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Sulfur-driven Switching of the Ullmann Coupling on Au(111)

Initial State

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We demostrate a method to selectively switch the Ullmann coupling reaction of 2,8-dibromodibenzothiophene on a Au(111) support. The Ullmann coupling reaction is effective already at low temperature, but complete inhibition of the same reaction can be achieved on Au(111) pre-exposed to H_2S . The marked difference in reactivity of pretreated Au(111) is explained by S-passivation of free Au atoms emerging from reconstruction sites. The inhibited state can be fully lifted by removing the S by hydrogen gas post-exposure.

Surface-assisted Ullmann coupling reactions of targeted organic precursors have in recent years obtained strong attention due to the possibility of controlling the assembly of covalent architectures of different dimensionality, 1D or 2D nanostructures¹⁻³, such as polymers and graphene⁴⁻⁶. A high level of control of this reaction on surfaces is crucial for nanofabrication and for applications in sensing^{7, 8}, catalysis^{9, 10}, molecular electronics, and optical devices¹¹. The dehalogenation of the precursors (aryl halides, C-Br, C-I) can result in 2D covalent networks (C-C) through the Ullmann coupling mechanism. It has been reported that the noble metal substrate plays an important role, and depending on the substrate type, temperature and the halogen species used, the reactivity of the molecular precursors can be tuned^{2, 3, 12, 13}. In particular, precise bottom-up fabrication of graphene nanoribbons (GNRs) can be achieved through coupling of halogenated molecular precursors^{6, 14}.

The reaction temperature is the primary intrinsic variable that can use to control Ullmann coupling reaction. However, motivated by the challenge to scale-up production of these 1D and 2D structures with high quality. It is of utmost importance also to understand the influence of co- adsorbed intermediates



Scheme 1. Ullmann coupling reaction scheme of 2,8-Dibromodibenzothiophene. The initial state of an intact molecule transform into a final state where the molecules have been debrominated and interlinked by C-C bonds.

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or adsorbates present on substrate, which can hinder or promote long-range ordering of the structures. It has previously been reported, that excess halogen atoms¹⁵ or Dysprosium coadsorbed atoms¹⁶ on the substrate can partially suppress the Ullmann coupling reaction.

In this communication we report the possibility to switch off and then on of the Ullmann coupling reaction on the Au(111) surface by exposing to molecular gases (H₂S, H₂). The The 2,8dibromodibenzothiophene (DBDBT) molecule used in our study consists of a thiophene center flanked by bromine benzene groups on either side (Scheme 1). The bromine groups in 2,8 position of DBDBT act as precursors in the Ullmann coupling mechanism (Scheme 1). It has been reported that the Ullmann coupling reaction usually has no intermediate state (organometallic state) on Au¹⁷⁻¹⁹, except when the precursors are sterically hindered from reaching the final state²⁰⁻²³.

Fig. 1a shows typical STM images, obtained at 110 K after deposition of DBDBT onto a Au(111) surface held at 150 K. The DBDBT molecules adsorb on the substrate in patches, that are observed to be surrounded by ridges of a modified $22 \times \sqrt{3}$ herringbone reconstruction of the Au(111) substrate, thus

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Fig.1 a) Large STM-images (V=+0.3 V, I=+0.4 nA), acquired at 100 K, of Au(111) after deposition of DBDBT molecules at 150 K. b) High-resolution STM images (V=+0.2 V, I=+0.4nA), showing a network of chains. A tentative model is superimposed on the chains. The green and blue ellipses enclose an intact and partially debrominated molecule, respectively.

indicative of a chemisorption reaction. The DBDBT molecules self-assemble into a characteristic chain network as shown in Fig. 1b, where the proposed chain model is superimposed. The chain formation is strongly indicative of debromination of the molecules, thus signalling the onset of the Ullmann coupling reaction and formation of a chain consisting of debrominated dibenzothiophene (DBT). Most of the molecules are debrominated, as shown in Fig. 1b, but a few intact molecules (initial state) are still observed. These intact molecules have a characteristic bow shape, exhibiting two bright lobes at the terminal positions, assigned to bromine atoms. Such an intact molecule is highlighted by the green ellipse in Fig. 1b.

