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Supplementary Information

Role of Isomerization in Kinetics of Self-Assembly: p-Terphenyl-m-Dicarbonitrile on Ag(111) Surface

David Abbasi-Pérez and J. Manuel Recio

MALTA-Consolider Team and Departamento de Química Física y Analítica, Facultad de Química,
Universidad de Oviedo, 33006 Oviedo, Spain

Lev Kantorovich*

Physics Department, King's College London, Strand, London, WC2R 2LS, United Kingdom
lev.kantorovitch@kcl.ac.uk

Monomers on the surface

To explore the potential energy surface of a monomer on the silver surface, we started by selecting six sites on the surface, Fig. S1, where one N atom of the molecule was placed, and then, using the chosen N atom as a pivoting point, considered various orientations of the molecule by rotating its molecular backbone prior to full geometry optimization.

An extended selection of DFT relaxed adsorption geometries of the C and T monomers on the surface is shown in Figs. S2 and S3, respectively. The mean distances to the surface of the carbon skeleton of the monomers is around 3.25 and of the N atoms is around 2.61 and 2.68 for the cis and trans isomers respectively. The dihedral angle between rings for trans monomers lay in the range of 9-15°, and between 18-20° for the cis.

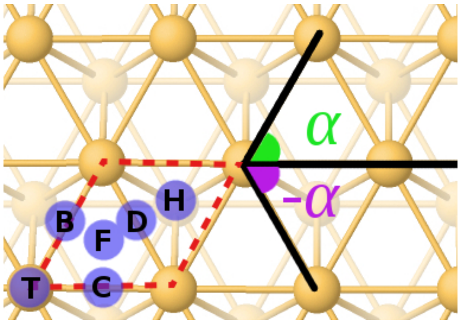


Figure S1 Docking sites on the Ag (111) surface. T label is used for top sites, B, C and D are used for the different bridge sites, and F and H are used for the fcc and hcp hollow sites, respectively. Red doted line indicates the primitive surface unit cell. The angle the backbone of the molecule makes with respect to one of the Ag-Ag surface symmetry directions (chosen as the horizontal axis in the picture) are considered positive if measured in the counterclockwise (green alpha) and negative if measured in the clockwise directions (purple alpha), respectively. Orange balls represent silver atoms

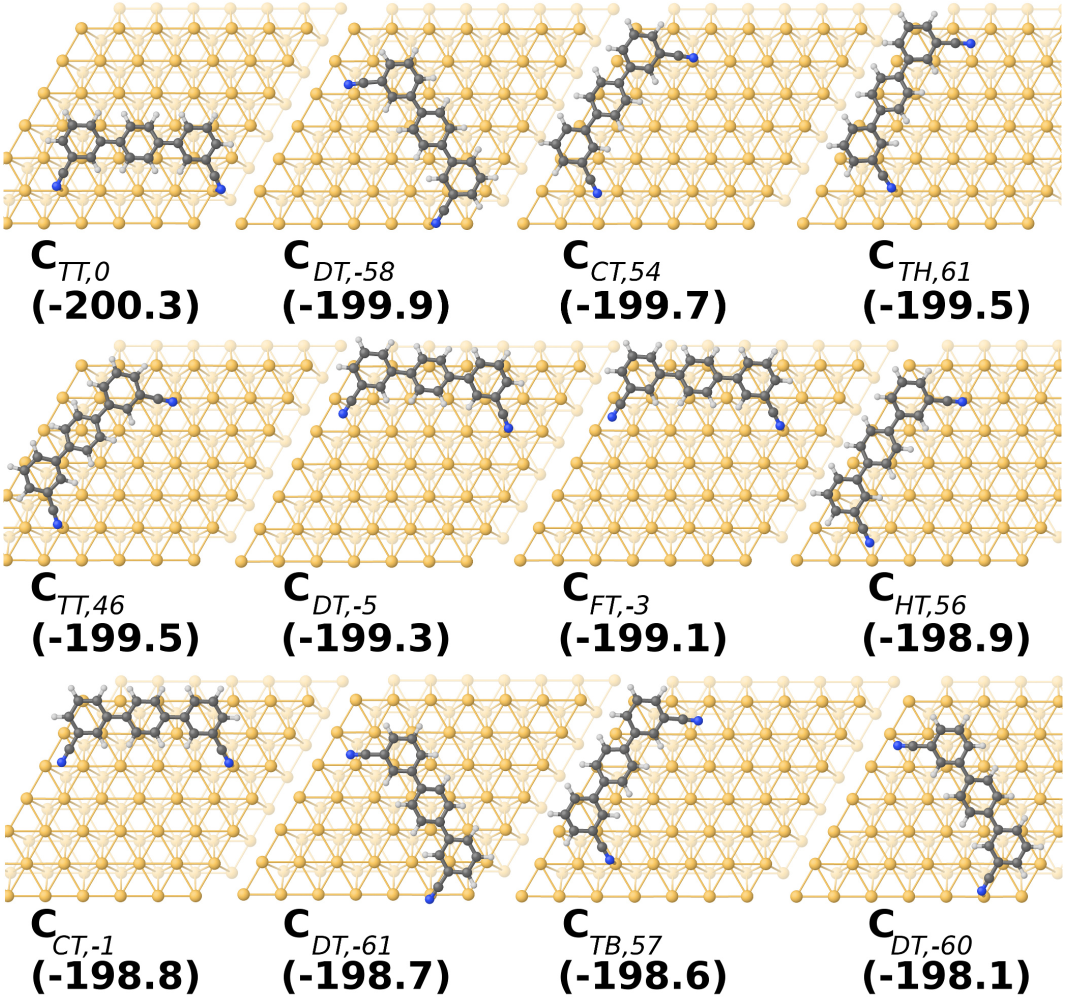


Figure S2 Twelve most stable cis conformers (C) on the surface found after the DFT geometry relaxation. The suggested nomenclature is meant to indicate the adsorption site and orientation of the molecule. The first subscript indicates the docking site of the left N atom, the second subscript indicates the docking site of the right N atom, and the number after the comma indicates the alpha angle (see Fig. S1). The corresponding binding energies (in kJ/mol) are also given underneath the symbol of the structure in round brackets. Orange, gray, white and blue balls correspond to Ag, C, H and N atoms, respectively.

