007), 8020–8023.
[2] Y. Wang, M. Alcamí and F.Martín. Chem. Phys. Chem (in press)

Figures:

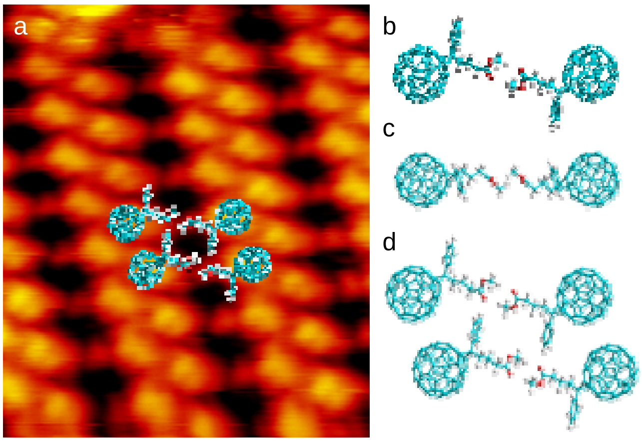

Figure 1 a) STM image of the Au(111) surface after depositing ~0.6 ML of PCBM. b) Top and c) side views showing the optimized calculated structure for a PCBM dimer. d) Optimized structure for a PCBM tetramer. The dotted lines mark the weak hydrogen bonds responsible for this conformation.

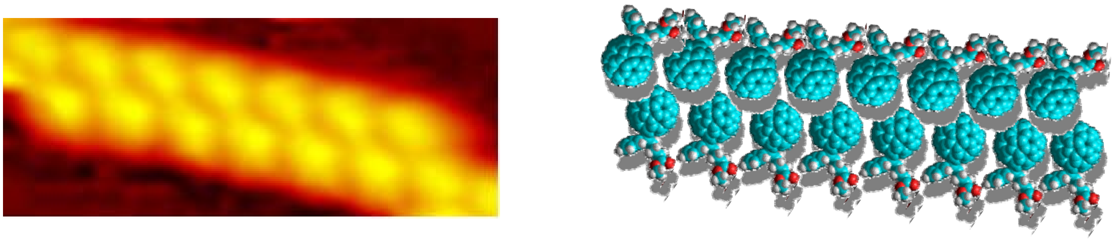

Figure 2. The 1D arrangement of the PCBM twin chain at low coverage

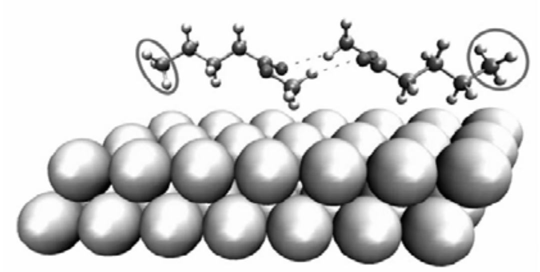

Figure 3. The optimized geometry of a supercell of the model dimer on Au-(111) surface by VASP. At the two ends of the model dimer, the circles indicate the methyl groups with fixed positions during the geometry optimization.