Collective Radical Oligomerisation Induced by STM tip on a Silicon Surface

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Methods

Materials. All reagents were purchased (Sigma Aldrich) and used as received. Detailed synthetic procedure is described below.

Elaboration of Si(111)√3x√3R30°-B

The Si(111)√3x√3R30°-B reconstruction surface was prepared by annealing in UHV the (111) surface of a highly B-doped Si wafer (0.001Ω·cm resistivity). The Si(111) surface was carefully outgassed and cleaned in situ by a series of rapid heating stages up to 1200 °C under a pressure lower than 5 x 10^{-10} mbar. A thermal process (1 h at 800°C) activated the boron segregation at the surface which meant a maximum boron atom concentration of 1/3 monolayer (ML) could be obtained (one ML is referred to the Si(111) ideal surface atomic density with 7.8 x 10^{14} atoms·cm^{-2}). In these conditions, the surface was found to exhibit a perfect √3x√3R30° reconstruction. [1]

STM experiments. STM experiments were performed in an ultrahigh vacuum chamber with a base pressure lower than $2 \cdot 10^{-10}$ mbar equipped with a variable temperature Omicron Scanning Tunnelling Microscope. STM images were acquired in a constant current mode at 110 K or at

room temperature. All the molecules were deposited from a quartz crucible at 443 K. The Si(111)-B substrate was kept at room temperature during the sublimation. Each image process was carried out using SPIP software.

Synthesis of PDB-OC10

All manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques. All solvents were degassed with nitrogen prior to use. Silica gel (type G) used for chromatography was purchased from Macherey Nagel GmbH. All precursors were purchased from Sigma-Aldrich, and used as received. Deuterated NMR solvents were purchased from Euriso-top SAS. NMR spectra were recorded using a Bruker AVANCE III 400 HD spectrometer.

Procedure for the synthesis of PDB. 1,4-dibromo-2,5-bis(decyloxy)benzene (1.0g, 1.8 mmol) and 4-pyridylboronic acid (1.2 mmol) were dissolved in 40 mL of DMF. Then, an aqueous solution of Cs_2CO_3 (0.5 M, 6 mL) and $Pd(PPh_3)_4$ catalyst (42 mg, 0.03 mmol) were added. The resulting mixture was heated at 150°C for 48 hours. Then, the solvent was removed under reduced pressure. The crude solid was dissolved in 100 mL of chloroform. The organic solution was washed three times with 100 mL of water. The solvent was removed under reduced pressure. The resulting white solid is purified by column chromatography (silica gel, acetone/petroleum ether 1:1).

**PDB-OC10**: 1,4-di(4',4''-pyridyl)-2,5-bis(decyloxy)benzene

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.65 (d, J = 6.4 Hz, 2H), 7.62 (d, J = 6.4 Hz, 2H), 7.03 (s, 2H), 3.99 (t, J = 6.4 Hz, 4H), 1.74 (p, J = 6.5 Hz, 4H), 1.32-1.28 (m, 28H), 0.90 (t, J = 7.4 Hz, 6H), ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.5, 148.1, 147.1, 128.9, 124.5, 115.3, 85.1, 69.6, 31.9, 29.6, 29.5, 29.3, 29.2, 26.1, 22.7, 14.1.

