

EPAPS : Supplemental Material for “Surface-induced optimal packing of two-dimensional molecular networks”,

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Here we provide 1) further details on the computer simulation methods used, and give additional results for: 2) the calculated kinetic barriers between the LD and HD phases, and 3) new experimental synthesis and STM data, obtained at two different molecular deposition rates.

I. DETAILS ON SIMULATION METHODS

DFT. Structures of the isolated TCNBB molecule in void were firstly optimized by DFT, as implemented in Gaussian-03 single-point calculations, with the B3LYP/6-311g functional. Charge distributions were assigned by the Merz–Singh–Kollman (MK) definition of the molecular electrostatic potential. H charges are always comprised between neutral and 0.2e; C–C bound atoms are between neutral and +0.3e. C bound to H are between −0.1 and −0.3e, and C neighboring the C–N function are at about +0.1e, while N atoms are at −0.05e. The charge of the surface Si and B atoms was set at neutral, according to the indications of the experimental STM images, which show no charged sites on the free surface.

Molecular dynamics. Molecular dynamics simulations were run using the DL_POLY v.2 and v.4 code, with a custom interface to input the MM3 force field, supplemented by ab-initio calculated spring constants for missing dihedrals in the TCNBB molecule. Intermolecular forces were described by the standard Van der Waals parameters of MM3; molecule-surface VdW forces instead were described by the improved treatment developed in our previous work (G. Copie et al., J Phys Chem C 118 (2014) 18217), based on the time-dependent DFT study of Oliveira et al. (PCCP 13 (2011) 15055). MD at finite T and P was performed with Nose-Andersen thermostats, with fictitious masses ranging from 1 to 50 times the total mass of the molecular system (since the Si and B surface degrees of freedom are frozen in the simulations). The integration time step was always 1 fs, a value ensuring energy conservation better than 10^{-5} in the isolated molecular system.

Metadynamics. We performed Meta Dynamics simulations (A. Laio, M. Parrinello, PNAS 99 (2002) 12652) by using the PLUMED v.1.0 plugin (M. Bonomi et al. Comp. Phys. Comm. 180 (2009) 1961) for DL_POLY v.2. Several MtD simulations were performed by placing a molecule at random sites on the surface, and subsequently relaxing the total system energy by steepest-descent method. We used only two collective variables, the x_{CM} and y_{CM} positions of the molecular center of mass, while all the other degrees of freedom were unconstrained. The MtD Gaussian functions had a width of 0.35 Å, height of 0.4 kcal/mol, and were introduced at every 1 ps, during a typical 2-ns simulation. In order to limit the size of the collective variables space to be explored, and thanks to the symmetry of the surface, we restrained the search to a periodic 23.1×13.4 Å² portion covering 2x2 unit cells of the Si:B(111) surface.

Energy barrier path sampling. Energy barriers were estimated by an approximate Molecular Dynamics reaction-path searching method (called in the article text “elastic-band method”). Our algorithm is a modified version of the one proposed by Elber & Karplus (Chem. Phys. Lett. 139 (1987) 375), which later gave origin to the “nudged-elastic-bands” method. We add elastic springs to the center of mass of each molecule, between two known states \mathbf{R}_{in} and \mathbf{R}_{fin}

(each of the vectors $\mathbf{R}=\{\mathbf{R}_1,\dots,\mathbf{R}_N\}$ representing the set of coordinates of all the atoms in all molecules in the system). Generally, finding the minimum energy path between the two known states consists in minimizing the integral:

$$S_L(\mathbf{R}_{in}, \mathbf{R}_{fin}) = \frac{1}{L} \int_{\mathbf{R}_{in}}^{\mathbf{R}_{fin}} [E(\mathbf{R}) d\mathbf{l}(\mathbf{R})]_L$$

where $E(\mathbf{R})$ is the function describing the total energy of the system in the state \mathbf{R} , and $d\mathbf{l}(\mathbf{R})$ the element of displacement along one of the (infinitely many) paths L connecting \mathbf{R}_{in} and \mathbf{R}_{fin} . The discretised version of the integral, including the explicit form of the elastic-spring energy, is:

$$S_L(\mathbf{R}_{in}, \mathbf{R}_{fin}) = \sum_i \left\{ E(\mathbf{R}_i) \Delta \mathbf{l}_i^L + \frac{k}{2} (\Delta \mathbf{l}_i^L)^2 \right\}$$

with $\mathbf{R}_{fin} = \mathbf{R}_{in} + \sum_i \Delta \mathbf{l}_i^L$, and the displacements $\Delta \mathbf{l}_i^L$ corresponding to a given path L . In the state \mathbf{R}_{fin} all the displacements are zero and the recall force of the springs is null. On the other hand, in \mathbf{R}_{in} the recall force is maximal, and pulls the molecules toward the target state.