The STM image also shows molecules that are partially debrominated, with a single bromine atom still attached, as indicated by the blue ellipse in Fig. 1b. The isolated DBDBT molecules are very mobile even at 110K, as observed by consecutive STM-images showing movement of molecules. This is seen for instance when comparing Fig. 1b and Fig. S1 (supplementary information). In addition, the noisy edges of the patches in Fig. 1a are indicative of molecules that are mobile/diffusing around the patches. After the debromination reaction, the bromine atoms surround the molecules, and it has been reported that thanks to these interstitial bromine atoms, the chains are stabilized and joined together via weak electrostatic C-H···Br···H-C interactions, as previously reported^{3,} ^{16, 24, 25}. There are different chain lengths as shown in Fig. 1 and the average distance between neighbouring sulfur atoms in the chains is 8.2 + 0.4 Å. These results are in good agreement with other experiments of molecules deposited on Au(111), where the intermediate state has not been observed^{4, 26}. The same oligomer has been reported on Cu(111), obtaining similar results²⁷. Thus, we conclude that the Ullmann coupling reaction occurred for this molecule on a gold substrate resulting in covalently linked polymers.

It is surprising to observe an almost complete Ullmann coupling reaction of DBDBT at a low temperature of 150 K, when compared with other Ullman coupled molecular networks that usually require thermal activation around room temperature³. We speculate that the modification of the herringbone reconstruction seen in Fig. 1a is important. The reconstructed clean surface reflects a ~4% compacted hexagonal close packed layer overlay compared with bulk



Fig. 2 STM-images of S-Au complex on Au(111) after deposition of H₂S vapour and subsequent annealing at 673 K for 10 min. The step edges are fully covered by S-Au complex and there are still mobile even at 110K, blue circles denoted some missing portion of sulfur atoms. a) V= -0.6 V, I=-0.5 nA; b) V=-0.6 V, I=-0.5 nA.

-terminated Au(111)²⁸. When the reconstruction is partially lifted by the presence of the DBDBT, the excess Au is expelled onto the surface as adatoms that can facilitate the debromination step (scheme 1). In this way a concerted mechanism involving lifting of the reconstruction and subsequent reaction between Au adatoms and DBDBT result in the structure seen in Fig 1b. The thiophenic S in DBDBT might be key in this process, as we believe that the molecule S-Au interaction drives the lifting of the herringbone reconstruction ^{29, 30}, even suppressing or modifying the herringbone, similar behaviour has been reported in other noble metals^{31, 32}.

Next, we repeated the experiment on a H_2S (1x10⁻⁷ mbar) pre-exposed Au(111) sample (60 L). Following the H_2S exposure alone, the high-resolution STM images in Fig. 2a,b reveal two significant changes to the Au surface. Firstly, it is noted that protrusions appears on the gold substrate. The protrusions are distributed on the terraces and the step edges are fully covered as shown in Fig. 2 and Fig. S2. Secondly, on the terraces the herringbone reconstruction is completely lifted after the H_2S exposure ³³⁻³⁵. We attribute the protrusions to Au adatoms originating from the lifting of the herringbone, which are decorated with S to form S-Au complex ^{30, 36-40}. The STM images were acquired at 100 K. Even at this temperature, some of the S-Au are slightly mobile (circles in Fig. 2a) reflecting that the S-Au complex is strongly coordinated with S and weakly bound to the Au(111) substrate itself.



Fig. 3 STM-images after deposition of DBDBT molecules on Au(111). We can observe intact molecules and S-Au complex on the terrace, marked by the green ellipse. Some of the molecules are interacting by pairs and the bromine terminations are observed as bright protrusions. A tentative model was superimposed. a-b) V= -0.3 V, I=-0.5 nA.

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In the next step, we deposited DBDBT on top of the Sreacted Au(111) surface. As the Au adatoms have become passivated already, Fig. 3a,b shows that no Ullmann coupling reactions occurred on the surface. Instead, intact molecules are observed, as we can identify the bromine attached to DBDBT by the bright protrusions, as shown in Fig. 3b. The molecules are ordered by pairs and stabilized by Br-H interactions. It is even possible to observe the S-Au complex on the terraces with similar distribution as shown in Fig. 2, indicated by the green ellipse in Fig. 3a. As mentioned before, both S-Au complex and DBDBT are mobile even at this temperature, judged from the fuzzy edges of islands in Fig. 3.

