



Substrate-controlled linking of molecular building blocks: Au(111) vs. Cu(111)



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ARTICLE INFO

Article history:

Received 7 January 2014

Accepted 22 April 2014

Available online 2 May 2014

Keywords:

Scanning tunneling microscopy (STM)

Cu(111) surface

Au(111) surface

Metal–ligand bond

On-surface polymerization

Hexabenzocoronene (HBC)

ABSTRACT

The coupling of dibromohexabenzocoronene (Br₂-HBC) as a precursor molecule is investigated by scanning tunneling microscopy (STM) on two noble metal surfaces: Au(111) and Cu(111). It is found that the on-surface polymerization of molecular building blocks equipped with halogen atoms is strongly influenced by the choice of the substrate. While on Au(111) a heating step of up to 520 K is required to activate the molecules and form polymers, on Cu(111) the catalytic reactivity causes activation already below room temperature. Due to the different substrates, the intramolecular bonds in the polymers between the HBC units differ: The HBC molecules are covalently coupled on Au(111) while on Cu(111) a copper adatom mediates the bonding. This effect is proven by the comparison with gas phase calculations and by lateral manipulation with the STM tip. The choice of the substrate thus does not only define the activation temperature but also lead to different bonding strengths between the molecular building blocks.

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1. Introduction

Controlling the arrangement of molecules with high precision paves the way to a new class of materials to be used in future technology [1,2]. The study of such processes on surfaces is of particular interest as the growth is confined to two dimensions. Scanning tunneling microscopy (STM) is a suitable technique for the characterization of the growth because it allows not only to observe the different stages of the experiment in submolecular resolution [3] but also to manipulate single molecules [4]. In a bottom-up approach, molecular building blocks are deposited and then linked on the surface. As a consequence of on-surface polymerization the molecular weight is not a limit for the in situ preparation of large organic structures. However, the role of the surface has to be investigated to control the arrangement of the molecular building blocks. Depending on the molecule–molecule and molecule–surface interactions they typically arrange on a surface by weak non-covalent forces [5]. These supramolecular arrangements are stable at low temperatures but break up as soon as the molecules thermally overcome the diffusion barrier [5] and stronger bonds are necessary to guarantee stable connections and structural integrity. First, an improved stability can be achieved by the coordination of a metal to functional groups (ligands)

attached to the molecule [6]. After addition of a metal atom, which is supplied from the surface or by separate deposition to the available ligand-containing molecule, a coordination bond is formed [7,8]. Second, the on-surface synthesis process [9,10], which produces more stable covalent nanostructures, takes advantage of the comparably low bond dissociation energy of the halogen–carbon to achieve selective activation at the halogenated sites. In addition to STM-tip induced dissociation as shown on the single molecule level by Hla et al. [11], the halogen–carbon bond can also be dissociated thermally in a controlled way [9], even offering the possibility of halogen-specific sequential activation via the heating temperature [12]. This creates a reactive species, probably a surface-stabilized radical [13], that ideally leads to the formation of a covalent bond at predefined positions with other activated molecules [9,10,13–18].

In such molecular polymerization processes, the surface is not only a supporting template, but has also a strong influence on the molecular growth. This concerns on the one hand the geometric arrangement that can be confined by an anisotropic surface [10,19,20] as the molecules prefer a certain orientation and/or diffusion direction. On the other hand, it has been reported that the linking process differs strongly when using the same surface orientation of different materials in fcc crystal structures (gold, silver and copper) [13]. While closed-packed islands grow on Ag(111), rather chain-like structures prevail on Cu(111) instead of islands [13]. In addition to influencing molecular diffusion, the surface can also lower the energy barrier needed for coupling reactions by its catalytic activity. The activation temperature

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for cleaving a carbon–bromine bond is typically below room temperature on Cu(111), while on Au(111) a heating step of at least 370 K (and typically 520 K for efficient dissociation) is required [21]. This difference is essential for molecules with low desorption or dissociation temperatures as they for instance decompose before covalent linking on Au(111). Furthermore, metal–ligand bonds can be formed on a Cu(111) surface due to the availability of copper adatoms [22].

