

Cooperative action for molecular debromination reaction on Cu(110)

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Supporting Information Placeholder

ABSTRACT: Copper is the paradigmatic catalyzer of the Ullmann cross-coupling reaction. Despite this, its role in the reaction is still under debate. Here, we shed light on the mechanistic steps of debromination, characterizing a prototypical molecule, namely 4,7-dibromobenzo[c]-1,2,5-thiadiazole (2Br-BTD), deposited on a Cu(110) surface. By means of scanning probe techniques and first principle calculations, we demonstrate, the oxidative addition of Cu atoms leading to -C-Cu-Br metal-organic complex. The scission of the strongly bound bromine atoms requires the cooperative action of neighboring complexes resulting in the formation of Cu-coordinated BTD structures.

The metal-catalyzed coupling of halobenzene derivatives leading to biaryls and larger carbon-based structures is a fundamental reaction in chemical synthesis. Discovered by Fritz Ullmann and Bielecki in 1901 [1] by adding copper particles to a solution containing bromine derivatives of benzene, the Ullmann reaction is undergoing a considerable revival in the last decade. Its application allowing the reliable synthesis of extended polymers has opened a fruitful path in surface chemistry, leading to the formation of polyphenyls, graphene structures of well-defined shape, or covalently assembled structures with engineered electronic and functional properties [2-7]. This reaction offered an unprecedented opportunity to access the molecular functionality by improving the mechanical stability and electron conductance, which are essential to advance in the realization of organic-based electronics.

In the classical Ullmann reaction, the oxidation of copper with the formation of molecular cuprate intermediates and copper halides as side reaction products, precede the cross-coupling reaction [1-8]. Whereas there is general agreement that at a certain point of the reaction a copper-coordinated structure is formed [9-11], the mechanism responsible for the initial debromination step is still under debate [13]. Latest investigations on copper surfaces have allowed visualizing the final reaction products as the intermediate Cu-coordinated phase and the aryl-aryl coupling-reaction [4,13-16]. These steps have been observed by scanning probe techniques and by x-ray photoemission spectroscopy monitoring the oxidation state of C 1s and Br 3p or Br 3d core levels. Changes in the photoemission lines have been assigned to the scission of the Br atom and to the formation of -C-Cu bonds [9,10,17]. Still, the debromination mechanism, which is the rate-limiting step of the reaction, has been scarcely investigated and the question whether the formation of radicals or the copper oxidative-addition precede the formation of the intermediate phase remains open [12,13].

Here, we have addressed this question characterizing the molecular debromination reaction of a prototypical molecule, namely 4,7-dibromobenzo[c]-1,2,5-thiadiazole (2Br-BTD) adsorbed on Cu(110). We demonstrate by scanning tunneling probe techniques and density functional theory (DFT) calculations the oxidative addition of Cu adatoms leading to the formation of a -C-Cu-Br structure. Moreover, we show that the scission of the halogen atom requires the concerted action of neighboring precursors. Thus, the formation of the Cu-coordinated intermediate phase is observed only in self-assembled structures.

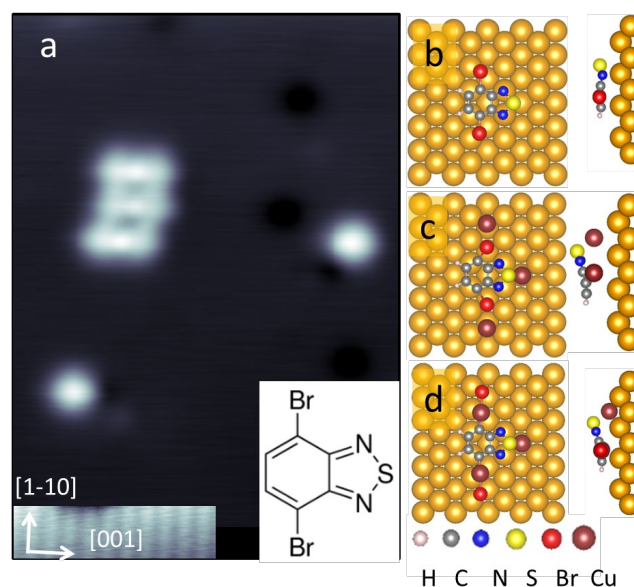


Figure 1: Dibromo-benzothiadiazole (2Br-BTD) deposited on Cu(110) surface. **a.** Topographic image showing isolated monomers and self-assembled dimeric structures (16x12nm). Insets: sketch of the 2Br-BTD molecule in gas-phase and high resolution of the Cu(110) surface **b.** Theoretical model showing the equilibrium position of the pristine 2Br-BTD molecule on the Cu(110) surface; **c.** Intermediate configuration. **d.** Lowest energy configuration: oxidative addition of Cu adatoms.

