Surface Supported Gold–Organic Hybrids: On-Surface Synthesis and Surface Directed Orientation

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The surface-assisted synthesis of gold–organic hybrids on Au (111) and Au (100) surfaces is reported by thermally initiated dehalogenation of chloro-substituted perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs). Structures and surface-directed alignment of the Au–PBI chains are investigated by scanning tunnelling microscopy in ultrahigh vacuum conditions. Using dichloro-PBI as a model system, the mechanism for the formation of Au–PBI dimer is revealed with scanning tunnelling microscopy studies and density functional theory calculations. A PBI radical generated from the homolytic C–Cl bond dissociation can covalently bind a surface gold atom and partially pull it out of the surface to form stable PBI-Au hybrid species, which also gives rise to the surface-directed alignment of the Au–PBI chains on reconstructed Au (100) surfaces.

1. Introduction

On-surface reactions of large organic molecules have attracted increasing attention of chemists and surface scientists by providing new materials[1] and new insight into traditional reactions.[2–6] Various types of surface supported reactions have been intensively investigated in past decades, producing materials with formation of metal-organic coordination bonds,[7–10] carbon-carbon covalent bonds[11,12] and covalent metal-carbon bonds.[13] Among these on-surface synthesized products, gold-organic hybrids are of particular interest, as its local electronic structures studied by scanning tunnelling spectroscopy (STS) may allow a basic understanding of the electron transport through covalent Au-C bonds,[14–17] which is an effective connection between a gold electrode and organic molecules in molecular electronics.[18–20] However, due to the difficulty of such experiments only a few examples of gold-organic structures have been reported by means of single-molecule chemistry in a scanning tunnelling microscopy (STM) junction.[14–17]

Gold is known to cleave the C-X bonds by thermal or photochemical dissociation of alkyl halides[21] and has recently
been used as a catalyst in Ullmann coupling reactions,[22] which are traditionally considered as copper-mediated coupling reactions of aryl halide.[23] On Au (111) surfaces, thermally-initiated Ullmann coupling reactions have been reported as an effective way for aryl-aryl coupling under ultrahigh vacuum (UHV) conditions.[1,11,24-26] Covalently-connected metal-organic polymers have been predicted as an intermediate state by theoretical simulations both on Cu (111)[27] and Ag (111)[26] and verified experimentally in recent STM studies.[28] However, to the best of our knowledge, it has never been reported that such a stable gold–organic hybrid intermediate exists in aryl–aryl coupling reactions on gold surfaces.

In this work, we report the on-surface synthesis and the alignment of gold-organic linear polymers via a surface assisted coupling reaction between chloro-substituted perylene-3,4,9,10-tetracarboxylic acid bisimides (PBIs, specifically tetrachloro-PBI (1)) and gold atoms on Au (111) and Au (100) surfaces in a UHV environment. The reconstructed Au (100) surfaces are able to align the polymerized Au–PBI chains. The length of the Au–PBI chains is only restricted by the area of the terraces and thus can extend over several hundred nanometers. To investigate the mechanism of the formation of these gold-organic hybrids we adopt a similar precursor, one-side chloro-substituted PBI (dichloro-PBI 2, Scheme 1) as a model molecule. Systematic investigations on the influence of substrate temperature reveal an intermediate state (M-PBI-Au) at lower substrate temperatures before the formation of dimers (Au–PBI dimers) at higher temperatures. Density Functional Theory (DFT) calculations show that a dehalogenated dichloro-PBI will bind a surface Au atom, thus forming a complex that we identify as the M-PBI-Au species. This complex is able to form an especially stable dimer structure, which we identify as the Au–PBI-dimer. These results demonstrate that we can provide an effective way to build gold-organic hybrids with Au-C covalent bonds and gain deep insight both in reaction pathways and on the self-patterning of the polymers.