DFT calculations

Density Functional Theory (DFT) calculations were carried out at T = 0 K with Siesta [2] and NWChem [3] packages, and the results were visualized with the Chimera software [4]. For calculations with Siesta, we used periodic boundary conditions with vdW-DF2 (or LMKLL) functional that includes van der Waals corrections. The computations were performed with norm-conserving Trouillier−Martins pseudopotentials and double-ζ polarized atomic basis sets. The mesh cut-off used to form the real space grid in the DFT calculations was 300 Ry, and the structural relaxation and geometry optimization were carried out using conjugate-gradient method until the forces and the variation of total energy were less than 0.04 eV/Å and 0.001 eV, respectively. We considered a vacuum region of 50 Å to minimize the interactions between periodic images in the direction normal to the slab. The molecular species in the supercell were fully optimized while the reconstructed Si(111)($\sqrt{3}\times\sqrt{3}$) R30°-B surface slab (528 atoms) was fixed to the bulk geometry [5,6], and where bottom Si atoms were saturated with H atoms to avoid the presence of lone pairs that may appear in the band gap region of the substrate. Total energy on optimized structure was calculated with a 9x9x1 Monkhorst-Pack k-point grid. With NWChem, we used the generalized gradient approximation using the PBE0 functional [7] and include energy correction for the van der Waals interactions [8]. We used 6-31G** basis sets to describe all H, C, O and N atoms. All gas phase calculations on PDB-OC10 and its fragments were carried out with the geometry of PDB-OC10 as the adsorbed phase on Si(111)-B found with Siesta.
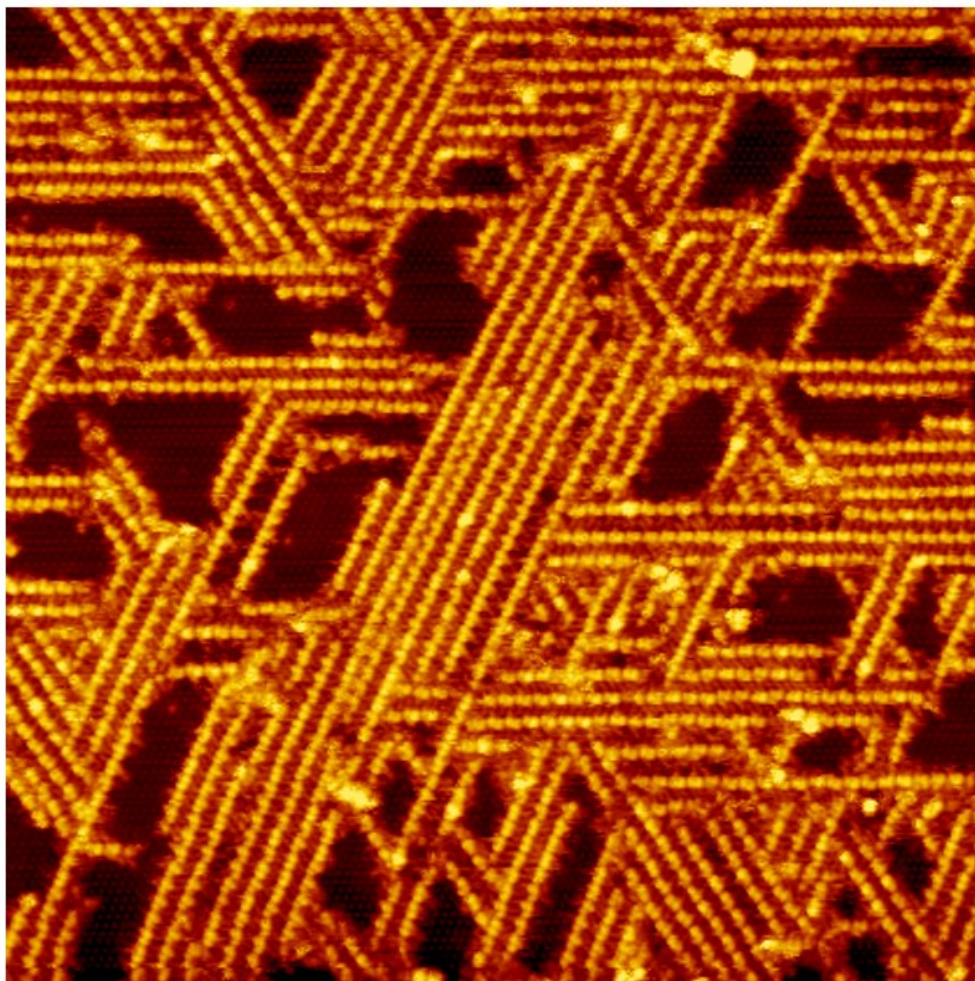
Figure S1. Large scale STM image shows the supramolecular assembly structure of PDB-10OC molecules deposited on Si(111)-B surface under UHV conditions (80x80 nm^2, V_s = -1.5 V, I_t = 7 pA, T = 110 K)
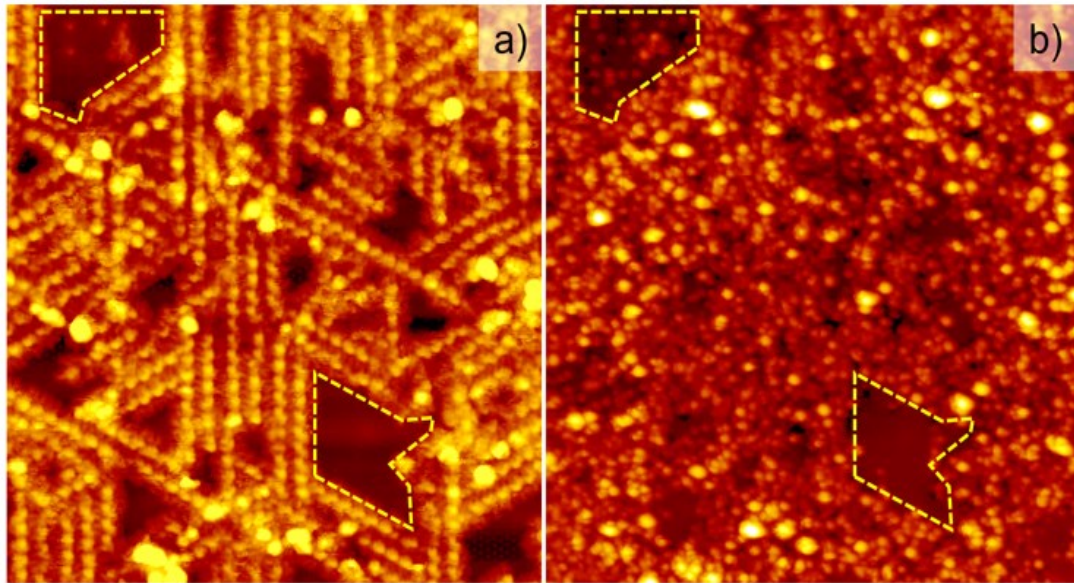
Figure S2. Two STM images (50x50 nm^2, V_s = -1.3 V, I_t = 7 pA, T = 110 K) showing the same zone referenced by the yellow dashed shapes pointing on non-covered parts of the Si(111)-B surface. a) intact network is presented. b) image reveals the complete destruction of the network after scanning at V_s = -4.5 V and I_t = 750 pA.


