Supplementary Information

Coverage-Modulated Halogen Bond Geometry Transformation in Supramolecular Assemblies

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Methods

SPM experiments

Experiments were performed in a custom-build STM/nc-AFM microscope (CreaTec Fischer & Co. GmbH) in an Ultra-High Vacuum (UHV) chamber with a base pressure below 5 × 10−10 mbar. The Au(111) surface was prepared by several cycles of Ar-ion sputtering and annealing at 800 K. Commercially available TBF molecules (Tokyo Chemical Industry Co., Ltd.) were outgassed in UHV for several hours and then deposited on a freshly cleaned Au(111) by thermal sublimation from a Ta pocket. Then, the molecular decorated sample is cooled down to 4.5 K for STM/nc-AFM inspection. Images were acquired with a FIB sharpened Pt/Ir tip mounted onto a Qplus sensor[1] (k=1300 Nm; Q=70k; Fr=30k). STM images were obtained at constant-current mode, except as otherwise mentioned. For nc-AFM imaging we used frequency modulation method by keeping the oscillation amplitude constant at 50 pm. Conductance dI/dV spectra and maps were acquired with conventional lock-in technique with a modulation of 1 mV and 10 mV, respectively (at a frequency of 934 Hz). WSxM[2] software was used to standart analysis of the data.

Xenon was dosed in the UHV chamber containing the nc-AFM/STM by means of a leak valve with the sample kept at < 20 K, in order to allow the diffusion of Xe on the surface. The sample temperature was again cooled down to 4.5 K, at which the measurements were done.

Theoretical calculations

Density functional theory (DFT) calculations were performed with the FHI-AIMS package[3] using the PBE[4] functional. The force and energy tolerances were set at $10^{-2} \, eV/Å$ and $10^{-5} \, eV$ respectively. First, the TBF molecule was relaxed on a 7x8 3L Au111 supercell, to properly describe its absorption configuration. Then, due to size of the systems, the dimers of the 1D phase where relaxed on a 1L Au111 orthogonal 16x10 supercell, to ensure no interaction with its periodic images. The 2D phase clusters were deposited on a 10x10 3L hexagonal supercell which lattice vectors are $|\vec{a}| = |\vec{b}| = 24.975 \, Å$. The calculation of the molecule-molecule interaction energies where calculated using gas phase molecules with the coordinated obtained from their relaxation deposited on the surface.

The simulated AFM images were obtained using the Probe Particle Model[5] using a quadrupolar tip to mimic the experimental CO decoration of the tip,[6] using a tip's lateral stiffness of the tip of $0.25 \, Nm^{-1}$ and a charge factor of $q = -0.1$. To properly describe the tip-sample electrostatic interaction, the DFT calculated Hartree potential of the different molecules were used.
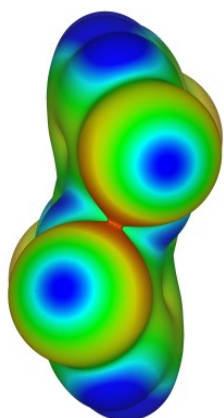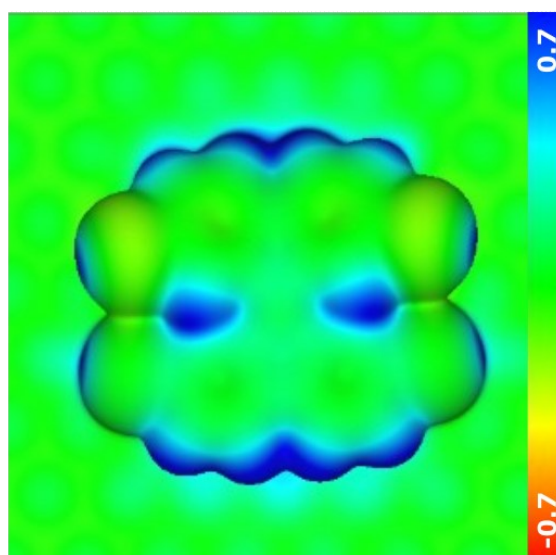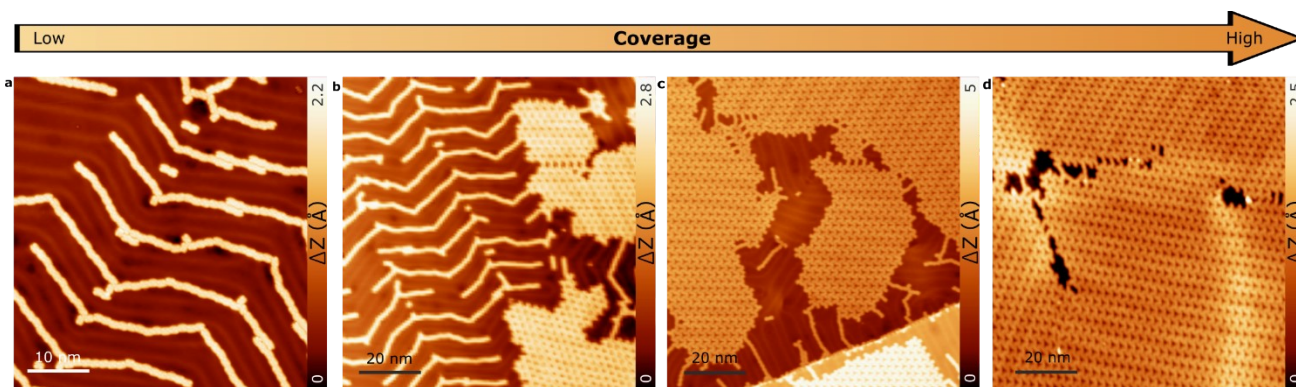
Figures S1 to S6

