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Supporting information for

Halogen-adatom Mediated Phase Transition of Two-dimensional Molecular Self-assembly on Metal Surface

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Table of Content

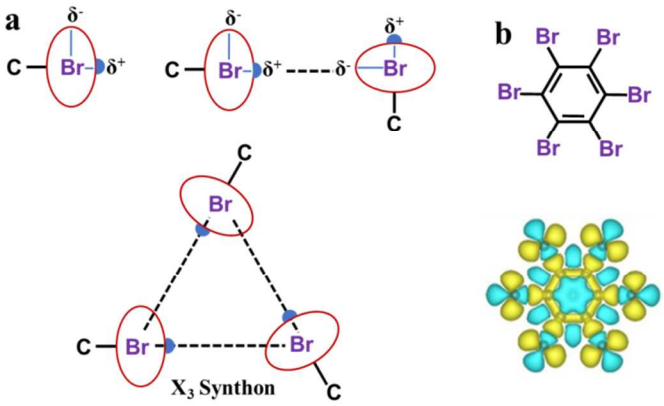

Figure S1. (**a**) Schematic view of positive polarization along covalent bond axis and negative polarization in the perpendicular direction of Br atom, which leads to halogen bonding between molecules including C-Br$^{\delta+}\cdots$Br$^{\delta-}$-C and X_3 synthon. (**b**) Molecular structure of HBB (Top panel) and charge density redistribution (Bottom panel) with an isovalue of 0.0002 e/Å^3. Here, charge density difference was calculated by $\Delta\rho=\rho_{HBB}-(\rho_{C6}+\rho_{Br6})$, where ρ_{HBB}, ρ_{C6} and ρ_{Br6} represent charge density of HBB molecule, six C and six Br atoms, respectively. Yellow (blue) isosurface indicates charge accumulation (depletion).

As schematically shown in Fig. S1a, charge distribution of Br atom in a halogenated molecule is characterized by positive polarization along the bond axis and negative polarization in the perpendicular direction. This leads to electrostatic attraction between molecules, including C-Br$^{\delta+}\cdots$Br$^{\delta-}$-C and X_3 synthon. Figure S1b shows the molecular structure of hexabromobenzene (HBB) and its charge density redistribution formed from single atoms. It is clearly seen that peripheral Br atoms are positively polarized along the C-Br bond, and negatively polarized in the perpendicular region.

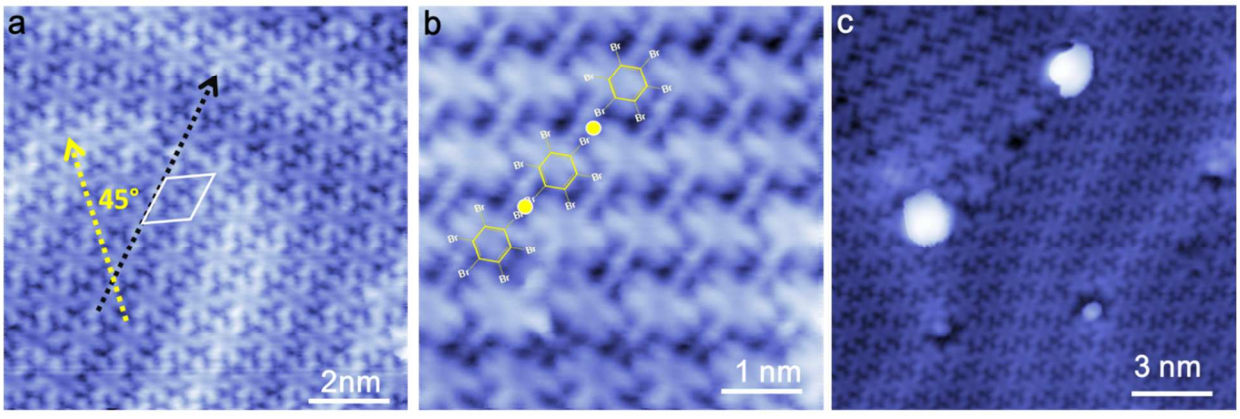

Figure S2. Molecularly resolved STM images showing (**a**) densely packed hexagonal phase, (**b**) tetragonal phase after annealing at 60 °C, and (**c**) a domain boundary between hexagonal phase and tetragonal phase (-200 mV, 500 pA).

Figure S2 is STM image taken with a modified tip to show the molecularly resolved topology of the densely packed hexagonal and tetragonal phases. It is clear that the HBB

molecules in the tetragonal phase (Fig. S2b) were deformed to two-fold symmetry while hexagonal phase remained six-fold symmetry. This also confirms that the observed molecular deformation is due to charge redistribution instead of tip effect during scanning.