STM tip trace in manipulation mode
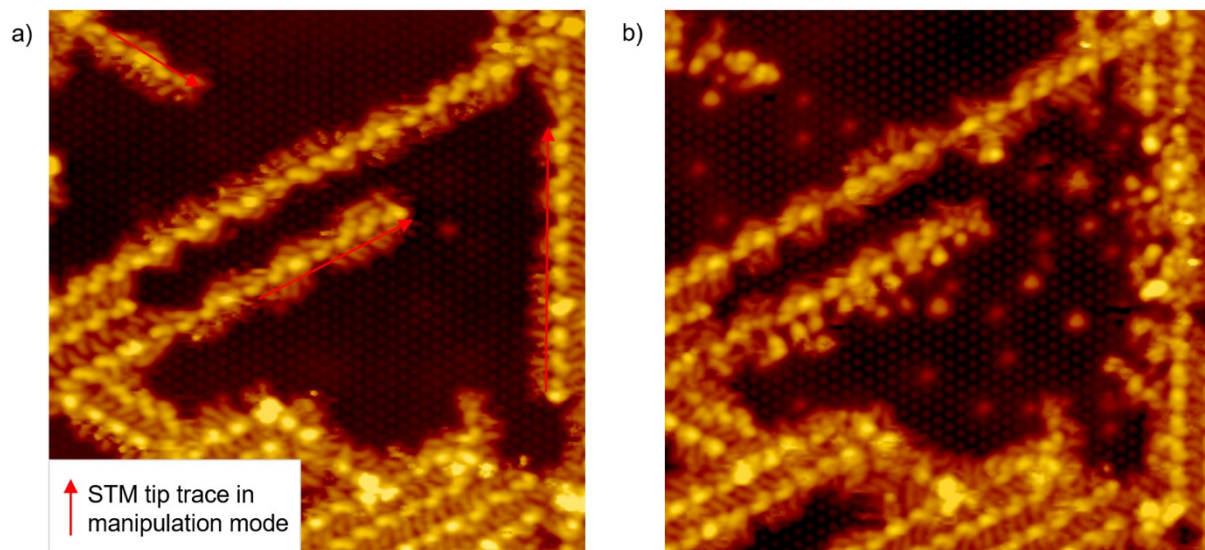
Figure S3. a) STM image (25x25 nm^2, Vs = -1.8 V, It = 7 pA, T = 110 K) representing part of the network before applying locally vectors (red arrows) in omicron atom manipulation mode at bias voltage -4.5 V while regulation loop is maintained on to control current at 750 pA. b) STM image (25x25 nm^2, Vs = -1.8 V, It = 7 pA, T = 110 K) showing the same zone affected only where the vectors are applied.