![Figure 1](image-url)  

**Figure 1.** (a) STM image (10 × 10 nm²) of the self-assembled structures of tetrachloro-PBI (1) prepared at room temperature on Au (111). The white ellipse marks a single molecule of 1, in which the bright bump on both sides of the molecule corresponds to the position of the chloro substituent. (b) Polymerized molecular chains of 1 on Au (111) surfaces prepared by depositing the molecules on the hot substrate (490 K) with a deposition rate of ~0.1 ML per hour. (c) High resolution STM image of a polymerized PBI-Au chain, obtained with tunnelling conditions of $V_{bias} = 1$ V and $I = 10$ pA, exhibiting bright protrusions of the gold atoms in the middle of the PBI units. (d) Proposed structural model of the polymerized PBI-Au chain.

### 2. Results and Discussion

#### 2.1. Surface Assisted Polymerization of Tetrachloro-PBI (1) on Au (111)

Shown in Figure 1a is an STM image of the self-assembled monolayers (SAMs) of tetrachloro-PBI (1) prepared on a Au (111) surface at room temperature (RT). Each single molecule appears as a combination of two small bumps and a big rod, corresponding to the short alkyl chains and the aromatic core of the PBI molecule, respectively. The bright spot on both sides of the core corresponds to the position of chlorine atoms, as the twisted structure caused by the repulsion of chloro substituents (see Scheme 1) can enhance the tunnelling probability correspondingly. A large-scale STM image (supporting information (SI) Figure S1) shows the herringbone like reconstructed ridges of Au (111), indicating that the adsorption and self-assembly of 1 cannot lift the reconstructed structures of Au (111). Linear molecular chains were prepared on hot Au (111) surfaces with either very low deposition rates (490 K, ca. 0.1 ML per hour) or at more elevated temperatures (510 K, ca. 0.1 ML per minute). Figure 1b displays a large scale STM image of the Au (111) surface, in which linear molecular chains with a maximum length of 70 nm can be observed. The directions of the molecular chains are mainly found along <110> directions of the Au (111) surfaces. Detailed structures of the linear chains can be observed.
from a high resolution STM image, as shown in Figure 1c. The chain is composed of parallel connected PBI units, visible as the enhanced tunnelling probability between two PBI units in the STM image at positive bias voltage ($V_{bias} = 1 \text{ V}$). The bumps on both sides of the chain correspond to the short alkyl chains of the PBI molecule. The significant higher noise level obtained on top of the bumps indicates that the chain is flexible and should be perpendicular to the surface plane.

The robust nature of the molecular chains has been proven by STM manipulation (Supporting Information, Figure S2). Although lateral movement and bending is observed, the interconnection between the PBI units is intact, indicating a strong coupling between the units. Since X-ray photoelectron spectroscopy (Supporting Information, Figure S2) of the sample prepared at RT and elevated temperature (490 K) shows the cleavage of the C–Cl bonds, it is thus reasonable to assume that the strong coupling of the PBI units results from the polymerization of the precursors. The measured periodic distance along the chain direction is $0.83 \pm 0.04 \text{ nm}$, which is very close to the distance (0.82 nm) obtained from the optimized structures of the Au–PBI chains by DFT calculations and notably larger than that of the covalently connected PBI dimer (0.66 nm). Our results indicate that the polymer should consist of gold-organic hybrids rather than covalently connected monomers, as shown in the model of the polymerized Au–PBI chains (Figure 1, panel d). To further confirm the formation of covalent Au–C bonds, we have performed differential conductance ($dI/dV$) measurements on different sites of the polymerized chain and compared with DFT simulations on the projected density of states (PDOS) of the PBI and Au in the Au–PBI chain (Supporting Information, Figure S3). The unoccupied states around 0.5 eV and 1.2 eV in STS agree well with the calculated results of the electronic states at positive energy (given with respect to the Fermi level $E_F = 0 \text{ eV}$) and differ from the unoccupied state (ca. 1.25 eV) of I. The mixing of the Au state with the $\pi$ orbitals of the PBI unit further confirms the formation of the covalent Au–C bonds.[16]

### 2.2. Oriented Alignment of the Polymerized Au–PBI Chains on Reconstructed Au (100)

Most of the Au–PBI polymerized chains are adsorbed on the reconstructed Au (111) surfaces along the <110> directions (Figure 1b). Correspondingly, the PBI units in the chains are adsorbed on the surface with its long axis along the <112> directions, the next-nearest-neighbour directions (the NNN directions, see Supporting Information Figure S1). The preferential orientation of the polymerized chains indicates that the substrate structure can be used to adjust the orientation of the polymerized chains. However, the reconstructed Au (111) surfaces with the herringbone ridges are too complex to align the polymerized chains. Featured with similar hexagonal structure in the first layer, the reconstructed Au (100) surfaces (Supporting Information, Figure S4) provide another possibility for the preferential adsorption of PBI molecules, similar to that on the Au (111) surfaces. In addition, the straight and uniform reconstructed ridges of the Au (100) surfaces are advantageous over the Au (111) for the long-range alignment of the polymerized chains.

