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On-surface synthesis of ethynylene bridged anthracene polymers

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Abstract: *Engineering low band gap π-conjugated polymers is a burgeoning area in basic and applied research. The main synthetic challenge lies in the solubility of the materials during the chemical synthesis which precludes the advance of the field. Here, we report an unprecedented on-surface synthesis protocol to overcome such difficulties, being able to design poly(p-anthracene ethynylene) molecular wires on an Au(111) surface. To this aim, a quinoid anthracene precursor endowed with =CBr₂ moieties is deposited and annealed to 400 K resulting in anthracene-based polymers, with a measured electronic bandgap of 1.5 eV. High-resolution non-contact atomic force microscopy with a CO functionalized tip unambiguously corroborates the nature of the ethynylene bridge bond between anthracene moieties. Complementary theoretical simulations of the reaction pathways illustrate the mechanism of the chemical reaction, highlighting three major steps: dehalogenation, diffusion of surface-stabilized carbenes, and homocoupling enabling the formation of an ethynylene bridge. Our results introduce a ground-breaking chemical protocol to design π-conjugated polymers based on oligoacene precursors and pave new avenues for advancing the emerging field of on-surface synthesis.*

The design and study of π-conjugated polymers has received great attention during the last decades, due to the relevant optical and electronic properties that emerge from the delocalization of their π-electrons. Such materials find use in different applications including light emitting devices, solar cells, organic field-effect transistors, photocatalysis and biosensors. Notably, they exhibit a large bandgap, which is tunable by chemical functionalization.[1-3]

However, despite great advances in the field from the synthetic point of view, there are enormous efforts from emerging areas of chemistry targeting to overcome the concomitant limitation of solubility, which precludes highly interesting conjugated nanomaterials to be synthesized by wet chemistry.[2, 3]
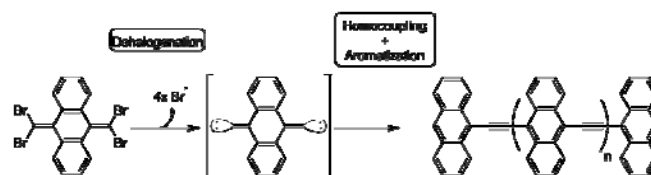
Contemporarily, on-surface synthesis has become a powerful discipline to design with atomistic precision a new plethora of molecular compounds, polymers and nanomaterials,[4-12] some of them not reachable by standard synthetic methods. In addition, on-surface chemistry enables the structural and electronic characterization of the designed products with advanced surfaces science techniques.[10, 13, 14]

Recently, and within the scope of on-surface synthesis, particular success has been achieved in the field of oligoacenes, where anthracene,[15] tetracene,[16] hexacene,[17] heptacene,[18, 19] nonacene[20], decacene[21] and undecacene[19] precursors have been deposited on coinage metals and transformed into oligoacene derivatives through external stimuli.

However, despite the great potential of such acene compounds for plastic optoelectronics, the design of high quality π-conjugated polymers exclusively based on oligoacene building units remains elusive.

Here, we report a comprehensive scanning tunneling microscopy (STM), non-contact atomic force microscopy (nc-AFM) and density functional theory (DFT) study of the on-surface synthesis of poly(p-anthracene ethynylene) molecular wires on Au(111). Our novel chemical approach is based on the dehalogenation, homocoupling and aromatization of a quinoid anthracene precursor endowed with =CBr₂ moieties at their 9- and 10- positions. The deposition of such precursor (11,11,12,12-tetrabromoanthraquinodimethane), abbreviated **4BrAn**, on Au(111) gives rise to a close-packed assembly. Annealing to 400K enables debromination, and, after diffusion of the species, long molecular wires based on ethynylene bridges are formed, unambiguously corroborated by the excellent agreement of experimental non-contact atomic force microscopy with theoretical simulations. A final step of annealing to 500 K induces the removal of peripheral bromine atoms and the subsequent emergence of isolated, high quality, robust, and long anthracene-based polymers. Scanning probe microscopy reveals the shape and the energy location of the frontiers orbitals, resulting in a bandgap of 1.5 eV. The theoretical study of the reaction pathways, complemented with high resolution scanning probe microscopy with CO-tip, illustrates that the homocoupling process is based on an efficient dehalogenation of the molecular precursors and diffusion of the surface-stabilized carbenes, finally leading to coupling and aromatization of the polymeric chain.

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Scheme 1. Scheme of the reaction sequence of **4BrAn** (11,11,12,12-tetrabromoanthraquinodimethane) precursor after being deposited on Au(111) and annealed.

Our study introduces a novel strategy to homocouple anthracene precursors, which could be extended to the whole family of oligoacenes. We envision that these results will notably contribute to the development of the field of on-surface chemistry, while providing novel avenues to design vanguard π-conjugated polymers in the form of molecular chains.

