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Supporting information

Title: 2D supramolecular network of dibenzonitrilediacetylene on Ag(111) designed by intermolecular hydrogen bonding

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1. Sub-monolayer coverage of DBDA on Ag(111)

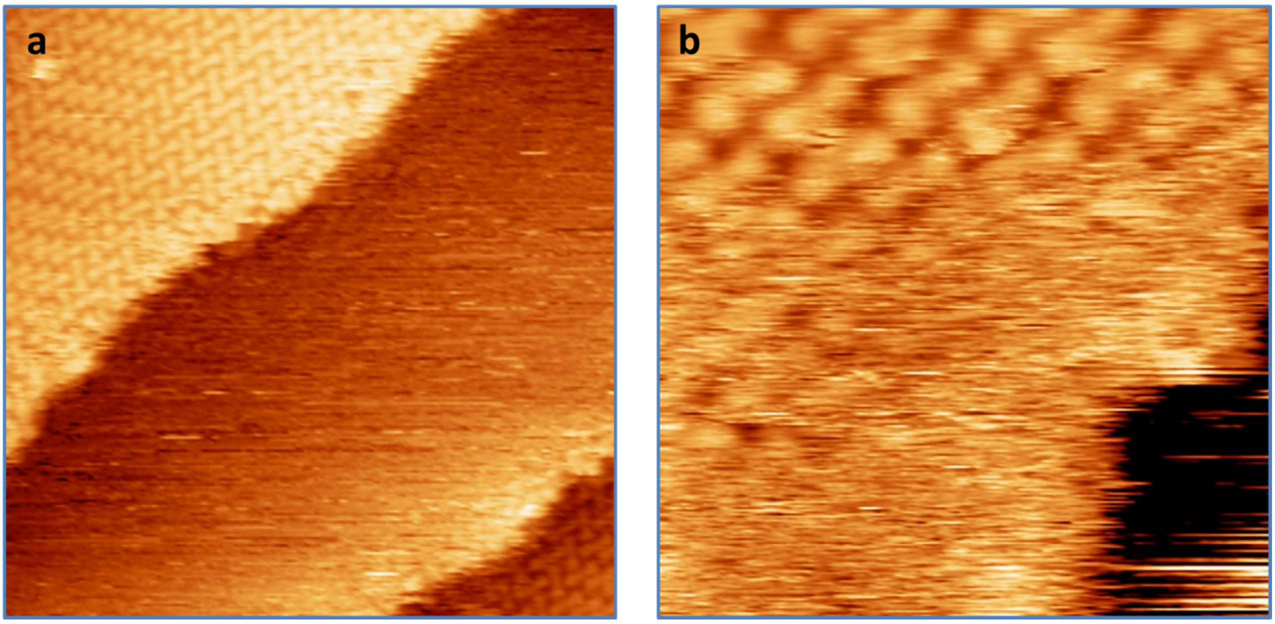


Figure S 1. 25×25 nm^2 (a) and 9×9 nm^2 (b) STM images of a sub-monolayer of DBDA on Ag(111). Molecules start to aggregate and form domains, whose borders are not defined (b), showing that the molecules have an appreciable mobility on the surface, until a complete ML is formed.