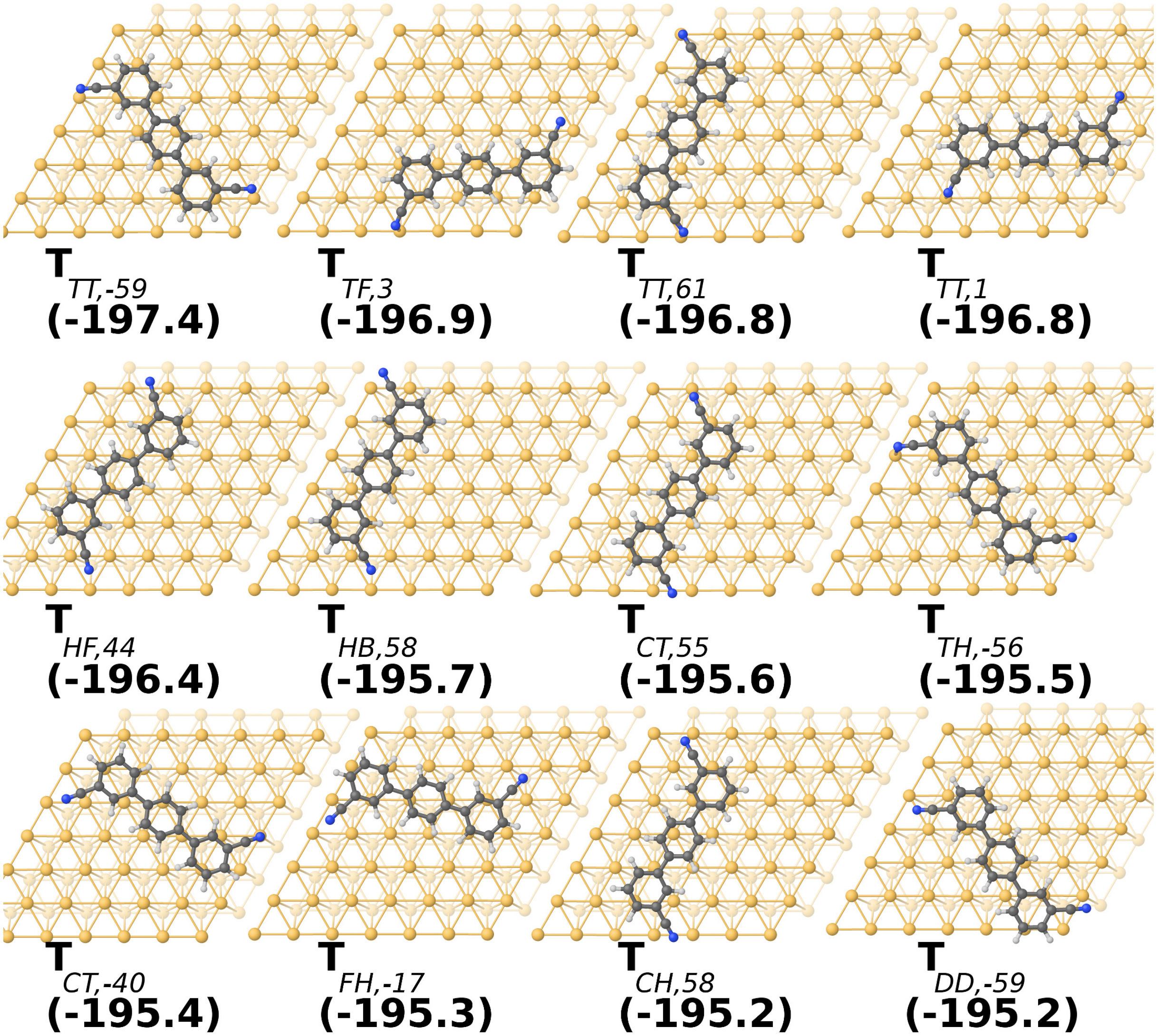


Figure S3 Twelve most stable trans conformers (T) on the surface found after the DFT geometry relaxation. The subscript of the nomenclature for each structure and the color code used are the same as in Fig. S2. When both N atoms align along a vertical line, then the first subscript reefers to the bottom atom. The corresponding binding energies (in kJ/mol) are also given. Only L isomers are shown for clarity; the corresponding D isomers with identical binding energies are obtained by appropriate flipping of the molecules (not shown).