**Figure 2a** shows the overview STM image of the polymerized Au–PBI chains prepared on the reconstructed hot Au (100) surfaces (ca. 500 K). The Au–PBI chains are located consistently along the [011] direction, namely the direction of the reconstructed ridges. PBI molecules in the chains are correspondingly adsorbed on the substrate with its long axis along the [011] direction (one of the NNN directions), which is a similar adsorption geometry as that on the Au (111) surfaces. The polymerized chains can extend to the whole area of the terrace with an approximate length of several hundred nanometers (Supporting Information, Figure S4). With a closer view of the highly oriented Au–PBI chains, the STM image of Figure 2b shows the structural relationship between the reconstructed Au (100) surfaces and the Au–PBI chains. Most of the polymerized chains are terminated on the reconstructed ridges of the Au (100) surface, as marked selectively by the white arrows in the image, indicating the favorable sites for the polymerization. Accordingly, a schematic model of the oriented Au–PBI chains on a reconstructed Au (100) surface is established on the basis of the STM observations, as shown in Figure 2c.

### 2.3. Mechanism for the Formation of the Au–PBI Hybrids and Surface Directed Alignment

To understand the mechanism for the formation of the Au–PBI chains and the substrate directed orientation, one-side chloro-substituted PBI (dichloro-PBI, 2) is adopted as a model
molecule for STM investigations on the surface-supported coupling reactions. Shown in Figure 3a is a STM image of the self-assembled monolayers (SAMs) of dichloro-PBI (2) prepared on a Au (111) surface at room temperature. A single molecule 2 is marked by a white ellipse for better recognition. Enhanced tunnelling probability on one side of the molecule shows the position of chloro substituents, indicating the stability of the C-Cl bonds during sublimation. When the molecule is deposited on hot Au (111) surfaces (ca. 500 K), different self-assembled structures are obtained by STM, as depicted in Figure 3b. A rectangular unit cell can be observed with unit parameters of $a = 1.76 \pm 0.04$ nm, $b = 3.30 \pm 0.04$ nm and $\gamma = 90^\circ \pm 2^\circ$. The unit cell marked in Figure 3b is composed of two coupled products. It is reasonable to propose that the coupled product should be Au–PBI dimer, as the product has similar structural characteristics with that of polymerized Au–PBI chains of 1, such as an obvious bump between two PBI units and measured intermolecular distance ($0.80 \pm 0.04$ nm) between aromatic cores. The formation of Au-C covalent bonds is also corroborated by the high resolution STM image (SI, Figure S5). Accordingly, a structural model of the SAMs of Au–PBI dimer is established, as shown in Figure 3c (cell parameters: $a = 1.76$ nm, $b = 3.3$ nm, $\gamma = 90^\circ$), in which both the Au-C bond length (2.1 Å) and the shortest molecule-molecule distance (e.g., C--O distance, 3.2 Å) are in a reasonable range.