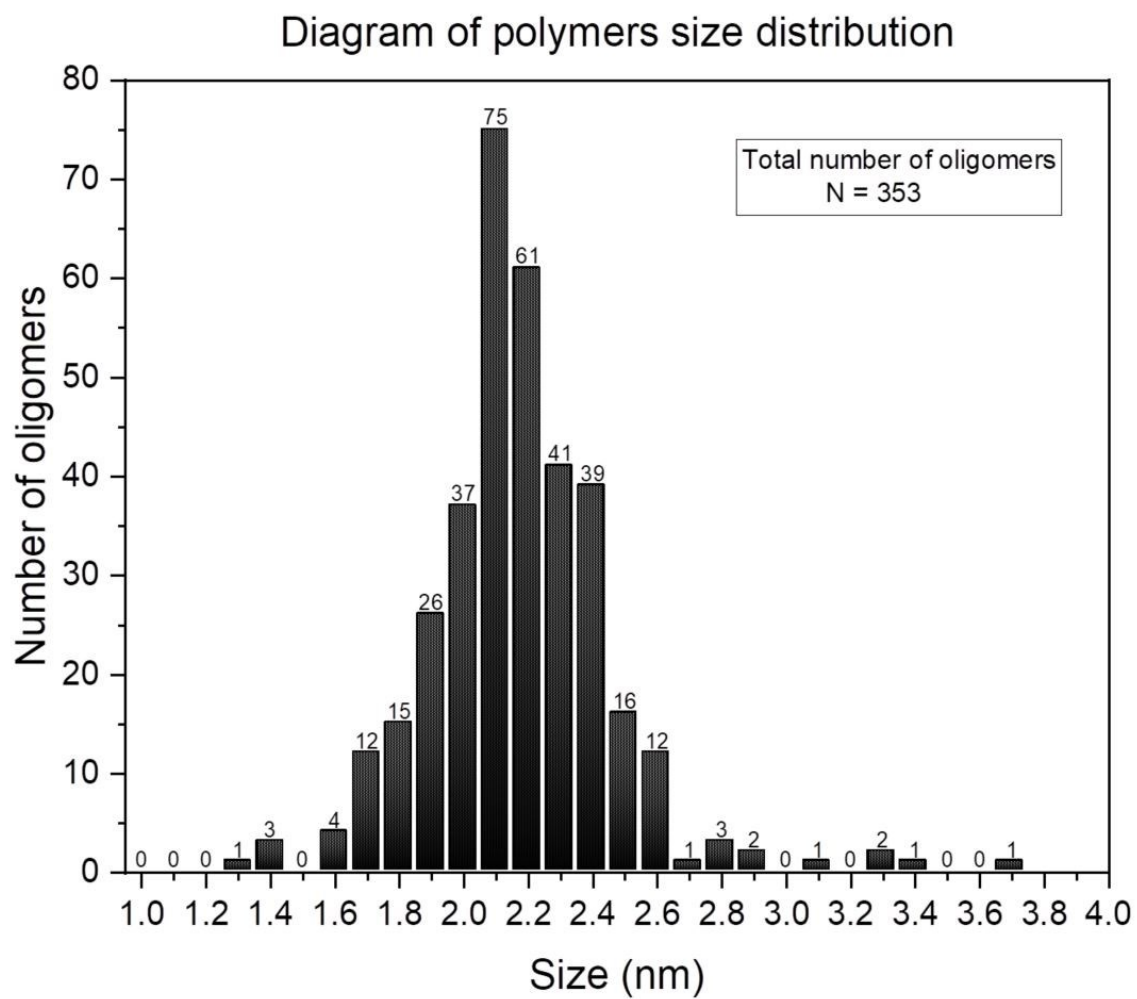
Figure S4. Statistical analysis of the size distribution of nanorods over 353 oligomers from 20 STM images. The size repartition is centered at a length of 2.1 nm.
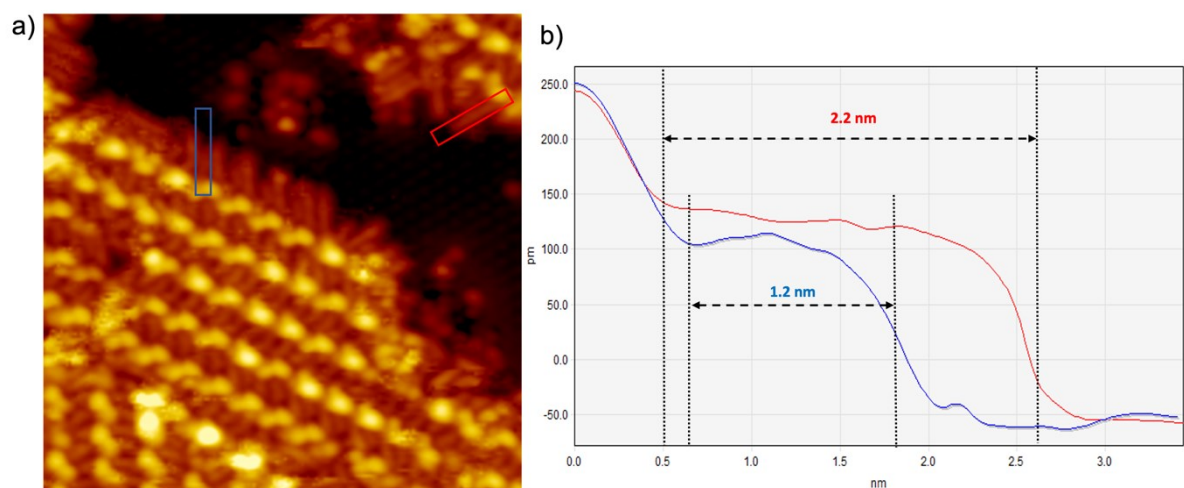
Figure S5. a) STM image (20x20 nm², Vs = -1.3 V, It = 7 pA, T = 110 K) of the supramolecular network (one alkyl chain of entire PDB-OC10 