In the present study, we chose dibromohexabenzocoronene molecules ($\text{Br}_2\text{-HBC}$; Fig. 1a) as they represent a very small flake of graphene. Due to their extended aromatic system, this class of molecules is of interest for the bottom-up synthesis of covalent [23,24] and supramolecular [25] constructs for efficient charge transport. A detailed understanding of their (covalent) polymerization behavior on surfaces could lead to the formation of planar polymers with various shapes and chemical compositions [23,24]. The pure HBC molecules have been deposited onto copper and gold metal surfaces [26] by sublimation under ultrahigh vacuum (UHV) conditions, which is not possible for larger graphene flakes [27], and were found to adsorb in a planar configuration due to their van der Waals interaction with the substrate [28]. The Br atoms were attached in a trans geometry to result in linear chains after polymerization as has been shown in previous experiments for halogen atoms at opposite termini [9,10,12,29].

2. Material and methods

All experiments were performed in an ultra-high vacuum chamber with a base pressure of about 10^{-10} mbar. Au(111) and Cu(111) surfaces were cleaned before molecule deposition through neon sputtering and subsequent annealing at 780 K. The molecules were then evaporated from a Knudsen cell onto the substrates kept at room temperature. The molecular flux, monitored by a quartz micro balance, was between 0.01 and 0.1 monolayers per minute. After transferring the sample into the STM chamber, measurements were done with a low temperature scanning tunneling microscope (modified Createc version) at 10 K. HyperChem was used to calculate the gas phase molecular structure with a molecular mechanics approach.

3. Results and discussion

3.1. Au(111)

After deposition onto the Au(111) sample, we observed that the molecules assemble in large islands (Fig. 1c–d), due to their mobility at room temperature on this surface. A single $\text{Br}_2\text{-HBC}$ molecule appears as a rectangle with two bright lobes attached at opposite ends (highlighted by the green circle in Fig. 1d). The dimensions of

a single $\text{Br}_2\text{-HBC}$ molecule (determined from the full width half maximum of the height profile with respect to the metallic surface) are 1.93 ± 0.04 nm along the Br axis and 1.29 ± 0.05 nm perpendicular to it, which are in good agreement with previous experiments of pure HBC molecules [26,30]. Thus, the hexagon corresponds to the HBC core while we assign the bright lobes at the termini to the bromine atoms.

In addition to the $\text{Br}_2\text{-HBC}$ molecules, we found three more species on the surface that also have a hexagonal shape but different numbers of Br substituents (Fig. 1b): $\text{Br}_3\text{-HBC}$ molecules with three lobes attached (outlined by the blue circle in Fig. 1d), $\text{Br}_1\text{-HBC}$ with one Br substituent (black circle) and the HBC without halogen atoms (gray circle). The length perpendicular to the Br axis is the same for all four cases, pointing to an equivalent molecular core. By counting the different species ($n = 256$ in total), we found that 87% of the molecules are intact (two Br atoms), 5% have three Br substituents, 6% have only one and less than 2% have none (Fig. 1b). This is probably also the composition of the synthesized substance that is filled into the evaporator (note that analysis after the final cyclodehydrogenation step in the chemical synthesis is severely limited by the very low solubility of the material [31]). An alternative explanation would involve molecular activation on the surface, which however seems unlikely as no Br dissociation has been observed so far on Au(111) at room temperature [9,10,22] and would furthermore hardly explain the presence of $\text{Br}_3\text{-HBC}$ molecules. Moreover, this is in agreement with the complete absence of polymer structures on the surface, which would be created if molecular activation had taken place on the surface (and the molecules are sufficiently mobile which is apparently the case as molecular islands are formed; see Fig. 1c). This interesting observation indicates that the $\text{Br}_1\text{-HBC}$ and HBC molecules are not a reactive species because they were not formed by Br dissociation (in the evaporator or on the surface, hence under ultrahigh vacuum conditions). In contrast, they were produced in the molecular synthesis and are therefore saturated and have no radical character. In addition to the molecules, small protrusions are filling the free space inside the molecular islands. Their precise nature is unclear, but they are likely individual Br atoms deposited from the evaporator. However, most of them (>50%) desorb already at around 250 °C, in contrast to typically much higher desorption temperatures for bromine on noble metal (111) surfaces [32].