To reveal the detailed reaction process, the effect of substrate temperature has been accessed by depositing molecule 2 on hot Au (111) surfaces maintained at various temperatures with the same evaporation rate of the precursor (ca 0.05 ML per minute). As shown in Figure 4, panels (a) to (f)
are typical STM images of Au (111) surfaces after the deposition of 2 at various substrate temperatures of 430 K (a), 460 K (b, c), 470 K (d), 490 K (e) and 500 K (f). At surface temperatures lower than 430 K, only dichloro-PBI molecules are observed on the surface (see Figure 4a). Domains of Au–PBI dimer (colored in green) are observed in the STM image occasionally when the substrate temperature reaches 460 K, as shown in the upper left corner of panel b. At the same time, the intact molecules and a new structure (colored by orange) coexist on the surface. The new structure, based on the STM image of the domain boundary and STS investigations, is considered as a mono-PBI-Au compound (hereafter, M-PBI-Au, see Figure S6 for more detailed information of the assignment). This is also supported by DFT calculations that a dehalogenated 2 will bind a Au atom from the substrate (see below). For a better view of the M-PBI-Au, a high resolution image and a structural model are displayed in Figure 4c. A commensurate \((4 \times \sqrt{3}T)\) structure of the M-PBI-Au SAMs is established on basis of the cell parameters of \(a = 1.16 \pm 0.04 \text{ nm}, b = 1.65 \pm 0.04 \text{ nm and } \gamma = 69^\circ \pm 3^\circ\). Such a commensurate structure is further supported by the measured angle \((19^\circ)\) of the long axis of the unit cell between adjacent mirror domains of M-PBI-Au SAMs (Supporting Information Figure S7).

As the temperature of the substrate further increases, the area of the self-assembled molecule 2 on the Au (111) surface decreases considerably. The STM image of the sample prepared at a substrate temperature of 470 K reveals that only large areas of M-PBI-Au, and small islands of the Au–PBI dimer could be observed on the surface (see Figure 4d). By further increasing the substrate temperatures to 490 K, the ratio of the covered areas between the Au–PBI dimer and the M-PBI-Au on the Au (111) surfaces are found to increase steadily and reach almost a ratio of 1:1 (see Figure 4e). An obvious difference between the domains of the M-PBI-Au and the Au–PBI dimer can be observed upon a closer inspection of reconstructed structures of the Au (111) surfaces in Figure 4, panel d and e. The reconstructed ridges of the Au (111) surface are lifted underneath the domains of the M-PBI-Au. The change of the reconstruction of the substrate also provides evidence for the structure of commensurate M-PBI-Au SAMs, as M-PBI-Au has strong interactions with the unreconstructed gold substrate and therefore lifts the surface reconstruction of the substrate (see following DFT calculations). The Au (111) surfaces covered predominantly by the Au–PBI dimer can be prepared by depositing PBI molecules on the substrate at a temperature of 500 K (Figure 3, panel f).

Regarding the substrate temperature effect, some important points should be emphasized: 1) the M-PBI-Au rather than the PBI radical prevails on the surface when the substrate temperature reaches an appropriate level (460 K) to dissociate the C-Cl bond; 2) the Au–PBI dimer can coexist with the M-PBI-Au at the beginning of the dehalogenation but the yield is remarkably lower than that of the M-PBI-Au; 3) an excess of Au–PBI dimer domains can be prepared on the surfaces at a substrate temperature of 500 K that is about 40 K higher than the onset temperature for the C-Cl bond dissociation.

DFT calculations have been performed to understand the above discussed points and the formation of the Au–PBI hybrid structures. The initial adsorption geometry of the molecule is predefined with the long axis of the molecule adsorbed along \(<112>\) directions, which is consistent with the adsorption geometry of the molecules observed from STM images (see Figure 4). As shown in Figure 5a, the calculations of a dehalogenated 2 on Au (111) indicate that a dehalogenated molecule will covalently bind and partially pull out a gold atom from the substrate thus forming the experimentally observed M-PBI-Au. Free radicals are often observed in Ullmann reactions occurring on copper surfaces, especially at the beginning of the dehalogenation on surfaces with low coverage of reactant. However, both our experiments and simulations indicate that the stable structure of dehalogenated 2 should be a gold-PBI hybrid rather than a free PBI radical. The gold atom bound to the PBI molecule is only partially pulled out of the surface and retains interactions with the substrate atoms (see Figure 5a). In this case, the adsorbate-substrate interaction should be relatively strong thus lifting the reconstructed structures of the Au (111) surfaces underneath (see Figure 4d). To further confirm the thermal stability of M-PBI-Au on the Au (111) surface, the adsorption energy of M-PBI-Au and intact molecule 2 on the Au (111) surface is calculated according to the formula:

\[
E_a = E_{\text{mol-sub}} - (E_{\text{mol}} + E_{\text{sub}})
\]

where \(E_{\text{mol-sub}}\) is the total energy of the adsorbed system, \(E_{\text{mol}}\) and \(E_{\text{sub}}\) represent the energies of the free molecule and the gold substrate, respectively. The calculated energy is 51.7 kcal/mol and 88.3 kcal/mol for intact molecule 2 and M-PBI-Au, respectively. The higher adsorption energy of M-PBI-Au suggests that M-PBI-Au is more thermally stable than molecule 2 on the Au (111) surfaces. The high adsorption energy (88.3 kcal/mol) of M-PBI-Au can also explain the observation of M-PBI-Au at substrate temperatures around 460–490 K.