a
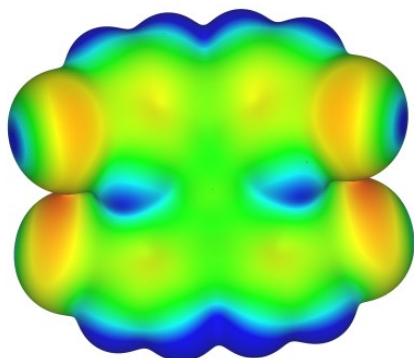
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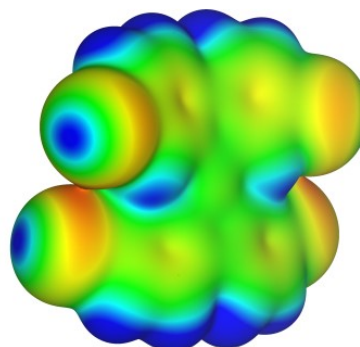
c


d

Fig. S1 a) Top and b) perspective views of the calculated electrostatic potential surface (EPS) of the TBF molecule. c) Lateral side views of the TBF molecule showing the sigma-hole charge distribution around the bromine atoms. d) EPS of t0068e relaxed TBF molecule on top of the Au(111) surface.

Fig. S2 STM topography overviews about the evolution of the 1D and 2D phases of the TBF molecule with the coverage a) <0.4 ML, b) 0.4 ML, c) 0.8 ML and d) >0.8 ML, approximately on the Au(111) surface.
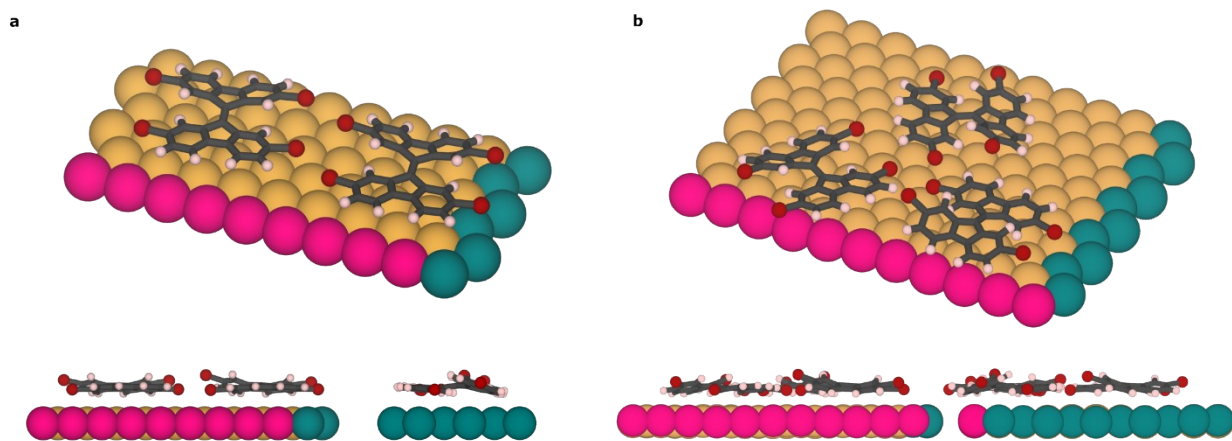
Fig. S3 3D DFT molecular model of the a) 1D phase and b) 2D phase of the TBF molecule with the lateral perspective views and the corresponding tilt with respect to the gold surface.
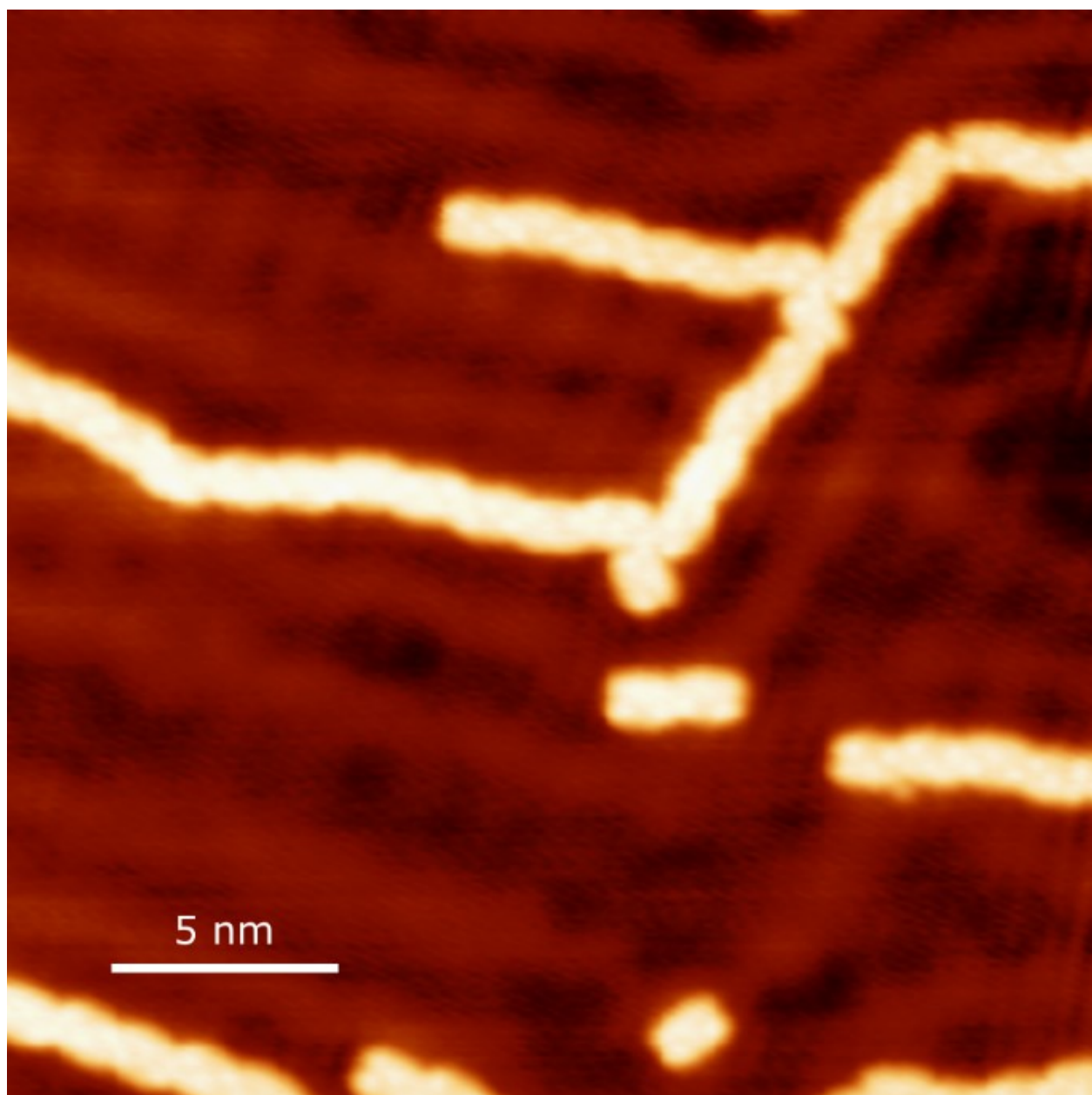
**Fig. S4** Overview STM image of the transition from 1D to 2D phases of the TBF molecule.

