Electronic Supplementary Information

Supramolecular self-assembly of brominated molecules on a silicon surface

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Molecule and Substrate Preparation.

4,4"-dibromo-*p*-terphenyl molecules were purchased from Aldrich and then purified by column chromatography on silica gel and then sublimated.

The Si(111)-B $\sqrt{3}x\sqrt{3}R30^{\circ}$ reconstruction surface is prepared by annealing of the (111) surface of a highly B-doped Si wafer (0.001 W·cm resistivity). Si(111) surface is carefully outgassed and cleaned *in situ* by a series of rapid heating up to 1200°C under a pressure lower than 5 $\cdot 10^{-10}$ mbar. A thermal process (one hour at 800°C) activates the boron segregation at the surface and a maximum boron atom concentration of 1/3 monolayer (ML) can be obtained (one ML is referred to the Si(111) ideal surface atomic density with 7.8 $\cdot 10^{14}$ atoms ·cm⁻²). In these conditions, the surface exhibits a perfect $\sqrt{3}x\sqrt{3}R30^{\circ}$ reconstruction.

STM experiments

STM experiments were performed in an ultrahigh vacuum chamber with a base pressure lower than 2x10⁻¹⁰ mbar equipped with a variable temperature Omicron Scanning Tunneling Microscope (STM). STM images were acquired in a constant-current mode at room temperature or 100 K. 4,4"-dibromo-*p*-terphenyl molecules were deposited from a Quartz crucible at 135°C. The Si(111)-B substrate was kept at room temperature (RT) during the sublimation. Each image process was carried out by using WSXM software.^[1] The artwork was produced with Blender.^[2]



Fig S1. Large-scale STM image (V_s = 3.0 V, I_t = 20 pA, 62x62 nm², 100 K) of DBT network on a Si(111)-B surface.



Fig S2. STM image (V_s = 2.0 V, I_t = 160 pA, 30x15 nm², 100 K) showing the lack of a row of DBT molecules in an island of DBT network on a Si(111)-B surface. The width of this lacking row corresponds to the width of the elemental cell.



Fig S3. STM image ($V_s = -2.0 \text{ V}$, $I_t = 100 \text{ pA}$, 30x30 nm², 100 K) showing step island of DBT network on a Si(111)-B surface. The formation of the network requires at least two DBT molecules to achieve the formation of the elemental cell.

Simulations

All calculations were carried out with the Gaussian 09 (revision C.01) program package ^[3] using density functional theory applying the efficient B3LYP for the exchange and correlation functionals. The calculation have been performed with the 6-311G* basis set for all atoms in the system. Some preliminary tests have been done using smaller levels of theory without giving any fundamental changes in the geometrical arrangement of the molecular systems. Energy minimum of the molecular structures were located by minimizing energy, with respect to all geometrical coordinates and without imposing any symmetrical constraints.

The route to obtain the optimal structures was progressive. We first optimized the monomer geometry. Then we relaxed the dimers, in lateral and opposite directions, and finally the tetramers.

Three molecular arrangements were optimized for dimers. When only Br-Br interactions are responsible for the dimer formation (Fig. S4), the interaction energies are low (minimum of -18.5meV).

On the other side, when π - π stacking fault and Br-H interactions guide majoritarly the dimer arrangement (Fig. S5), the interaction energy is drastically diminished (-99.8meV) indicating a preferential organization of the DBT in a vertical way. Finally, the trimer arrangement (Fig. S6) in horizontal way confirms the lower influence of the Br-Br interactions on the energy (-30meV). The formation of DBT tetramers (Fig. S7) in vacuum is more difficult to achieve. However, when correctly optimized without any substrate constraints, it leads to a strong interaction energy (-843,8meV) conjointly due to π - π stacking fault and Br-H interactions (distance between each entities is also lowered in this configuration).

Taking into account additive interactions, we could estimate the different contributions of each interaction in the total energy. As shown in Figs. S4 and S6, we could estimate the Br-Br interaction to about -15meV. From results obtained in Figs. S5 and S7, the π - π stacking fault could be counted for -14meV while Br-H interaction would lead to about -72 meV in interaction. On the basis of these DFT results in vacuum, we can conclude on the specific organization of the DBT depending on the Br-H positions and, equivalently Br-Br and π - π interactions. The SiB substrate serves as a template to position the molecules according to the atomic lattice.





Fig. S4: DBT dimers optimized in vacuum in horizontal way. A) Only Br-Br contributions are preponderant and lead to an interaction of -13.8meV. B) Br-Br contributions (distance=4.1Å) are organized in quasi perpendicular position and lead to an interaction of -18.5meV.



Fig. S5: DBT dimers optimized in vacuum in vertical and parallel way. Two π - π systems (distance=4.5Å) and two Br-H interactions (distance=3.4Å) are optimized here and lead to an energy of -99.8meV.



Fig. S6: DBT trimers optimized in vacuum in horizontal way. Only two Br-Br contributions (distance=4.1Å) are preponderant and lead to an interaction of -30.0meV.



Fig. S7: DBT tetramers optimized in vacuum in horizontal and vertical ways. Only two Br-Br contributions (distance= 4.4 ± 0.5 Å) are present due to the optimization of 11 Br-H interactions (distance=3.1Å ±0.1) and four π – π stackings (distance= 3.4 ± 0.1 Å). In such tetramer, the interaction is of -843.8meV. In the tetramer, the energy is optimized in such a way that the distance between each Br atoms is increased while Br-H distance and π – π stacking is shortened.

References

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