2. Intermixed phase domains

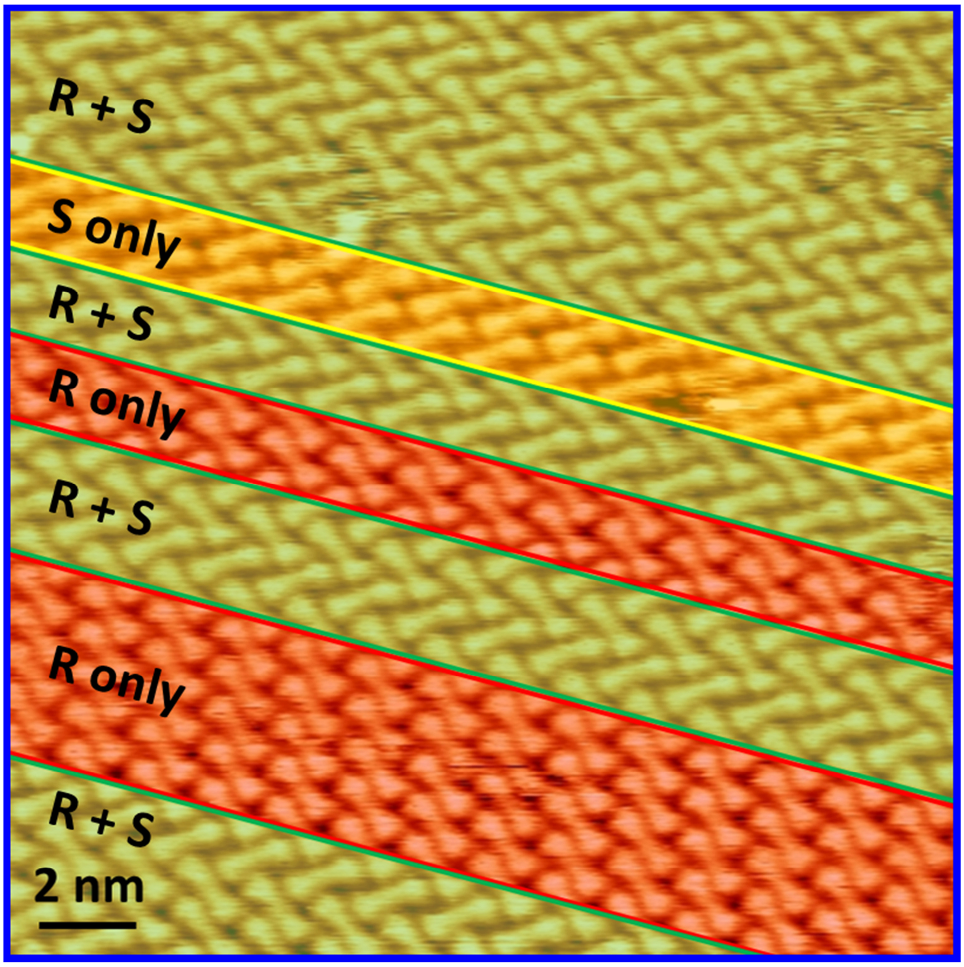


Figure S 2. 20×20 nm^2 STM image of DBDA deposited on Ag(111) at RT, with superimposed colored-mapping indicating the enantiomeric molecular domains: red for *R*-only (parallel phase), yellow for *S*-only (parallel phase) and green for mixed *R* and *S* enantiomers (chevron phase).

3. Isomer recognition by STM

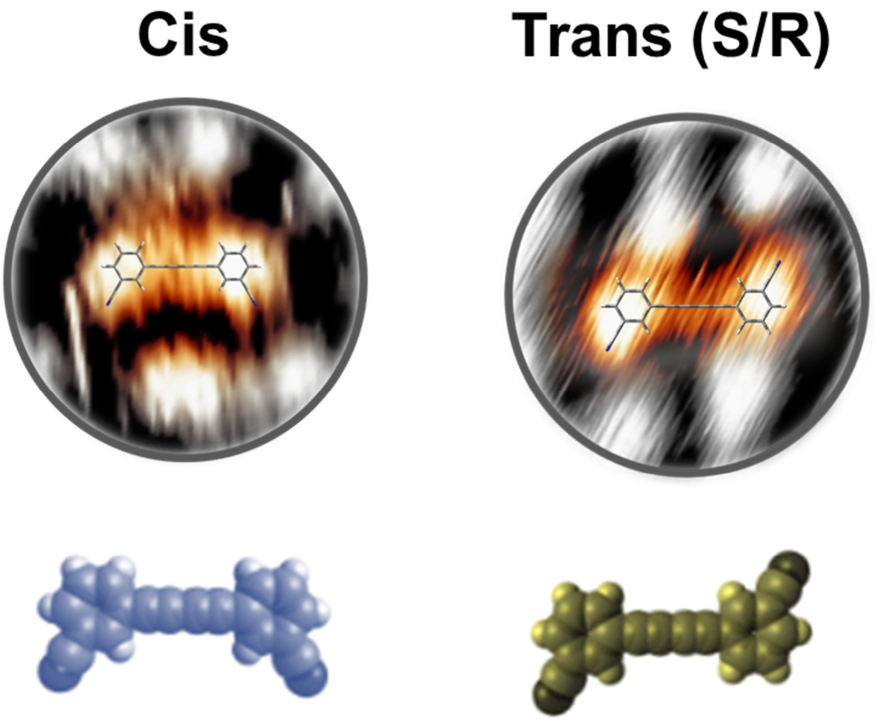


Figure S 3. STM images of DBDA on Ag(111). While *cis* and *trans* isomers appear differently in the STM images, the resolution was not sufficient to distinguish between the *R* and *S* enantiomers.

4. Additional DFT calculations

4.1 Some details on the dimensions of the large supercells used for simulation

In the small (primitive) unit cell (Figure 2, Manuscript), only the molecules (imaged as bright features in STM) and not the surface atoms are included. For the simulation, in order to self-calibrate the dimensions of the cell with respect to surface atoms, the epitaxy of the adsorbed molecules was taken into account. This procedure required choosing a larger supercell with different dimensions and orientation than the small unit cell.

The molecular density remained unchanged in the larger supercell (Figure 2, Manuscript), and different combinations of three isomers (*cis*, *R-trans*, *S-trans*) in the supramolecular networks were calculated. Therefore, the large supercells consisting of the molecules with respect to the direction of surface atoms were first measured based on the experimental data for the three observed (chevron, parallel, and butterfly) phases. Following the common procedure of calibrating STM images, the dimensions of these supercells, measured based on the Ag-Ag bond length of 2.93 Å, gave ± 2.5% error. We set the dimensions of the supercell for simulation according to our calibration of the silver lattice constant using Ag-Ag 2.9247 Å (**See Section 4.5, SI**), which, therefore, bears 0.17% error with respect to the mentioned calibrated experimental data. Although most of the calculations on SAMNs in this study were performed in the gas phase, the mentioned self-calibration allows to carry the effect of the surface on the supramolecular arrangement which would have been otherwise neglected in the simulations.