To activate the molecules by dehalogenation, we heated the surface for five minutes at 520 K, similar to previous studies [9,10]. This causes a coverage reduction from 0.25 to 0.16 monolayers, indicating that the molecules desorb at this temperature. Most importantly, HBC chains were formed by this heating step as intended. The majority of the HBC oligomers appear as dimers and their limited chain length (maximum of nine HBC units) is probably caused by two effects: First of all, the

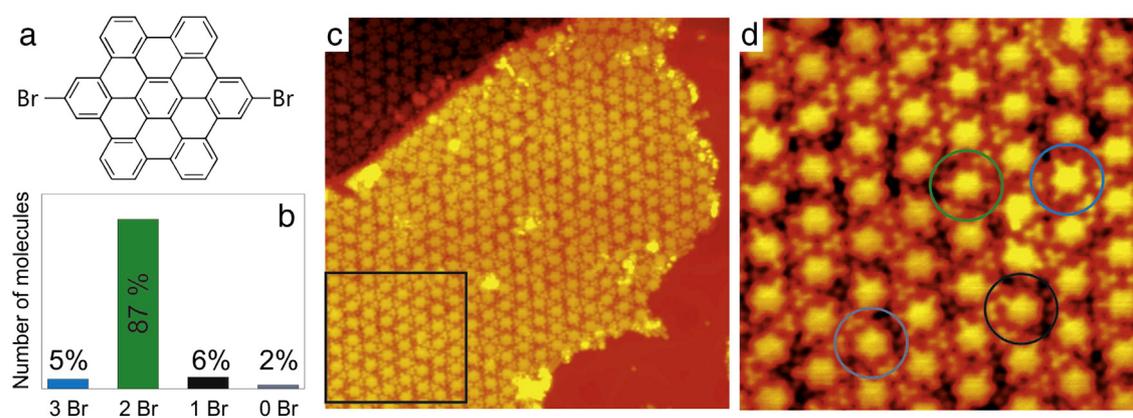


Fig. 1. (a) Chemical structure of $\text{Br}_2\text{-HBC}$. (b) Percentage of the HBC with three, two, one and none Br attached after deposition at room temperature (from 256 molecules in total). (c) STM image (39×38 nm²) of $\text{Br}_2\text{-HBC}$ deposited on Au(111) with a zoom (in the indicated rectangle) in (d) (13×13 nm²). The circles in (d) indicate individual HBC molecules with either three (blue), two (green), one (black) or no (gray) bromine substituent attached. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

substrate–molecule interaction is enhanced with increasing chain length and simultaneously the diffusion barrier rises. This barrier is indeed expected to be higher for the planar aromatic system of HBC than for more weakly interacting molecules [10,29,33]. Second, in contrast to other studies, molecules ($\text{Br}_1\text{-HBC}$) are available that terminate the polymerization process, since they can only form a bond on one side. However, the latter argument is of minor importance as the relative abundance of $\text{Br}_2\text{-HBC}$ and $\text{Br}_1\text{-HBC}$ on the surface (see above) would statistically result in chains of 15 units.