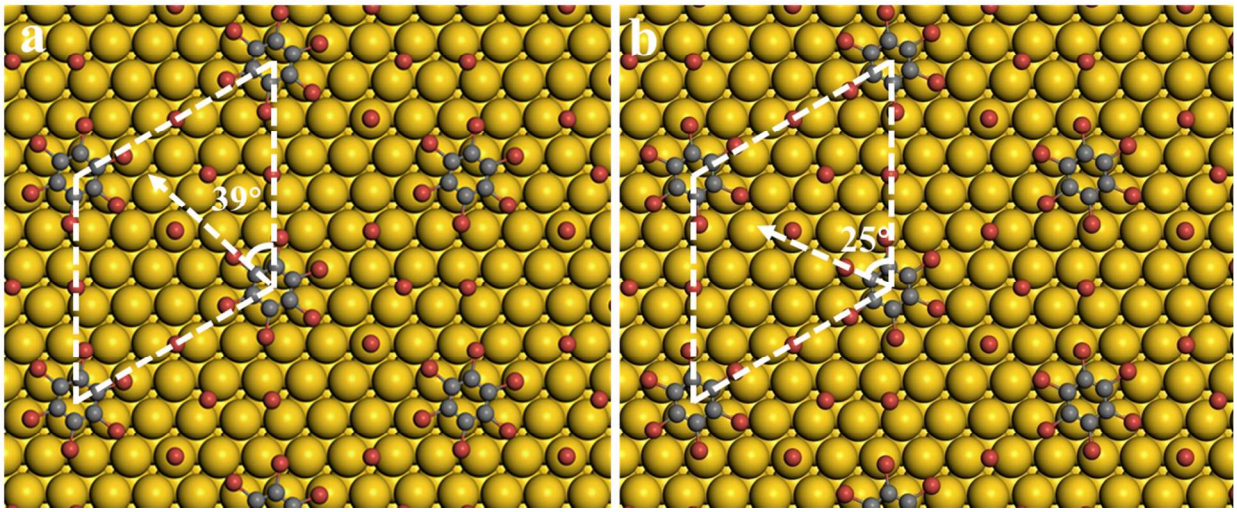

Figure S3. DFT optimized two metastable states of HBB in the expanded hexagonal phase on Au(111), with molecular orientations highlighted.

Figure S3 shows the DFT optimized two metastable structures with different orientations in the expanded hexagonal phase, which have adsorption energies smaller by ~0.02 eV compared to the ground state as shown in Fig. 5d in the main text. This suggests that HBB molecules may flexibly change their orientation in this phase.

