Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for: Temperature-induced molecular reorganization on Au(111) driven by oligomeric defects

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1. STM vs DFT distances

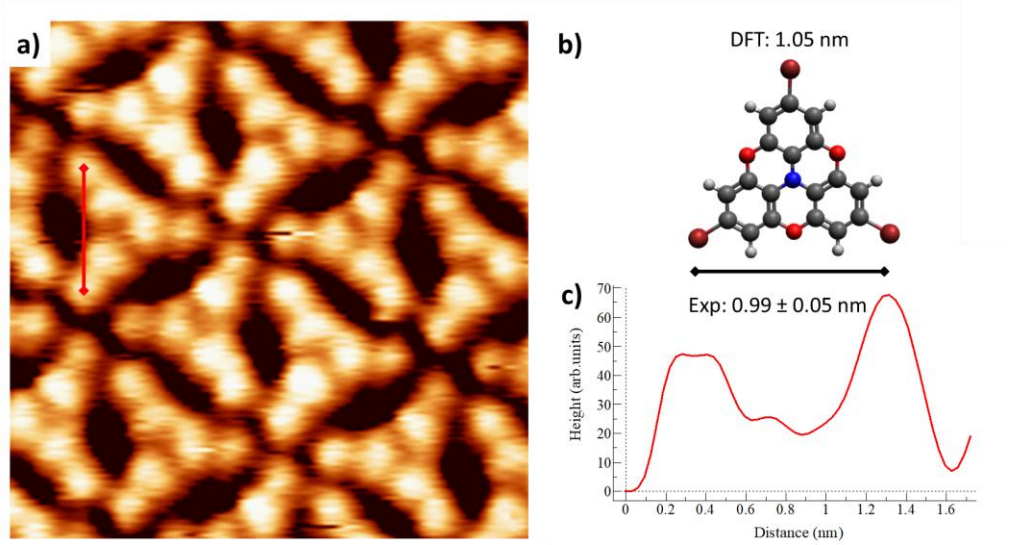

Figure S 1. 2.5×2.5 nm² STM image of TBTANG on Au(111) at RT. b) gas phase DFT model of the intact model, with the calculated Br-Br distance, compared with the experimental one obtained from STM line profile (c).

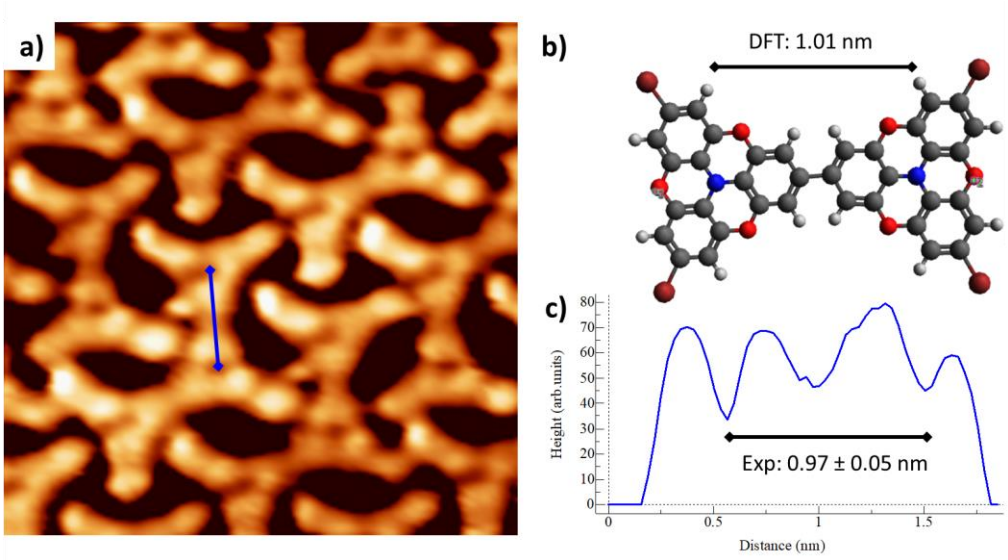

Figure S 2. 3×3 nm² STM image of TBTANG on Au(111) at 100 °C. b) gas phase DFT model of a dimer, with the calculated N-N distance, compared with the experimental one obtained from STM line profile (c).