molecule surrounded by blue rectangle) with some deposited rods (surrounded by red rectangle). b) Profile along a C10 alkyl chain of an entire PDB-OC10 molecule (blue) and a nanorod. They differ only by their length.
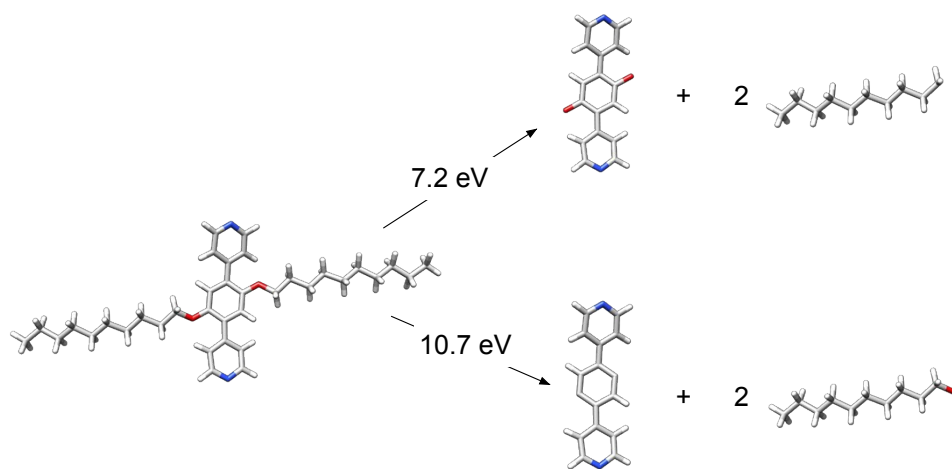
Figure S6. Determination of dissociation energy of the PDB-OC10 molecule in gas phase through the breaking of C-O bonds at DFT/PBE0/vdW/6-31G** level. The dissociation energy reported