4.2 Chevron phase structures

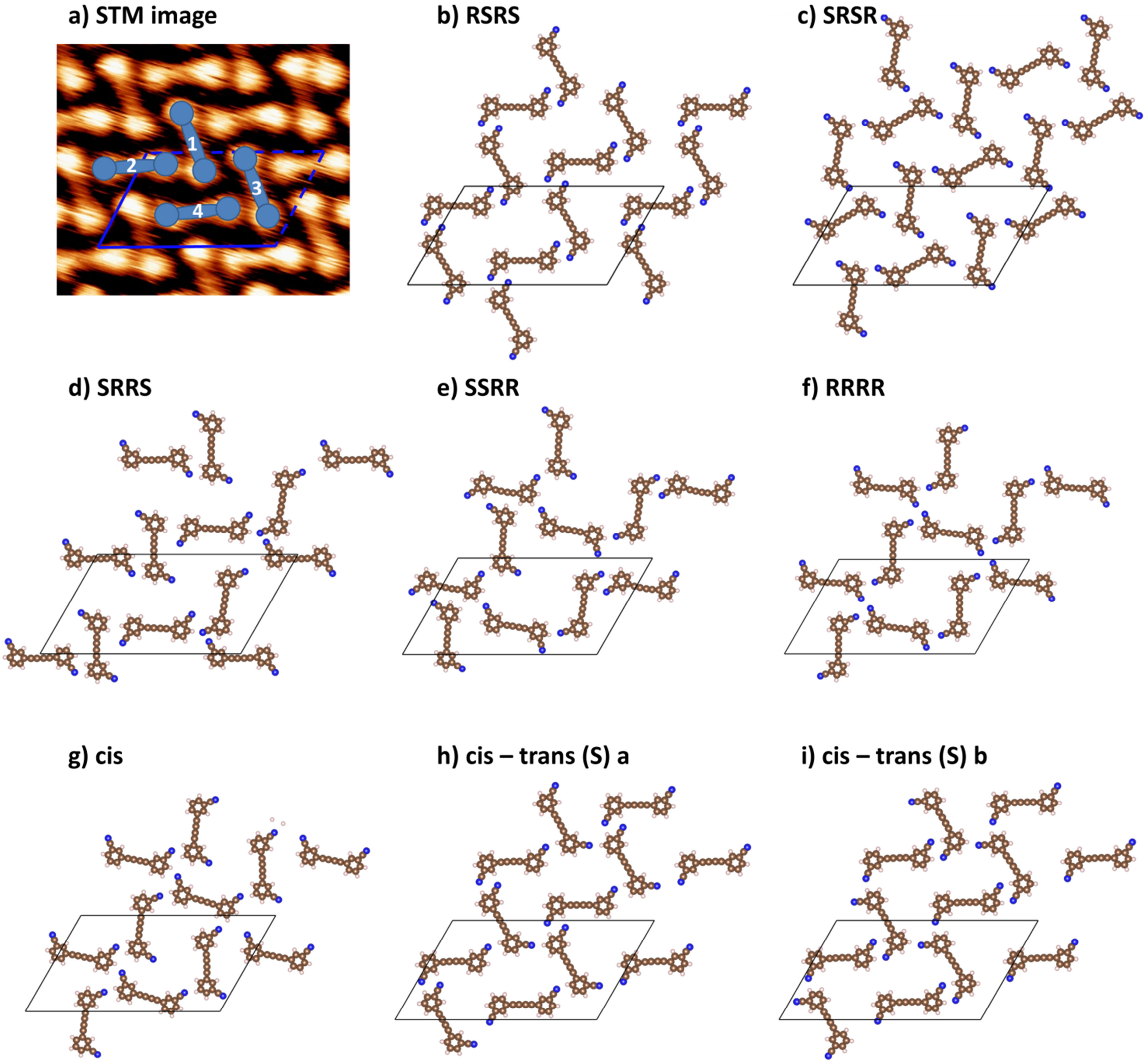


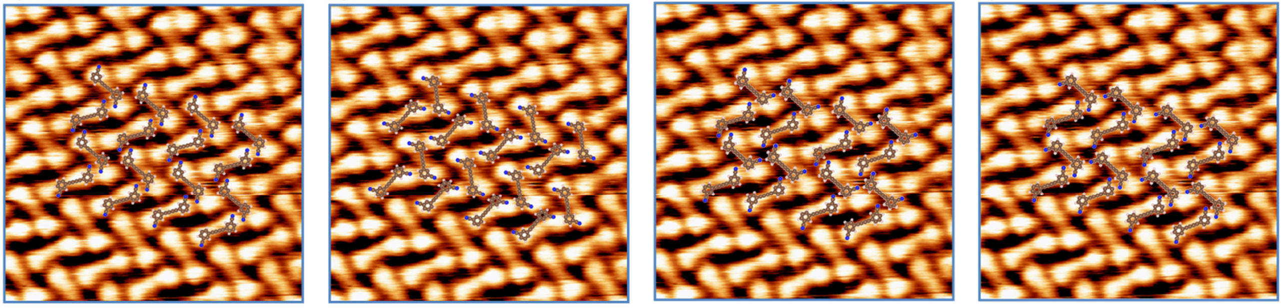
Figure S 4. a) STM image of the chevron phase, with the super cells used for the DFT calculation and the stylized ball-and-stick molecules corresponding to the molecular positions; b-i) structures obteined by DFT starting from different compositions of *cis*, *R* and *S* isomers. The closest structures to STM images are b) and c) which are presented in Figure 3, Manuscript.

4.3 Comparison between different DFT methods

Table S1: Comparison between DFT calculated energy for the simulated chevron, parallel and butterfly phases - combinational conformations consisting of *cis*, *R-trans*, and *S-trans* DBDA. The most stable configuration for each structure is reported in bold. Results from three different DFT methods are reported here. See Section 2, Materials and methods, Manuscript for the descripttion of the methods.