To determine the bond type formed between the HBC molecules we measured the molecule–molecule distance within a chain by taking the full width half maximum (FWHM) with respect to the substrate. STM images have been calibrated by atomically resolved images of the Au(111) surface. From various images, we found an average distance of 1.33 ± 0.05 nm between the molecular centers. This value is in very good agreement with gas phase calculations performed with the molecular mechanics package of HyperChem that predicts 1.29 nm and thus reveals that the HBC molecules are linked by covalent carbon–carbon bonds (see scheme in Fig. 2b). In contrast, a metal–ligand bond via a gold atom that links two HBC molecules can be excluded since the distance between the molecular centers would be 1.52 nm, according to our HyperChem calculations (in the gas phase), and thus is much larger. A further proof for the covalent nature and stability of the chemical bond can be obtained by STM manipulation to laterally displace the entire polymer in contrast to monomer detachment that happens for metal–ligand bonds [9,22]. During such an experiment, the tip is first approached vertically from the scanning position to the surface and then moved over the molecule along a predefined path (indicated by the blue line in Fig. 2d–f) at constant current (150 nA with a bias voltage of 25 meV). STM images before (Fig. 2c) and after manipulation (Fig. 2d–f) illustrate the induced changes. In this manipulation sequence, we first moved small trimer chains off the island (Fig. 2d). Then, we separated the hexamer chain by displacing it to the left (Fig. 2e) and then downward (Fig. 2f) in the image area. Note that we started every manipulation at the end of the chain. The rest of the chain follows the manipulation pathway without decomposing, which points to a covalent carbon–carbon bond in contrast to weaker bonds that are destroyed [22]. These experiments are started at a rather large tip height, i.e. weak tip–molecule interaction that is then reduced step-

by-step until a molecular displacement is obtained. By following this strategy, it turns out that a relatively small tip–surface distance is required to move a chain (tunneling resistance of about 170 k Ω), indicating a relatively strong surface–molecule interaction, which is in agreement with the interpretation of the rather small average chain length above.

3.2. Cu(111)

To study the influence of the surface on the polymerization we then turned to Cu(111) as a substrate, which is more reactive than Au(111) and is known to support catalytic reactions [34–36]. The energy required to remove an atom from a Cu(111) step is lower than for Au(111) [37], which results in more diffusing copper adatoms at room temperature. Due to the higher catalytic activity, we found that most of the molecules are already partially activated after molecular deposition and have lost at least one Br while only 1% of the molecules are intact (Fig. 3b in comparison with Fig. 1b). The appearance and dimensions of a single $\text{Br}_2\text{-HBC}$ molecule on Cu(111) are similar as on Au(111).

It becomes clear from Fig. 3a that in many cases two HBC molecules are connected through a bright bridge, indicating a bond formation between them. Thus, chains are created on the Cu(111) surface without a heating step, which can be advantageous if the dissociation temperature of the molecules is low. Importantly, chains are assembled in a linear fashion, following the trans configuration of the Br substituents at the initial building blocks (Fig. 1a). In comparison to the Au(111) surface, the average length of chains is smaller on Cu(111). The major fraction of chains (33%) are dimers, larger oligomers appear at a smaller abundance (trimers: 24%, tetramers: 14%, pentamers: 8%, oligomers with at least 6 units: <1%). In the vicinity of the molecules small protrusions – particularly visible at the edges of the molecular island in Fig. 3a – are observed, which are probably due to individual bromine atoms. Since they are present on both studied surfaces (see Fig. 1d for the Au(111) case), they seem not to cause the observed difference in intermolecular linking on the two surfaces. Note that on Cu(111) the distance of 4.4 ± 0.1 Å between these protrusions is in good agreement with the reported ($\sqrt{3} \times \sqrt{3}$)R30° structure (with interatomic distances of 4.41 Å) of a mixed Cl/Br overlayer on Cu(111) [38], supporting our interpretation.