a

3.2

ΔZ (nm)

0

50 nm
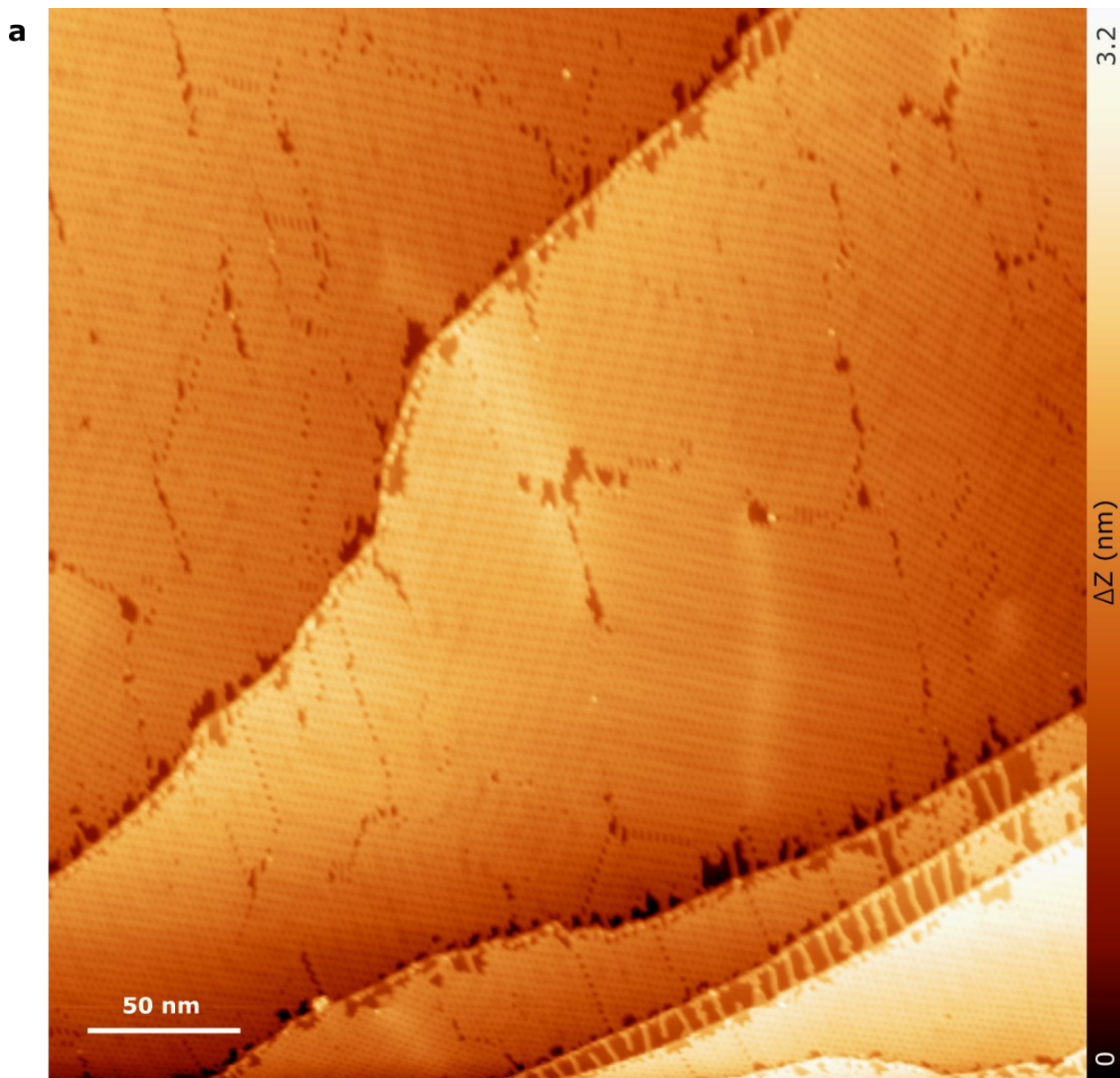
Fig. S5 a) STM topography overview at high scale showing the sub-micrometer size of the 2D phase coverage on the Au(111) surface.
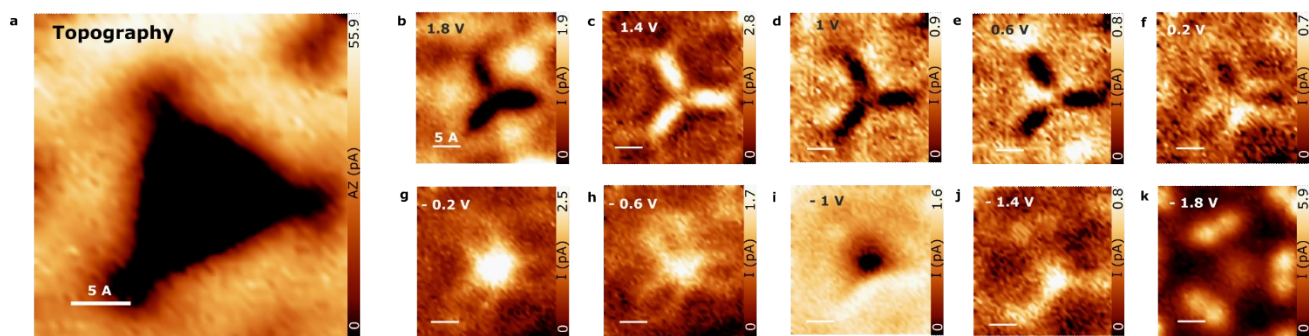
Fig. S6 dI/dV images of the center of the pore in the 2D phase of the TBF molecule. The images show a) a STM topography and dI/dV maps at b) 1.8 V, c) 1.4 V, d) 1 V, e) 0.6 V, f) 0.2V, g) -0.2 V, h) -0.6 V, i) -1 V, j) -1.4 V and k) -1.8 V.