Simulated Phases	**Structure**	**dE_{total} (eV) DFT [per molecule]**	**dE_{total} (eV) DFT-D2 [per molecule]**	**dE_{total} (eV) DFT-D3 [per molecule]**
Chevron phase	***trans-RSRS***	**-0.8119 [-0.2030]**	**-1.1561[-0.2890]**	**-1.1572[-0.2893]**
	trans-SRSR	-0.7456 [-0.1864]	-0.9154[-0.2289]	-0.9208[-0.2302]
	trans-SSRR	-0.2495 [-0.0624]	-0.8616[-0.2154]	-0.8745[-0.2186]
	trans-RRRR	-0.0441 [-0.0110]	-0.2363[-0.0591]	-0.2597[-0.0649]
	trans-SRRS	-0.2427 [-0.0607]	-0.4691[-0.1173]	-0.5068[-0.1267]
	cis	-0.6191 [-0.1548]	-0.8659[-0.2165]	-0.8718[-0.2180]
	cis-trans(S) a	-0.7401 [-0.1850]	-0.9206[-0.2302]	-0.9281[-0.2320]
	cis-trans(S) b	-0.6403 [-0.1601]	-1.0179[-0.2545]	-1.0259[-0.2565]
Parallel phase	***trans-RRRR***	**-0.7829 [-0.1957]**	**-1.0574[-0.2644]**	**-1.0880[-0.2720]**
	cis	-0.5841 [-0.1460]	-0.7512[-0.1878]	-0.7924[-0.1981]
Butterfly phase	***cis***	**-0.1589 [-0.0794]**	**-0.2065[-0.1033]**	**-0.2150[-0.1075]**
	trans	-0.0984 [-0.0492]	-0.1630[-0.0815]	-0.1757[-0.0879]

4.4 STM *vs* DFT structures

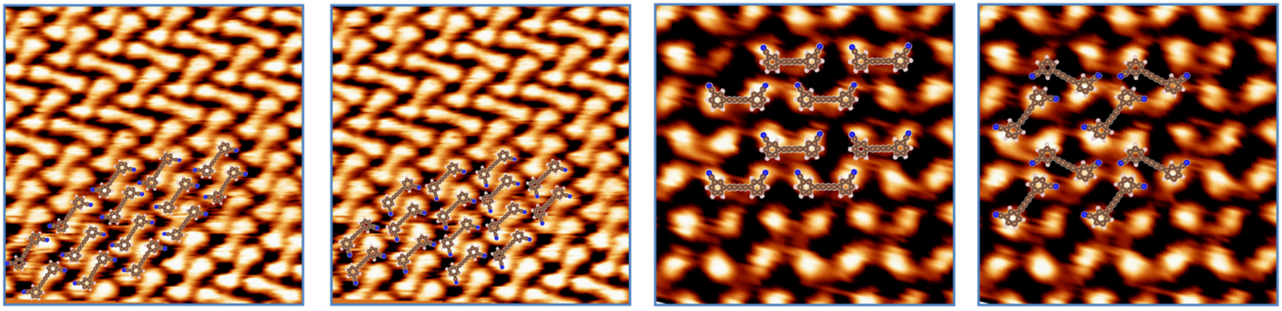


a) Chevron – RSRS

b) Chevron – SRSR

c) Chevron – cis-trans (S) a

d) Chevron – cis-trans (S) b



e) Parallel – RRRR

f) Parallel – cis

g) Butterfly – Cis

h) Butterfly – RS

Figure S 5. The most energetically stable structures and/or the structures which fit the STM images, overlaid on their respective STM image for each phase. For the chevron phase, the four most energetically stable structures are shown (a-d), while two structures are displayed for parallel (e, f) and butterfly (g, h) phases.

The DFT energies reported in Table S1 are based on gas phase simulations (approximated at 0 K). The energy available at room temperature could however determine the molecular arrangement observed in the STM images, favoring a configuration which is less energetically stable. Due to the large size of the supercells, surface atoms were not included in the simulations, which could have otherwise determined a better fit of the molecular structures with the experimentally observed images. In Figure S 5, the STM images are superimposed by the DFT calculated structures (based on their cohesive energy and/or a better fit to the imaged features), to propose molecular structures for each phase. For parallel (e) and butterfly (g) phases, the most energetically stable structures also provide a better match to the STM images. For the chevron phase, the *trans*-only phases indicate a better fit (a, b) to the STM images, in contrast to the mixed *cis*-*trans* isomers (c, d). From the two *trans*-only molecular structures, the best overall match is observed for *SRSR*, which is 60 meV less stable than *RSRS*. Since the type of *trans* enantiomer (*R* or *S*) cannot be determined experimentally, the simulation data indicates that the chevron phase is formed by a mixture of *R* and *S* enantiomers (*RSRS* or *SRSR*), while parallel and butterfly are made of one isomer only, *R* (or *S*) and *cis*, respectively.