Differently from the version of Elber & Karplus, which uses an explicit minimisation algorithm on a fixed lattice of points, on which a finite number of paths L can be defined and explored exhaustively, we let molecular dynamics to do the job. In practice, by progressively decreasing the strength of the spring constant, and at the same time increasing the temperature (although remaining always at quite low values $T < 100$ K) of the MD simulation, the system explores the most probable paths for the transition, and the energy profile along the reaction coordinate can be followed. Although the method does not ensure a rigorous search of the complete configuration space, after averaging over many simulations (which run very fast), statistics on the points \mathbf{R}_i visited by the paths are accumulated, allowing to identify with reasonable accuracy the best transition paths.

Kinetic Monte Carlo. We set up a discrete lattice of N^2 rhomboidal unit cells, with a unit of length $a=6.63$ Å, each unit containing 2 hollow and 1 top site. The lattice reproduced the geometry and topological constraints of the Si:B surface. TNBB molecules were modelled as equilateral-triangular objects with C_{3v} planar symmetry, with side $3.15a$ ($=20.9$ Å) equal to the length of the segments joining the terminal N atoms. Note that this implies that many of the N lattice sites (27, for every position occupied by a molecule) are inaccessible, due to the steric occupation of the triangles. A lattice of N^2 units has a total of $M=3N^2$ sites, and can accommodate a maximum of $0.126M$ molecules in the LD phase, or $0.1405M$ in the HD phase. The results from the MD simulations, in particular the relative values of intermolecular interactions between triangle sides and corners, and between triangles and surface, were used as energy parameters in the MC sampling. Allowed MC moves are: jumps from occupied to any empty site, and on-site rotation in steps of $\pm\pi/3$ rad, for the $\{NVT\}$ -ensemble simulations; or, jumps from occupied to a neighboring empty site, rotation as above, and deposition/evaporation at/from an empty site, for the $\{\mu VT\}$ -ensemble simulations. A standard Metropolis rejection technique was implemented at values of $\Delta E/k_B T$ such that acceptance ratio was about 0.5 per move.

II. ENERGY BARRIERS BETWEEN THE TWO PHASES

In Figure S1, we plot the components of the energy along the reaction coordinate for each of the two types of molecules composing the base dimer unit (black and red curves). It is seen that both the intermolecular energy and the molecule-surface energy display a barrier (migration energy E_M) in going from the HD to the LD, of about 1.5 kcal/mol for the former and about 4 kcal/mol for the latter, both quite larger than room-temperature fluctuations. Therefore, patches of molecules locally arranged in the HD lattice could be kinetically trapped, and would not spontaneously transform into the (thermodynamically more favorable) LD phase, even for densities above the critical activity n_C , until a threshold temperature is reached.

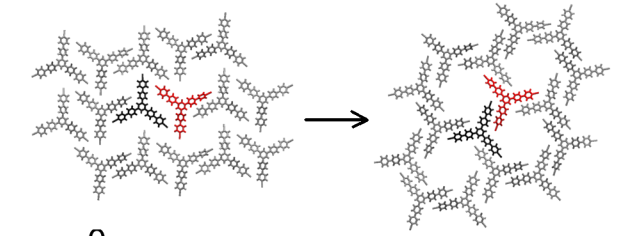
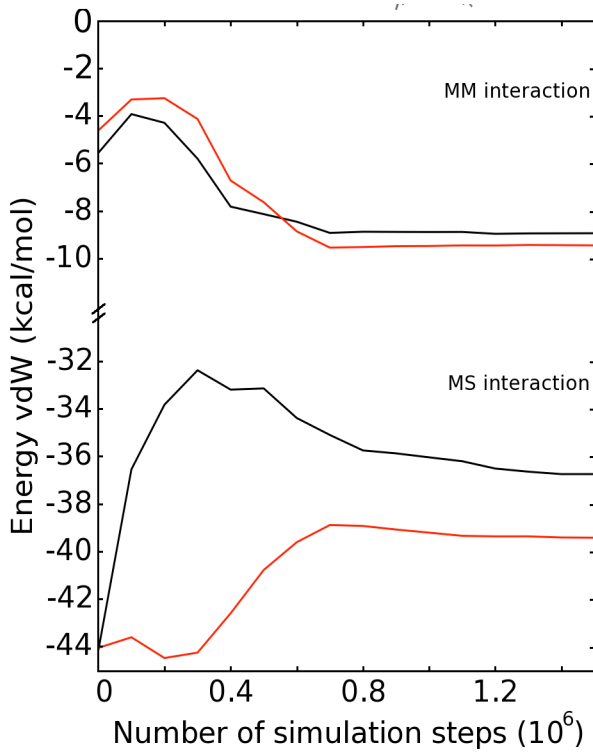