Scheme 1 illustrates the suitably synthesized molecular precursor **4BrAn** used for building up the desired anthracene-based polymers. Notably, it incorporates a =CBr$_2$ moiety at the positions 9 and 10 of anthraquinone backbone to steer dehalogenation and subsequent homocoupling upon thermal annealing[22] by undergoing an unprecedented reaction pathway as detailed below.
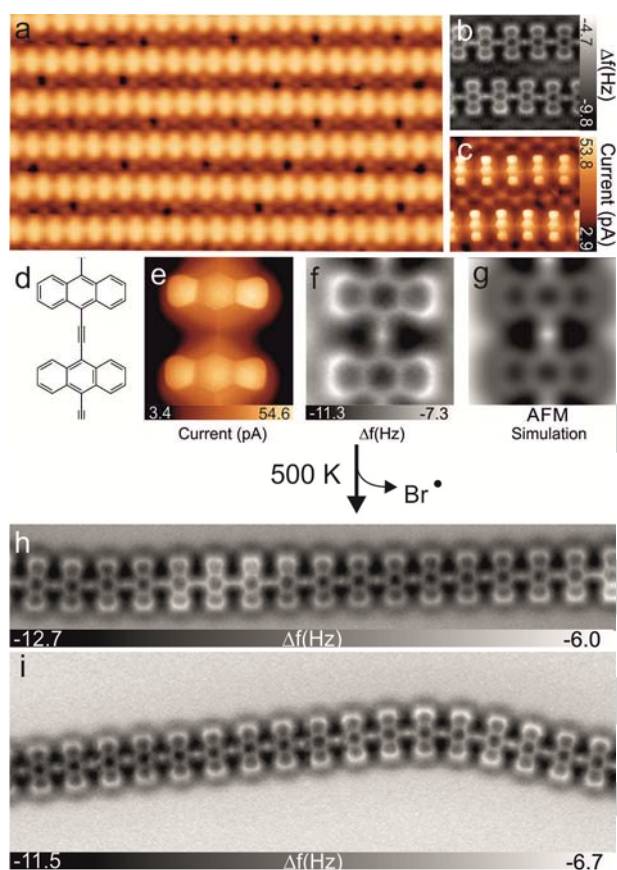

Figure 1. a) Large scale STM image of the on-surface design of ethynylene linked anthracene polymers, aligned in a parallel fashion and coexisting with bromine atoms, after depositing a submonolayer coverage of **4BrAn** on Au(111) and subsequent annealing at 400 K (Vbias = 100 mV, I = 10 pA, Size = 14.9 x 8.4 nm^2). b) Zoomed-in simultaneously acquired constant height nc-AFM and c) STM image (Size = 3.6 x 3.2 nm^2) of selected area of a). d) Chemical structure of an ethynylene bridged anthracene region. e) Constant height STM and f) nc-AFM image resolving the ethylene bond, which matches very well with g) the nc-AFM simulation (1.3 x 1.3 nm^2). h) Constant height nc-AFM image of a linear (size = 12 x 2 nm^2) and i) of a curved (size = 12 x 4 nm^2) ethynylene linked anthracene polymer after annealing a) to 500 K.

The deposition of a submonolayer coverage of **4BrAn** on Au(111) results in the formation of close-packed islands, featuring a rectangular unit cell (cf. Figure SI1). At this stage of

the reaction no bromine atoms are detected isolated on the surface, highlighting the integrity of the molecular precursors.

A first step of annealing to 400 K gives rise to the emergence of long polymeric wires (cf. Figure 1a and Figure SI2). The molecular precursors have now lost their bromine atoms, which can be found either forming 1D atomic chains over the surface, or being located in between the polymers directing their alignment in a parallel fashion (cf. Figures 1a and SI2). As illustrated by high resolution AFM imaging with CO-tip, the polymers are formed by anthracene moieties linked by ethynylene bridges. For adequate tip-sample height, the triple bond can be unambiguously distinguished as a bright protrusion (cf. Figure 1b,f and SI3), in agreement with recently synthesized poly(p-phenylene ethynylene) molecular wires on Au(111) by a distinct synthetic route.[23] The excellent agreement between experiment and simulated AFM images corroborates the ethynylene nature of the bridge (cf. Figure 1f,g) and differs from the previously reported formation of cumulene bridges by dehalogenative homocoupling of alkenyl gem-dibromides.[22]

At this step of annealing a small fraction of ethynylene bridged anthracene dimers and trimers is present. High resolution AFM resolves the conformation of such oligomers (cf. Figure SI4). Dimers are not planar due to the presence of the terminal C atoms from the =CBr$_2$ moiety at each termini of the dimer, which interact strongly with the substrate. Such assumption is proven through the excellent match between the experimental images and the simulated ones. Notably, the trimer exhibits a planar central anthracene, whereas the two terminal moieties are bent due to the interaction of the carbon termini with the gold support. Statistically, 90% of molecular precursors are engaged in the polymeric wires for a typical annealing of 30' at 400 K, the edge of which always present the same -C termination, resulting in that terminal anthracene moieties are bent towards the surface (cf. Figure SI4).