4.5 H-bonding distances for the three phases

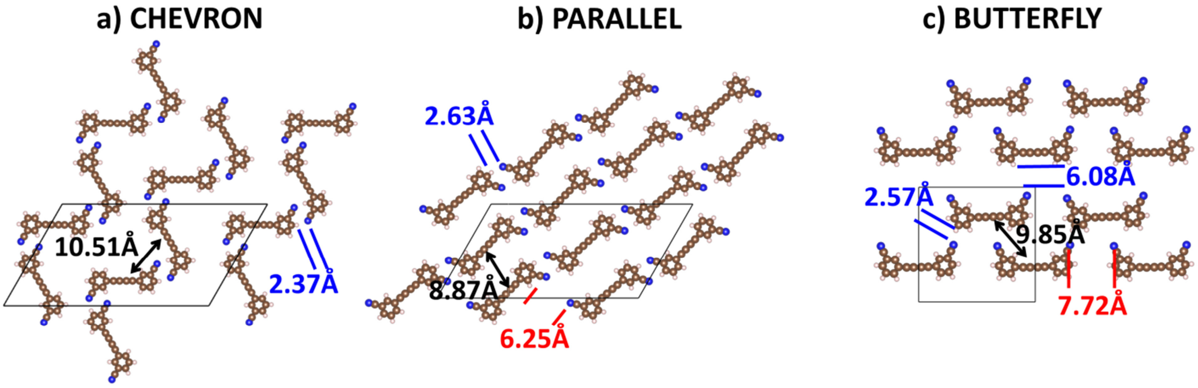


Figure S 6. The most energetically stable DFT-calculated structures for each phase. Some distances are displayed for attractive hydrogen bonding (in blue), repulsive N···N (in red) and for acetylene-acetylene (in black) interaction. It can be seen that the acetylene groups are far apart in all the structures, therefore, hindering the possibility of topochemical polymerization. Also, in all the phases the CN···H-Ph interaction seems to be the driving force of the molecular arrangements of SAMNs.

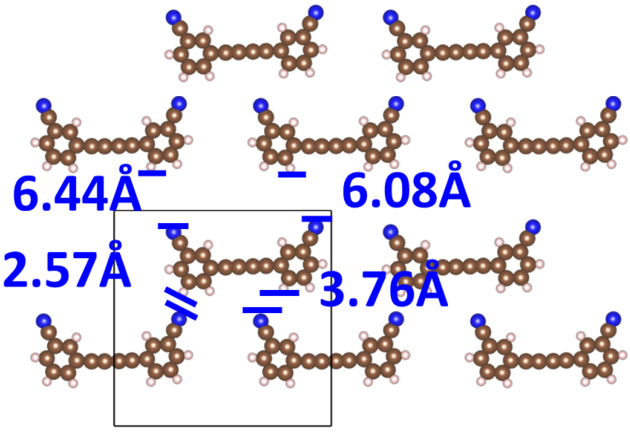


Figure S 7. Different CN···H-Ph hydrogen bonding distances for the butterfly phase.

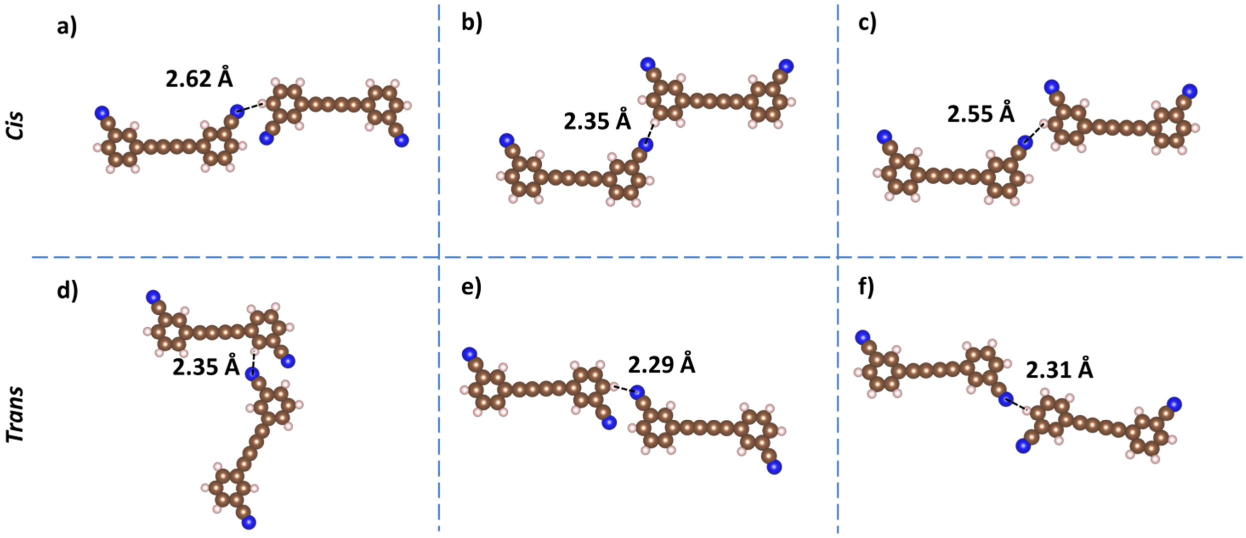


Figure S 8. Different orientations for forming two hydrogen bonds between two molecules (*trans*···*trans* and *cis*···*cis*) were calculated by DFT. For the *trans* isomer, *RS* (d) and *RR* (e) pairs were calculated, giving the 2.35 Å and 2.29 Å bond lengths. Three different cases for having only one hydrogen bonding were also calculated as a reference (b, c, f). Depending on the geometry, the *cis*···*cis* pair (a, b, c) gives a longer bond length distance range (2.35-2.62 Å) than the *trans* isomers (d, e, f).