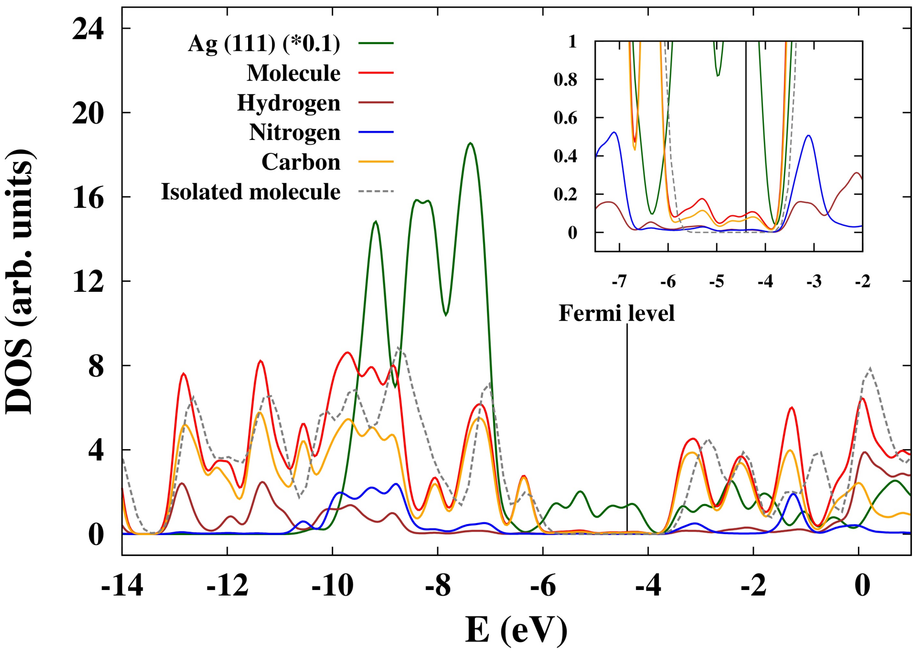


Figure S4 Comparison of PDOS for the cis structure $C_{TT,0}$ (solid lines) and the molecule in the gas phase (dashed line). The inset shows the region around the metal Fermi energy in more detail. Notice the negligible contribution of the monomer to the DOS in this region

A projected density of states (PDOS) of a cis molecule $C_{TT,0}$ (see Fig. 2 of the main text) placed on the surface is compared with the PDOS calculated for an isolated molecule. We see that the HOMO and LUMO levels of the molecule are clearly positioned on the left and right of the Fermi energy of the surface, with small variations with respect to the isolated molecule.

In Fig.S5 the DFT+NEB calculated diffusion path for a T monomer on the surface is shown exploiting two mechanisms: pivoting and sliding. The latter mechanism results in higher energy barrier similarly to the case of diffusion of a C monomer, Fig. 5 of the main text.

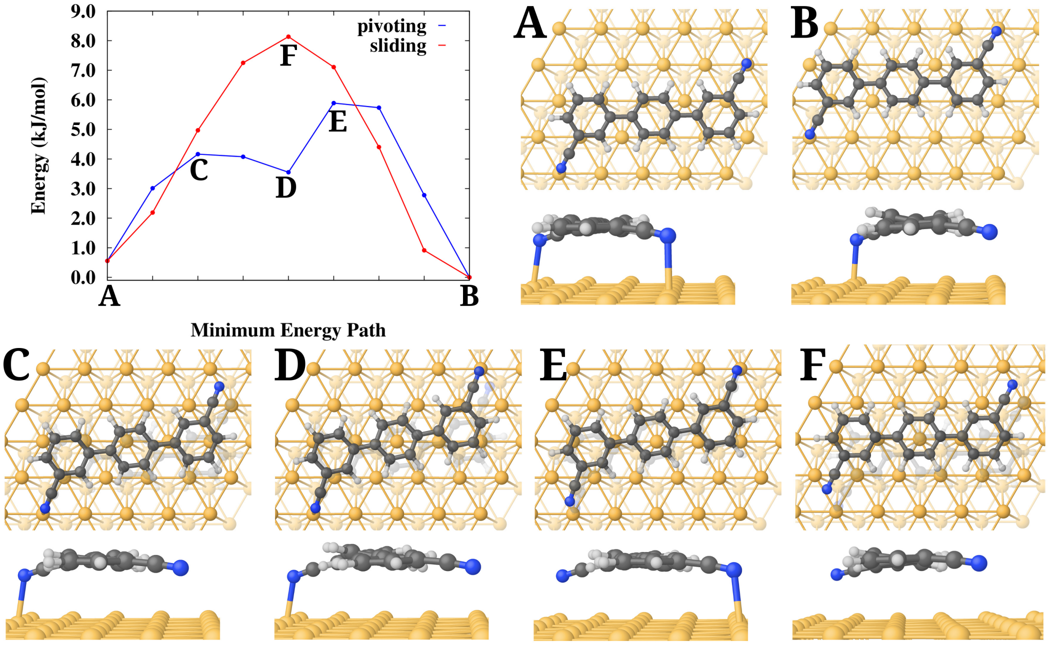


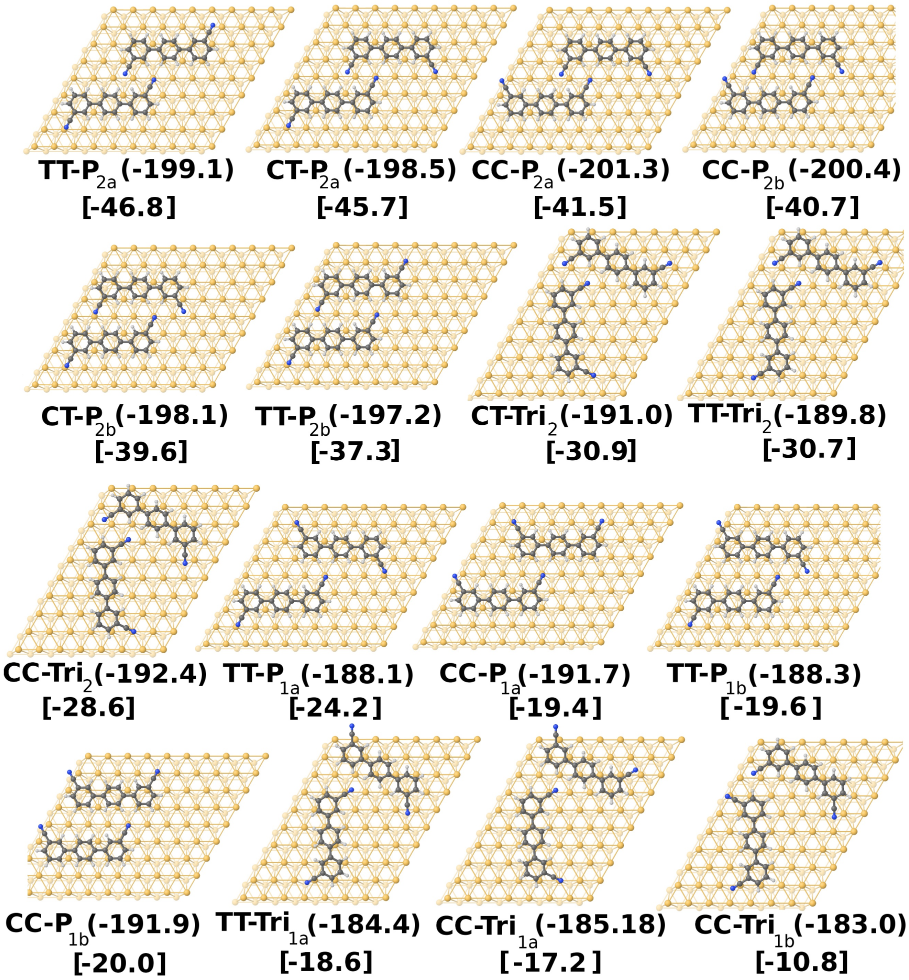
Figure S5 Diffusion paths for a T monomer on the Ag(111) surface. For the explanations, see the caption to Fig. 5 of the main text.

