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ARTICLE

Predicting Supramolecular Self-assembly on Reconstructed Metal Surfaces

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Thomas J. Roussel*, Esther Barrena, Carmen Ocal, and Jordi Farauo

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The prediction of supramolecular self-assembly onto solid surfaces is still challenging in many situations of interest for nanoscience. In particular, no previous simulation approach has been capable to simulate large self-assembly patterns of organic molecules over reconstructed surfaces (which have periodicities over large distances) due to the large number of surface atoms and adsorbing molecules involved. Using a novel simulation technique, we report here large scale simulations of the self-assembly patterns of an organic molecule (DIP) over different reconstructions of the Au(111) surface. We show that on particular reconstructions, the molecule-molecule interactions are enhanced in a way that long-range order is promoted. Also, the presence of a distortion in a reconstructed surface pattern not only induces the presence of long-range order but also is able to drive the organization of DIP into two coexisting homochiral domains, in quantitative agreement with STM experiments. On the other hand, only short range order is obtained in other reconstructions of the Au(111) surface. The simulation strategy opens interesting perspectives to tune the supramolecular structure by simulation design and surface engineering if choosing the right molecular building blocks and stabilising the chosen reconstruction pattern.

1. Introduction

The theoretical prediction of self-assembly processes in materials sciences in general and in nanomaterials in particular is still challenging. As emphasized in a recent review,¹ there are few attempts to refine existing concepts and algorithms in computational physics and chemistry to tackle the intrinsic difficulties present in self-assembly processes (multiple time and length scales, for example). This is in contrast with other areas of science¹ (or even other problems in nanoscience)² in which simulations employing basic physics and chemistry are used as a tool for design. Our particular interest here is in the prediction of supramolecular assembly onto solid surfaces, a question of interest for many problems of nanoscience (organic electronics, surface engineering, molecular sensors, for example).^{3,4} In certain cases, it is possible to simulate (with atomistic detail) the supramolecular patterns experimentally observed by using techniques such as Molecular Dynamics⁵ or Monte Carlo simulations.¹ However, these simulations are very demanding computationally and they are limited to a small number of adsorbed molecules. Several groups are trying to tackle this problem by developing novel, alternative simulation methodologies. One popular option is to replace costly models with atomistic resolution by coarse grain models with resolution at the level of chemical groups or at the level of molecules. For example, a recent proposal⁶ extends the popular coarse grain “Martini” methodology⁷ in order to simulate efficiently large patterns of adsorbed organic molecules onto solid/liquid interfaces, obtaining an excellent agreement with

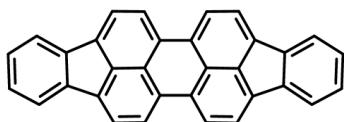
the different supramolecular patterns observed in experiments. Another option, which is extremely challenging, is to develop new algorithms to improve the efficiency of atomistic simulations in order to simulate problems in which atomistic details are important. In this line, one of us (TR) has recently introduced a novel methodology⁸ called SANO (Self-Assembly of Nano-Objects), which speeds up classical Monte Carlo simulations of self-assembly onto solid surfaces by a factor of 10⁴ or more. The method allows one to simulate, with atomistic resolution, the self-assembly of thousands of molecules over large length scales, typical of scanning probe microscopy (AFM/ STM) experiments. In this article we will employ this novel technique to address a difficult problem which was up to now outside the scope of simulation techniques. Relaxation and reconstruction phenomena at metallic surfaces^{9,10,11} offer potential substrates as pattern candidates for self-organization.^{12,13,14,15,16,17} The question at hand is how the reconstruction of metal surfaces affects or even drives the self-assembly of organic molecules at room temperature.

The description of the self-assembly of molecules onto reconstructed surfaces requires atomistic precision, otherwise essential mechanisms such as interaction of molecules with discommensuration lines, kinks and other symmetry-breaking features at the surface will be lost. In addition, reconstructed surfaces have periodicities over large distances, so one is forced to consider an extremely large number of surface atoms and a large number of adsorbing molecules. To our knowledge, no previous simulation approach has been capable to bring these

insights spanning over the relevant atomistic scale and the entire molecular self-assembly.

The particular case studied here will be the self-assembly of diindenoperylene (DIP, see scheme 1) at room temperature onto different reconstructions patterns of the Au(111) surface, a benchmark system of weakly interacting molecules on surfaces. There is a substantial wealth of experimental studies of self-assembly of DIP molecules adsorbed on metals.^{18,19,20} A particularly interesting feature is that DIP molecules show long-range order when adsorbed onto gold,²¹ in spite of the weak molecule-substrate interaction, an order which is absent when adsorbed onto other metals (copper, for example). The analysis of our large scale simulations reported here and the comparison with scanning tunnelling microscopy (STM) experiments provide a rich and complex picture of the key-role played by the surface reconstructions, and the substantial contribution of defects and dislocations, on the resulting supramolecular self-assembly.

We show that only on particular reconstructions of the Au(111) surface molecule-molecule interactions are enhanced in a way that long-range order is promoted. Our simulations also reveal that the presence of distortion in a reconstructed surface not only induces long-range ordering but also the organization of DIP into two coexisting homochiral domains, with predicted unit cells which are in excellent agreement with STM experimental results. This latter aspect is one of the main motivations of this present work: can we predict and engineer the surface (controlling defects and reconstructions) to obtain long-range chiral domains formed by achiral molecules?



Scheme 1. Chemical structure of diindenoperylene (DIP).

2. Outline of the Simulation Methodology

In this work we employ the recently developed SANO methodology⁸, which we will briefly outline here. The method consists in a two-dimensional (*off-lattice*) Monte-Carlo (MC) approach that replaces the computationally expensive direct calculation of molecule-molecule and molecule-surface interaction energies by a fast grid interpolation of precalculated potential energies.²² The main approximation involved in this approach is to consider that the internal (vibrational) degrees of freedom of both the substrate and the molecular building blocks are frozen, an approximation which is reasonable in many self-assembly problems, as those considered here.

SANO simulations involve two different steps. In a first preliminary step, we model and pre-calculate the molecule-molecule interaction and the interaction of a single molecule with the different substrates. This first step requires the selection of a methodology for the calculation of potential energies (for example, a suitable force field or a quantum mechanical method), the building of atomistic models of the substrate and the pre calculation of molecule-substrate and molecule-molecule potential energies with a given precision.

Then (second step), the adsorption of a large number of interacting rigid molecules onto a substrate is simulated at a given temperature using a Monte Carlo simulation. At each Monte Carlo attempt interpolated values for potential energies are obtained from the grid values pre-calculated in the preliminary stage.

In the present paper, we have employed this methodology to simulate the self-assembly of a large number of DIP molecules at 300K on different reconstructions of the Au(111) surface. Reconstructions of the gold surface are usually found in experiments, but they are extremely difficult to tackle in simulations. Depending on the type of contraction (from fully uniaxial to isotropic), the surface strain relief exhibits different geometric patterns that bring broad periodicities (spanning over nanometric scale) with small but consequent surface roughness and a variety of adsorption sites (line and point defects which release the tensions on the metal surface). Four kinds of gold reconstructions have been considered here: namely the striped, distorted herringbone, herringbone and *rosetta*. For the sake of completeness, we have also performed SANO simulations corresponding to the adsorption of DIP on the unreconstructed Au(111) surface. The different simulations performed here are summarized in Table 1. All technical details of our simulations and full details of the employed models are given in Appendix A (Simulation Methods). The results of our simulations are reported in the next section, except in the case of the simulations of adsorption over the unreconstructed Au(111) surface which are discussed in the Supporting Information (SI). As seen in the SI, in absence of surface reconstruction we do not found any supramolecular order, only short rows of few molecules aligned along with the $[1\bar{1}0]$ direction.

