Electronic Supplementary Material (ESI) for ChemComm.


Supporting information for

# Real-space visualization of sequential debromination of polybrominated benzenes on Ag(111)

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## Experimental and Theoretical Methods

All STM experiments were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 1 × $10^{-10}$ mbar. The whole system was equipped with a variable-temperature, fast scanning "Aarhus-type" STM using electrochemically etched W tips purchased from SPECS[1, 2], a molecular evaporator, and standard facilities for sample preparation. The Ag(111) surface was cleaned by several cycles of 1.5 eV $Ar^+$ sputtering and annealing at 780 K. After thoroughly degassing, the three polyhalogenated aromatics, namely, 1,2,3-TBB, 1,3,5-TBB, and 1,2,4,5-TBB molecules, were deposited onto the Ag(111) surface from a molecular evaporator separately. The sample was thereafter transferred within the UHV chamber to the STM head. All the STM measurements were performed in a typical temperature range of 100 – 150 K, and the typical scanning parameters were $V_t$ = ± 700 – 1000 mV and $I_t$ = 0.5 –1.2 nA. STM images were further smoothed to eliminate noise. All the calculations were performed based on periodic density functional theory (DFT) by using the Vienna ab initio simulation package (VASP) code[3, 4]. The projector-augmented wave method was used to describe the interaction between ions and electrons[5, 6], and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation of the exchange-correlation functional was employed[7]. Van der Waals (vdW) corrections to the PBE density functional were also included using the DFT-D3 method reported by Grimme[8]. The atomic structures were relaxed until the forces on all unconstrained atoms were ≤ 0.03 eV/Å. The simulated STM images were obtained by using the Tersoff–Hamann method[9], in which the local density of states (LDOS) is used to approximate the tunneling current. DFT calculations on the monomer and two kinds of organometallic dimers from 1,2,3-TBB were performed including Ag(111) substrate. The Ag(111) substrate was modelled by a four-layered slab separated by a ~15 Å vacuum region for the structural models, where the bottom two layers were fixed. As for the situations of 1,3,5-TBB and 1,2,4,5-TBB, the structural models were optimized in gas phase.

## Additional Data

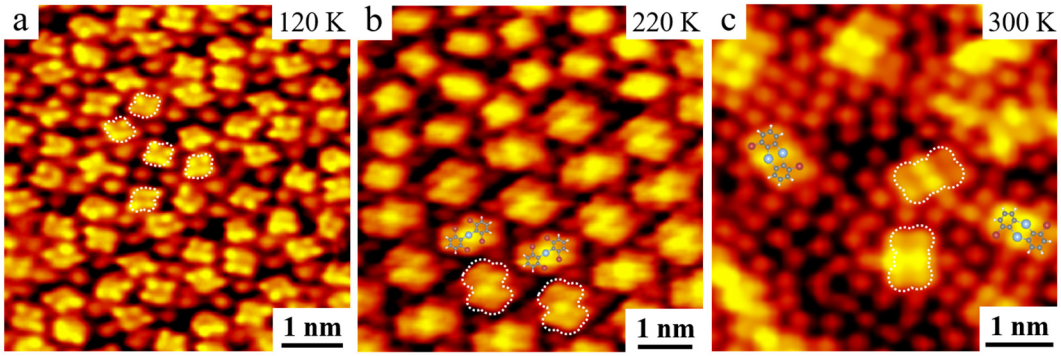


**Figure S1**. Large-scale STM images of (a) 1,2,3-TBB monomers, (b, c) organometallic dimers obtained upon deposition at (a) ~120 K, (b) ~220 K, and (c) 300 K. The white contours indicate individual motifs, respectively.