A representative topographic image of a submonolayer coverage of 2Br-BTD deposited on Cu(110) surface is displayed in figure 1a. These molecules, constituted by benzene and thiadiazole heterocycles (see inset), are part of a family of similar functional molecules widely used in organic electronics. The electron acceptor character and the good electrical conductance conferred by the thiadiazole functional group and the benzene aromatic cycle, make the 2Br-BTD molecules ideal components of bipolar transistors, photovoltaic systems etc. [18-23]. As shown in figure 1, the 2Br-BTD molecules adsorb on Cu(110) parallel to the surface, forming singly isolated or dimeric units with their back-

bone orthogonal to the [1-10] direction, as confirmed by DFT. The adsorption configuration adopted by the 2Br-BTD monomers reflects the dominating interaction of the molecular functional groups, ended by sulfur (S) and bromine (Br) atoms. The calculated energetically most favorable configuration indicates that Br atoms settle close to long-bridge positions along the channels formed parallel to the closed-packed rows of Cu(110), while N atoms bind in the top sites above one of the Cu rows (figure 1b).

In order to clarify the role of the surface in the catalyzed scission of the bromine bond, we have considered the role of copper adatoms self-diffusing already at low temperatures along [1-10] crystallographic direction, which has the lowest energy barrier for diffusion on this copper surface [24-26]. It might be expected that these Cu atoms are sufficient to promote the chemical exothermic reaction that leads to the scission of the halogen bond. Our calculations (figure 1b-d and SI) demonstrate that the molecule interact with a Cu adatom at the S termination. **The formed metal-organic complex lowers the energy of the system about 400 meV and induces a small tilt of the molecular plane (~22°).** This adsorption configuration brings the benzene and the Br functional groups closer to the surface, favoring a stronger interaction. Still, the scission of the bromine-carbon bonds followed by the saturation of the molecular radicals with copper atoms, i.e., **the transmetalation of the 2Br-BTD molecule is not yet energetically favorable.** **The huge energy gain of about 10.2eV is observed** when Cu adatoms bind to the 4,7 carbon atoms of the BTD molecule, shifting laterally the Br atom of about 2.3Å (see figure 1d). Therefore, the insertion of Cu atoms between carbon and bromine results in a -C-Cu-Br structure extended along the Cu(110) closed-compact rows. This configuration suggests that the interaction with copper adatoms is not sufficient to induce the scission of the Br bonds from the molecule. The interaction energy of each of the Br atoms bound to the Cu-metalated system has been calculated to be about 1eV (see Supp. Info.), which is in line with the predicted strong bond of Br to Cu [11].

Local spectroscopic characterization confirms the chemical composition of the 2Br-BTD molecule adsorbed on Cu(110). Figure 2a displays the dI/dV spectra measured at the positions indicated in the topographic image (inset). **The nature of the electronic features observed in the dI/dV spectra can be understood comparing the spatial distribution of the dI/dV signal in constant energy maps with the corresponding topographic image (figure 2b-e).** This intuitive identification of the molecular orbitals is fully corroborated by calculations. Particularly interesting for the aim of this work is the electronic state observed at 1.2 eV (figure 2c) and imaged in the Br-Cu region. DFT calculations support the assignment and confirm that **this energy feature characterizes exclusively the Br-functional terminations of the 2Br-2Cu-BTD molecular complex.** In order to reproduce these energy-resolved images, we have plotted (in orange) the local density of states (LDOS), projecting the total density of states uniquely on the atomic orbitals that have an out of plane symmetry (see details in the Supp. Info.). The good agreement between the experimental and theoretical results confirms that Cu adatoms are inserted between the C and Br atoms in the 2Br-BTD molecular precursors. Besides, the presence of Br atoms attached to the metal-organic system is decisive to mimic the symmetry and spatial distribution of the electronic states according to the predicted model displayed in figure 1.