Table 1. Summary of simulated systems. (a) Pre calculation of molecule-substrate interaction (preliminary step) (b) Monte Carlo SANO simulations.

Surface model	Unit Cell [\AA^2] ^{a)}	Simulation box size [\AA^2] ^{b)}	Number of molecules ^{b)}	Density ^{b)} [mol nm ⁻²]
Au(111)	5.78×4.99	520×450	619 and 725	0.26 and 0.31
Stripes	65.04×66.35	520.3×530.8	913	0.33
Herringbone	325.4×69.8	650.8×698.0	600, 900, 1200, and 1893	0.13, 0.20, 0.26 and 0.41
Roseta	69.5×120.3	695.0×601.9	1313	0.31

3. Results

3.1. Self-assembly with long-range order at the striped gold surface

The striped gold surface is the simplest reconstruction of the Au(111) surface^{23,24,25}. It is shown in Figure 1. It is obtained as the result of a small uniaxial contraction along the $\langle 1\bar{1}0 \rangle$ -type (next neighbours directions). It contains face-centered cubic (fcc) and hexagonal close packing (hcp) domains separated by one discommensuration line along $[11\bar{2}]$. The resulting striped superstructure is known by its unit cell name, i.e. “ $23\times\sqrt{3}$ ”, and

has lattice parameters equal to 6.6 and 0.489 nm ($\sqrt{3}a_{111}$ with $a_{111} = 0.288\text{nm}$).

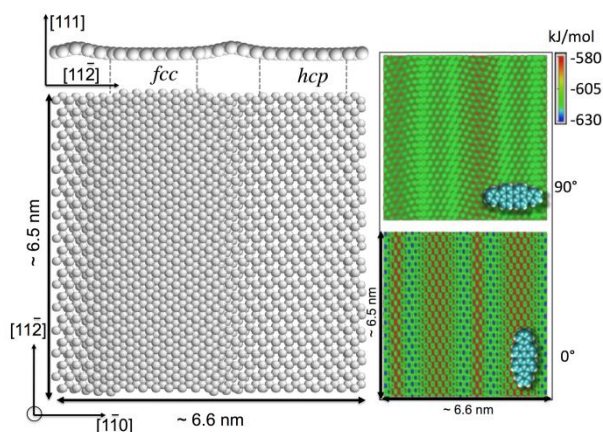


Figure 1. (Left) Atomic structure of the Au(111)-(23xv3) Striped gold surface obtained after relaxation (see Methods). We show here 13 unit cells stacked along the $[11\bar{2}]$ direction. Longitudinal fcc and hcp domains are indicated. These are separated by one discommensuration line along $[11\bar{2}]$ (see text). Above the image we also show a magnification of the first layer (coordinate z multiplied $\times 5$) to highlight the roughness of the surface. (Right) Potential energy landscape for the interaction of a single DIP molecule with the surface for two molecule orientations: 0° (top), and 90° (bottom).

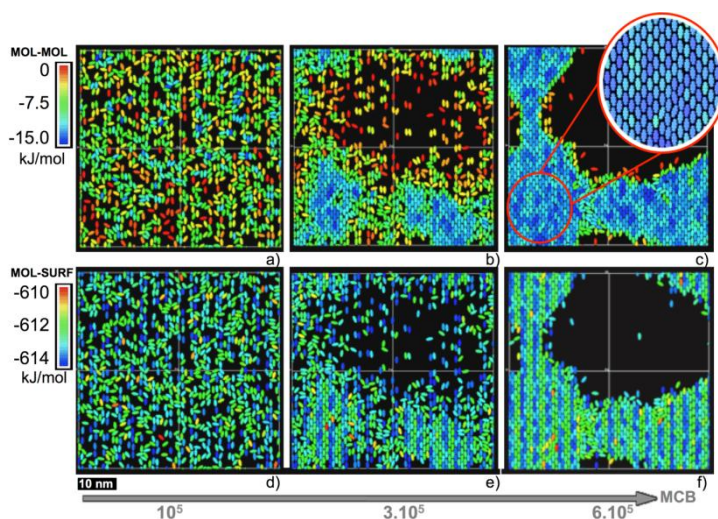


Figure 2. Simulation snapshots of 913 DIP molecules self-assembled on the striped reconstructed gold surface: (a, d) At the very beginning, (b, e) at an intermediate stage, and (c, f) at the end of the (NVT) Monte Carlo run after 5.107 blocks (regions I, II and III, respectively, in Figure SI.3). Note the difference in absolute values of the colour scales (kJ mol^{-1}) corresponding to the intermolecular (a, b, c) and the molecule-substrate (d, e, f) potential energies.

We build a fully atomistic model of the substrate with size $65.04 \times 66.35 \text{ \AA}^2$ containing 7202 gold atoms (Table 1), with the methods described in the Appendix. This model was employed for the pre calculation of the interaction between a single DIP molecule and the substrate. The result of this calculation is also illustrated in Figure for two particular orientations of the DIP molecule (parallel and perpendicular to the discommensuration lines, indicated as 0° and 90° , respectively). It can be seen in

the substrate-molecule potential energy that favourable adsorption sites (which reach -630 kJ mol^{-1}) for a single DIP molecule are near discommensuration lines along the $[11\bar{2}]$ direction. After pre calculation of the molecule-surface interaction, we performed simulations with 913 DIP molecules adsorbed onto a surface of $52.03 \times 53.08 \text{ nm}^2$ (see table 1) which means 8×8 unit cells and corresponds to a density of $0.33 \text{ molecules nm}^{-2}$.

We found substantial long-range order induced by the stripes of the surface reconstruction with DIP molecules adopting a head-to-tail stacking. The emergence of the long-range order is shown in figure 2 with illustrative snapshots of the evolution during simulation time. These snapshots correspond to configurations selected at three different stages during the MC simulation: at the beginning of the self-ordering (fig. 2.a, 2.d), at an intermediate step (fig. 2.b, 2.e) and at the end of the Monte Carlo run corresponding to the equilibrated configuration (fig. 2.c, 2.f). The colour of the molecules corresponds to their intermolecular (top) or their molecule-substrate (bottom) potential energies. The evolution of the different contributions of the potential energy during the simulations is shown in figure SI.3 of the supporting information. Figure 2 shows that after a few MC cycles, the molecules aggregate forming rows on a head-to-tail configuration. As the MC simulation proceeds, the clusters expand forming large ordered domains. The final snapshot reveals that the DIP molecules orientate with the long molecular axis aligned with the discommensuration lines of the reconstruction, i.e. along the $[11\bar{2}]$ direction of the gold surface. The overall evolution of potential energy during the MC simulation is addressed in the Supporting Information (Figure SI.3), which shows a decrease of the molecule-molecule potential energy with only a modest increase of the molecule-surface energy.

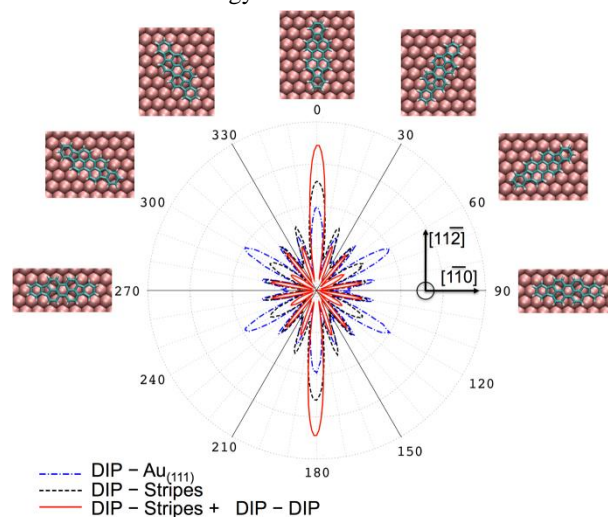


Figure 3. Molecular orientation distribution (MOD) for DIP molecules in different simulations. Red solid line: Results for Monte Carlo simulations with 913 interacting molecules onto striped reconstructed surface. Black dashed line: infinitely diluted DIP (no molecule-molecule interaction) adsorbed onto striped reconstructed surface. Blue dotted-dashed line: again infinitely diluted system but adsorbed onto the non-reconstructed gold (111) surface. Ball and stick representations show the molecular matching with the non-reconstructed Au(111) surface. DIP molecules are drawn at scale along the $\langle 1\bar{1}0 \rangle$ -type and $\langle 11\bar{2} \rangle$ -type directions.