Dimers on the surface

A number of stable dimer structures, fully relaxed with our DFT method, together with their total binding energies per molecule and H bond binding energies (in round and square brackets, respectively) are shown in Fig. S6. The H bonding binding energies of dimers on the surface can be directly compared with those for the dimers in the gas phase reported previously.[?] The tendency in both cases is the same, but the H bond is up to 1.5 times stronger on the surface than in the gas phase. In fact, dimers with a single H bond and a totally planar geometry that are unstable in the gas phase, become stable on the surface with the central ring slightly rotated by the dihedral angle of around 12.5.

We also defined a (positive) *deformation energy* $\Delta E^{A}_{def} = E_A - E^0_A$ for any component (surface and/or molecule) of the whole system, where E_A is the energy of the component A in the complex. This energy shows the cost for the component A to be in the complex. Cis and trans monomers have a mean deformation energy of 6.4 and 12.9 kJ/mol, respectively, when they are bound to the surface, and this deformation energy increases to 13.0 and 14.0 kJ/mol when they form a dimer. On the other hand, the surface has a deformation energy of around 1.8 kJ/mol when a monomer is bound to it and increases to a mean value of 4.8 kJ/mol in the case of dimers. This suggests that it is easier for a trans conformer to form a dimer once it is deposited on the surface.

An example of the EDD is shown for the dimer CC-P_{2a} in Fig. S7. It is seen by comparing panels E and F of the same Figure that the contribution of the dispersion interaction between molecules increases when the dimer is placed on the surface. Similar analysis has been conducted for other dimers as well, and in all cases qualitatively similar EDD were observed for the dimers in the gas phase and on the surface. This observation confirms that binding between monomers in dimers on the surface can still be characterized in terms of the H-bonding with significant contribution coming from the dispersion interaction, as discussed above and in our previous study.[?] The H bond distances also follow the same tendency as in the gas phase; however, on the surface these distances become around 0.04 shorter for P geometries (with a distance around 2.44 for the bond where the carbonitrile groups and the H atoms lie along a line) and more than 0.10 shorter for Tri geometries, where the H bond is around 2.25 for the shortest non-linear H bond as in the CC-Tri_2 geometry. The mean distance of the molecule to the surface is 3.29 and 3.18 for the N atoms.



TT-P$_{2a}$(-199.1) [-46.8]
CT-P$_{2a}$(-198.5) [-45.7]
CC-P$_{2a}$(-201.3) [-41.5]
CC-P$_{2b}$(-200.4) [-40.7]

CT-P$_{2b}$(-198.1) [-39.6]
TT-P$_{2b}$(-197.2) [-37.3]
CT-Tri$_{2}$(-191.0) [-30.9]
TT-Tri$_{2}$(-189.8) [-30.7]

CC-Tri$_{2}$(-192.4) [-28.6]
TT-P$_{1a}$(-188.1) [-24.2]
CC-P$_{1a}$(-191.7) [-19.4]
TT-P$_{1b}$(-188.3) [-19.6]

CC-P$_{1b}$(-191.9) [-20.0]
TT-Tri$_{1a}$(-184.4) [-18.6]
CC-Tri$_{1a}$(-185.18) [-17.2]
CC-Tri$_{1b}$(-183.0) [-10.8]

Figure S6 A more extense selection of dimers. The legend used to denote the dimers means: the first two characters are composed of either C or T corresponding to the cis or trans conformations of the constituent monomers; the next letters are either P or Tri referring to either parallel or triangular forms, respectively; the index 1 or 2 that follows corresponds to the number of hydrogen bonds in the dimer; finally, a subscript *a* or *b* is used to differentiate between similar parallel and triangular structures.