on the figure corresponds to the simultaneous breaking of two C-O bonds in the molecule.
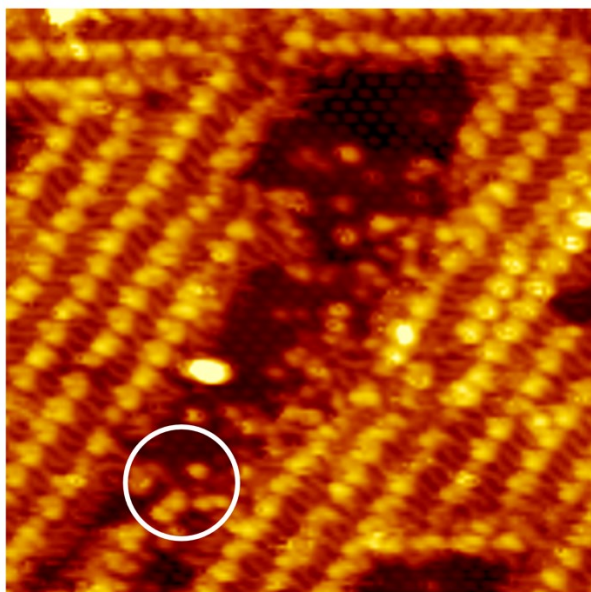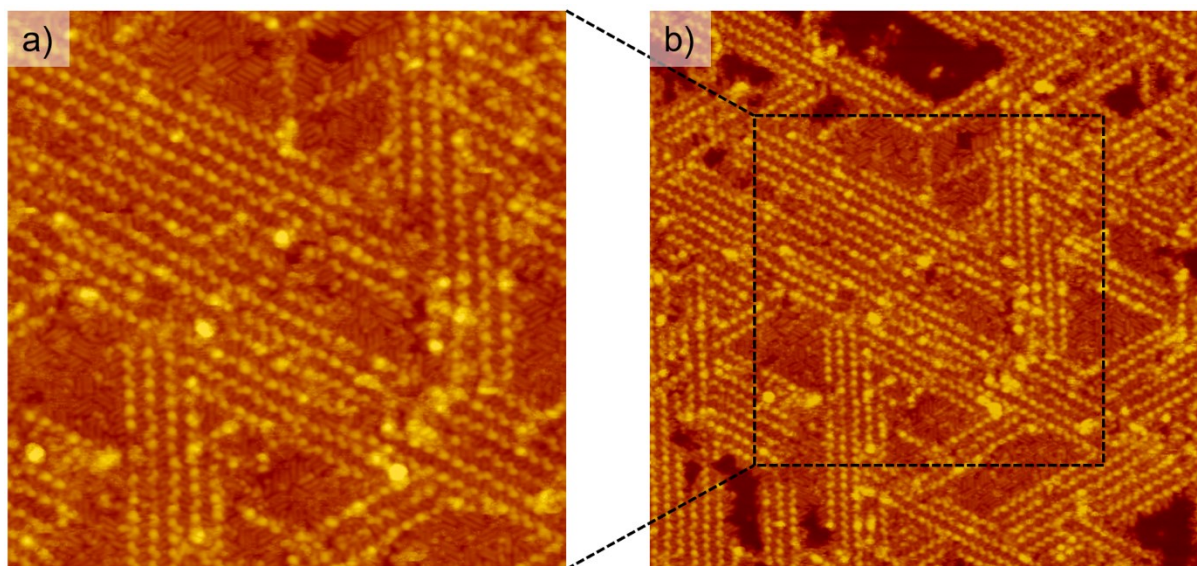
Figure S7. a) STM image (20x20 nm^2, Vs = -1.3 V, I$_t$ = 7 pA, T = 110 K) after cleavage of the C-O bonds. Two bright spot attributed to phenoxide moieties without any lateral chains are surrounded by a white circle.
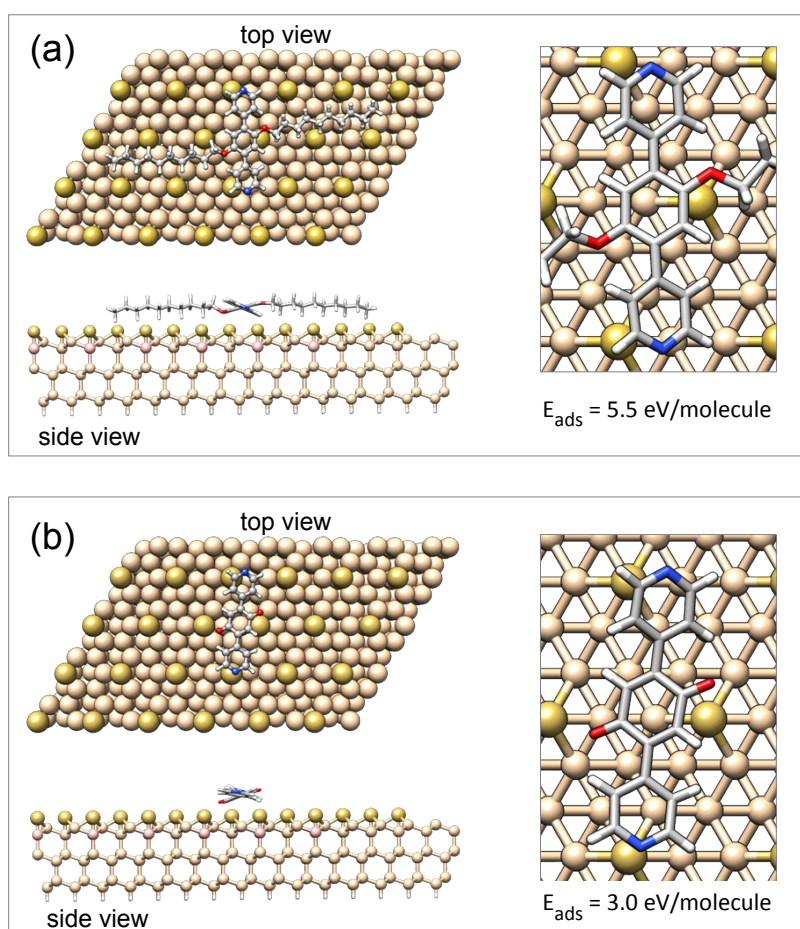