The preferred orientation of DIP molecules observed in the snapshots can be quantitatively described by the molecular orientation distribution (mod) shown in Figure 3 (red line). A prominent peak in the $[1\bar{1}\bar{2}]$ direction can be clearly observed, corresponding to the alignment of molecules with the stripes of the substrate. Though other possible orientations are also correlated every 20 degrees, all $\langle 1\bar{1}0 \rangle$ -type directions are avoided.

It is worth discussing the role-played by molecule-molecule and molecule-substrate interactions in the emergence of the long-range order. To this end, we have performed additional ancillary simulations for a system of infinitely diluted DIP molecules adsorbed onto the stripped reconstruction (dashed black line in the figure 3). In these simulations, where molecule-molecule interactions are absent, the same molecular orientations are explored but the peak in the $[1\bar{1}\bar{2}]$ direction is substantially reduced. In other words, the intermolecular interactions enhance the preferential orientation of DIP molecules along the direction of the surface stripes. The underlying mechanism is that by following the stripes of the substrate (as dictated by the anisotropic potential energy landscape), the molecule-molecule interaction can be optimized promoting long-range self-assembly. The symmetry break due to the presence of discommensuration lines reduces the rotational freedom degree of molecules, imposing a preferential molecular orientation and drastically modifying the interaction between molecules and inducing a cooperative, self-ordering process.

To get more insight on the role of the substrate, we have plotted in the Figure 3 the MOD corresponding to the simulations of the infinitely diluted DIP molecules adsorbed onto the Au(111) flat surface (not reconstructed) which therefore serves as a reference. As expected, the molecules statistically align equally and preferentially every 60 degrees, but surprisingly along the three equivalent $\langle 1\bar{1}\bar{2} \rangle$ directions of the non-reconstructed gold surface. Interestingly the $\langle 1\bar{1}0 \rangle$ -type directions, which correspond to the densest crystallographic directions of the Au(111) surface, are avoided as in the previous cases. By superposing one DIP molecule on the Au(111) surface and along these directions (Figure 3), it discloses that the whole perylene group (centre of DIP molecule) matches five gold atoms positions when DIP aligned with the $\langle 1\bar{1}\bar{2} \rangle$ -type directions, while with the $\langle 1\bar{1}0 \rangle$ -type directions only three benzene units match.

3.2. Long-range order and the emergence of homochiral domains

As demonstrated above, surface symmetry break due to the presence of one dimensional features, here discommensuration lines or stripes, plays a fundamental role in generating large ordered domains of DIP molecules onto the gold surface. On the other hand, it is known that rupture of surface symmetry can be used to drive the generation of chiral domains made out of adsorbed achiral molecules. Exploiting this idea, we have introduced an additional surface symmetry break now in a direction perpendicular to the stripes. To this end, we have considered the presence corrugation lines following the $[1\bar{1}0]$ direction superposed to the striped reconstruction, as shown in the atomistic model of Figure 4 (top left). This feature has a deep impact in the results of DIP self-assembly simulations, as illustrated in the snapshot of Figure 4 (bottom, right). Now we observe long-range ordering consisting of two coexisting

enantiomorphic homo-chiral domains with a mirror plane along the $[1\bar{1}0]$ direction. For comparison, an experimental STM image of DIP on Au(111) is depicted at the left. Note that the packing and orientation of the domains seen in the simulation snapshot are in excellent agreement with the experimental observations by STM.²¹ The molecular orientation distribution of the final DIP configurations on this substrate is given in the Figure 4 (top right) where for the sake of comparison the results for the infinitely diluted phase of DIP on Au(111) are also shown. The orientation of the DIP molecules presents two peaks, corresponding to directions $\pm 10^\circ$ deviated with respect to the $[1\bar{1}0]$ direction in excellent agreement with the deviation of $15^\circ \pm 3^\circ$ measured in the STM experiments.²¹ These results show that the enantiomorphic homo-chiral domains are a consequence of the competition between the tendency of molecules to align with the corrugation lines and the unfavourable molecular orientation along the $[1\bar{1}0]$ direction. Hence, imposing parallel corrugation lines along the dense Au(111) direction captures the main features of the herringbone distorted pattern induced by the molecular deposition and experimentally observed (addressed in figure 10). Interestingly, these distorted herringbone patterns were also observed for perylene molecular deposition.^{26,27}

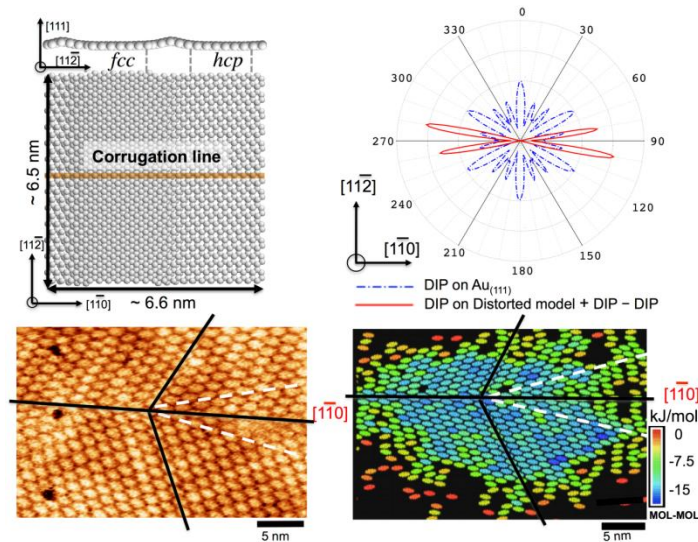


Figure 4. Top: (Left) Substrate consisting on the superposition of corrugation lines along the $[1\bar{1}0]$ direction on the atomic structure of the Au(111)-(23xv3) striped gold surface after relaxation. (Right) Molecular orientation distributions (MOD) for the final self-assembled DIP domain on the latter surface model (solid line), and superposed on the MOD of infinitely diluted phase adsorbed on the non-reconstructed flat gold (111) surface (dotted-dashed line). Bottom: (Left) STM image for DIP deposited at room temperature on Au(111) ($I=0.1$ nA and $V=0.60$ V) showing two coexisting enantiomorphic homo-chiral DIP domains with a mirror plane along the $[1\bar{1}0]$ direction ($\langle 1\bar{1}0 \rangle$ -type directions are indicated by the black solid lines). (Right) Simulation snapshot of the obtained equilibrium configuration.

3.3. Absence of Long-range Ordering on the Herringbone and Roseta reconstructions

The results of the simulation have shown the essential role of the striped pattern, caused by uniaxial strain relief of the Au(111) surface, to achieve long-range DIP ordering. However, as we will see in the following, other surface

reconstructions with isotropic strain relief result in short range order.

Let us first consider an atomistic model for the herringbone reconstruction of the Au(111) surface (Figure 5). This reconstruction is found when two 120° rotated domains of parallel discommensuration lines coexist on the surface. When they meet, they do not cross but bend forming “chevron” or “herringbone” patterns that give name to what is the most encountered reconstruction in experiments¹⁶. Similarly to the striped pattern, it contains fcc and hcp regions separated by discommensuration lines which in this case form zig-zag patterns following alternately the $[\bar{2}\bar{1}1]$ and $[\bar{1}\bar{2}1]$ directions.