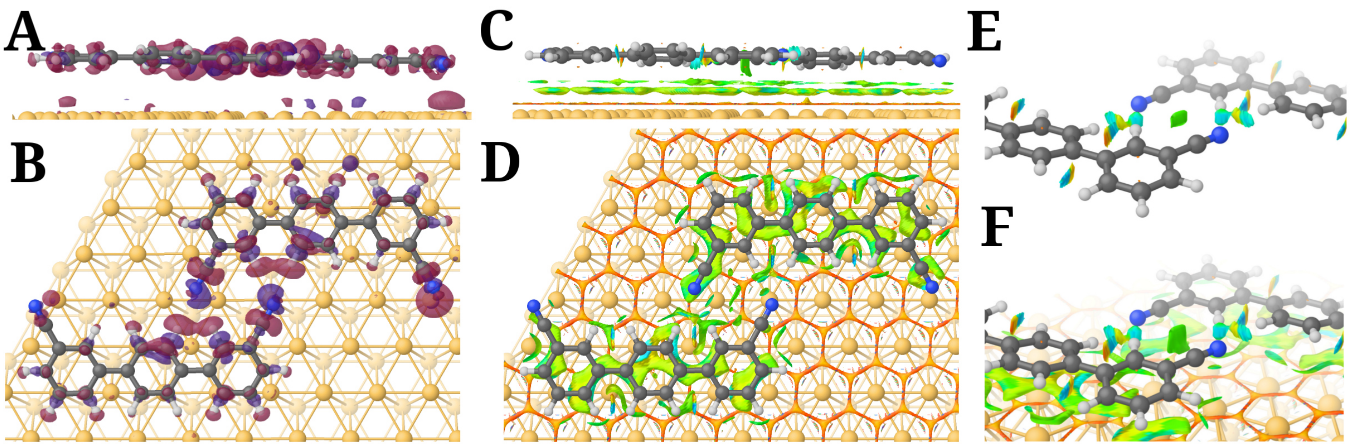


Figure S7 Electron density plots of the dimer CC-P$_{2a}$ on the surface shown either via EDD (side (A) and top (B) views) or NCI (side (C) and top (D) views). NCI shows the H bonds and attractive dispersion interaction between the carbonitrile groups in a dimer without (E) and with (F) the surface. Note the bigger green area in (F) related with the dispersion interactions between carbonitrile groups. The same color scheme as in Fig. 3 of the main text is used.

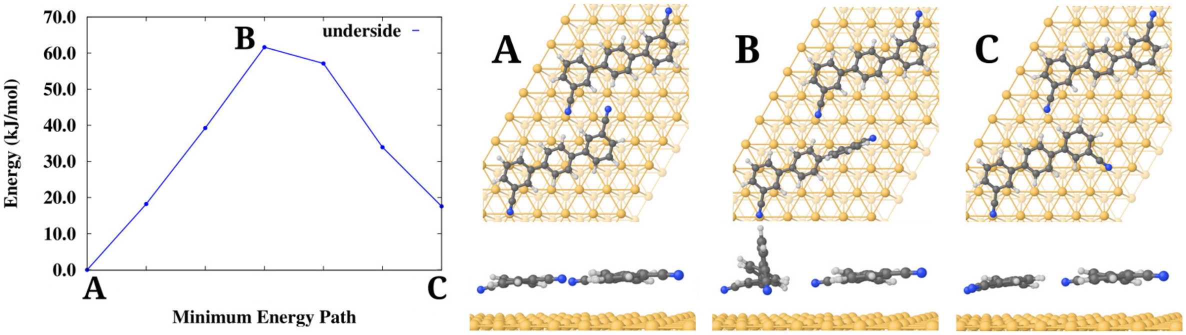
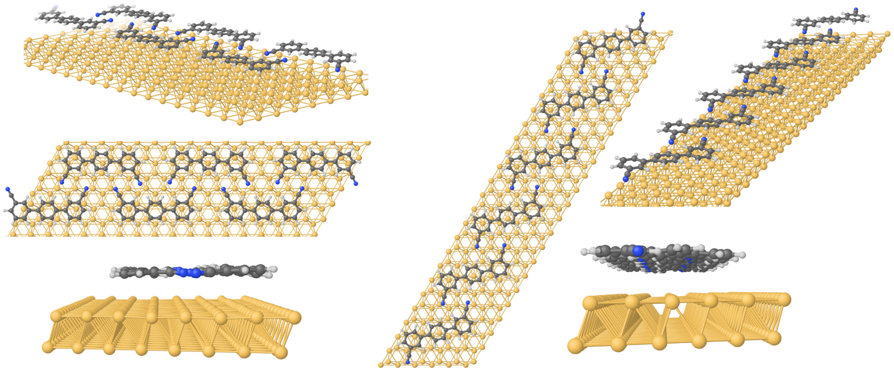


Figure S8 The MEP (the left panel) and the initial (A), final (C) and transition state (B) geometries for the NEB+DFT relaxed under-side isomerization transition between T-T and a T-C dimers.

The isomerization reaction between T-T and T-C dimers is shown in Fig. S8. Only the under-side mechanism was studied as it is bound to be more favourable as follows from other calculations discussed in the main text.

Ribbons and linkers on the surface

More views of the two studied ribbon structures are given in Fig. S9. The mean distance of the N atoms to the surface in the ribbons is between 3.2 and 3.3 due that the carbonitrile group being not bent towards the surface when engaged in the H bond. The dihedral angle is about 10° which is very close to the value in the gas phase.

