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Intermolecular repulsion through interfacial attraction: towards engineering of polymorphs

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Experimental Section

Computational

The gold surface and its bulk phase are described by a form of the Embedded Atom Model called “glue model”.¹ The atomic energy of the Gold atoms consists of a contribution from an atom-atom potential energy function plus a contribution from a many-body term that is a function of the number of nearest neighbors. This term ensures that the atoms cohesion due to the conduction electrons of the metal is accurately reproduced. The metal-organics interactions are the sum of long-distance and short-distance terms. The long-range Coulomb interactions are calculated with charges obtained on-the-fly as a function of the interatomic distances by the charge equilibration (QEq) scheme of Rappe and Goddard.² The short-range interactions are described by a Born Mayer

potential, which is needed to tune the long-distance contribution, to account for higher order terms such as van der Waals interactions, and to balance attractive Coulombic metal-molecule attraction. The organic molecules are simulated by a standard force field,³ which was also used for the calculations for the PHB/graphite physisorption.

This model was previously used to investigate a variety of processes such as (i) the dynamics of C₆₀ on gold surfaces,^{4a,b} (ii) the adsorption of alkanes and 1-alkenes on Au(111),^{4c} where the adsorption energies of short chains, up to C10, were reproduced with an average deviation from the experiments of less than 1 kcal mol⁻¹ and the unexpected transition to disorder that occurs for the deposition of alkyl chains between 18 and 26 carbon atoms was explained, (iii) the apparent symmetry breaking of a macrocycle on the Au surface,^{4d} (iv) the substitution kinetics and dynamics of thiols in self-assembled monolayers,^{4e,f,g} (v) the mechano-chemistry of a polymer on the Au surface,^{4h} and (vi) the adsorption and dynamics of DNA bases on Au(111) where the energies of adsorption were also within 1 kcal mol⁻¹ from the experimental values,⁴ⁱ and the adsorption dynamics in the presence of voltage.^{4j}

The model does not define *a priori* the bonds between the atoms of the molecules and those of the metal. Molecules are free to drift on the surface, which, in turn, can reconstruct. Its relative simplicity (which, however, requires the inversion of large matrices) has allowed us to investigate rather large unit cells (with hundreds or even thousands of atoms) and to perform long-time molecular dynamics simulations (of the order of the nanosecond). Under the same conditions, the use of modern Density Functional Theory or *ab initio* programs would be too demanding for the present computer hardware, especially for applications where large unit cells are necessary in conjunction with long dynamics runs.

All calculations were carried out with an in-house modified version of the TINKER program⁵ on a slab of 16*16*4 Au atoms with periodic boundary conditions. Geometries were optimized to RMS deviation of the energy gradient smaller than 0.01 kcal mol⁻¹ Å⁻¹.

Although not ab initio, the present model, accounts for charge flow and metal-organic interactions in a more thorough way than the Born Mayer potentials,⁶ or even when the metal is described by an Embedded Atom Model,⁷ and may be comparable in complexity to the treatment with the Universal Force Field⁸ which, however, may use predefined Gold-Gold or the Gold-organic connectivities. The hexagonal surface of graphite is simulated by a 36*36*3 slab. The border atoms are saturated by hydrogen atoms.

Preparation of Substrates.

Au(111) was prepared by evaporation of 99.99% gold, Umicore Materials AG, on freshly cleaved mica sheets, Ted Paella, Inc., at 10⁻⁷ mbar in a home-built evaporator at the Zernike Institute for Advanced Materials, University of Groningen. The thickness of the gold layer was ~150 nm. Prior to formation of the self-assembled monolayer, reconstruction of the Au(111) surface was checked for by STM in *n*-tetradecane.

Highly oriented pyrolytic graphite (HOPG) was bought from Goodfellow Cambridge Ltd. and freshly cleaved prior to deposition of the molecules.

MoS₂ single crystals were provided by Dr. E. Lacaze, for which she is gratefully acknowledged. They were freshly cleaved before use.