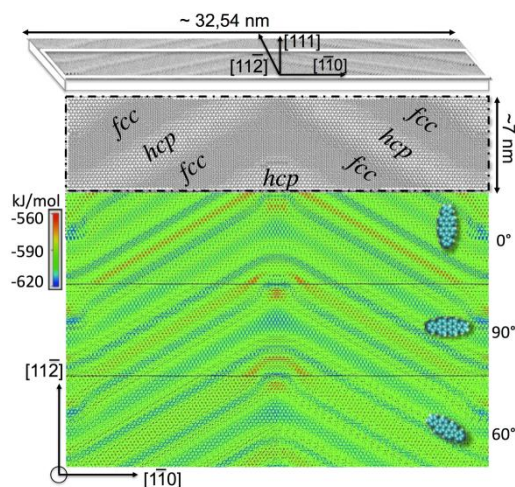


Figure 5. Top panels: Atomic structure of the Au(111) *Herringbone* surface after relaxation. Only the three first layers are represented to emphasize the different stacking. An oblique view is represented with magnified z ($\times 5$) to highlight the surface roughness. Bottom: Three potential energy landscapes of the interactions between a single DIP molecule oriented at 0° , 90° and 57° , respectively, and the surface. The colour scale is given in kJ mol^{-1} of molecule.

The employed atomistic model was obtained from a previous work²⁸ and has a unit cell with an area of $325.44 \times 69.84 \text{ \AA}^2$ and a total of 47613 atoms (see Figure 5). The obtained surface corrugation is around 0.33 \AA , slightly higher than the experimental value obtained by STM ($0.20 \pm 0.05 \text{ \AA}$) and substantially larger than that of the unreconstructed surface (0.05 \AA). In Figure 5 we also illustrate the obtained potential energy maps for the interaction between a single DIP molecule and the substrate for three particular orientations of the DIP molecule. The obtained molecule-surface potential energy shows a substantial dependence with the orientation of the DIP molecule and its particular location at the surface relatively to the discommensuration lines.

We emphasize here that the surface considered for the simulation of the self-assembly is extremely large ($650.8 \times 698 \text{ \AA}^2$) for a simulation with atomistic detail and includes several unit cells of the substrate. In Figure 6, we show a snapshot of the self-assembly for the higher coverage investigated ($0.41 \text{ molecules nm}^{-2}$). We observe that the DIP molecules form a large compact domain but though it is possible to find small ordered clusters with molecules lining up along the channels formed by the discommensuration lines, other molecules follow different orientations (see insets) and no long-range order is

achieved. It is noticeable by looking to the colour scale that molecules in more ordered and compact clusters (blue regions) have the lowest intermolecular potential energy (top), even though the molecule-surface one (bottom) is not favourable. Contrary to the striped reconstruction case, there is no clear correlation between the molecular orientations and the regions with most favourable molecule-surface interaction (compare Figures 5 and 6). The MOD obtained is shown and addressed in the supporting information (figure SI.4). We emphasize here only the fact that the distribution has a more complex structure than in the previous cases with a slightly preference orientations along the discommensuration lines present in the herringbone surface, i.e. along the $[\bar{2}\bar{1}1]$ and $[\bar{1}\bar{2}1]$ directions, while avoiding the $[11\bar{2}]$ direction.

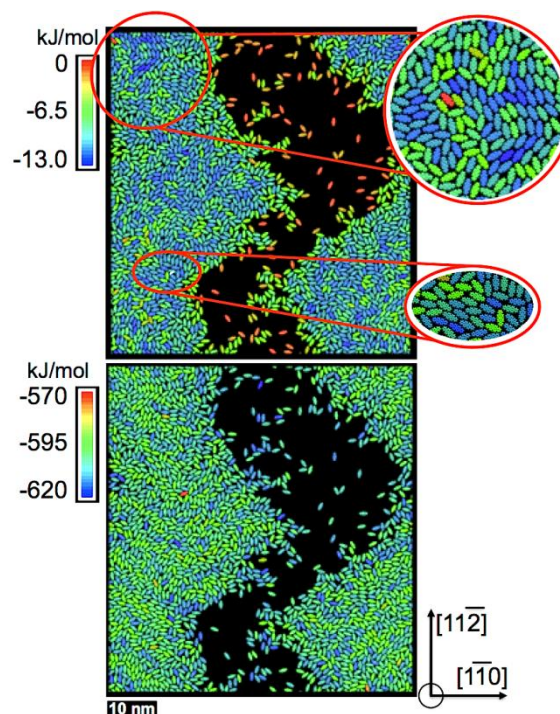


Figure 6. Snapshots of equilibrium configurations from the simulation of DIP molecules on the herringbone gold surface ($0.41 \text{ molecules nm}^{-2}$). Colour scales represent the intermolecular (top) and the molecule-surface potential energies (bottom). Only short-range ordering is achieved. The insets show zoom views.

In the Supporting Information we also report results for simulations performed at lower coverage. At very low coverage (fig. SI.5a), the DIP molecules preferentially decorate the pinched and bulged kinks of the reconstruction. As the coverage increases, the occupancy of DIP molecules is notably related to regions with most favourable molecule-substrate interaction and form rows with a tendency to orient the molecular axis with few degrees (about 10°) of deviation from the $[11\bar{2}]$ direction. As the coverage increases further, DIP molecules form compact aggregates without long-range order giving rise to the structure seen in Figure 6 at the highest coverage simulated.

From these simulations it can be concluded that the herringbone reconstruction is not able to induce the cooperative effect between molecule-substrate and molecule-molecule interactions

observed for the striped reconstruction and only results in short range order. This agrees with the distortion of the herringbone pattern observed experimentally and induced by the molecular deposition, which confirms the cooperative process during the self-ordering.

Finally, we will discuss our results on the so-called *Roseta* reconstruction of the Au(111) surface. Due to the three-fold symmetry of the Au(111) surface, an isotropic surface strain can be relieved if three discommensuration lines running along the three $\langle 1\bar{1}0 \rangle$ -type directions meet together. As can be seen in Figure 7, in this case, the crossing discommensuration lines separate triangular domains with fcc and hcp stacking to form a regular pattern that can be seen either as an orthorhombic lattice (black dash-dotted line) or a hexagonal one with (22×22) unit cell (white dashed line). The greater surface compression imposes gold atoms at the unit cell vertices to expel from the surface, which enhances the surface roughness.

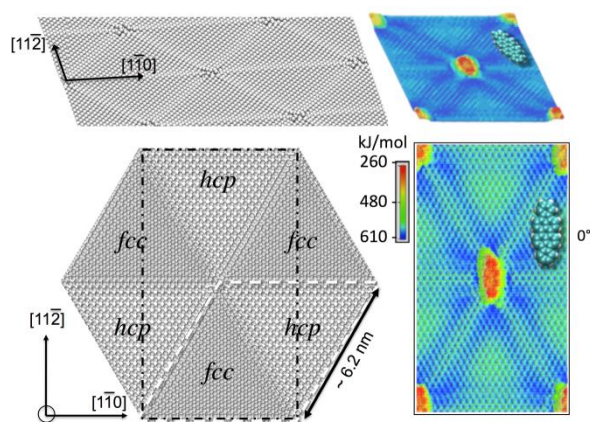


Figure 7. Atomic structure the Au(111)- (22×22) (*Roseta*) surface after relaxation. Only the three first layers are represented to emphasize the different fcc and hcp stacking at each half of the unit cell (white dashed line). An oblique view of the first layer is represented (top panel) to highlight the roughness of the surface due to outcropped atoms (adatoms) at the unit cell vertices. Right: Colour scale represents the absolute value of the (attractive) molecule-surface potential energy (kJ mol^{-1}) calculated for one orthorhombic unit cell as seen by one DIP molecule oriented at 0° respect to the $[11\bar{2}]$ direction.