4.6 DBDA adsorbed on Ag(111) surface

DFT simulation for the adsorption of a single DBDA molecule on a Ag(111) surface was performed. The lattice constant of Ag was found to be 4.1362 Å corresponding to 11×11×1 k-point. A 5-layer 7×4 supercell containing 140-Ag atoms was used for this calculation, while the bottom two layers were kept frozen, and the remaining atoms were relaxed. The method and accuracy level are the same as the other calculations data in the manuscript. The orientation of the molecule with respect to the surface was obtained from STM images, while for the adsorption position of each isomer, three different structures based on the position of nitrile over top, hollow and bridge surface adsorption sites were optimized. Figure S8 presents the most stable geometry, whose adsorption energy was calculated to be within 0.04 eV greater than that of other configurations. This data shows that for both isomers, the nitrile group slightly approaches the surface, while the diacetylene, owing to its *sp*-orbitals, prevents the molecular backbone from tilting. The average adsorption height of a molecule having one central phenyl ring derived with three acetyl groups was found to be 3.12 Å to 2.93 Å (the most stable configuration).[1] Our calculation yields an adsorption height of 3.4 Å of the diacetylene backbone to the surface, while the nitrile groups (adsorption height 2.9-3.1 Å) located ~ 0.3-0.5 Å closer to the surface than diacetylene.

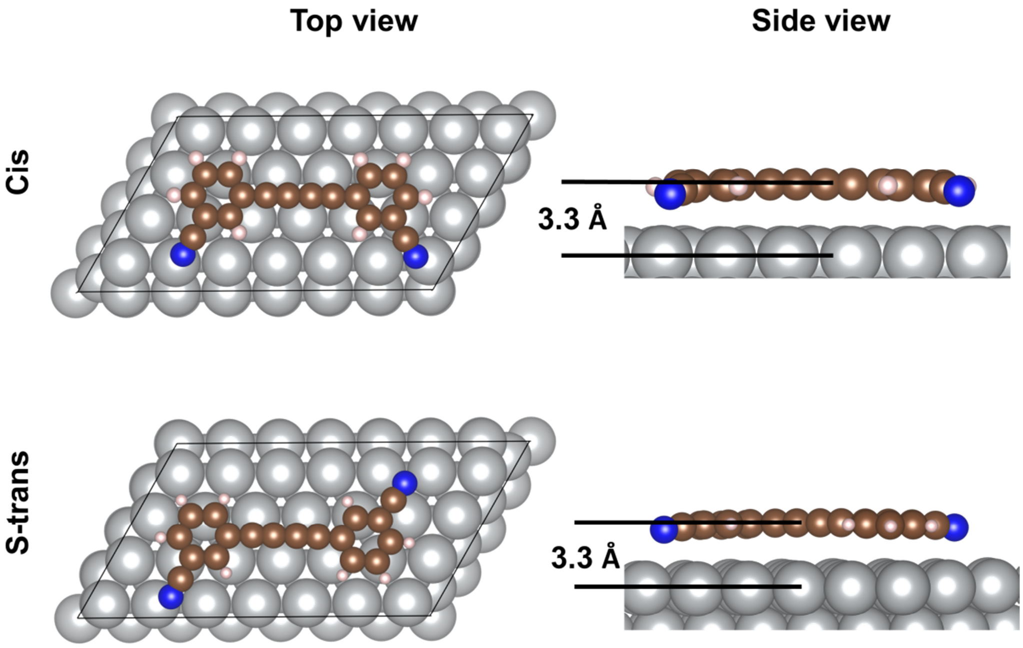


Figure S 9. Top and side views of DFT calculated structures for *cis* and *S-trans* isomers on Ag(111). The molecules remain nearly planar on the surface. The adsorption energy is dE= -1.857 eV (this value is for the most stable geometry, among three calculated structures based on the position of nitrile over top, hollow and bridge surface adsorption sites), for both isomers. The average distance of the molecule's carbon atoms to the surafce atoms is 3.3 Å for both isomers. Nitrile groups are located ~0.3-0.5 Å closer to the surafce than their respective diacetylene backbones.