Putting two PBI radicals on the Au (111) surfaces in a face-to-face geometry results in the energetically stable structure of the Au–PBI dimer (Figure 5, panel b). The Au–PBI dimer is calculated to be a stable organogold product generated by pulling out substrate gold atoms to form a flat
geometry. Compared with the structure of the M-PBI-Au, the gold atom is completely pulled out of the substrate in the case of the Au–PBI dimer, which implicates a weak interaction with the substrate. Therefore the reconstructed structure of the Au (111) surfaces is observable again underneath the SAMs of the Au–PBI dimer (see Figure 4f).

The Au–PBI dimer is observed on the surfaces simultaneously with the M-PBI-Au, but only prevails on the surface at a substrate temperature about 40 K higher than the onset temperature for the dehalogenation. Inversely proportional relationship of the M-PBI-Au and the dimer can be concluded from the STM results regarding the effect of substrate temperature on the reactions. Accordingly, it is reasonable to propose that M-PBI-Au is an intermediate state for the formation of the Au–PBI dimer. To verify this hypothesis, DFT calculations for the coupling reaction from M-PBI-Au to Au–PBI dimer have been performed by using the climbing image nudged elastic band (CI-NEB) method. The initial state (IS) is assumed to be two M-PBI-Au facing each other and the final state (FS) to be the Au–PBI dimer. As we find an intermediate state (IM in Figure 6), we carry out two separate CI-NEB calculations with 16 images to find the transition states from IS to IM and from IM to FS. The first reaction step involves the relative shift of the two M-PBI-Au structures, while the second one involves the back-donation of one Au atom to the substrate and simultaneous formation of the Au–PBI dimer. As demonstrated in Figure 6, the transition states TS1 and TS2, are similar in energy. TS1 is found to be up-hill by 17.8 kcal/mol with respect to the IS, and can be considered as the rate-limiting step in the reaction sequence. The formation of Au–PBI dimer (FS) from two M-PBI-Au involves an energy gain of 31.4 kcal/mol. Because of the low activation barrier, the formation of Au–PBI dimer can thus be expected to occur at relatively mild conditions. This calculation result can readily explain the simultaneous formation of M-PBI-Au and Au–PBI dimer since the energetic barrier from the M-PBI-Au to the Au–PBI dimer is quite low (17.8 kcal/mol). However, we must emphasize here that the energetic barrier might be slightly underestimated, since the two lower layers of the Au (111) slab are fixed and alkyl chains are not involved for simplification of the simulation. When two M-PBI-Au meet each other on the surface with a face-to-face geometry (see Figure 6, IS), the surface kept at the onset temperature for dehalogenation (460 K) may provide enough thermal energy to surmount the activation barrier from IS to TS1, leading to the formation of Au–PBI dimer. However, when two M-PBI-Au entities meet each other with the same adsorption geometry, SAMs of M-PBI-Au tend to form instead of the reaction to form Au–PBI dimer. Since the adsorption energy of M-PBI-Au is relatively high (88.3 kcal/mol), a higher substrate temperature (e.g., 500 K) can increase the mobility of the M-PBI-Au rather than desorb the molecule, thus increasing the probability of M-PBI-Au with face-to-face geometry. Therefore the Au (111) surfaces fully covered by Au–PBI dimer can be prepared at a substrate temperature 40 K higher than the onset temperature of dehalogenation with deposition rate of 0.05 ML per minutes. Such a rough explanation in kinetics is further supported by STM investigations on the product with sufficient reaction time. When the temperature of the Au (111) surfaces is controlled at the onset temperature for dehalogenation (ca. 460 K), long-time deposition of molecule 2 (e.g., 1 h) with a lower deposition rate (ca. 0.8 ML per hour) can lead to the formation of dominant SAMs of Au–PBI dimer (see Supporting Information, Figure S8). No SAMs of M-PBI-Au are observed from STM images of the sample, which further support the understanding that M-PBI-Au should be an intermediate state in the formation of Au–PBI dimer.