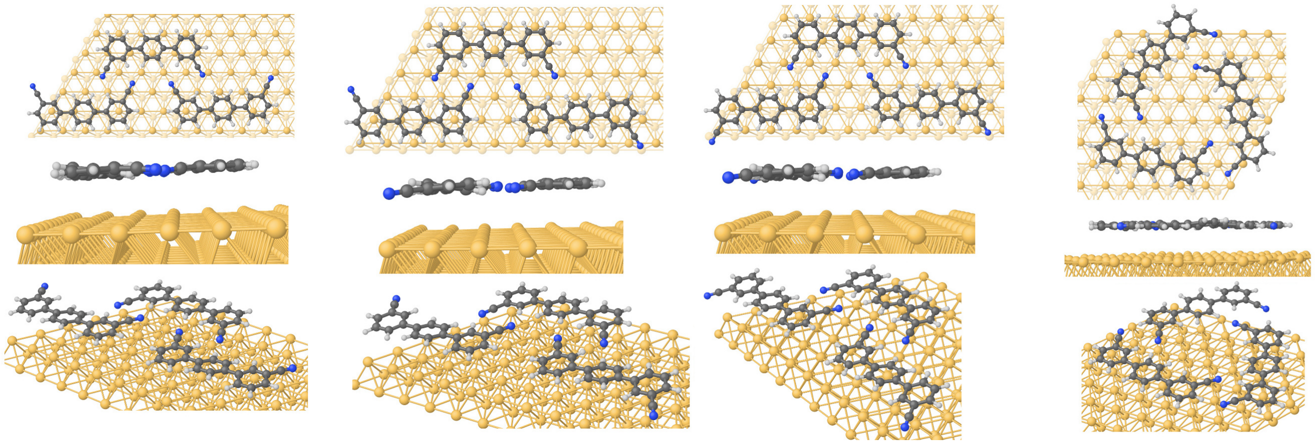


CC$_A$ (-214.8) **TT$_A$ (-212.9)**

Figure S9 Relaxed geometries and corresponding binding energies (per molecule, in brackets and in kJ/mol) of the CC$_A$ and TT$_A$ ribbons on the silver surface (perspective, top and side views).

More studied linker structures are shown in Fig. S10. The molecules in the linker structures are at 3.29 above the surface and the carbonitrile groups, involved or not in the H bonds, become parallel to the surface.

We showed previously that in the gas phase the linear H bond is stronger than the non linear one.[?] The same happens on the surface as we can see comparing the H bond binding energies of the P and Tri dimers, Fig. S6. This explains why the CCC-Tri linker, which has 3 linear and 3 non linear H bonds, is more stable than the other linkers with 4 linear H bonds.



CCC-Lin (-201.1) **CCT-Lin (-201.5)** **TCT'-Lin (-202.5)** **CCC-Tri (-222.9)**

Figure S10 Relaxed geometries and corresponding binding energies (per molecule, in brackets, in kJ/mol) of several linker clusters on the silver surface (top, side and perspective views).

Molecules in brickwall islands

The MEP and the relaxed geometries of the initial, final and transition states (both top and side views) of the isomerization reaction of a monomer in the T island is shown in Fig. S11.

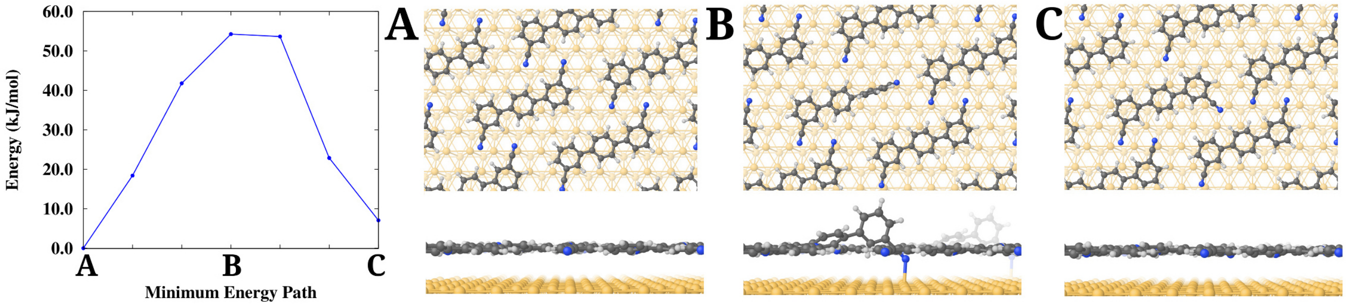


Figure S11 MEP (left panel) of the cis-trans isomerization of a monomer inside a monolayer with the corresponding initial (A), transition (B), and final state (C) relaxed geometries (top and side views) obtained with the NEB+DFT method.

A typical STM image of a brickwall T monolayer from? is shown in Fig. S12. The superimposed molecular images correspond to the structure proposed in? and consisting only of the T isomers. However, bright white areas on the other sides of the corresponding benzonitrile groups (some of these areas are circled) indicate that a portion of the time during the scan of these regions the group was directed the other way round. An animation of this effect can be seen in the movie Isomerization_In_Island.mp4 provided.

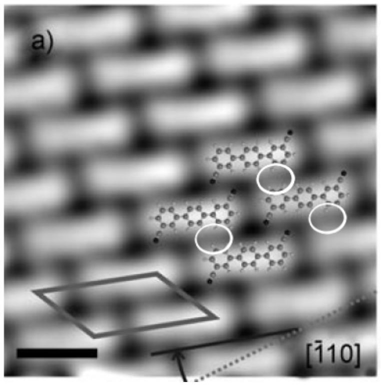


Figure S12 High resolution STM image (adapted with permision from Ref. **?**) of a pTmDC island on the silver surface at room temperature. White circles indicate additional bright areas between chains.

KMC simulations

In Figs. S13-S15 snapshots of KMC simulaitons for several coverages are displayed. We also provide several movies of the KMC runs in which every 500000-th move has been displayed.

