

Supporting information for: “Self-assembly of 5,6-dihydroxyindole-2-carboxylic acid: polymorphism of a eumelanin building block on Au(111)”

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Table of Contents

1) STM calibration details	2
2) Additional details on brick wall phase DFT calculations	2
3) Additional details on Monte Carlo calculations	3
4) Additional STM images	4

1) STM calibration details

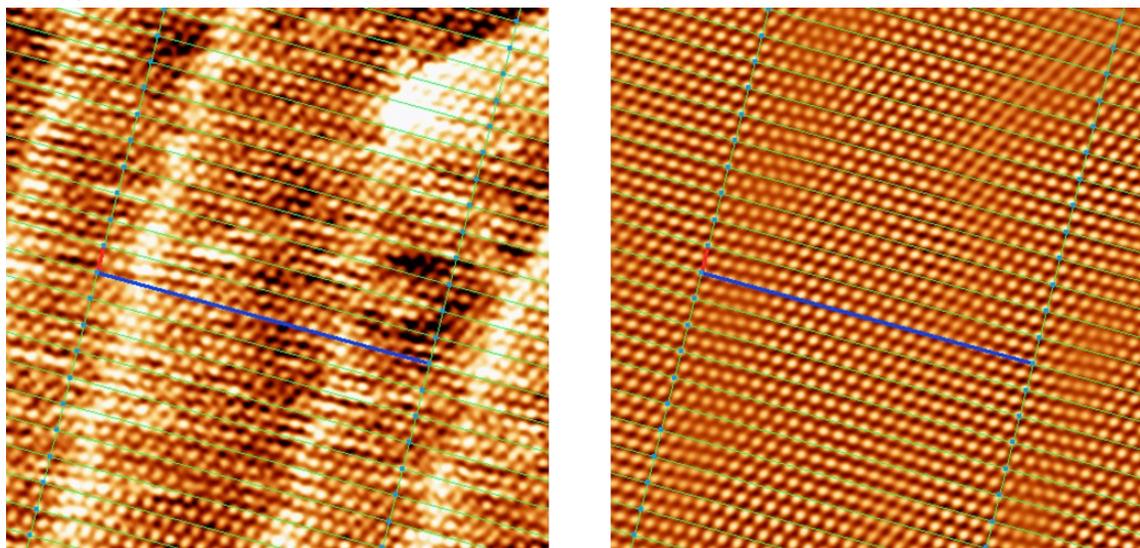


Figure S1. An example of the calibration adopted for the DHICA/Au(111), where the clean Au substrate image (3.30 nA, 0.01 V, 10x10 nm²) is processed and filtered until the single atoms are properly visible. The image is calibrated by using the 6.23 nm herring bone reconstruction dimension ([1-10], blue vector in the image) at 90° respect to the direction of the solitons ([112], red vector in the image) as the distance between 23 atoms.

2) Additional details on brick wall phase DFT calculations

The observed brick wall phase is formed by all DHICA molecules, as shown by STM in Figure 2b in the main text. The molecules can assemble in different configurations, with either a head-to-head or a head-to-tail interaction. Although in the case of two isolated molecules, the head-to-head interaction is preferred (Figure 4 main text), additional side interactions are present in a four-molecules unit cell. Nevertheless, our DFT calculations under PBC conditions show that the head-to-head yields the SAMNs with the lowest energy. In addition to being a more stable self-assembly, the head-to-head configuration also has a better agreement with the STM experimental images, preserving the observed symmetry.