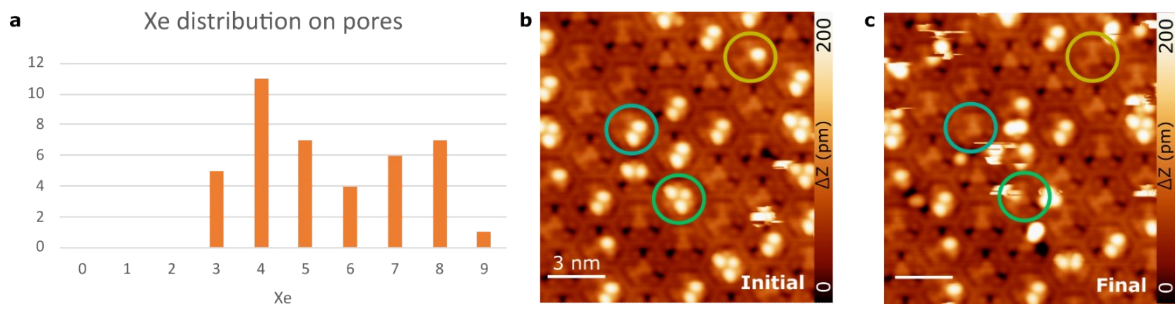
Fig. S7 Xe deposition on the 2D phase of the TBF molecule. a) Xe distribution statistics of the number of Xenon atoms found in the pores of the hexagonal structure. The highest probability is to find four Xe atoms within the hole. b,c) Manipulation of the Xe atoms in the b) initial, c) final state of their interaction with the tip at high voltages (>1 V).

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