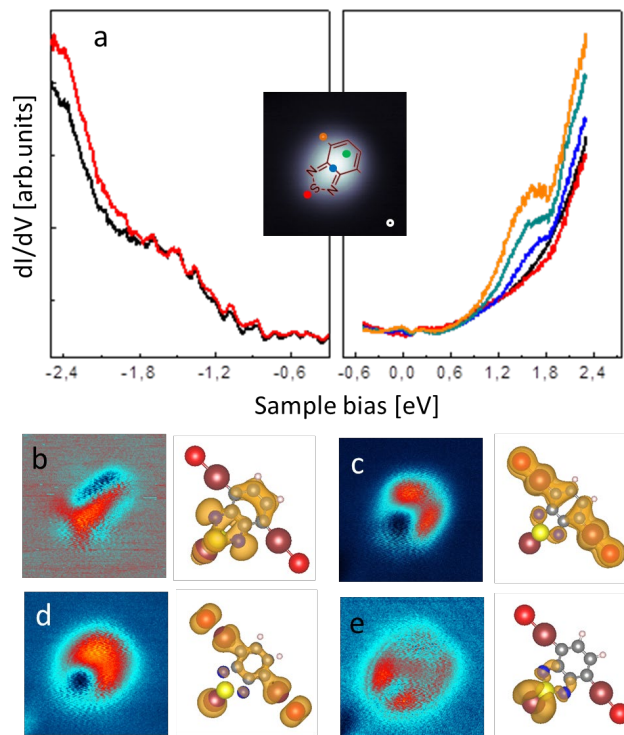


Figure 2: Density of states of the metal-organic molecule. a. dI/dV spectra measured at various molecular positions indicated by circles in inset. **b-e.** Constant energy maps of the molecule (b. -2.1eV; c. 1.2eV; d. 1.6eV; e. 2.1eV); (3.5nm \times 3.5nm) Corresponding simulated local density of states (LDOS) are plotted in orange beside each spectroscopic image.

The Bader analyses of charge distribution [27] at Br and C atoms further substantiate our findings. In figure 3, the charge distribution in the pristine molecule and the molecules with -C-Cu, and the -C-Cu-Br terminations are compared. Remarkably, the oxidative addition of Cu atoms (about 0.6 electrons) between the C and Br chemically reduces both C and Br. It is worth noting, that these reduction processes recalls the ones observed by x-ray photoemission measurements indicating energy shifts of the C1s and Br 3d core levels towards lower binding energies [14-16]. These changes in the oxidation state have been previously assigned to the formation of distinct structures containing Br-Cu and C-Cu bonds, always assuming the scission of the C-Br bond and the consequent reaction of the molecular radical and the Br atoms with Cu atoms of the surface. Here, we demonstrate instead that the oxidative addition of a Cu atom leading to the -C-Cu-Br structure is energetically more favorable and it can equally explain the reported photoemission evidences.

In order to simulate the scission of the halogen bond we have progressively strained the Cu-Br bond of the 2Br-2Cu-BTD adsorbate complex starting from its equilibrium configuration. The variation of the Bader charge assigned to C, Cu and Br atoms sampled by increasing distances along the bond linear direction are shown in the right panel of Figure 3. As the distance from the molecule gets larger, the Br atom recovers its valence configuration while the C and Cu atoms approximate to the charge distribution observed for the Cu-BTD molecule, also shown in the left panel of figure 3.

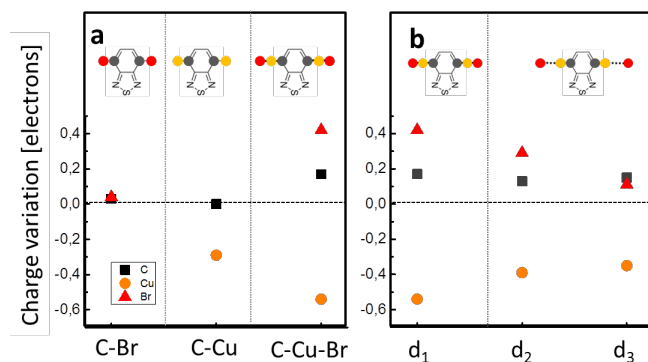


Figure 3: Redistribution of charge calculated at specific atomic position. **a.** Charge variation with respect to the valence electrons, as a function of chemical termination. **b.** Charge variation at the -C-Cu-Br as a function of an increasing Br-Cu distance. Distances d_1 , d_2 , d_3 indicate the equilibrium distance, one lattice constant further along Cu [1-10] direction, and infinite distance, respectively.