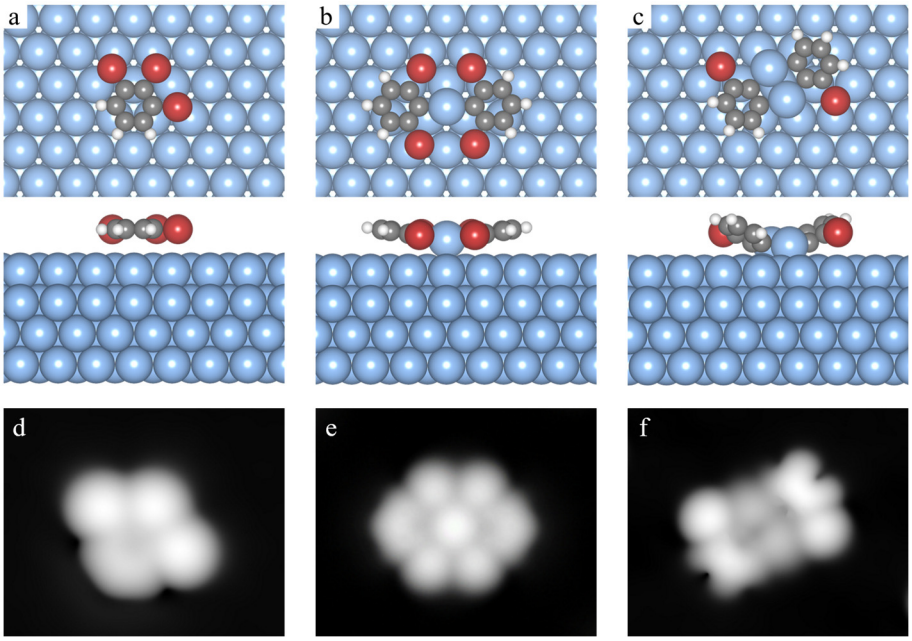


**Figure S2**. (a)-(c) DFT optimized structural models of the (a) monomer and (b), (c) two kinds of organometallic dimers from 1,2,3-TBB on Ag(111). (d)-(f) Corresponding STM simulations based on the structural models.

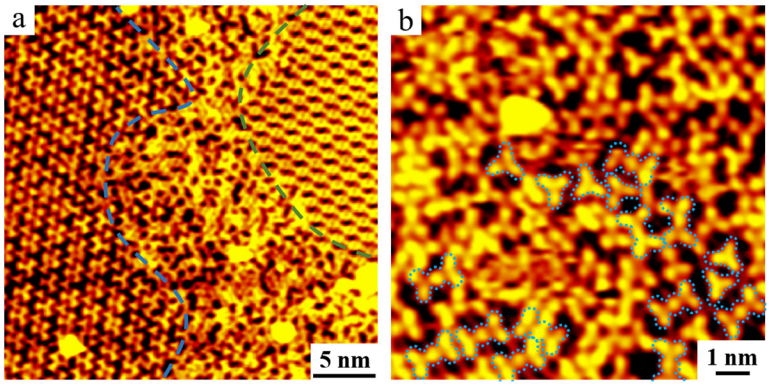


**Figure S3**. (a) Large-scale STM image showing the coexistence of monomers and dimers after deposition of 1,3,5-TBB onto Ag(111) at 300 K. (b) Typical zoomed-in high-resolution STM image showing the details of the disordered phase involved, which is dominantly made up of monomers and organometallic dimers coexisting with some impurities.

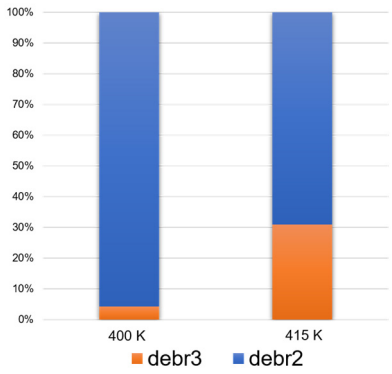


**Figure S4.** Statistics showing the proportion of doubly- (debr2) and triply-dehalogenated (debr3) 1,3,5-TBB involved in the structural phases obtained after annealing at ~400 K and ~415 K.

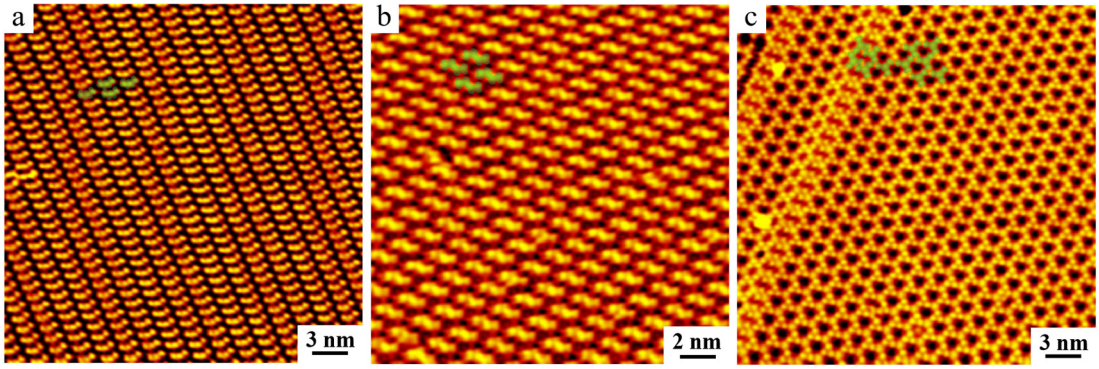


**Figure S5**. Large-scale STM image of organometallic (a) dimer 1 and (b) dimer 2 of 1,2,4,5-TBB obtained upon annealing at ~200 K. (c) Large-scale STM image of organometallic trimers of 1,2,4,5-TBB obtained upon annealing at ~250K. Individual motifs (i.e., organometallic dimers and trimers) involved in the debromination process are highlighted in green.

## References


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