This reconstruction was first observed decades ago by STM after alkaline intermixing alloys²⁹, as the result of releasing the local constrain arising from the small size of the hetero-atom. The first proposed atomic structure was already a hexagonal unit cell consisting of fcc and hcp domains^{30,31}. This reconstruction has been also observed for transition metal alloys^{32,33}, or after molecular deposition²⁶ and interestingly, it was also stabilized after local electrical pulses in pure gold³⁴ (Figure SI.6). The crossing dislocations separating fcc and hcp stacking domains produce periodic stark-like patterns with a hexagonal 22×22 unit cell and a lattice parameter of 6.2 nm along NN directions at which vertices several ad-atoms emerge out of the surface plane level. We are not aware of any previous simulation study of this rosetta reconstruction model, so we had to build up an atomistic model for the substrate (Appendix Methods section and SI). The precalculation of the potential energy for the interaction of a single DIP molecule with the substrate was performed for one orthorhombic unit cell of the

(22×22) (i.e. $69.5 \text{ \AA} \times 120.38 \text{ \AA}$). As one example of that, Figure 7 shows the molecule-surface potential energy map obtained for one given molecular orientation parallel to $[11\bar{2}]$. As it can be seen, the discommensuration lines play a similar role than before but, in addition, the presence of Au ad-atoms on top of the reconstructed surface has a substantial impact on the potential energy map.

The simulation box size is $695.0 \times 601.9 \text{ \AA}^2$ and therefore contains several unit cells of the substrate structure. We considered 1313 DIP molecules, meaning a molecular coverage of $0.31 \text{ molecule nm}^{-2}$. A snapshot of the obtained equilibrium configuration is shown in Figure 8.

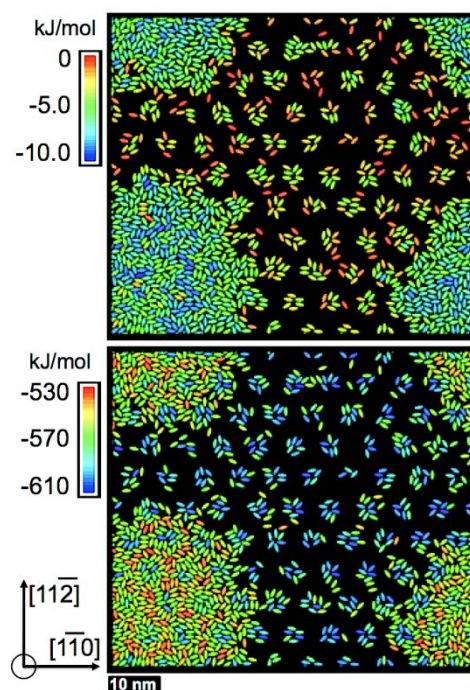


Figure 8. Snapshot of the obtained equilibrium configuration from the simulation of the self-assembly of DIP on Roseta gold surface (coverage of $0.31 \text{ molecule nm}^{-2}$). Colour scales represent the intermolecular (top) and the molecule-surface potential (bottom) energies.

As seen in Figure 8, the adsorbed molecules decorate the vertices of the surface surrounding the gold *ad*-atoms, avoiding them and without preferred orientation. Note that the DIP molecules with the most favourable molecule-substrate interaction (blue colour) are located at the vicinity of these surface defects forming disordered aggregates. At high local coverage, the molecules are shown to condense and form a broad disordered domain that maximizes their molecule-molecule interaction without any long-range order observed. At this point, it is interesting to note that this behaviour is opposite to that observed for organic molecules able to make chemical bonds with gold atoms (such as certain phthalocyanine derivatives), which prefer to locate on top of ad-atoms which are more accessible for chemical bonding³⁵.

4. Discussion

The results obtained in the simulations reported so far demonstrate that surface reconstruction can either induce or conversely restraint long-range ordering of DIP molecules.

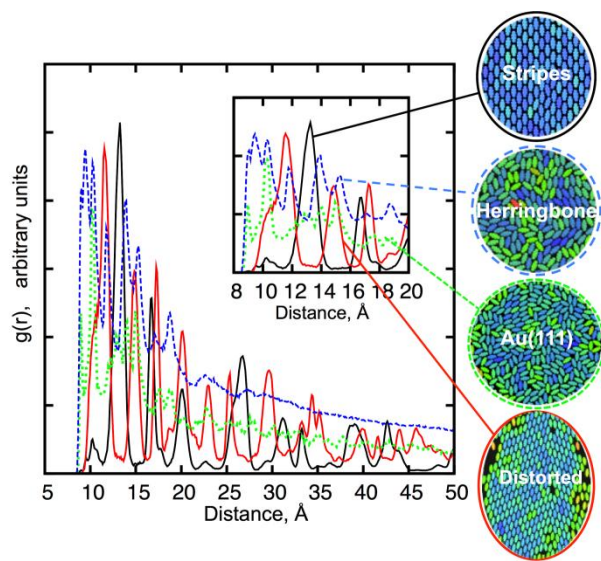


Figure 9. Radial distribution (or correlation) function in arbitrary units, $g(r)$, calculated for DIP molecules adsorbed on each substrate as computed from our simulations. $g(r)$ is plotted for shorter distances in the inset for clarification; images of the corresponding obtained structures are also shown.

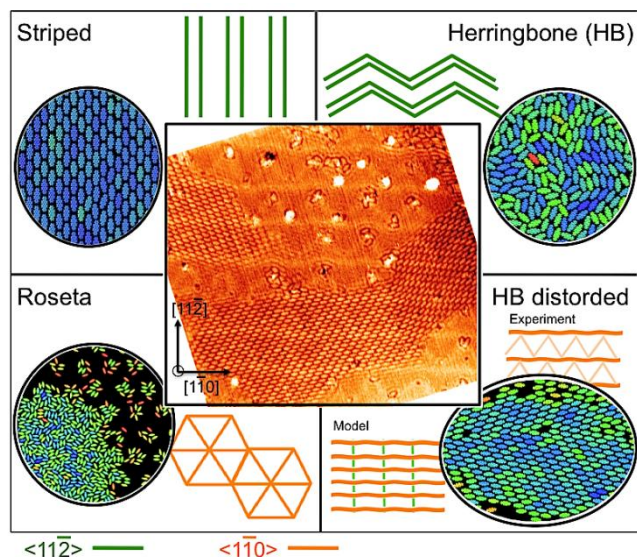


Figure 10. The central image was obtained by STM experiments²¹ (1.8 V, 0.05 Å) for a submonolayer coverage of DIP on Au (111). The four illustrative schemes depict the different discommensuration line patterns (with colours, green and orange meaning respectively the $\langle 11\bar{2} \rangle$ and $\langle 1\bar{1}0 \rangle$ -types of the Au(111) crystallographic directions) and the corresponding self-assembly patterns of DIP obtained from simulations. All the structures are shown with the $\langle 1\bar{1}0 \rangle$ direction horizontal.

These results are summarized in Figure 9, where we show the radial distribution (or correlation) function, $g(r)$, calculated for DIP molecules adsorbed on each substrate as computed from our simulations. This function measures the deviations of the local density of DIP molecules from that expected from a random distribution of molecules. Therefore, peaks in $g(r)$

indicate the presence of structures and their typical correlation distances. Snapshots of relevant configurations are also shown to help interpretation of $g(r)$.

In the case of simulations on either the non-reconstructed Au(111) surface or on the herringbone reconstruction, no significant evidence of order is found. For both, the peak between 8 to 11 Å has a simple interpretation: it corresponds to first neighbour molecules in contact in disordered aggregates. In the striped reconstruction case, the head-to-tail stacking leads to a regular lattice spacing (first correlation peak) $a \approx b \approx 13.25$ Å (± 0.7 Å), with an angle between lattice vectors of $\gamma = 98.5^\circ$ ($\pm 2^\circ$). The angle is directly extracted from structural analyses for the same number of configurations used to calculate the $g(r)$ function and for molecules first neighbours.