5. Two chosen isomeric combinations fit to *Butterfly* phase

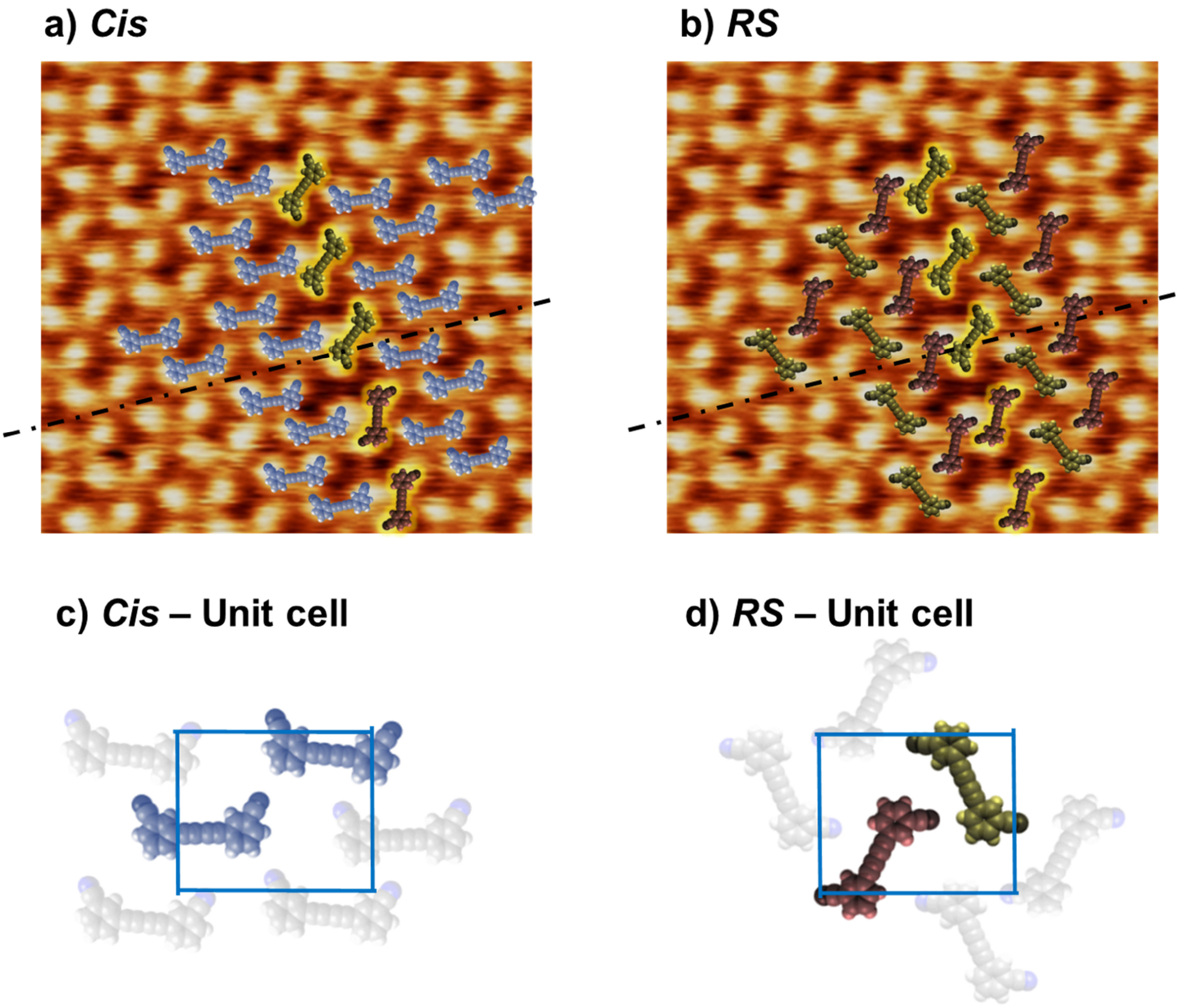


Figure S 10. STM image of *butterfly* phase of DBDA on Ag(111) at RT. A stacking fault (molecules with the golden shade) can be seen in the self-assembly, and both of the proposed molecular structures could be overlayered well with the STM images (a, b). Therefore, DFT calculation was performed on both proposed structures (c, d). Each enantiomer is represented by a different color scheme: blue, red and green for *cis*, *R* and *S*, respectively. Because it was not possible to distinguish between *R* and *S* with STM only, a and b were divided in two areas by the black dotted line. The above and below regions were superimposed with *S* and *R*, respectively, which both fit with the STM images. This allowed to check the boundaries between the proposed structures and the stacking fault for both cases presented in (a,b).

6. Additional XPS data

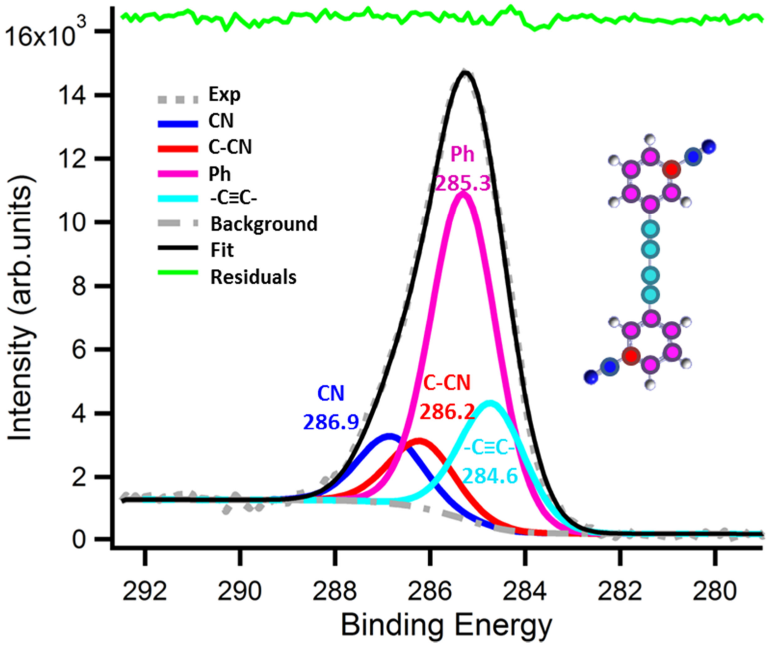


Figure S 11: XPS C 1s spectra of DBDA on Ag(111). The experimental data, and spectral composition are reported. The C 1s spectrum was fitted with four components, presented in the same color as their respective carbon atoms, as shown in the molecular scheme next to the spectrum. Both the peak positions and their relative surface area are consistent with intact molecules. The residual peak of the peak-fitting is shown in green.

