Surface-confined [2+2] Cycloaddition Towards One-dimensional Polymers Featuring Cyclobutadiene Units

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Surface-confined synthesis has been offering a wide range of opportunities for the construction of novel molecular nanostructures. Exploring new types of on-surface coupling reactions is considered essential for being able to deliberately tune the materials properties. Here, we report on the formation of a covalent C–C bonding motif, namely 1,3-cyclobutadiene, via surface-confined [2+2] cycloaddition between pyrene moieties using low temperature scanning tunneling microscopy (LT-STM) and X-ray photoemission spectroscopy (XPS) measurements. By employing a hydrogen dosing treatment together with low-temperature activation, we were able to both eliminate residual byproducts and obtain covalent 1D polymers through the formation of 1,3-cyclobutadiene units. The results present a C–C bonding motif hardly explored in surface chemistry and provide substantial evidence that the hydrogen treatment is crucial towards the removal of byproducts in surface-confined polymerization.

Introduction

Around one decade ago, surface-confined synthesis under ultra-high vacuum (UHV) conditions was introduced as an alternative method to traditional solution-based synthesis for the bottom-up fabrication of low dimensional π-conjugated nanostructures.1–8 This method has opened up new possibilities for the construction of extended molecular nanoarchitectures on surfaces in a controlled fashion, offering a versatile playground for potential applications in future electronic devices.8–12 In this context, different types of chemical reactions have been employed for the fabrication of tailored 1D and 2D covalent nanostructures, including Ullmann-type coupling,1,10,13–19 cyclodehydrogenation,10 condensation reactions,20 acetylenic homocouplings (i.e., Glaser or Hay coupling),21,22 alkane dehydrogenation23 and others.3,24–26 To date, Ullmann-type coupling has been the most frequently used reaction. However, the halogen atoms split off during the polymerization reaction have been often observed to chemisorb on the metal surface and thus, are an undesired reaction byproduct, which can in turn cause structural modifications of the surface,27–30 and may even hamper the diffusion of the monomers which is important during the polymerization process. Therefore, it negatively influences the formation of well-ordered polymer structures. To desorb the split off halogen atoms from the metal surface, one generally needs to anneal the sample at high temperatures (> 523 K).31–33 However, such high temperatures may negatively influence the formed polymer networks or even destroy them. Recently, an alternative approach based on hydrogen dosing during the activation of the on-surface reaction and verified by temperature-programmed desorption measurements was presented for desorbing the split off halogen atoms during the polymerization reaction.34 However, hitherto there has been no direct microscopic visualization of the outcome of this process.

The formation of covalent C–C bonds of a 4-membered 1,3-cyclobutadiene ring, involving two endocyclic C=C bonds through a [2+2] cycloaddition of intermediate arynes (or biradicals), has been already known in solution.35–38 However, reports for such an interesting covalent dimerization are scarce under UHV conditions. A recent related work focused on the surface-confined formation of phthalocyanine derivatives on Au(111), where the 4-membered ring was formed by dimerization of alkenes and hence, it does not possess any endocyclic C=C bonds.39 Another interesting study employed a perylenetetracarboxylic dihydride derivative to synthesize graphene-type nanoribbons involving 4- and 8-membered rings which were formed via a stepwise process.40 Hence, up to now no direct experimental evidence of such a dimerization involving arylene intermediates in surface chemistry has been reported.

In this work, we also present a new on-surface synthesis protocol under UHV conditions for the formation of 1,3-butadiene units connecting pyrene derivatives into a 1D...
covalent polymer. Using 4,5,9,10-tetrabromo-2,7-di-tert-butylpyrene (1) as a molecular precursor, we investigated both the self-assembly and on-surface polymerization on coinage metal surfaces by STM and XPS measurements. We obtained well-ordered 2D self-assembled networks for the deposition of 1 on Au(111) held at room temperature. Upon thermal activation above 450 K combined with hydrogen dosing, the network undergoes covalent polymerization through the formation of 4-membered rings between the pyrene units. However, for the more active Cu(111) surface, we directly obtained 1D metal-coordinated polymer chains by deposition of 1 on the substrate held at room temperature.

**Results and discussion**

Deposition of submonolayer coverage of 1 on Au(111) held at room temperature results in self-assembled structures in two different arrangements with a relatively equal distribution: phases A and B. Fig. 1a and 1c present detailed STM images of phases A and B, respectively (for an overview STM image see Fig. S1). The characteristic Au(111) herringbone reconstruction is visible through the molecular adlayer and remains unaffected, which we ascribe to a weak molecule-substrate interaction.\(^4\) In the close-up STM image (Fig. 1a), the molecular structure of 1 is superimposed. The bright protrusions are ascribed to the tert-butyl groups.\(^4\) Fig. 1b shows the tentative model revealing the intermolecular interactions for the observed 2D pattern. The molecules are arranged in a rhombic unit cell with parameters \(a_1 = 1.30 \pm 0.12 \text{ nm}, a_2 = 1.60 \pm 0.14 \text{ nm}\) and \(\alpha = 44 \pm 2^\circ\). The direction \(a_2\) draws an angle of about 80° with the Au [110] direction. Taking into account the possible non-covalent interactions,\(^4\) we conclude that both weak intermolecular hydrogen bonds (along \(d_1\)) and van der Waals forces (along \(d_2\)) are responsible for the well-ordered phase A. Here, the average interaction distances are \(d_1 = 3.7 \pm 0.1 \text{ Å} \) (between Br and H in the tert-butyl groups of the neighboring molecules, marked by the red dotted lines) and \(d_2 = 2.7 \pm 0.1 \text{ Å} \) (between H and H in the neighboring tert-butyl groups, marked by the black dotted lines), which are in good agreement with literature.\(^4\) Note that in our interpretation the halogen bonds between Br-Br of two neighboring molecules are neglected since the Br-Br distance \(d_{Br-Br}\) is too large (> 4.5 Å).