Figure S1. Above: schematic of the driven transition from the HD (left) to the LD (right) phase. Left: Intermolecular (upper curves) and molecule-surface (lower curves) van der Waals energy profiles, while switching from the HD (at time $t=0$) to the LD (at time $t=1.5 \cdot 10^6$) lattice by constrained minimization with the elastic-band MD simulation. The black and red curves correspond to the black and red molecule in the dimer base unit, from the above scheme. Each curve is averaged over similar molecules in all dimers.

III. INFLUENCE OF THE DEPOSITION RATE (experimental)

Additional experiments were performed at different deposition rates, so that the molecular activity was variable. The deposition rate was controlled through the increase of pressure during the evaporation of the molecules. The STM images shown in Figure S2 were obtained at a coverage rate much smaller than the saturation coverage. In the left image, corresponding to a low pressure during the evaporation ($<10^{-10}$ Torr), the LD network is the only phase seen. At higher pressure during the evaporation ($>10^{-10}$ Torr), both networks are visible (right image), demonstrating the role of the deposition rate on the formation and survival of the HD phase. Although difficult to put in correspondence on a more quantitative basis, this finding goes in the same direction as the Monte Carlo simulations, showing that a faster deposition rate may allow portions of the HD phase to survive to the surface diffusion, which instead promotes the phase change into LD.

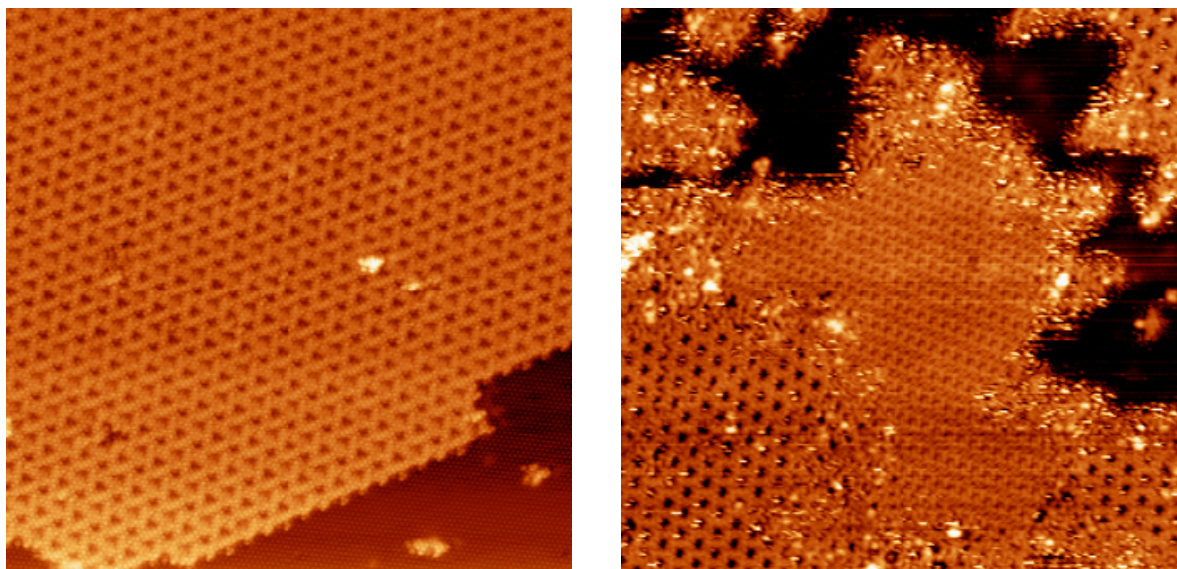


Figure S2. STM images showing the typical supramolecular structures obtained after the adsorption of TCNBB on a Si:B(111) surface for two different deposition rate: (Left) evaporation pressure $< 10^{-10}$ Torr, (Right) : evaporation pressure $> 10^{-10}$ Torr. Image size: $80 \times 80 \text{ nm}^2$.