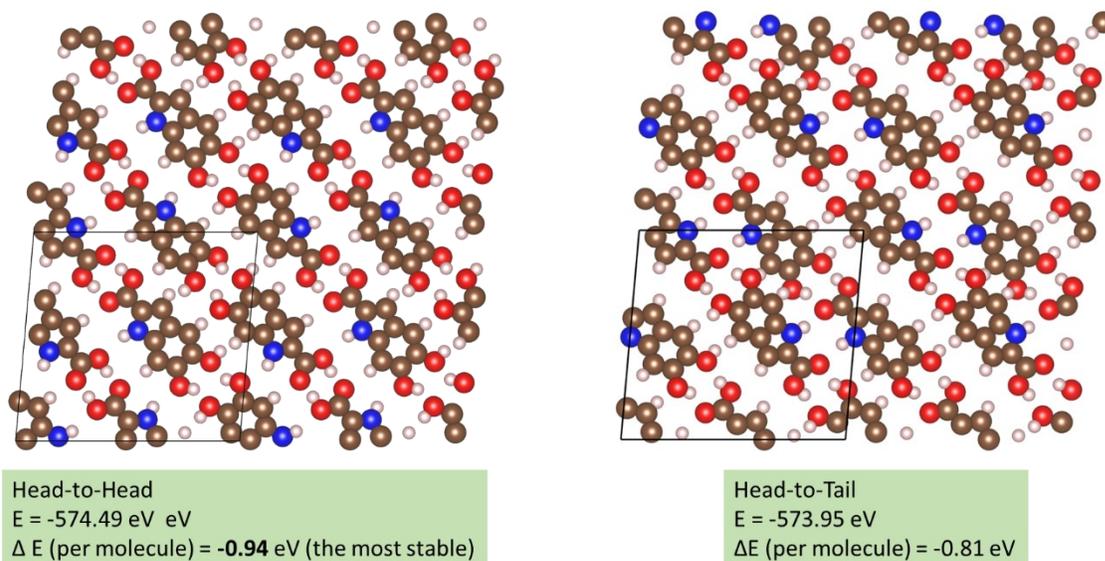


Figure S2. Comparison between the cohesive energy of a head-to-head and a head-to-tail conformation

3) Additional details on Monte Carlo calculations

To describe the ordering of DHICA, we constructed a statistical model which involves four molecular states and main dimeric interactions (see Figure S3). First of all, we took into account three axial bondings that occur when two molecules interact via carboxyl (further called head-head, e_{hh} interaction), carboxyl and catechol (head-tail e_{ht}) and catechol (tail-tail, e_{tt}) groups. The gas phase DFT calculation provided the following values of these interaction energies: $e_{hh} = -25.12$, $e_{ht} = -11.58$ and $e_{tt} = -8.60$ kcal/mol (see Figure 4a).

We also included and evaluated interactions caused by nearly perpendicular geometries of two interacting molecules. These interactions are obtained from the two-molecule as well as from the three-molecule complexes. In the latter case, the system comprises the main axial dimeric interaction and perpendicular interaction as well. These interactions are called in a same manner as the main axial interactions, but with a superscript “p” for perpendicularity: e_{hh}^p , e_{th}^p and e_{tt}^p (Figure S3). The magnitudes of these interactions determined from the three-molecule DFT geometry (see Figure 4b) are: $e_{hh}^p = -17.09$ and $e_{th}^p = -6.61$ kcal/mol. We also obtained the value of the trio complex when the third molecule is not in a perpendicular tail-to-head geometry (i.e. directed to one of the dimer molecules), but has its catechol group directed towards the dimeric bond itself. Such a complex is a bit more stable (-34.95 kcal/mol) than the one with dimeric e_{th}^p interaction (-31.73 kcal/mol), but their energy difference is quite small (3.2 kcal/mol). The interaction $e_{tt}^p = -7.32$ kcal/mol was taken from the three-molecule geometry with an additional tail-tail axial interaction (see Figure 4b).

Finally, we considered two interactions potentially characteristic to the brick wall and ladder phases when two molecules interact from their sides (Figure S3). The denotation of interactions has the superscript “s” for the “side”. The magnitudes of these interactions are $e_1^s = -5.09$ and $e_2^s = -3.78$ kcal/mol (Figure 4c). Note that in our model we did not take into account the chirality of DHICA, as nitrogen atom barely affects the side interactions. In our model we also take into account that two

molecules within a certain close distance cannot coexist, because they either overlap or induce strong repulsion. Such configurations are subjected to infinite exclusion.

The model was solved using MC simulations on a square lattice. The choice of such a lattice was motivated by the symmetry of the ordered phases. In our model, the distance between the interacting molecules is different for different types of interactions as indicated in Figure S3.

Note that we tolerate some freedom in the choice of interaction energies but try to keep a discrepancy from the DFT values as small as possible.