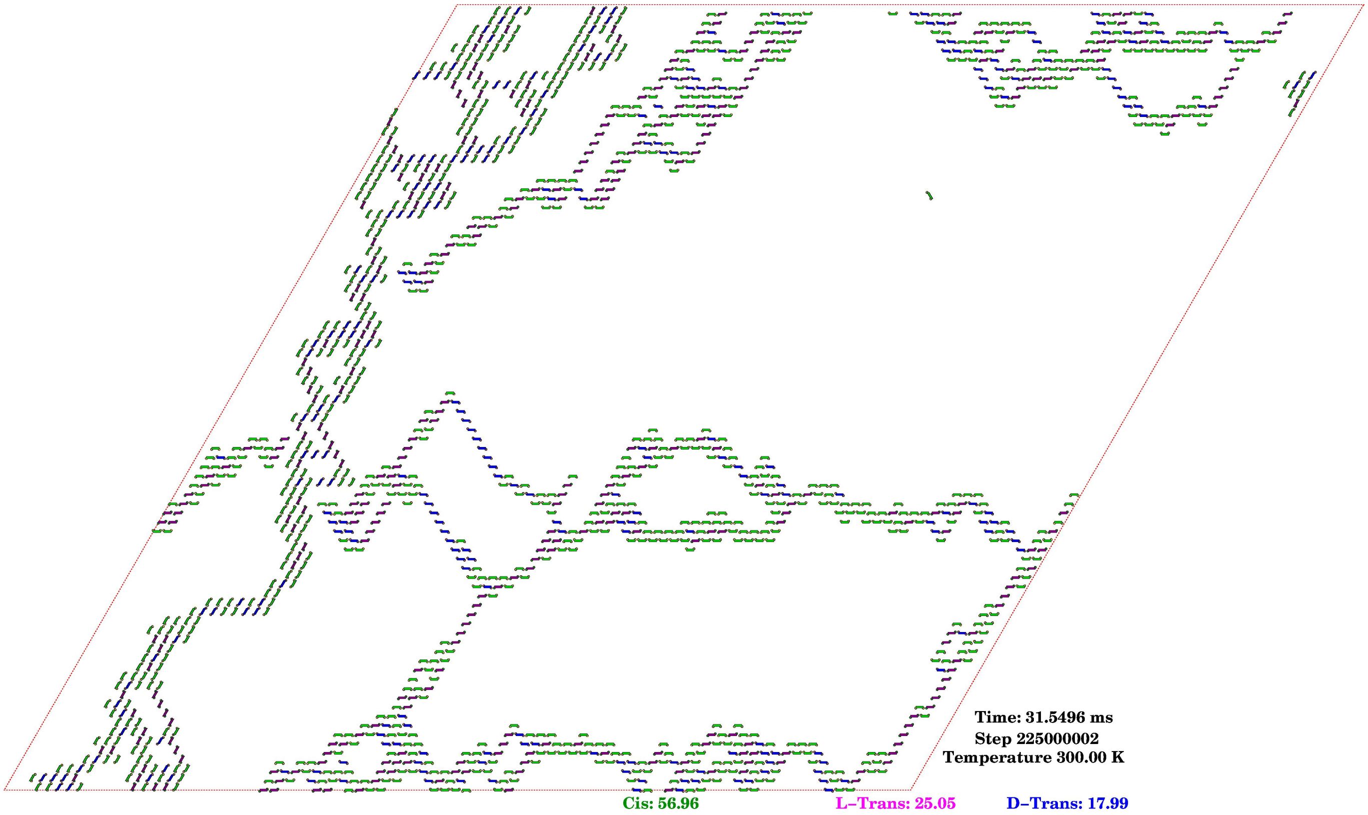


Figure S13 Snapshot of a KMC simulation at 300 K with the coverage of 20% in a 85x85 cell, and a deposition rate of 10^{-7}ps^{-1}. Green, purple and blue rectangles are cis, L-trans and D-trans monomers, respectively. Their proportions are given with the same color code at the bottom in the image. The KMC step number and the simulation time corresponding to the snapshot are also indicated.

Besides the snapshots, a number of movies of the KMC simulations at different temperatures and coverages are also provided (see Table S1 for details).

Movie number	Cell size	T (K)	Deposition rate (ps^{-1})	Coverage (%)
01	85	200	10^{-7}	20
02	85	175	10^{-7}	20
03	85	300	10^{-7}	20
04	85	300	10^{-7}	20
05	50	300	10^{-7}	50
06	50	300	10^{-7}	80

Table S1 Parameters of the different movies.