Interesting aspects of the reaction emerge surveying the characteristic spectroscopic fingerprint of the bromine atoms in the Cu-modified molecules forming molecular ensembles of increasing complexity. In figure 4, isolated and self-assembled dimeric structures are shown. The center of dimers, which are formed by two monomers facing at the sulfur terminations, contains the thiadiazole groups of the two molecules, bridged by copper adatoms (indicated with dark brown in figure 4b). The adsorption registry of each monomer in the dimeric structure is comparable with the one for the isolated monomer and orthogonal to the [1-10] direction (figures 1a and 4b). The constant energy-map at 1.2 eV measured for an isolated dimer shows again the density of states clearly localized at the Br atoms (red areas in figure 4c). Dashed lines drawn on the constant-energy map and on the topographic image are a guide for the eyes highlighting the four localized maxima of the Br terminations.

A different scenario is instead observed in larger structures, as dimeric pairs, formed along the [1-10] direction (figure 4d-f). The constant energy map at 1.2 eV (panel e) differs strikingly, since the fingerprint of the bromine atoms in the density of states is uniquely observed at the outermost side of the molecular ensemble. Indeed, only four of the eight maxima expected for a dimer pair are observed. Additionally, none of them are located at the coordinated side of the dimer pair. A similar situation is found in larger self-assembled structures as dimeric or monomeric chains, as shown in Supp. Info. The lateral distance (along the [1-10] direction) between the pairs of dimers, about 1nm, and the absence of the density of states assigned to the Br atoms at the center of the ensemble, account for the molecular structure shown in panel f. Both, the lattice periodicity of the structure and the absence of the signal in the density of states suggest that the scission of the Br bond requires the cooperative action of neighboring molecules.

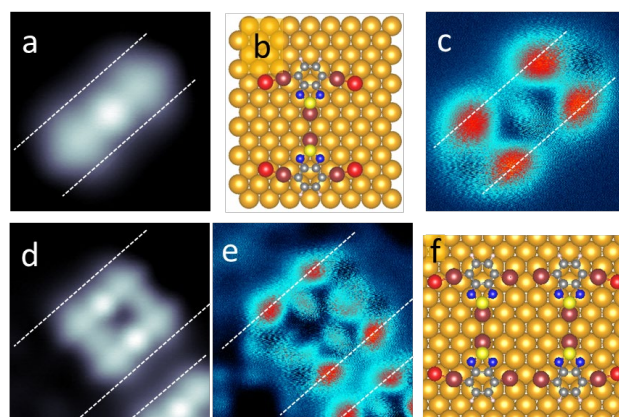


Figure 4: Spectroscopic fingerprint of Br atoms in self-assembled structures. **a,b.** Topographic image of a dimeric structure (3nm x 3nm) and structural model **c.** Corresponding constant energy map at 1.2eV; **d,e** Topographic image and constant energy map (1.2eV) of a self-assembled dimeric pair structure (4.5nm x 4.5nm); **f.** Model of the self-assembled dimeric structure: The dashed lines in panel a,c d, and e, are a guide to the eyes highlighting the topographic localization of the signal corresponding to the Br atoms in the structure.

Our experimental and theoretical investigation of the dehalogenation process of 2Br-BTD molecules on Cu(110) have enabled the identification of a mechanistic sequence of the Br-scission that is expected to precede the Ullmann coupling reaction on surfaces. Based on a step-by-step characterization of the adsorption of isolated single molecules, we have demonstrated that the scission of the halogen atom is consequential to the formation of -C-Cu-Br complexes and the concerted action of neighboring complexes. This mechanistic explains the debated role of the Cu atom in the debromination reaction, which is considered the rate-limiting step of the Ullmann reaction. Our findings provide insight into the largely discussed catalytic activity of the copper. **Furthermore, despite the formation of a metal intermediate complex has been less frequently observed also for other metal surfaces as Au or Ag [4, 28-30], the reaction steps of the dehalogenation process might have common characteristics with the ones here described.**

ASSOCIATED CONTENT

Supporting Information

Complementary experimental and theoretical results are included in the supporting information file. Firstly, methods are described, followed by two sections devoted to theoretical calculations. On the one hand, the interaction energy of Br atoms with the organometallic system when adsorbed in the substrate and, on the other hand, the projected density of states of the gas phase Br-Cu-BTD. Finally, a more complex self-assembled structure, together with its corresponding spectroscopic image is shown.

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(Word Style "Section_Content"). ‡These authors contributed equally. (match statement to author names with a symbol, if applicable)

Notes

The authors declare no competing financial interests.

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