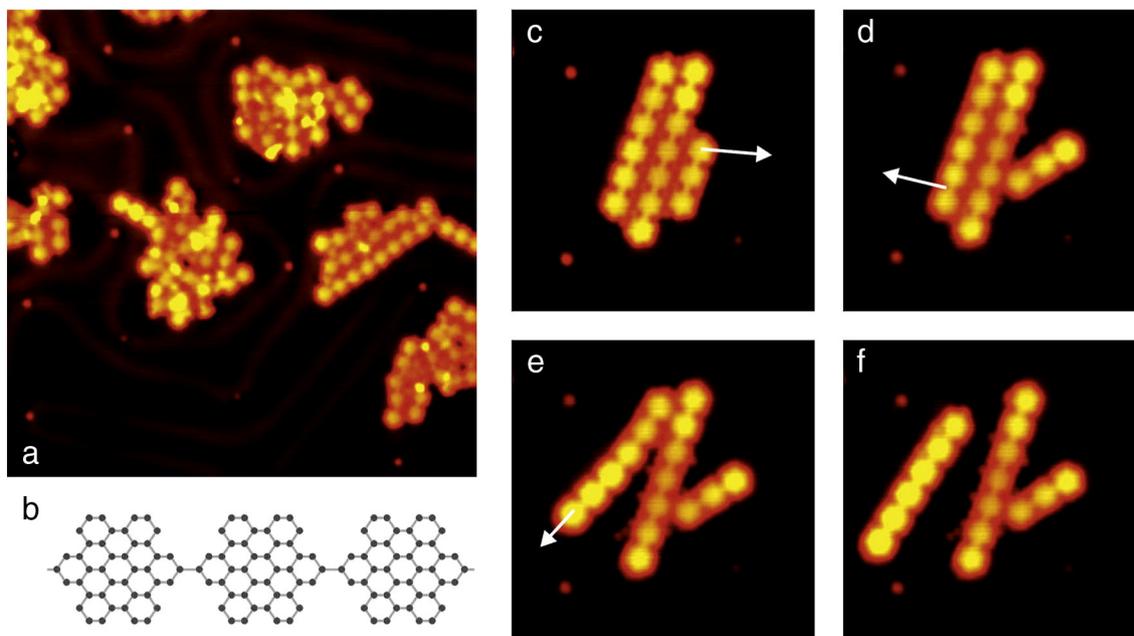


Fig. 2. (a) STM image of the Au(111) surface after heating at 520 K (37×37 nm 2). (b) Chemical model of the molecular chains formed on Au(111). (c–f) Manipulation series to prove the covalent nature of the bond (14×14 nm 2).

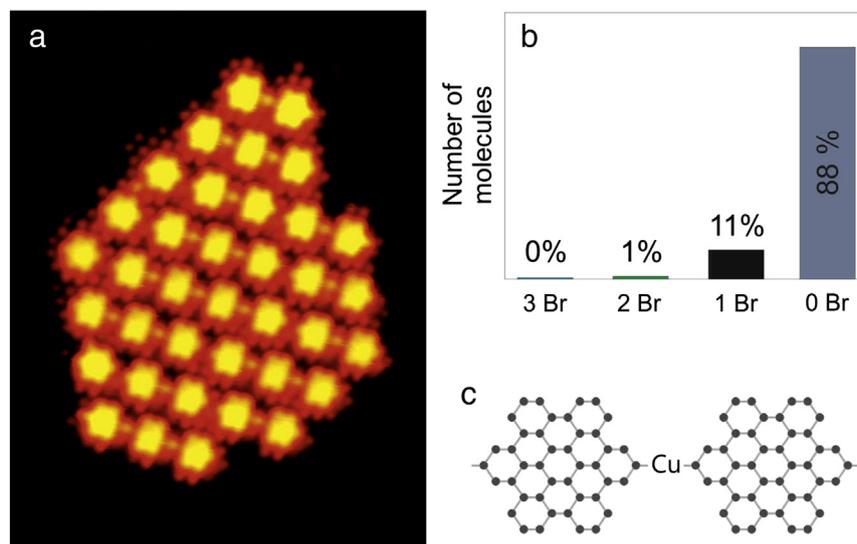


Fig. 3. (a) Image of diBr-HBC deposited at RT on Cu(111) ($13 \times 17 \text{ nm}^2$). The small protrusions are probably individual bromine, similar to the Au(111) case (Fig. 1d). (b) Percentage of the Br dissociation at RT (from 109 molecules in total). (c) Chemical model of the HBC chains formed on Cu(111).