Figure S11 reports the N 1s region spectra with increasing coverage of DBDA on Ag(111). At low coverage, the main peak is located at 399.5 eV, which shifts toward a higher BE at 399.8 eV at high coverage. XPS measurements of a molecule with the same terminal *m*-cyanophenyls group[2] showed the peak at 399.5 eV for the sub-monolayer coverages (up to 0.7 ML). In their work, Marschall *et al.*[2] assigned this peak to a physisorbed state, with N atoms interacting with neighboring molecules only. Increasing the molecular coverage resulted in the growth of two additional peaks: one at 398.4 eV, whose intensity increased by increasing the coverage up to 1.5 ML, and one at 400.2 eV, which appeared only at the coverage above 2 ML. They assigned the 398.4 eV peak to N atoms interacting with the surface, and the 400.2 eV peak to the molecules not in contact with the surface. In our study, no peak is observed around 398.4 eV, suggesting that dosing more molecules does not result in a different geometry in which the molecules stand-up on the surface with their N atoms interacting directly with surface atoms.

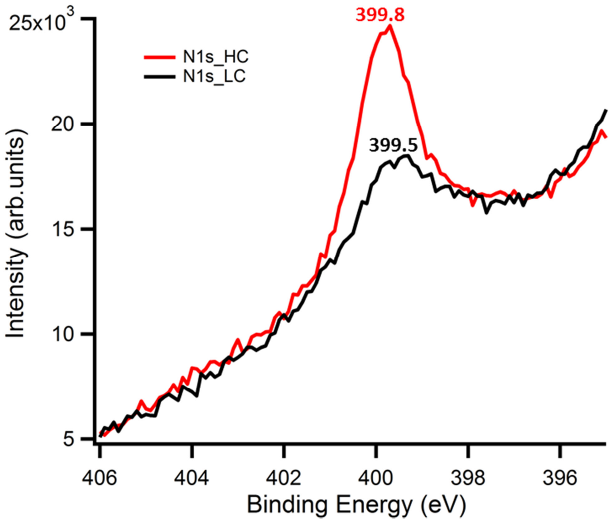


Figure S 12. N 1s spectra of DBDA on Ag(111). The spectra are for a sequential dosing, the black curve is relative to a low coverage (sub-monolayer), red curve to a high coverage (multilayer). Also in this case, as for the C 1s, a shift toward higher BE is observed when increasing the molecular coverage.

7. STM images after annealing/irradiating the surface covered with DBDA

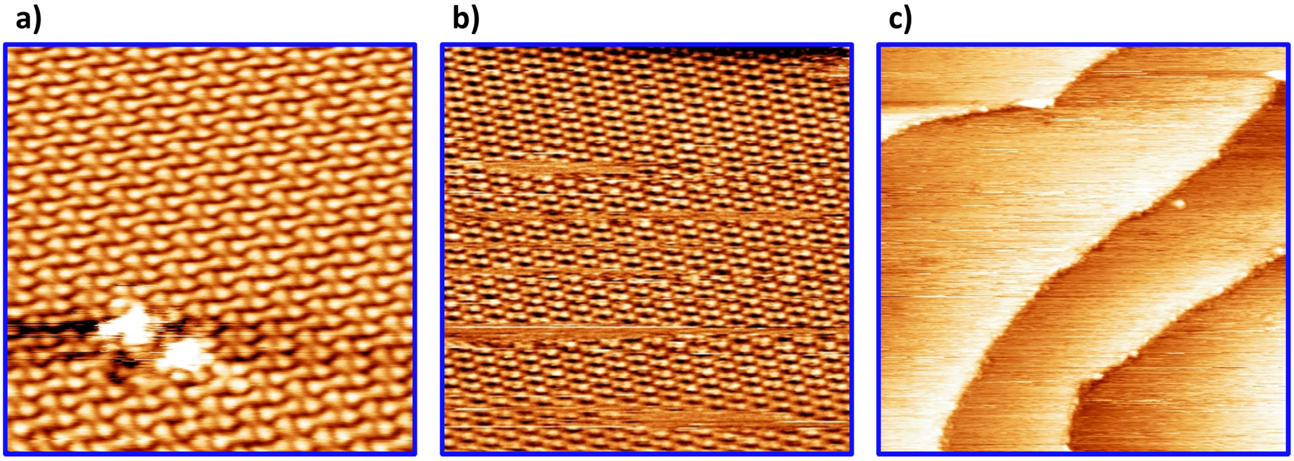


Figure S 13. STM images: a) 15×15 nm^2 after annealing at 100 °C for 30 minutes, showing a chevron phase domain; b) 30×30 nm^2 image after irradiation with UV light @ 254 nm for 3 hours, showing a parallel phase; c) 70×70 nm^2 image after annealing at 150 °C for 1 hour, showing a clean surface. In all cases (a, b, c) the surface was saturated with DBDA molecules after being deposited at RT.

6. Bibliography

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2. Marschall, M.; Reichert, J.; Diller, K.; Klyatskaya, S.; Ruben, M.; Nefedov, A.; Wöll, C.; Kantorovich, L. N.; Klappenberger, F.; Barth, J. V., Meta-Positioning of Carbonitrile Functional Groups Induces Interfacial Edge-On Phase of Oligophenyl Derivatives. *J. Phys. Chem. C* 2014, *118* (5), 2622-2633.