Fig. 1c shows a detailed STM image of phase B, which is, however, a rather complex molecular arrangement compared to phase A. From overview STM images (Fig. S2), one can observe a long-range periodicity of the groups of either three or four bright protrusions with the herringbone reconstruction easily visible underneath the molecular layer. These groups of three and four protrusions are labeled by triangles and ellipses in Fig. 1c. The molecules tend to align along the directions labeled \(a_1\) or \(a_2\), which draw an angle of ~22° with the Au [112] direction. The obtained phase B is stabilized by a combination of both hydrogen and halogen bonding.\(^4\) Here, the measured distances \(d_1\) (between Br and Br of the neighboring molecules) and \(d_2\) (between Br and H of the nearby molecules) amount to 3.3-3.9 Å and 2.1-3.6 Å, respectively. It should be noted that for this phase the repulsive interaction, due to the C–Br–Br–C angle (type-I interactions), between the halogens plays a role in forming the self-assembled network.\(^4\)
The formation of the chains as shown in a tentative model in Fig. 2d. The length distribution of the 1D polymers is presented in Fig. S4. The average distances between two nearest bright protrusions along and perpendicular to the chain amount to $a_n = 0.56 \pm 0.03$ nm and $b_n = 1.00 \pm 0.05$ nm, respectively (Fig. 2c). The experimental lengths are in excellent agreement with the distances determined from the proposed model structure for the bonding mechanism of the polymer chains, where $a_{nm} = 0.58$ nm and $b_{nm} = 1.03$ nm (Fig. 2d). In essence, the formation of the covalent polymer involving the 4-membered rings between the pyrene units is intriguing. The formation of such 1,3-cyclobutadienes via the [2+2] cycloaddition of intermediate arynes (or biradicals), has been well known in solution.30,31 Hence, our results provide clear evidence on the formation of covalent 1,3-cyclobutadiene-fused pyrene polymers under UHV conditions on a surface.

To gain further insight into the surface-assisted polymerization, we studied 1 on Au(111) by means of X-ray photoemission spectroscopy (XPS; Fig. 3). Fig. 3a shows the Br 3p XPS spectrum of the self-assembled network for the molecular deposition performed at room temperature. The spectrum was fitted with a single doublet showing two peaks located at 190.4 eV and 183.9 eV which correspond to the Br 3p$_{1/2}$ and 3p$_{3/2}$ component, respectively. The peak positions are indicative for intact Br–C bonds which is in good agreement with previous studies.47,48 The spectrum obtained for the sample annealed at 510 K was fitted with a single doublet, showing the Br 3p$_{1/2}$ and 3p$_{3/2}$ component situated at 188.2 eV and 181.8 eV, which can be associated with split off Br atoms residing on the Au surface. c) XPS spectrum after dosing hydrogen for 2 hours while keeping the substrate at 450 K obviously shows the absence of split off Br atoms on the surface.

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carried out to demonstrate the removal of Br atoms by the H-treatment. Thus, we conclude that with the help of thermal activation and hydrogen treatment, we are able to obtain covalent 1D 1,3-cyclobutadiene-fused pyrene polymers accompanied by a complete removal of halogen byproducts, which is corroborated by the excellent agreement between STM and XPS data.

Fig. 4. Deposition of 1 on Cu(111) held at room temperature. a) (50 x 50 nm²; 30 pA, -1.6 V) STM image visualizing 1D coordination polymer chains. b) (6.5 x 2.5 nm²; 30 pA, -1.8 V) Close-up STM image of a 1D polymer chain (the black dotted rectangle in a)). Two monomers are superimposed. c) Tentative model proposed for the 1D polymer chains.

Conflicts of interest
There are no conflicts to declare.

Experimental methods

4,5,9,10-Tetrabromo-2,7-di-tert-butylpyrene (1) was synthesized according to the literature procedure. All STM experiments were performed in a two-chamber UHV system (Oxford Instruments Omicron NanoScience) with a base pressure of 2 × 10⁻¹¹ mbar at liquid nitrogen temperature (77 K). The Au(111) and Cu(111) single crystals were cleaned by subsequent cycles of sputtering with Ar⁺ ions and annealing at 500° C and 480° C, respectively. The molecules were thermally evaporated from a glass crucible that was heated inside a home-built evaporator. A quartz-crystal microbalance was used to monitor the molecular deposition rate while the metal substrates were held at room temperature during deposition. All STM images were taken in constant current mode using a platinum-iridium tip. Image processing was done with the free software WSxM.

The XPS measurements were performed in another two-chamber UHV system using a hemispherical energy analyser employing Al Kα radiation with a photon energy of 1468.6 eV. The sample preparation was carried out in the same way as mentioned for the STM measurements. The Au 4f core level spectra were taken for referencing the XPS data.

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References


We report on the formation of 1,3-butadiene units between pyrene moieties through surface-confined [2+2] cycloaddition polymerization under ultrahigh vacuum conditions. We successfully demonstrated that the employed H-dosing treatment is a promising method for fabricating covalently linked nanostructures at reduced activation temperatures with improved structural ordering.