Hence, both on Au(111) and on Cu(111) molecular chains are formed from Br_2 -HBC monomers, but only on Cu(111) a lobe appears between the molecules (Fig. 4a–c). Furthermore, the distance between two molecules (extracted from the FWHM of the height profile above the metallic substrates) is $1.55 \pm 0.05 \text{ nm}$ on Cu(111). This distance is slightly larger than on Au(111) ($1.33 \pm 0.05 \text{ nm}$) and also than for a covalently bonded HBC dimer according to gas phase calculations (1.29 nm). Together with the protrusion between the molecules, this points to a carbon–copper–carbon connection and indeed a distance of 1.52 nm is found for such an arrangement through gas phase calculations (sketched in Fig. 3c), in very good agreement with the experimentally determined value. The protrusions therefore reflect the Cu atoms that form the bond and are in this case clearly visible (in contrast to other metal–ligand bonds [22]), probably due to the planar HBC structure. Note that even after heating the Cu(111) surface at 450 K no polymerization could be observed, but all molecules desorb at this temperature.

To compare the bond strength of the HBC chains on Cu(111) to the covalently bonded chains on Au(111) we again used lateral constant-current manipulation (Fig. 4d–e) and applied two manipulation sequences at different bias set points. During the first manipulation a tunneling current of 100 nA and a bias voltage of 50 mV, which correspond a tunneling resistance of 500 k Ω , are used to move the chain to the right side in Fig. 4d. In the second manipulation the same tunneling current is used but the applied bias voltage is reduced to 17 mV (a tunneling resistance of 170 k Ω) which leads to a smaller tip–sample distance during the lateral manipulation (note that high tunneling resistances correspond to large tip–sample separations and vice versa). The resulting interaction between the tip and molecule is apparently sufficient to cleave an intermolecular bond. Two HBC molecules are removed from the surface after the manipulation. In contrast to similar experiments [22], we could not identify the copper adatoms after bond cleavage. Note that during manipulation of the covalently bonded chains