The structure obtained in the simulations on the distorted herringbone substrate (red solid line) reveals two well-resolved and intense peaks in the $g(r)$ at $a \approx 12$ Å and $b \approx 14.6$ Å (± 1 Å). These results are in outstanding agreement with the STM experiments²¹, in which highly ordered molecular domains were reported with an asymmetric primitive unit cell of $a = 13.4$ Å (± 1) and $b = 14.8$ Å (± 1), with an angle of $\gamma = 97^\circ$ ($\pm 2^\circ$). In that work, it was also shown that, the submonolayer surface coverage presents more complicated scenarios that are a manifestation of the key role played by specific structural features of substrate surface.

In order to demonstrate the potential of the simulation methodology employed in the present work, a STM image corresponding to submonolayer coverage of DIP (~ 80 nm \times 80 nm) is shown in Figure 10 with four schemes representing characteristic results from our simulations. Clear similarities between experiment and simulations are evidenced. From which we highlight at least two: i) the presence of large homochiral domains (induced in our simulations by the combined effect of the presence of stripes along the $[11\bar{2}]$ and a parallel corrugated potential field along the $[1\bar{1}0]$ direction which captures the main features of the experimental distorted herringbone structure²¹, and ii) the neat decoration of the *Roseta*-like regions by nucleation of small disordered clusters of DIP at vicinity of surface defects.

4. Conclusions

Supramolecular self-assembly of organic molecules on metal surfaces involves a subtle and competitive balance between weak intermolecular and molecule-substrate interactions. This balance becomes even subtler in the presence of surface reconstruction. On the other hand, the large number of atoms needed for the whole self-assembly description results theoretically unaffordable with common methodologies. In this work we present simulations performed using the SANO strategy, which circumvent this issue permitting large-scale modelling. As a benchmark system of weakly interacting molecules on surfaces we have chosen the adsorption of DIP molecules onto diverse surface reconstructions of Au(111) resulted from different forms of strain relief.

The motivation of this work was triggered by the fact that no long-range order could be obtained with the flat Au(111) surface. Interestingly, the competitive self-assembly on the herringbone surface prevents the long-range ordering at a large scale. Initiated by diverse experiments, we have also considered the so-called *Roseta* surface reconstruction. In spite of being already observed for different systems, the relaxed atomic

structure is reported here for the first time. Though no long-range order could be obtained, the inherent ad-atoms on this surface endorse the role of nucleation sites and diffusion barrier, as observed experimentally.

Long-range order is fully achieved during self-assembly in the striped reconstruction, where the surface symmetry is broken by presence of parallel discommensuration lines. The consequent surface roughness helps aligning up cooperatively the molecules and improves their intermolecular interactions. Moreover, an interesting result appears when we include an extra symmetry break by adding a surface corrugation perpendicular to the stripes, which captures the essential features of the observed experimental distorted herringbone pattern. The simulation results obtained for self-assembly in such surface evidence the emergence of two homochiral domains equally deviated from the corrugation line at the origin of the rupture of symmetry, which has led to an impressive agreement with the experiment confirming the cooperative process during the self-ordering.

In summary, by performing large scale modelling of the entire supramolecular self-assembly at ambient temperature on different gold reconstructed surfaces, we predict and recover the overall picture of the experimental STM observations during DIP self-assembly. Our results provide understanding of the gearing role of the discommensuration lines of gold (111) surface on the self-ordering and demonstrate the subtlety of the cooperative/competitive driving force leading to long-range ordered domains and surface-induced chirality. Importantly, taking advantage of the symmetry break on the rotational degree of freedom of molecules, the simulation strategy opens interesting perspectives to tune the supramolecular structure, by surface engineering if choosing the right molecular building blocks and stabilising the chosen reconstruction pattern. For instance, this work represents the first milestone to further study tuneable symmetry and periodicity in binary supramolecular nanostructures on reconstructed surfaces.^{36,37}

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Appendix: Simulation Methodology

Atomistic Model for the DIP molecule and pre-calculation of the molecule-molecule potential energy of interaction

We consider a fully atomistic rigid model of the DIP molecules. The intermolecular interactions are described with the OPLS-AA force field^{38,39}, a transferable force field appropriate for organic molecules weakly interacting at room temperature. The force field includes both Lennard-Jones and electrostatic interactions between atoms. Electrostatic interactions between two neutral DIP molecules arise from an unequal charge distribution over the atoms of each molecule

and are described by placing partial charges on the atoms (as shown in table S1 and Figure SI.1 in Supporting Information). The partial charges were determined according to the Partial Equalization of Orbital Electronegativities (PEOE) algorithm also known as *Gasteiger-Marsili* method.⁴⁰

The interaction energy between two equal DIP molecules was computed for 200 intermolecular distances between 3.5 and 30 Å, therefore the spatial resolution is 0.13 Å. For each molecule-molecule separation, we considered 360 × 360 relative orientations, therefore the angular resolution was one degree. The results of these calculations were stored for further use in the MC runs.

Atomistic models for the substrates

In the case of the simple Au(111) substrate, the atomic coordinates were obtained by placing 4800 atoms in a 12-layers slab following a *fcc* structure. The top (111) surface has an orthorhombic unit cell of dimensions 5.78 × 4.99 Å².

Unlike the case of a *fcc* structure, in the case of the reconstructions of the Au(111) surface considered in this work, the atomic coordinates of the gold atoms (required for the calculation of the molecule-surface interaction) are not known *a priori*. Therefore, we need to generate the atomic coordinates using simulation techniques. In all the structures considered here, we started with an initial guess for the atomic positions as described below followed by optimization using quenched molecular dynamic simulations⁴¹ (qMD). To provide realistic structural features, the interactions between gold atoms were described by a semi-empirical many-body potential derived from the tight binding scheme in its second moment approximation⁴² (TB-SMA).

In the case of the striped reconstruction, each unit cell is constructed by inserting one additional atom every 23 nearest neighbour distances (dNN) along the [1 $\bar{1}$ 0] direction of an ideal (111) plane. Initial atomic coordinates correspond to a slab of 11 bulk layers stacked along the [111] direction and the 23 × √3 reconstructed topmost layer. The orthorhombic simulation box size is 65.04 Å × 66.35 Å in the *x* and *y* directions, respectively, and contains 7202 atoms. After optimization of the structure using the qMD simulations⁴¹, the compression along the [1 $\bar{1}$ 0] direction leads to two extended domains: a *fcc* stacking and an *hcp* stacking. These domains are separated by parallel DLs, therefore following [11 $\bar{2}$] directions, due to the gold atoms located at unfavourable bridge positions respectively to the underlying layer. This atomic position relaxation imposes a slight vertical displacement of the surface atoms (between 0.2 to 0.3 Å in *z*) that gives rise to a surface corrugation visible by scanning tunnelling microscopy (STM) measurements⁴³.

In the case of the herringbone reconstruction²⁸, the simulation slab consists of 15 (111) planes from which the 14 bulk planes and the slab bottom surface are unreconstructed (111) planes and contain 3164 atoms each whereas the overclose-packed (111) surface plane is the reconstructed topmost-layer and contains 3317 atoms (see Figure 3). The slab unit cell generated in this way has an area of 325.44 × 69.84 Å² and a total of 47613 atoms. The structure obtained after relaxation with qMD simulations retains the desired herringbone patterns and shows a strong dispersion of the in-plane surface nearest-neighbour distances, from 2.68 Å at the zig-zag kink positions to 2.86 Å in the *fcc* regions. The obtained surface corrugation is around 0.33 Å, slightly higher than the experimental value obtained by STM (0.20 ± 0.05 Å) and substantially larger than that of the unreconstructed surface (0.05 Å).