While in the disabled state consisting of unreacted DBDBT on Au(111) mixed with S-Au complex in Fig. 3, we can effectively switch on the Ullman coupling again by post-exposing the sample at hydrogen gas at 673 K. Fig. 4 shows the surface after hydrogen exposure $(1 \times 10^{-4} \text{ mbar})$, where we can observe the same Ullmann coupled chain network obtained by depositing DBDBT molecules on pristine Au(111) (Fig. 1). The reaction is clearly enabled again by the hydrogen dosing. We explain this switching by reduction of the Au-S complex by hydrogen leading to H₂S and subsequent liberation of free Au adatoms that can drive the Ullmann coupling.

In summary, we have shown that the Ullmann coupling reaction on Au(111), can be switched off by the presence of sulfur atoms and on again by hydrogen reduction, respectively. It is wellknown that sources for reactive metal atoms are step edges⁴¹, where the adatoms can be released to build molecular, organometallic, or 2D networks⁴²⁻⁴⁴. In our case, Au adatoms are available at low temperature due to the lifting of the herringbone by virtue of the S in DBDBT. However, when H₂S is pre-dosed the strong S-Au adatom interaction is modifying the atoms on the terrace, by lifting the herringbone reconstruction, and deactivating the step edges where the sulfur atoms are blocking the mobility of the Au atoms, so all the possible Au adatoms are already bounding in the form of S-Au complex. Due to this inhibition the debromination cannot be triggered and the molecules remain unreacted on the surface. This result is in good agreement with previous studies where it was observed that dehalogenation occurs until the saturation of surface reaction sites (steps edges and elbows of the gold herringbone



Fig.4 STM-images after dosing H_2 onto the sulfur-inhibited state of DBDBT molecules on Au(111) at 673 K for 10 min. Inset: Atomistic model of the chains consisting of 4 and 5 molecules, respectively. a) V= -0.4 V, I=-0.5 nA; b) V=-0.4 V, I=-0 4 nA

reconstruction) is reached^{29, 45}. For example, the Dy atoms are sequestering the Ag adatoms from the step edges, and the partial debromination is only possible from the Dy on the terraces. A similar effect occurs when iodine atoms are poisoning the step edges and only the initial molecules are debrominated. Contrary to the Dy and I cases, we can completely switch on the Ullman coupling again by removing the sulfur atoms from the substrate by exposing the sample at hydrogen gas. Our findings illustrates the general use of coadsorbates to disable and selectively enable an on-surface Ullmann coupling reactions on Au(111). The insight may facilitate new possibilities to design synthesis protocols involving gas exposure for complex 2D nanostructures and hybrid nanosystems on surfaces.

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Conflicts of interest

"There are no conflicts to declare".

Notes and references

‡ The experiments were carried out in ultra-high vacuum conditions (UHV), with a base pressure of 10⁻¹⁰ mbar, with a home-built Variable Temperature Scanning Tunneling Microscopy (VT_STM) "Aarhus" STM type. The STM images were acquired at 110 K with a mechanically cut Pt/Ir tip, and the bias voltage is applied to the sample. The substrate used for making the experiments was a single crystal of Au(111). The sample was cleaned by standard cycles of sputter/anneal. DBDBT molecules was sublimated from a glass crucible inside a homemade molecular evaporator held at 323 K, onto the clean copper or gold samples, which could be held at 150 K and 300 K. Sulfur deposition has been made by exposing the pristine Au(111) surface to H₂S vapor by backfilling the UHV system (1x10⁻⁷ mbar) using a doser tube to increase the local pressure at the sample surface, followed by annealing at 673 K for 10 min. The hydrogen deposition has been made by exposing the sample to H₂ by backfilling the system (1x10⁻⁴ mbar) using a leak valve, followed by annealing at 673 K for 10 min.

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