Chemisorbed and physisorbed structures for 1,10-phenanthroline and dipyrido[3,2-a : 2',3'-c]phenazine on Au(111)

Scanning tunneling microscopy (STM) images of 1,10-phenanthroline (PHEN) and dipyrido[3,2-a : 2',3'-c]phenazine (DPPZ) on Au(111) are recorded using both in situ and ex situ techniques. The images of PHEN depict regimes of physisorption and chemisorption, whereas DPPZ is only physisorbed. All physisorbed structures are not pitted and fluctuate dynamically, involving aligned (4 x 4) surface domains with shortrange (ca. 20 molecules) order for PHEN but unaligned chains with medium-range (ca. 100 molecules) order for DPPZ. In contrast, the chemisorbed PHEN monolayers remain stable for days, are associated with surface pitting, and form a (4 x root 13)R46 degrees lattice with long-range order. The density of pitted atoms on large gold terraces is shown to match the density of chemisorbed molecules, suggesting that gold adatoms link PHEN to the surface. For PHEN, chemisorbed and physisorbed adsorbate structures are optimized using plane-wave density-functional theory (DFT) calculations for the surface structure. Realistic binding energies are then obtained adding dispersive corrections determined using complete-active-space self-consistent field calculations using second-order perturbation theory (CASPT2) applied to cluster-interaction models. A fine balance between the large adsorbate -adsorbate dispersive forces, adsorbate-surface dispersive forces, gold ligation energy, and surface mining energy is shown to dictate the observed phenomena, leading to high surface mobility and substrate/surface lattice incommensurability. Increasing the magnitude of the dispersive forces through use of DPPZ, rather than PHEN, to disturb this balance produced physisorbed monolayers without pits and/or surface registration but with much longer-range order. Analogies are drawn with similar but poorly understood processes involved in the binding of thiols to Au(111).

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