In the case of the roseta reconstruction, the initial atoms coordinates (before optimization) were built from a slab containing 9 (111) atomic planes based on the Barth's model³⁰. The topmost surface layer is 8.8% denser than the (111) bottom layers (1152 and 1058 Au atoms, respectively). After optimization with qMD, in addition to atoms on bridge positions at the DLs that separate the two domains (*hcp* and *fcc*), few atoms outcrop from the surface at the vertices of the pattern, because of the too high dNN compression, a phenomenon also reported experimentally³⁴. The existence of these ad-atoms and the relatively short distance between them (6.2 nm along DL) imply a more pronounced surface roughness as compared to the aforementioned reconstructions ($\sim 0.5 \text{ \AA}$ to 1.5 \AA see Figure SI.8).

Pre-calculation of molecule-substrate potential energy

The force field for the interaction of a DIP molecule with gold substrate consists only of a Lennard-Jones interaction between Au and DIP atoms, employing the parameters recommended on Ref 39 for modelling the interaction of metals with organic molecules at room temperature, consistent with the OPLS-AA force field. In general, the use of the force-field methodology (OPLS, CVFF, CHARMM,...) is well justified for modelling molecule-surface interactions in the case of physisorption of organic molecules onto metal surfaces, as discussed for example in refs^{44,45}. Other contributions such as the induced polarization of the metal surface are very small here, and can be neglected (see also Refs 8 and 46).

In the case of the flat non-reconstructed Au(111) surface, the pre calculation of the DIP-surface potential energy was done by dividing the surface in a grid containing 50×50 points (about $0.11 \times 0.1 \text{ \AA}^2$ resolution). For each grid point, we have located the distance between the DIP centre of mass and the surface at which the potential energy of interaction between a horizontal DIP molecule and the surface is minimum. This calculation is repeated as a function of the molecular orientation with a resolution of one degree.

In the case of the other substrates, we have first to generate the atomistic models described above. After the gold atom coordinates relaxation, we can pre calculate the molecule-surface interaction with the a procedure similar to that employed in the case of the Au(111) surface. However, the higher roughness of the surface and the possible presence of ad-atoms at the surface introduce further complications in the calculation. In the Au(111) case without reconstruction, it was assumed that a DIP molecule will adsorb with its plane parallel to the plane of the surface. However, in the case of adsorption onto a reconstructed surface, other orientations of the plane of the molecule are possible. For this reason, in this case the molecule-substrate distance that minimizes the potential energy is further refined by permitting the molecule to rotate out of plane around its orientation axis. The final tilt is always smaller than 2 degrees from the initial one.

In the case of the stripes reconstruction, the surface was divided in 200×200 grid points which means that molecule-surface potential energy was precalculated with $\sim 0.3 \times 0.3 \text{ \AA}^2$ spatial resolution. Again, the resolution for the energy dependence with the orientation of the molecule was one degree. In the case of the herringbone reconstruction, the precalculation of the interaction energy between a single molecule and the surface was done as in the previous cases. Taking advantage of the mirror symmetry of the herringbone pattern, the computational time is reduced by calculating the potential energy for $250 \times$

150 points of half unit cell of the surface. The angular resolution with the molecular orientation for the energy precalculation was again one degree. Due to the large number of atoms per unit cell (47615 atoms), the pre-calculation of the molecule-substrate potential energy takes into account only the four first topmost surface layers, which still ensures including more than 99% of the potential energy well.

In the case of the roseta structure, the pre-calculation of the molecule-substrate potential energy was done for one orthorhombic unit cell of the (22×22) roseta structure (*i.e.* $69.5 \text{ \AA} \times 120.38 \text{ \AA}$) and performed for 150×200 points and 360 molecular orientations.

SANO Methodology for modelling the molecular self-assembly

Once the molecule-molecule and molecule-substrate potential energy are calculated, we can proceed to perform Monte Carlo simulations at the desired coverage and temperature. The movements introduced in the MC simulations are translation, rotation or translation plus rotation of molecules.⁸ As usual, each MC cycle requires the evaluation of the potential energy of the system, which is computationally very expensive. In our MC simulations, the potential energy of the system is derived from the (tri-)linear interpolation of the precalculated molecule-molecule (V^{MM}) and molecule-substrate (V^{MS}) potential energies. This approximation is essential in the SANO methodology.⁸ It improves the computational efficiency by a factor of 10^4 (or more) while keeping the atomistic description of the system and the desired accuracy for the potential energies. It allows performing standard Monte Carlo (MC) simulations on a two-dimensional large periodic box containing ($n \times m$) integer numbers of unit cells of the substrate. The size of the periodic simulation boxes and the number of DIP molecules was different in each case since the size of the simulation box requires to appropriately simulate each different reconstruction periodicity (see Table 1). For instance, the simulation with the stripes reconstruction involves a simulation box containing 8×8 unit cells. Note that in all cases, the simulation box is large enough to be able to simulate the possibility of self-assembly patterns that may extend beyond the size of a single unit cell of the substrate.

For each substrate, the initial configuration consists of a fixed number of molecules randomly dispersed on the bare surface. To avoid any early structure formation or overlap between molecules at the beginning of the simulation we perform a first run of 10^5 MC cycles per molecule at very high temperature (1000K). This case corresponds to a two-dimensional disordered (gas like) phase, with no structure. Then, the temperature is set at 400K and decreased until 300 K by steps of 20K between each equilibration. In order to correctly sample the accessible configuration space, at least 10^6 MC attempts (translation, rotation or translation plus rotation) are performed for randomly chosen molecules. At the first stage of the simulation, we perform an initial run of 10^5 MC attempts per molecule using an average displacement equal to half of the simulation box length, which insures a proper and rapid exploration of the accessible configurations. In a second stage, the average displacement is reduced progressively until reaching twice the thermal De Broglie wavelength of the molecule, which is approximately the molecular length. Finally, the average displacement was selected so that 50% of Monte Carlo attempts of molecular displacements are accepted. Once equilibrated, the average values for the physical magnitudes of interest (*i.e.* average potential energies, structural analyses) are

calculated during the last production run of 10^6 MC attempts per molecule.

The results obtained from the MC simulations of Table 1 contain both the effect of molecule-molecule and molecule-substrate interactions. In the analysis and discussion of the results, it could be helpful to be able to discriminate between these two main contributions. In order to help interpretation of the results, we have performed additional ancillary simulations corresponding to an ideal system of an infinitely diluted phase of DIP molecules adsorbed at the different substrates. These ancillary simulations are performed with a MC run at 300K taking into account only the molecule-surface interaction (the molecule-molecule interactions are ignored) during the calculations. In order to obtain good statistics, the simulations were performed for one thousand isolated adsorbed molecules. The runs consisted of 10^6 MC attempts per molecule and the simulations are reported for the Au(111) substrate, the striped and herringbone reconstructions.

All snapshots are made with VMD⁴⁷.

Notes and references

^a Address: Institut de Ciència de Materials de Barcelona ICMAB-CSIC, Campus de la UAB, E-08193 Bellaterra, Spain

(*) Corresponding Author: troussel@icmab.es

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1 C.-A. Palma, M. Cecchini, P. Samori, *Chem. Soc. Rev.*, **2012**, *41*, 3713-3730.

2 A. Aksimentiev, R. Brunner, J. Cohen, J. Comer, E. Cruz-Chu, D. Hardy, A. Rajan, A. Shih, G. Sigalov, Y. Yin, K. Schulten, in *Methods in Molecular Biology*, vol. 474: *Nanostructure Design: Methods and Protocols* (Edited by: E. Gazit, R. Nussinov) © Humana Press, Totowa, NJ pp 181-234 (2008).