2. Additional XPS data

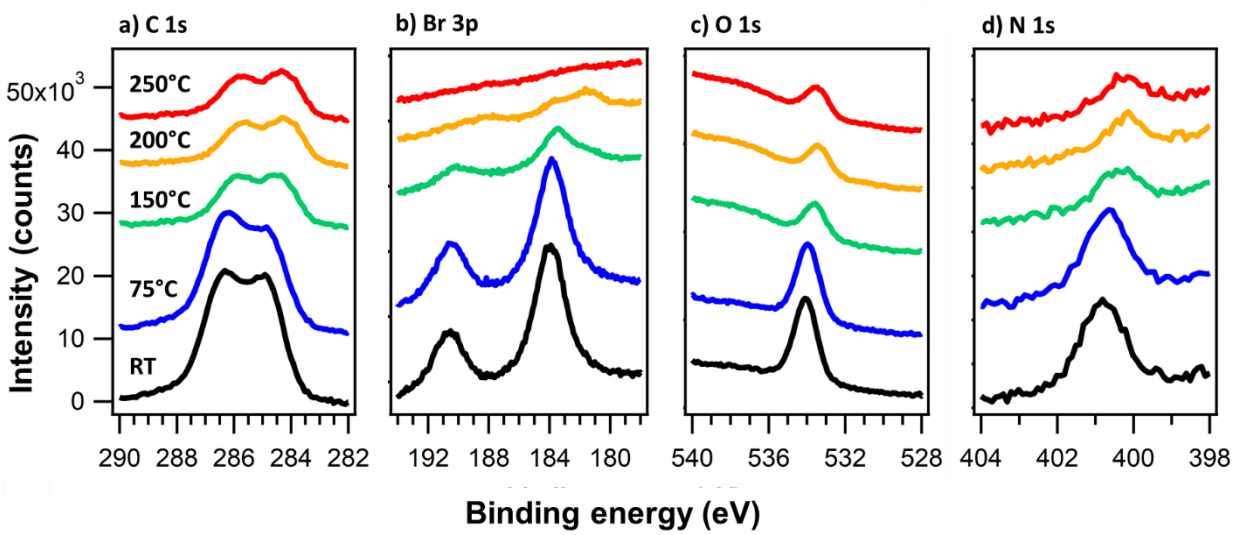

Figure S 3. C1s, Br3p, O1s and N1s XPS spectra of TBTANG at different temperatures.

3. Additional DFT data

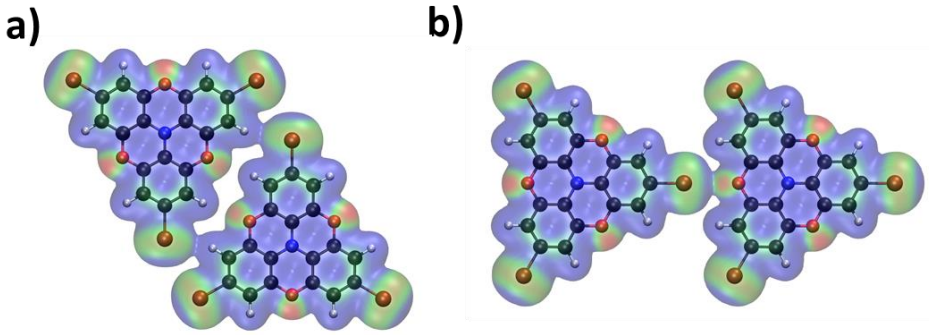

Figure S 4. Electrostatic potential (ESP) maps showing the interactions within a pair of molecules in the (a) Br···Br phase, showing Br–Br and Br–H halogen bonding and (b) the Br···O phase, showing primarily a Br–O interaction. The double polarization of the C–Br bond is reflected in the positive charge (blue) in the bond direction (σ-hole) and negative charge (red) around the Br atom (belt). The ESPs are expressed in atomic units (a.u., Rydberg/e) on 0.006 e/Bohr^3 isodensity surfaces with a color scale range of ±0.02 a.u..