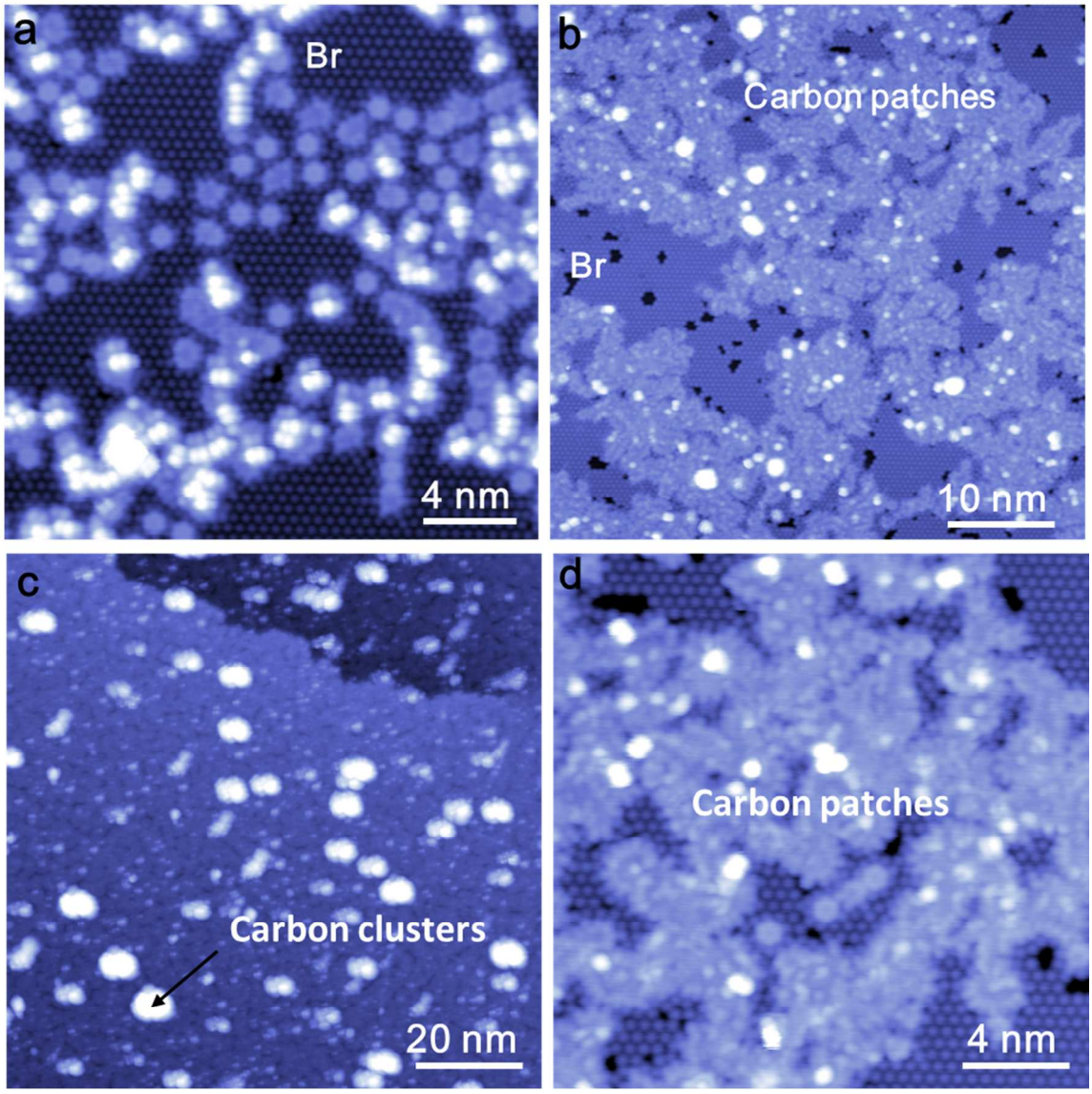

Figure S4. STM images of the evolution process with annealing treatment, showing decomposition of HBB, formation of coupled radicals, amorphous carbon clusters/patches, and ordered islands of Br adatoms. Annealing temperatures: (a) 150 °C; (b) and (c) 240 °C; (d) 420 °C. Scanning parameters: (a) -500 mV, 300 pA; (b) -2 V, 150 pA; (c) -1 V, 100 pA; (d) 2 V, 120 pA.

STM image in Fig. S4a was taken after further annealing the system to 150°C, where Br adatoms were aggregated to a hexagonal pattern. Bright areas are carbon clusters formed from decomposed HBB molecules, which could couple with each other to form chains. HBB molecules were fully decomposed into carbon clusters and Br adatoms after increasing the substrate temperature above 200 °C (Fig. S4b). We found that no ordered carbon nanostructures were formed (Fig. S4c). Further annealing the system to 420°C, only large carbon patches randomly distributed on Au(111) surface were observed (Fig. S4d).

