Supplementary Material (ESI) for PCCP

Supplementary Information
Role of van der Waals interaction in forming molecule-metal junctions: flat organic molecules on the Au(111) surface

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Here we present supplementary information about the diffusion calculations of the melamine and PTCDA molecules on the Au(111) surface. To investigate whether the surface potential is indeed flat, we performed extensive diffusion calculations for the melamine and PTCDA molecules on the surface in which a single carbon atom in their benzene-like core was moved in small steps along several directions, as is shown in Fig. 1, on the surface with subsequent relaxation of all other atoms of the molecule and the upper layer atoms of the surface; the vertical component of the chosen atom was also allowed to relax .

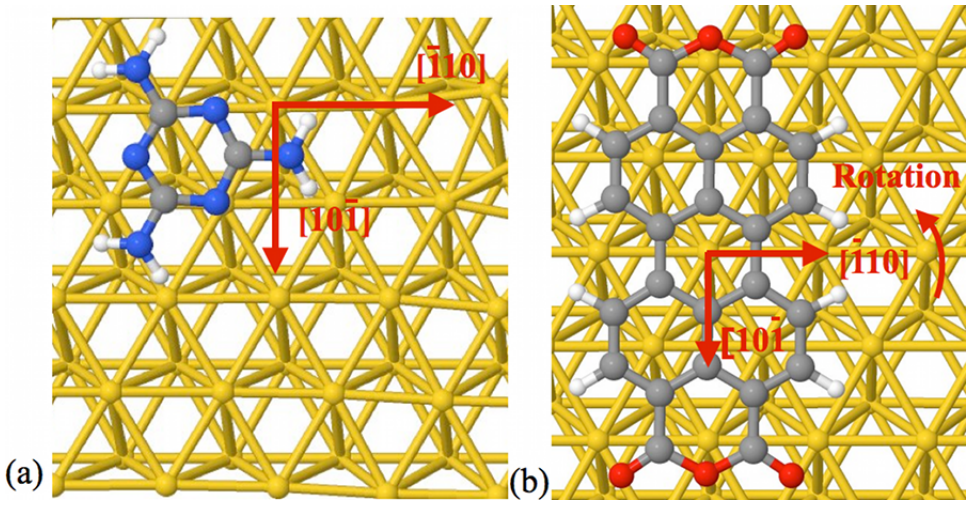

Figure 1: The starting geometry of the melamine (a) and PTCDA (b) molecules on the Au(111) surface. The red arrows indicate different directions considered to move the molecule across the surface; we also considered a rotation of PTCDA around its centre of mass.

We performed these calculations using both PBE and vdW-DF methods by translating the molecules in 0.1$\AA$ (PBE) or 0.05$\AA$ (vdW-DF) steps along several directions across the surface ([$\bar{1}$10] and [10$\bar{1}$]) as indicated in Fig. 1. In some of the PBE based calculations, we also rotated the PTCDA in 10° steps around its centre of mass. The results of these calculations are shown in Fig. 2 for the melamine and Fig. 3 for the PTCDA molecules, respectively. In some of the calculations the steps taken were rather big, so that the curves connecting the points are only used to guide the eye.

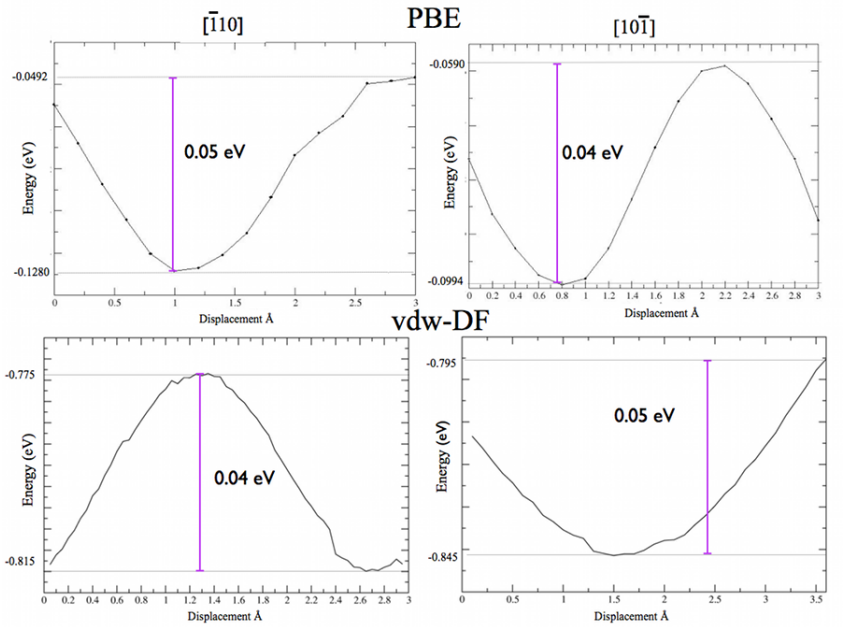

Figure 2: The relative total energy of a melamine molecule as a function of its position on the surface calculated using both PBE and vdW-DF functionals.

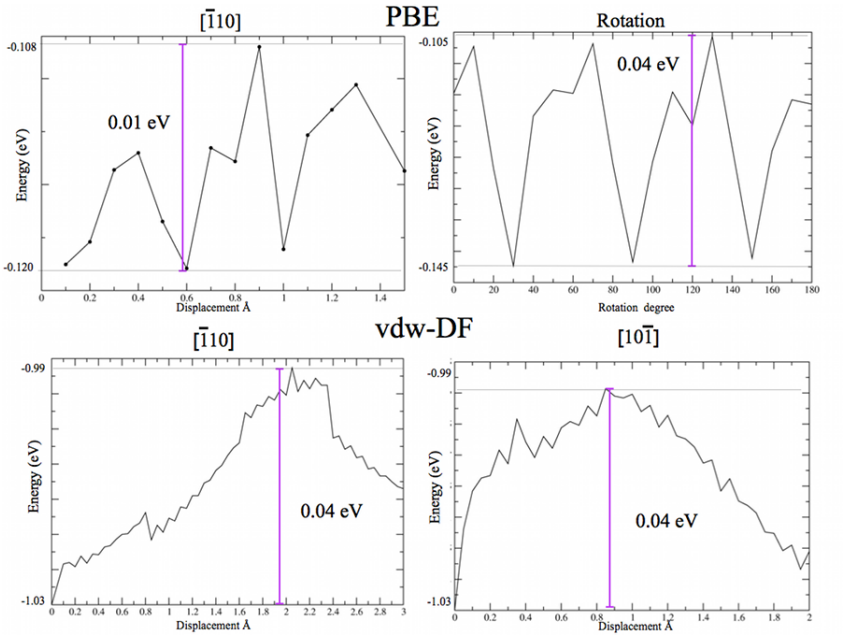

Figure 3: The relative energy of a PTCDA molecule calculated using both PBE and vdW-DF methods as a function of the molecule displacement along the surface directions as indicated, or when rotating the molecule around its centre of mass.

We find insignificant relaxations of both the gold and the molecules and a very small corrugation of the total energy: when moving the molecules in different lateral directions for up to 3 Å, the total energy changes by no more than 0.05 eV. This means that the surface potential predicted by the PBE and the vdW-DF method is very flat and hence the molecules must be extremely mobile on the surface at small coverages.