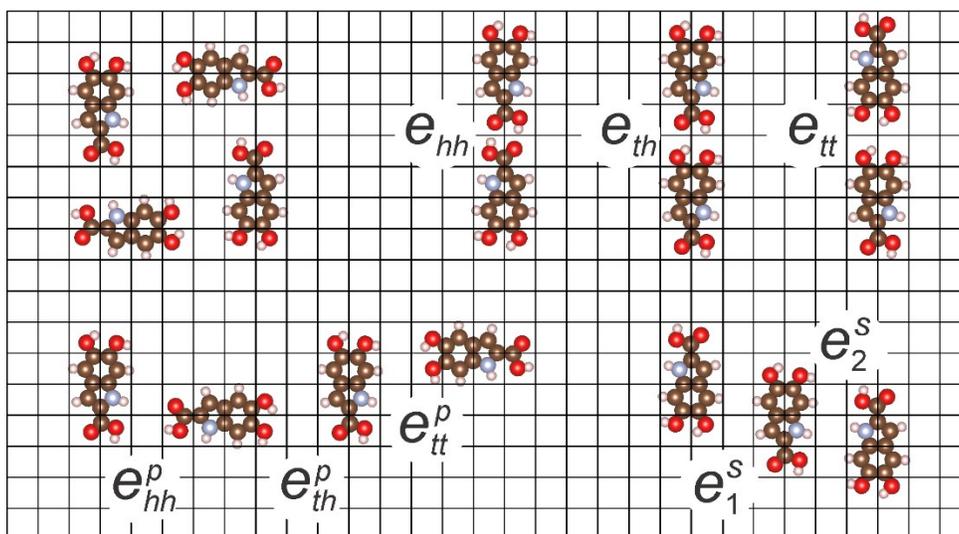


Figure S3. Four molecular states of DHICA on a square lattice (above, left) and the eight intermolecular interactions used in MC simulations.

4) Additional STM images

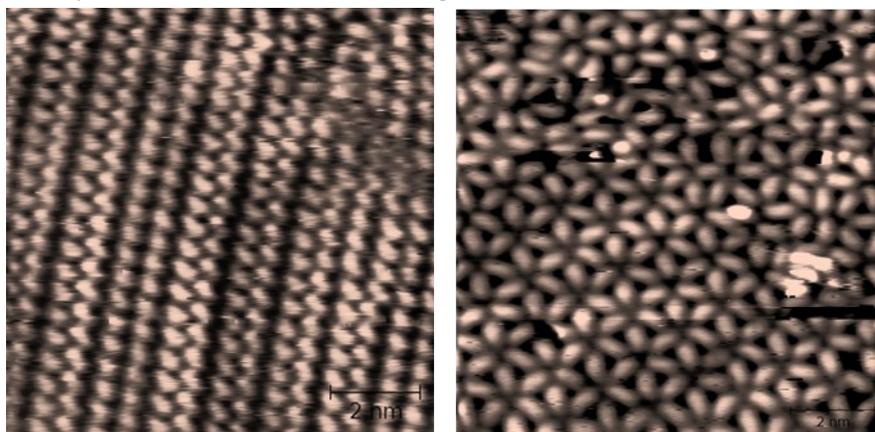


Figure S4: Other DHICA SAMNs phases formed on Au(111) at a) RT and b) LT

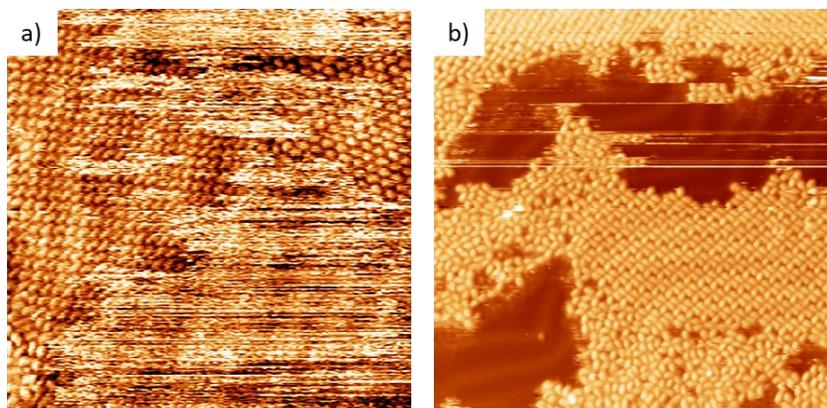


Figure S5: STM images of the a) brick wall and b) ladder close packed DHICA phase obtained at submonolayer coverages