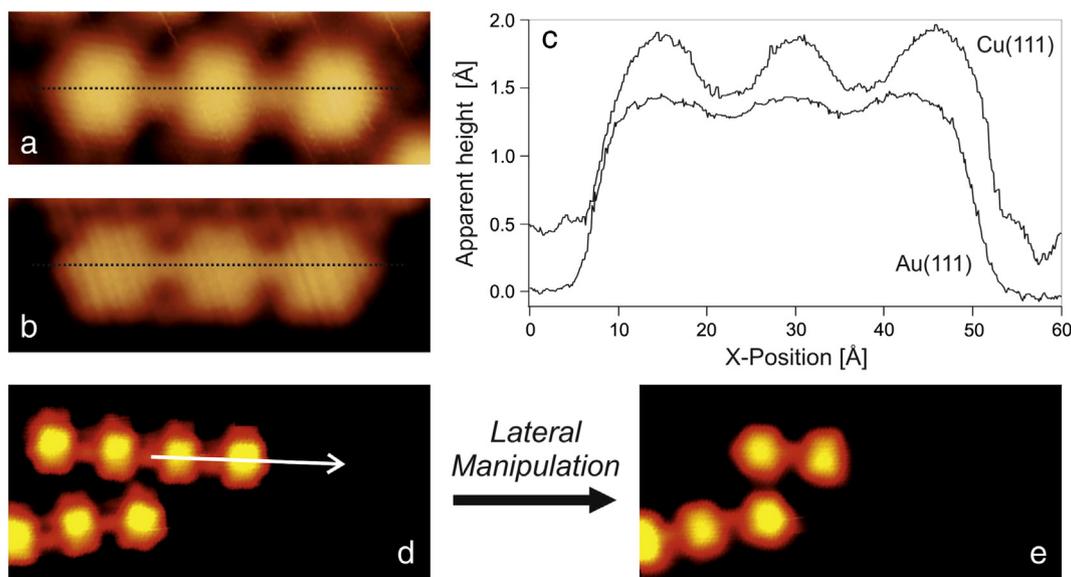


Fig. 4. (a) HBC chain on Cu(111) ($5.5 \times 2.0 \text{ nm}^2$, -300 mV , 0.3 nA). (b) HBC chain on Au(111) ($5.5 \times 2.0 \text{ nm}^2$, -300 mV , 0.1 nA). (c) Line scan along a HBC trimer on Cu(111) and Au(111). (d–e) Manipulation of a HBC chain on Cu(111) ($10 \times 5 \text{ nm}^2$).

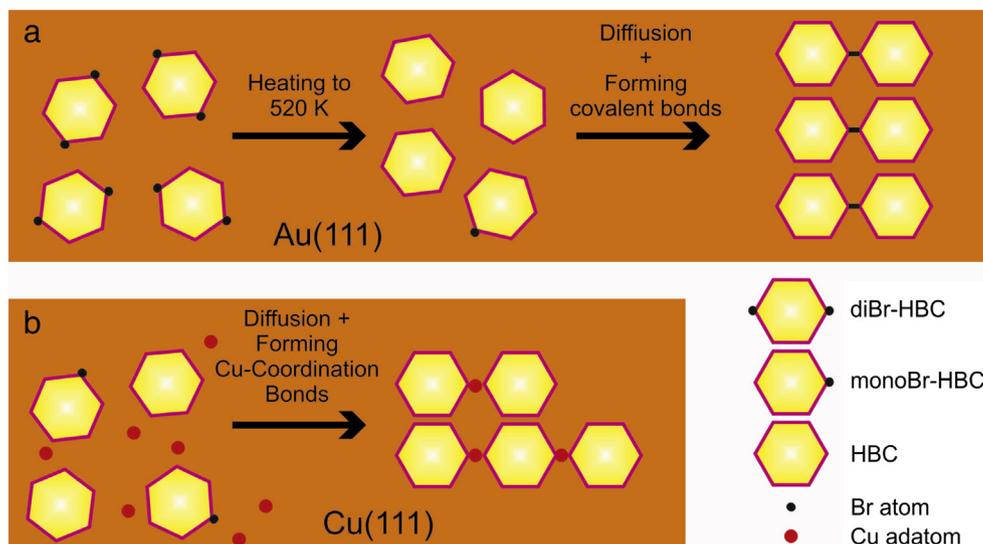


Fig. 5. Illustration of the chemical process on Au(111) (a) and Cu(111) (b).

on Au(111) the tunneling resistance and thus applied force was the same but no cleavage of the chains was observed, in agreement with the covalent nature of the bonds.

4. Conclusion

In summary, we could show that two qualitatively different types of covalent bonds are formed between two HBC molecules, depending on the type of noble metal substrate (as sketched in Fig. 5). On Au(111), a covalent carbon–carbon bond between the HBC molecules is formed after annealing the surface at 420 K. In the case of Cu(111), no heating step is required as the molecules are activated directly after deposition on the substrate at RT and connected via a central Cu-atom by two-fold metal–ligand bonds. In both cases, the connection between the HBC molecules is predetermined by the position of the halogen-substituent enabling precise molecular construction that depending on the choice of the substrate can involve either covalent (carbon–carbon) or metal–ligand (carbon–copper–carbon) linkages. The reason for this surface-mediated effect is on the one hand the spontaneous dehalogenation on Cu(111) at room temperature, which is absent on Au(111), and on the other hand the different desorption temperatures on the two metals. While we can heat (and polymerize) the molecules on Au(111) up to at least 250 °C, complete desorption is observed on Cu(111) already at 180 °C, thus probably not allowing to reach the temperature required to form a covalent carbon–carbon bond.

Acknowledgments

We thank the European Union for funding via the Projekts AtMol (grant number 270028) and ARTIST (grant number 243421).

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