Both DFT calculations and experimental results reveal the key intermediate of the M-PBI-Au in surface supported coupling reaction of chloro-substituted PBI. A reaction pathway on basis of the initial state of the M-PBI-Au is thus proposed, in which the gold substrate is involved in the reaction by playing the role of a reaction pool for exchanging of gold atoms between adsorbed intermediate and surface atoms. This mechanism can tentatively explain the oriented alignment of polymerized Au–PBI chains on reconstructed Au (100) surfaces. The reconstructed ridges of the Au (100) are formed by the mismatch of the first hexagonal layer (lattice parameters ca. 2.76 Å) and the second rectangular layer (lattice parameters ca. 2.88 Å) with a slight rotation angle (ca. 0.8°) of the first layer.[31] Elevated gold atoms showing as bright ridges in the STM image should be easier to be exchanged with the Au–PBI complex or pulled out of the substrate by covalent bonding of PBI radicals and thus can determine the position of the coupling reaction. Manipulation of the Au–PBI chains on the Au (100) surfaces shows the missing ridge of the reconstructed gold underlying the polymerized chain (SI, Figure S9), indicating the participation of the substrate gold atoms in the coupling reaction. In addition, PBI molecules favor the adsorption geometry with its long axis adsorbed along the [011]direction. Both factors together determine the position and adsorption geometry of the coupling reaction, leading to the substrate directed alignment of the polymerized PBI-Au chains on the Au (100) surfaces.

3. Conclusion

In summary, surface-supported linear polymerization of tetrachloro-PBI on reconstructed Au (111) and Au (100)
surfaces has been investigated by STM in UHV environment, revealing the formation of long range gold-organic hybrids and their oriented alignment directed by the substrate. Using one side chloro-substituted PBI (dichloro-PBI), experiments on the effect of substrate temperature, combined with DFT calculations, reveal a reaction pathway for the formation of the Au–PBI dimer. A PBI radical bonded with one gold atom (M–PBI–Au) is considered as the intermediate in the coupling reaction to form Au–PBI dimers. These on-surface synthesized products (M–PBI–Au and Au–PBI dimer) are ideal candidates for further STS study on the electronic state of the molecule to investigate the effect of bonding geometry of Au-C covalent bonds. Our results also provide a way for controlled alignment of the polymerized molecular chains on single crystal surfaces which is fundamentally useful for the assembly of nanosystems and practically useful for the measurement of the bandgap of conjugated polymer lines.\[32]\n
4. Experimental Section

Single crystalline Au (111) and Au (100) surfaces (Mateck GmbH, Germany, 9 mm in diameter, orientation accuracy better than 1°) were cleaned by cycles of Ar-ion sputtering and annealing under UHV (base vacuum $3 \times 10^{-10}$ mbar) and were checked by STM, showing herringbone and stripe reconstructed structures, respectively. PBIs were then deposited onto the substrate by means of the organic molecular beam deposition (OMBD) technique. The substrate, heated by a filament on the back side of the sample holder, was maintained at a constant temperature for at least half an hour and measured by an infrared thermometer mounted outside the chamber. The infrared thermometer has been calibrated by a thermocouple (K type, fixed on a sample holder) in air. The systematic error for temperature measurement was estimated to be less than ±5 K due to the adsorption of the alumina view port and uncertainty in temperature measurement of the thermocouple. An Omicron low temperature STM (base vacuum $< 1 \times 10^{-10}$ mbar) was used to investigate the as-prepared samples at 78 K. X-ray photoelectron spectroscopy (XPS) was performed under UHV conditions (base vacuum $3 \times 10^{-10}$ mbar) utilizing monochromated Al K excitation and a Phoibos 100 hemispherical electron analyzer from Specs. PBIs 1 and 2 were synthesized by a method reported in literature.\[13]\n
Periodic DFT calculations were carried out using the VASP program.\[34]\n
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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