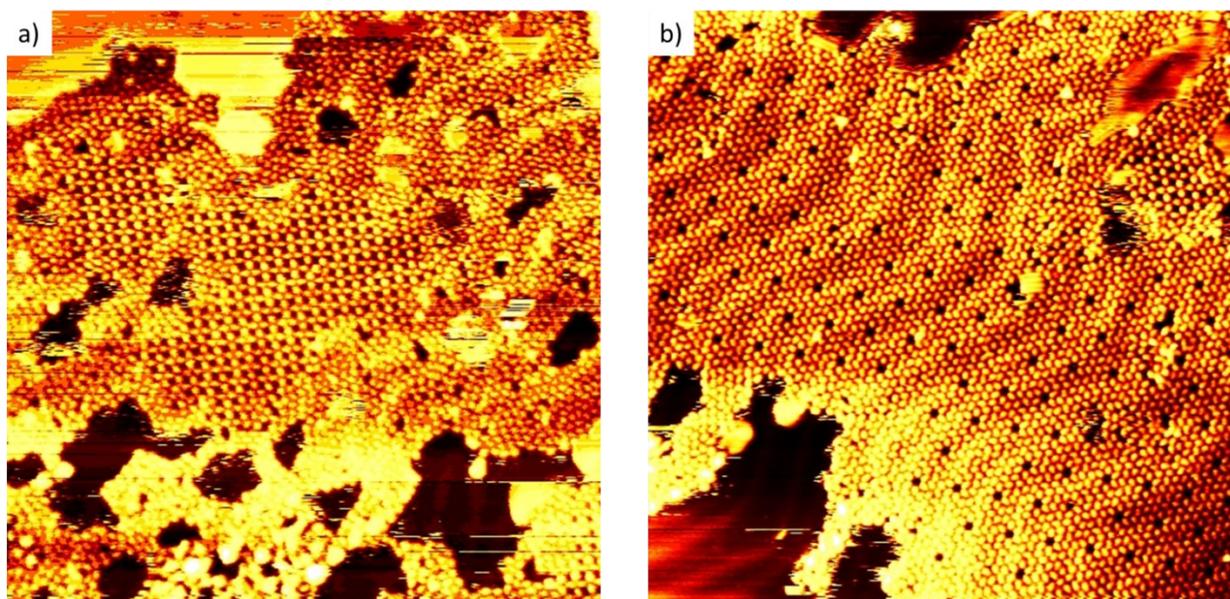


Figure S6: DHICA/Au after exposure to O_2 (a) and annealing to $100^\circ C$ (b). Small domain of open lattice phase is still visible across the surface.

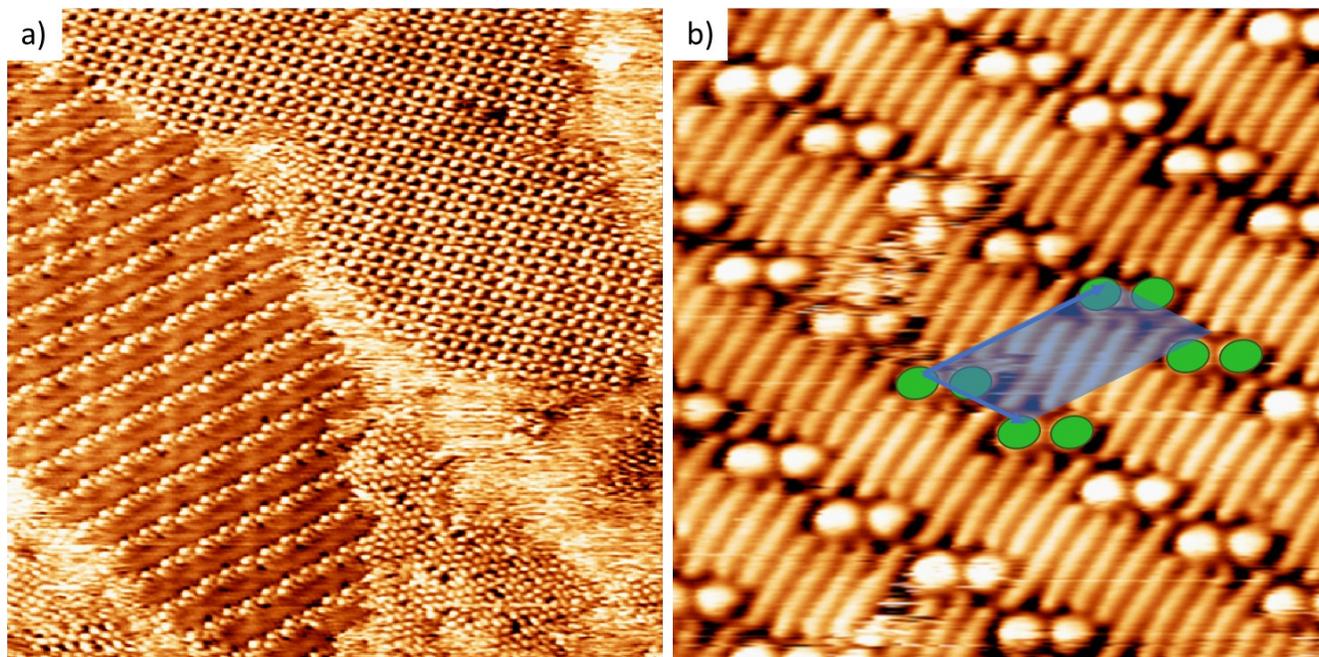


Figure S7: a) The DHICA/Au surface after exposure to O_2 . b) Detail of the phase formed exposing the molecule to 10^{-5} mbar of O_2