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

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ABSTRACT

The coupling of dibromohexabenzocoronene (Br_2-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.

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 (Br_2-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 Br_2-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 Br_2-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 Br_2-HBC molecules, we found three more species on the surface that also have a hexagonal shape but different numbers of Br substituents (Fig. 1b): Br_3-HBC molecules with three lobes attached (outlined by the blue circle in Fig. 1d), Br_1-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 Br_3-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 Br_1-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

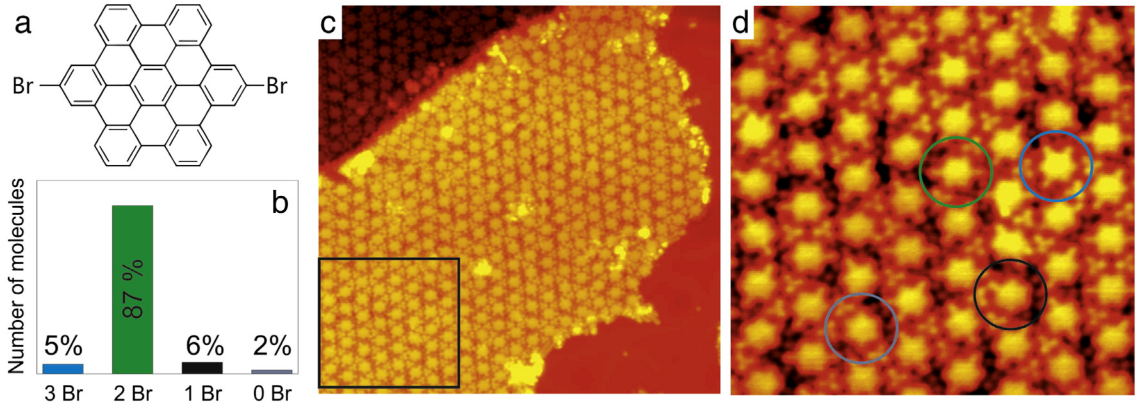

Fig. 1. (a) Chemical structure of Br_2-HBC. (b) Percentage of the HBC with three, two, one and none Br attached after deposition at room temperature (from 256 molecules in total). (c) STM image (39 × 38 nm^2) of Br_2-HBC deposited on Au(111) with a zoom (in the indicated rectangle) in (d) (13 × 13 nm^2). 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.)