3 S. Hecht, Welding, *Angew. Chem. Int. Ed.* 2003, **42**, 24.

4 A. Kühnle. *Curr. Opin. Colloid Interface Sci.*, 2009, **14**, 157-168.

5 J. Saiz-Poseu, A. Martínez-Otero, T. Roussel, J.K.-H. Hui, M.L. Montero, R. Urcuyo, M.J. MacLachlan, J. Faraudo, D. Ruiz-Molina, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11937-11943.

6 C. Gobbo, I. Beurroies, D. de Ridder, R. Eelkema, S.J. Marrink, S. De Feyter, J.-H. van Esch, A.H.J. de Vries, *Phys. Chem. C* 2013, **117**, 15623-15631.

7 S.J. Marrink, D.P. Tieleman, *Chem. Soc. Rev.*; 2013, **42**, 6801-6822.

8 T. Roussel, L.F. Vega. *Journal of Chemical Theory and Computation*, 2013, **9**, 2161-2169.

9 L. Burgi, H. Brune, K. Kern, *Phys. Rev. Lett.*, 2002, **89**, 17, 176801.

10 K.G. Huang, D. Gibbs, D.M. Zehner, A.R. Sandy, S.G.J. Mochrie, *Phys. Rev. Lett.*, 1990, **65**, 26, 3313-3316.

11 S.B. Darling, A.W. Rosenbaum, Y. Wang, S.J. Sibener, Coexistence of the $(23 \times \sqrt{3})$ Au(111). *Langmuir*, 2002, **18**, 7462-7468.

12 M. Bohringer, K. Morgenstern, W.-D. Schneider, R. Berndt, F. Mauri, A. De Vita, R. Car, *Phys. Rev. Lett.*, 1999, **83**, 324-327.

13 I. Chizhov, A. Kahn, G. Scoles, *Journal of Crystal Growth*, 2000, **208**, 449-458.

14 M. Yu, W. Xu, Y. Benjalal, S. Nagarajan, F. Masini, E. Lægsgaard, M. Mohamed Hliwa, X. Bouju, A. Gourdon, C. Joachim, F. Besenbacher, T.R. Linderoth, *Nano Res.* 2012, **5**, 903-916.

15 J. Mendez, R. Caillard, G. Otero, N. Nicoara, J.A. Martin-Gago, *Adv. Mater.* 2006, **18**, 2048-2052.

16 M. Corso, L. Fernández, F. Schiller, J.E. Ortega, Au(111)-Based Nanotemplates by Gd Alloying. *ACS Nano*, 2010, **4**, 1603-1611.

17 A.D. Jewell, E.C.H. Sykes, G. Kyriakou, *ACS Nano*, **2012**, *6*, 3545-3552.

18 A.C. Dürr, F. Schreiber, M. Munch, N. Karl, B. Krause, V. Kruppa, H. Dosch, *Appl. Phys. Lett.* 2002, **81**, 2276.

19 A.C. Dürr, N. Koch, M. Kelsch, A. Ruhm, J. Ghijsen, R.L. Johnson, J.-J. Pireaux, J. Schwartz, F. Schreiber, H. Dosch, A. Kahn, *Phys. Rev. B.* 2003, **68**, 115428.

20 M.A. Heinrich, J. Pflaum, A.K. Tripathi, W. Frey, M.L. Steigerwald, T. Siegrist. *J. Phys. Chem. C* 2007, **111**, 18878-18881.

21 D. Oteyza, E. Barrena, M. Ruiz-Oses, I. Silanes, B.P. Doyle, J.E. Ortega, A. Arnau, H. Dosch, Y. Wakayama. *J. Phys. Chem. C.* 2008, **112**, 7168-7172.

22 S.C.B. Mannsfeld, T. Fritz, *Mod. Phys. Lett. B*, 2006, **20**, 11, 585-605.

23 C. Goyhenex, H. Bulou, *Phys. Rev. B*; 2001, **63**, 235404.

24 C. Goyhenex, H. Bulou, J.-P. Deville, G. Tréglia, *Applied Surface Science*, 2002, **188**, 134-139.

25 P. Campiglio, V. Repain, C. Chacon, O. Fruchart, J. Lagoute, Y. Girard, S. Rousset, *Surf. Sci.*, 2011, **605**, 1165-1169.

- 26 J.T. Sun, L. Gao, X.B. He, Z.H. Cheng, Z.T. Deng, X. Lin, H. Hu, S.X. Du, F. Liu, H.-J. Gao, *Phys. Rev. B*, 2011, **83**, 115419.
- 27 G.E. Poirier, E.D. Pylant, *Science*, 1996, **272**, 1145-1147.
- 28 H. Bulou, C. Goyhenex, *Phys. Rev. B*; 2002, **65**, 045407.
- 29 J.V. Barth, H. Brune, R. Schuster, G. Ertl, R.J. Behm, *Surf. Sci. Letters*, 1993, **292**, L769-L774.
- 30 J.V. Barth, R.J. Behm, G. Ertl. *Surf. Sci. Lett.*; 1994, **302**, L319-L324.
- 31 H. Brune, H. Roder, C. Boragno, K. Kern. *Phys Rev. B*, 1994, **49**, 2997-3000.
- 32 K. Ait-Mansour, P. Ruffieux, W. Xiao, P. Groning, R. Fasel, O. Groning, *Phys. Rev. B*, 2006, **74**, 195418.
- 33 C. Giinther, J. Vrijmoeth, R.Q. Hwang, R.J. Behm. *Phys. Rev. Lett.*, 1995, **74**, 5, 754-757.
- 34 J. Mendez, J. Gomez-Herrero, J.I. Pascual, J.J. Saenz, J.M. Soler, A.M. Baro., *J. Vac. Sci. Technol. B*, 1996, **14**, 1145-1148.
- 35 L. Gao, Q. Liu, Y. Y. Zhang, N. Jiang, H. G. Zhang, Z. H. Cheng, W. F. Qiu, S. X. Du, Y. Q. Liu, W. A. Hofer, and H.-J. Gao, *Phys. Rev. Lett.* 2008, **101**, 197209.
- 36 D. Oteyza, I. Silanes, M. Ruiz-Oses, E. Barrena, B.P Doyle, A. Arnau, H. Dosch, Y. Wakayama, J.E. Ortega. *Adv. Funct. Mater.*, 2009, **19**, 259-264.
- 37 D. Oteyza, E. Barrena, H. Dosch, J.E. Ortega, Y. Wakayama, *Phys. Chem. Chem. Phys.*, 2011, **13**, 4220-4223.
- 38 W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.*, 1996, **118**, 11225.
- 39 H. Heinz, R.A. Vaia, B.L. Farmer, R.R. Naik, *J. Phys. Chem. C*, 2008, **112**, 17281.
- 40 J. Gasteiger, M. Marsili, *Tetrahedron*, 1980, **36**, 3219.
- 41 C. Mottet, G. Trégliat, B. Legrand, *Phys. Rev. B*, 1992, **46**, 16018.
- 42 V. Rosato, M. Guillope, B. Legrand, *Phil. Mag. A*, 1989, **59**, 321.
- 43 J.V. Barth, H. Brune, G. Ertl, R.J. Behm, *Phys. Rev. B*, 1990, **42**, 15, 9307.
- 44 H. Heinz, B.L. Farmer, R.B. Pandey, J.M. Slocik, S.S. Patnaik, R. Pachter, R.R. Naik, *J. Am. Chem. Soc.* 2009, **131**, 9704-9714.
- 45 J. Feng, J.M. Slocik, M. Sarikaya, R.R. Naik, B.L. Farmer and H.H. Heinz, *Small* 2012, **8**, 1049-1059.
- 46 H. Heinz, K. C. Jha, J. Luettmer-Strathmann, B. L. Farmer and R.R. Naik *J. R. Soc. Interface*, 2011, **8**, 220-232.
- 47 W. Humphrey, A. Dalke, K. Schulten, VMD: Visual Molecular Dynamics. *J. Mol. Graph. Model.* **1996**, 14, 33-38.