Figure S8. Calculated adsorption energy of (a) PDB-OC10 and (b) phenoxide species on the Si(111)-B surface. For each species, we show a top view, a side view and a zoom view of the optimized molecular species on the Si(111)-B surface. For clarity, we used a darker color for surface Si-adatoms than for bulk-like Si atom in the model, and pink atoms are B-dopants located directly under Si-adatoms. The supercell contains (a) 92 atoms (PDB-OC10) + 528 atoms (substrate), and (b) 30 atoms (phenoxide) + 528 atoms (substrate).

Figure S9. a) STM image (50x50 nm^2, Vs = -1.3 V, I$_t$ = 7 pA, T = 110 K) of fully filled zone by oligomers during scanning. b) STM image (80x80 nm^2, Vs = -1.3 V, I$_t$ = 7 pA, T = 110 K) at larger scale where the dashed inset is the same zone shown in image a) where the outer network holes remains empties.
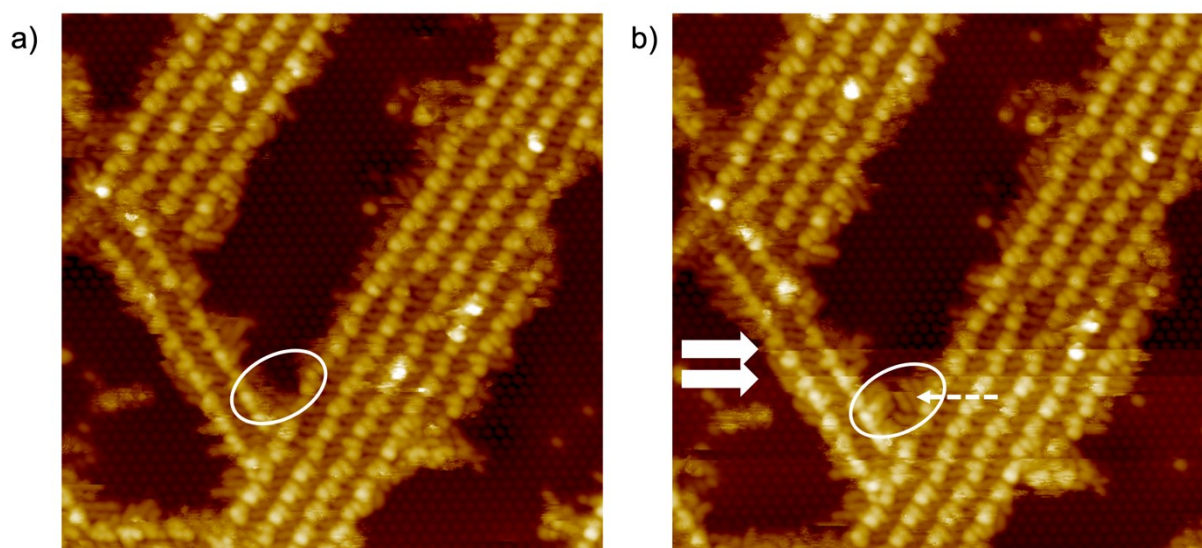
Figure S10. a) STM image (30x30 nm^2, Vs = -1.3 V, I$_t$ = 7 pA, T = 110 K) of network. b) STM image (30x30 nm^2, Vs = -1.3 V, I$_t$ = 7 pA, T = 110 K) showing tip instabilities (indicated by white arrows) after deposition of alkyl dimer onto the surface (white dashed arrow in white ellipse).

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