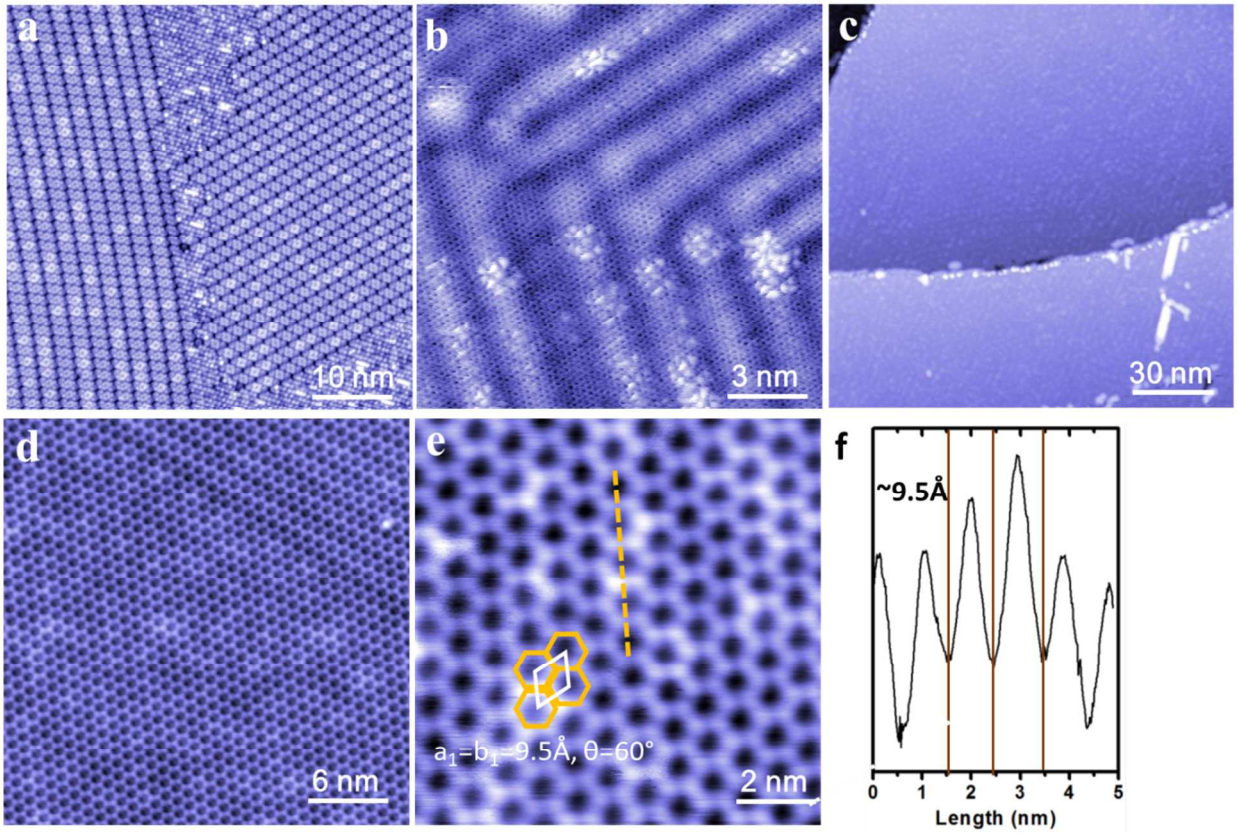

Figure S5. Monolayer HBB on graphene/Ge(110). (**a**) Large-area STM image of CVD graphene on Ge(110). (**b**) Atomically resolved STM image showing the honeycomb lattice of graphene. (**c**) Large-area STM image showing the densely packed monolayer HBB on graphene/Ge(110). (**d**) Zoom-in scan of the honeycomb pattern. (**e**) Enlarged STM image and corresponding (**f**) line profile shows pore-to-pore distance along the dashed line in (e). Unit cell is also indicated. Scanning parameters: (a) -2.0 V, 200 pA; (b) -200 mV,400 pA (c, d) 3 V, 100 pA; (e) 3.5 V, 100 pA.

Chemical vapor deposited (CVD) graphene on Ge(110) wafer[1] provides a flat and inert surface for molecular self-assembly. Figure S5a shows an STM image of CVD graphene on Ge(110). Periodic stripes are surface reconstruction of Ge(110) which could be selectively observed at empty state (negative bias). At a low bias of -200 mV, typical graphene honeycomb lattice can be identified, with bright stripes being underneath Ge reconstruction (Fig. S5b). Deposition of HBB on graphene/Ge(110) at room temperature leads to a well-ordered monolayer with a large domain that spans over the entire surface (Fig. S5c, d). HBB monolayer continuously flows over steps and wrinkles of the substrate, and defects do not perturb ordering of the HBB monolayer. Interestingly, HBB molecules pack into a honeycomb lattice with a unit cell of a=b= 0.95 nm, θ= 60° as measured from the molecularly resolved STM image (Fig. S5e) and the corresponding line profile (Fig. S5f). Inter-pore distance is close to 4√3 times of graphene lattice (9.84 Å).