4. Details of Monte Carlo simulations

The main intermolecular interactions between the TBTANG molecules used for the MC simulations were determined by using DFT (B3LYP, 6-31G(d,p)). We calculated five different pair

interactions (1-2, 1-5, 2-4, 2-5, 3-4) of the six-molecule hexagon of the Br···Br phase (Figure S5a) and also the main nearest neighbor interaction of the Br···O phase (Figure S5b). The molecular pairs for the calculations of the intermolecular energy were isolated without further optimization from the extended structures of both phases as obtained by the PBC DFT explained in the main text.

The obtained interaction energies are given in Table S1 demonstrating that the dominant interaction in the Br···Br phase is between the molecules "1" and "2". This interaction corresponds to e_1 in our model for the MC simulations (Figure 4a). In the halogen-halogen bonding scheme the 1-2 interaction is classified as combined X-bond and H-bond three-center binding motif (X_2H synthon).[1] Other calculated interactions are rather weak or weakly repulsive. Interaction 7-8 corresponds to e_2 interaction in our model for TBTANG ordering (Figure 4b). Note that $e_2 \approx 0.5e_1$.

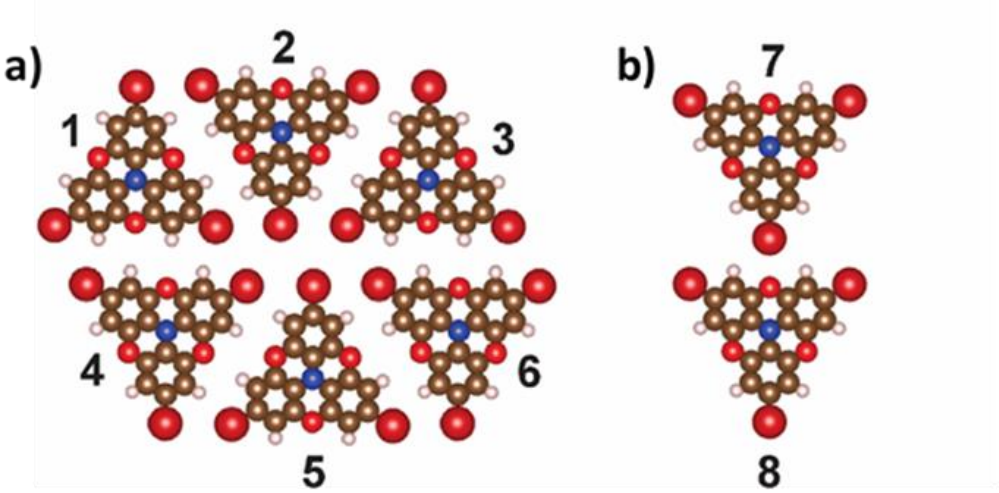

Figure S 5. a) Six-molecule hexagon of the Br···Br phase and b) fragment of the Br···O phase as obtained by the PBC DFT.

Table S1: Intermolecular interaction energies calculated by DFT (B3LYP, 6-31G(d,p)) using molecular arrangements obtained by the PBC DFT.

Phase	Br···Br					Br···O
Interacting molecules	1-2	1-5	2-4	2-5	3-4	7-8
Energy (kcal/mol)	-5.692	1.144	-0.284	0.139	0.586	-2.886

Bibliography

1. Gutzler, R.; Fu, C.; Dadvand, A.; Hua, Y.; MacLeod, J. M.; Rosei, F.; Perepichka, D. F., Halogen bonds in 2D supramolecular self-assembly of organic semiconductors. *Nanoscale* **2012,** *4* (19), 5965-5971.