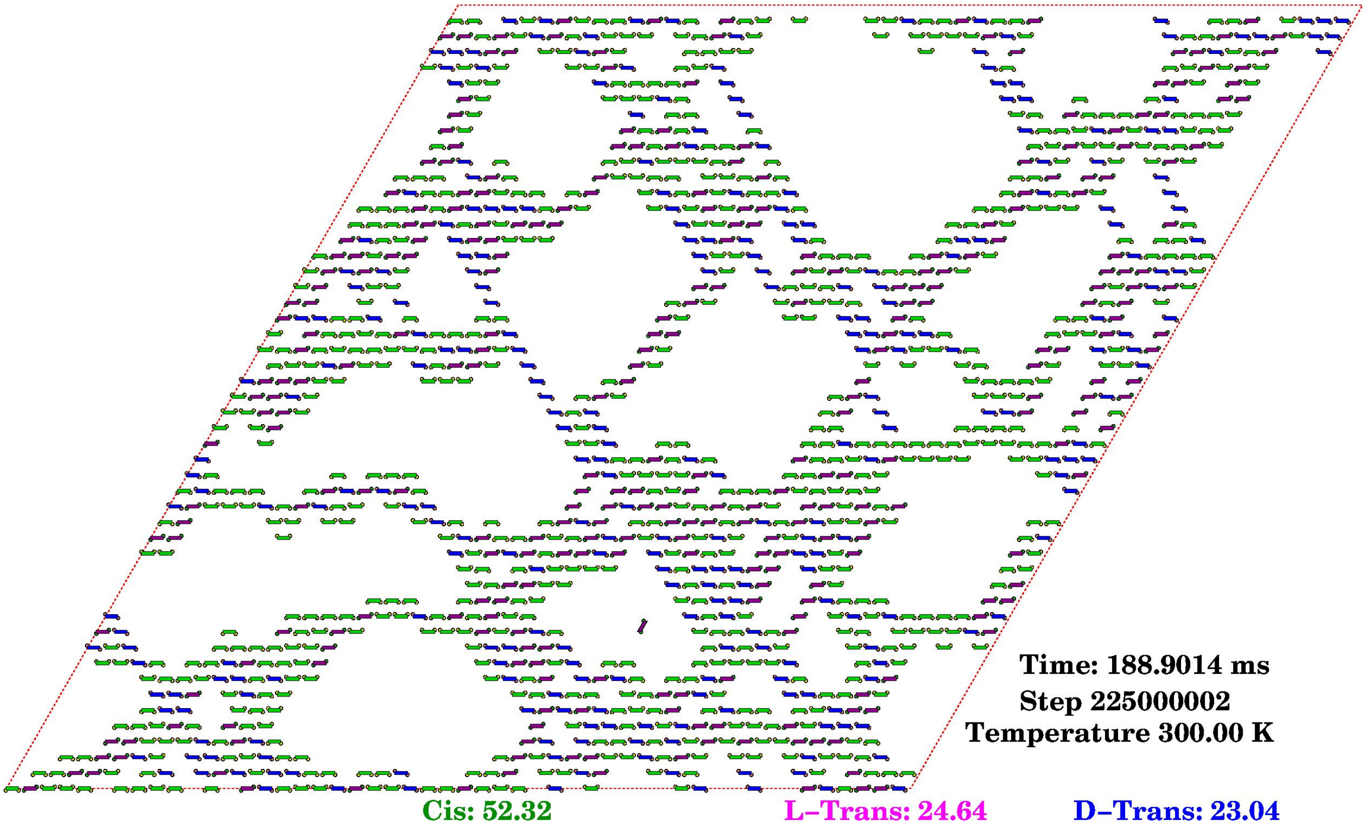


Figure S14 A snapshot of a KMC run corresponding to the 50x50 simulation cell for 300K, the coverage of 50% and deposition rate of 10^{-7}ps^{-1}. The same color code as in Fig. S13 is used.

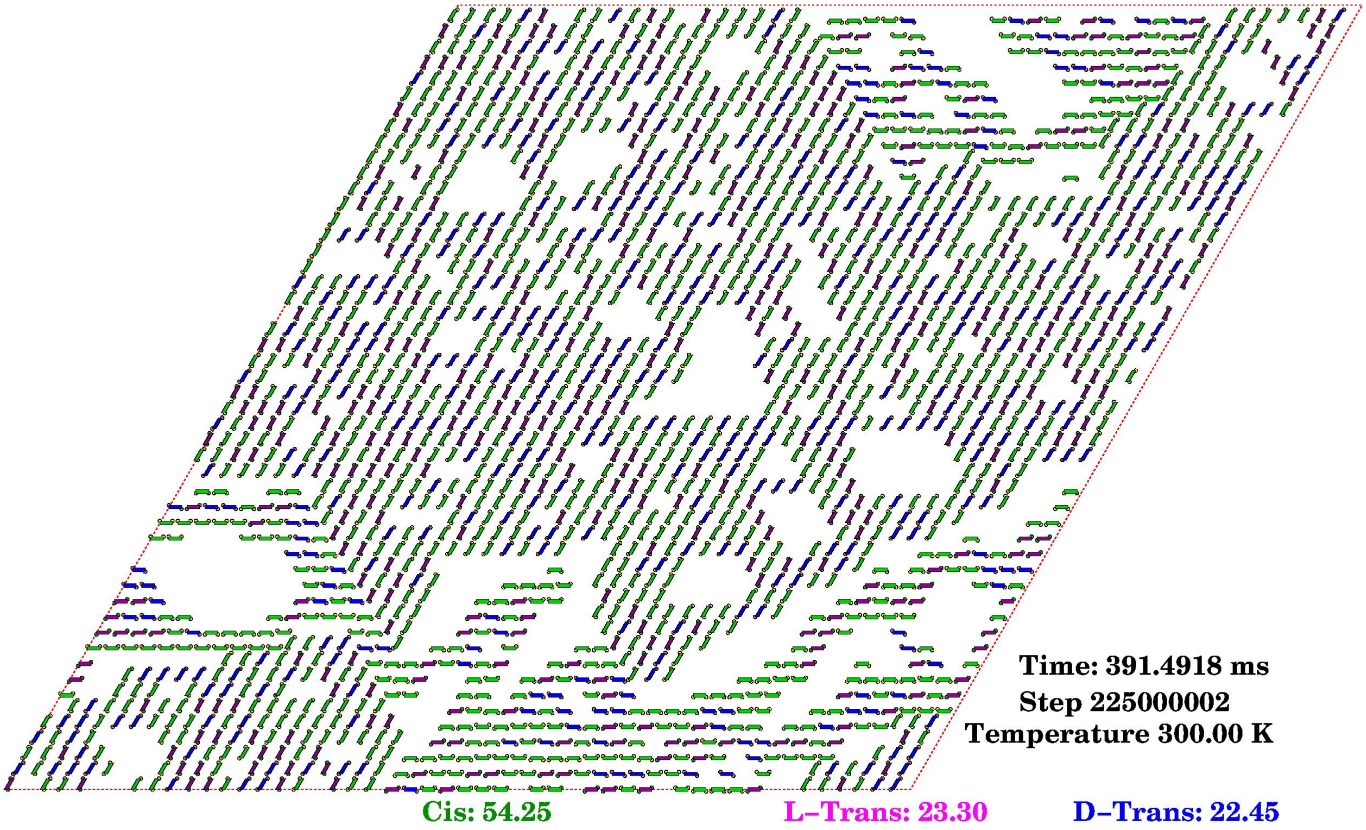


Figure S15 A snapshot of a KMC run corresponding to the 50x50 simulation cell for 300K, the coverage of 80% and deposition rate of 10^{-7}ps^{-1}. The same color code as in Fig. S13 is used.