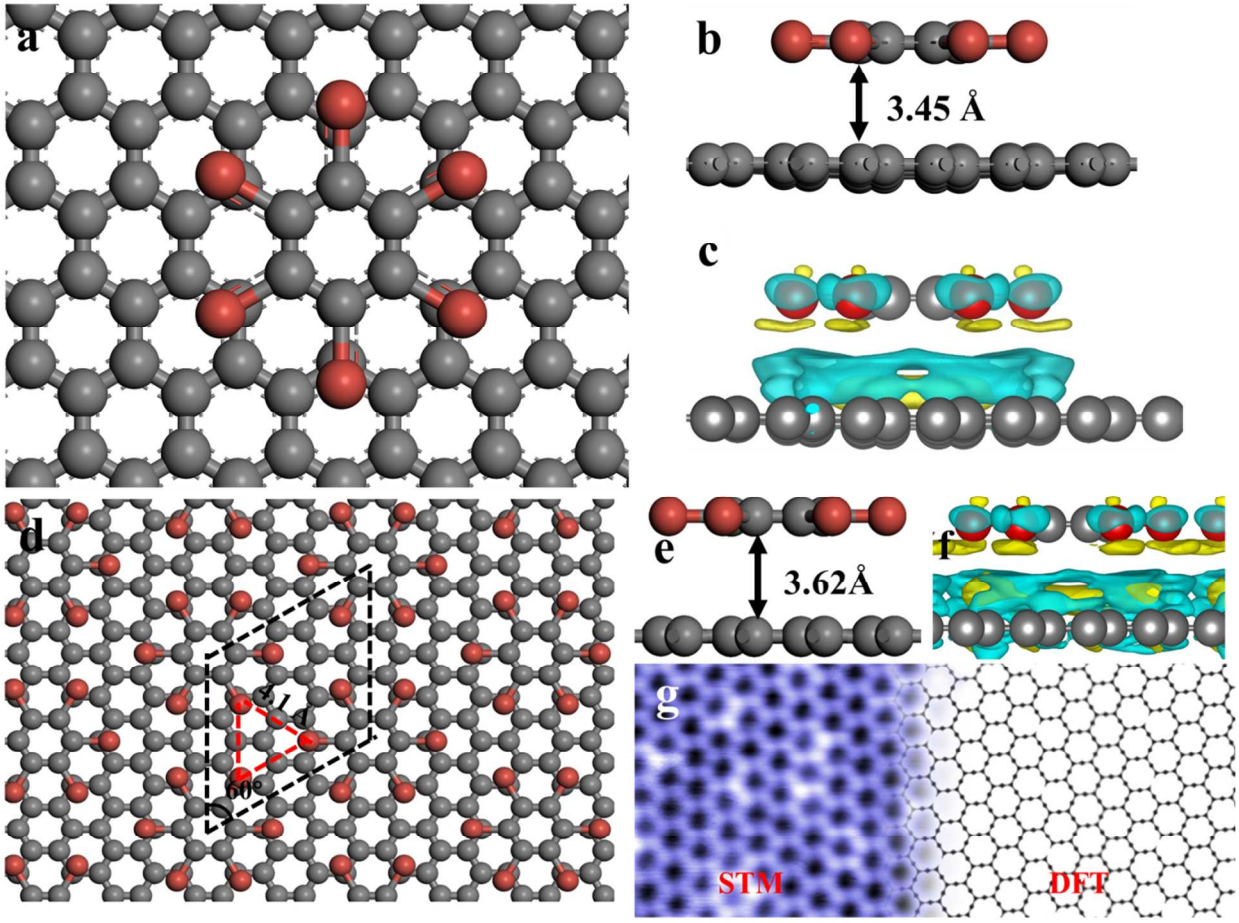

Figure S6. (**a**) Top and (**b**) side views of the most stable structure for individual C_6Br_6 adsorbed on graphene. (**c**) Charge density redistribution calculated by $\Delta\rho=\rho_{total}-(\rho_{HBB}+\rho_G)$, where ρ_{total}, ρ_{HBB} and ρ_G represent charge density of the adsorbed system, HBB molecule and graphene, respectively (isovalue=0.0002 e/Å^{-3}). Yellow (blue) isosurface indicates charge accumulation depletion, respectively. (d) Top and (e) side views of the most stable structure for a monolayer of HBB on graphene. (f) Charge density redistribution for (e). (g) Experimental and DFT simulated STM image.

To understand the STM images shown in Fig. S6, we also performed DFT calculations to investigate the adsorption of HBB on graphene. We first determined the ground state with lowest total energy and then calculated the adsorption energies and electronic structures. As shown in Fig. S6a and b, for a single molecule adsorption, benzene ring of HBB preferably resides on graphene honeycomb lattice with an adsorption distance of 3.45 Å and adsorption energy of 1.42 eV. Charge density redistribution in Fig. S6c shows that HBB loses charge, which was also confirmed by Bader charge analysis. When a monolayer of HBB is adsorbed, molecules remain identical conformation, forming a densely packed monolayer. The calculated adsorption distance was 3.62 Å with adsorption energy of 1.23 eV, indicating weaker interaction compared to single

molecule adsorption. As shown in Fig. S6d, distance between nearest Br atoms of three HBB molecules is 4.1 Å, with a typical feature of X_3 synthon.

References

[1] J. Y. Dai, *et al. Nano Lett.* 2016, **16**, 3160–3165.