Pentacontane-modified HOPG (n-C₅₀H₁₀₂/HOPG) was prepared by deposition of a warm droplet of saturated pentacontane (Fluka) solution in *n*-tetradecane (Aldrich), onto a freshly cleaved surface of HOPG. The formation of the pentacontane monolayer was observed by STM. The excess of

pentacontane was washed away with few droplets of tetradecane, before addition of the PHB monolayer.

Preparation of Samples.

A solution of PHB in *n*-tetradecane (Aldrich) was sonicated for 5 min and heated at 40 °C for 20 min so as to form a saturated solution. A drop of the warm solution was applied to the prepared substrates and the STM tip was immersed into the solution for imaging.

Scanning Tunneling Microscopy (STM).

All experiments were performed at room temperature, using a PicoSPM (Molecular Imaging, Scientec), at the interface between the surface and *n*-tetradecane. Pt/Ir STM tips were prepared mechanically from Pt/Ir wire (80:20, diameter 0.25 mm, Goodfellow Cambridge Ltd.). The parameters of the unit cells were measured after drift effects were corrected with the Scanning Probe Image Processor (SPIP) software (Image Metrology ApS). However, the presented STM images contain raw data and are not subjected to any processing other than routine plane correction.

Workfunction measurements.

For the workfunction measurements with the ultraviolet photoelectron spectroscopy (UPS) setup, 0.1 mg of the Schiff-base derivative (PHB) diluted in *n*-tetradecane (100 mg) was heated for 5 min at 60 °C and drop-cast onto freshly evaporated gold films on mica or onto a freshly cleaved HOPG surface. After drying under an argon gas stream, the samples were immediately introduced through a load lock system into a VG Scientific Clam 100 ultraviolet photoemission spectrometer, equipped with a VG He lamp ($h\nu=21.2$ eV). The base pressure in the spectrometer during the measurements was 10^{-9} mbar. We recorded the spectral region of the secondary electron cutoff for each sample

and for a clean Au film as reference, taking care to apply a voltage of -3.07 V to the sample during data acquisition in order to suppress any spectral features resulting from electrons generated inside the analyzer. The overall energy resolution was set to 30 meV.

Synthesis.

4-Dodecyloxy-2-hydroxybenzaldehyde was prepared as described before⁹ [1]. The Schiff base derivative 4-(dodecyloxy)-N-(4-dodecyl)-phenyl-2-hydroxybenzalimine (PHB) was prepared by refluxing 2.34 g (7.65 mmol) of 4-dodecyloxy-2-hydroxybenzaldehyde with 2 g (7.65 mmol) of 4-dodecylaniline in absolute ethanol for 18 h, with a few drops of glacial acetic acid as the catalyst. Solvent was evaporated and the crude product was crystallized several times from hot absolute ethanol. Yield 86% (3.6 g). M. p. 102-103 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.88 (t, 6H), 1.20-1.40 (m, 34H), 1.40-1.5 (m, 2H), 1.55-1.67 (m, 2H), 1.79 (quintet, 2H, *J*=7.7 Hz), 2.62 (t, 2H, *J*=7.7 Hz), 4.00 (t, 2H, *J*=6.6), 6.47 (d, 1H, *J*=8.3 Hz), 6.51 (s, 1H), 7.16-7.21 (m, 4H), 7.23 (d, 1H, *J*=8.3 Hz), 8.52 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 14.1 (s), 22.7 (d), 26.0 (d), 29.1 (d), 29.2 (d), 29.3 (d), 29.5 (d), 29.6 (d), 29.6 (d), 29.7 (d), 31.5 (d), 31.9 (d), 35.5 (d), 68.2 (d), 101.5 (t), 107.5 (t), 120.7 (t), 129.3 (t), 133.3 (t), 141.4 (q), 145.8 (q), 160.5 (t), 163.4 (q), 164.0 (q) ppm. MS (EI): 549 [M⁺]; HRMS: calcd. for C₃₇H₅₉NO₂ 549.455, found 549.454.

Scheme 2. Synthesis of PHB.

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