Importantly, the carbon termini of the dehalogenated species do for metal-organic complexes with gold adatoms, but diffuse as surface-stabilized carbenes until they connect forming the ethynylene bridged anthracene polymers. Such behaviour is also typically encountered on Au(111) for homocoupling of aryl halides.[22-25] It is worth to highlight that the formation of anthracene polymers results in the aromatization of the quinoid precursors, since the ethynylene bridges are preferred over the cumulene ones, regardless of the length of the polymer. The pro-aromatic nature of our quinoid precursor seems to be the driving force leading to the aromatization of the anthraquinoid core through electronic rearrangement. This scenario is fully supported by total energy DFT simulations, which also reveal the presence of the ethynylene bridges. The optimized structure of polymer is almost planar, located 3.4 Å above the Au(111) substrate, and being coupled dominantly via dispersion forces.

Further annealing of the sample to 500 K enables the desorption of the remaining bromine atoms, giving rise to isolated, long and very high quality ethynylene bridged anthracene polymers (cf. Figure 1h and Figure SI5). Notably, the wires exhibit a remarkable degree of flexibility, allowing open curvatures up to 130º through minute bending of the ethynylene links (cf. Figure 1i). In addition, the bond is robust and stands tip induced lateral manipulation processes, which results in a change in the curvature of the polymer, while preserving its chemical structure

(cf. Figure SI6), thus heralding promising prospects for flexible electronics.

At this stage of annealing, the major termini of the polymers have lost the remaining carbon and are passivated by residual atomic hydrogen, as illustrated in Figures SI7, SI8. Defects within the molecular chain are rare and structurally perfect ethynylene-bridged anthracene polymers with a length up to 30 nm are frequently observed.
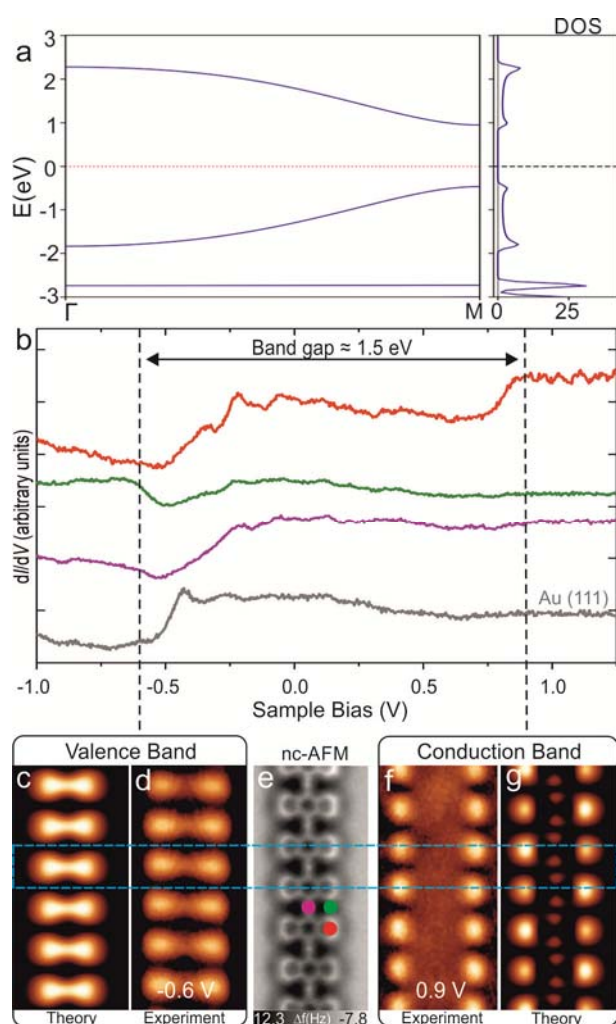

Figure 2. a) Calculated electronic structure of a free-standing ethynylene linked anthracene polymer with DFT-B3LYP. b) dI/dV scanning tunneling spectra acquired on the polymer on Au(111) at selected points indicated by the colored dots. c) Simulated image of the valence band. d) experimental dI/dV map at constant current of the valence band. e) nc-AFM image of a ethynylene linked anthracene polymer (size = 1.9 x 4.3 nm²). f) experimental dI/dV map at constant current of the conduction band. g) Simulated image of the conduction band . The dotted blue line is a guide for the eyes.

In order to elucidate the electronic structure of the π-conjugated polymers, we first calculated the electronic structure of freestanding polymer using B3LYP-DFT (cf. Figure 2a), which reveals the presence of dispersive valence (VB) and conduction (CB) bands separated by a band gap of ~ 1.4 eV. Calculated projected density of states of polymer on Au(111) indicates that

the dispersion of CB/VB remains practically unaltered, with only a slight reduction of the band gap due to additional electron screening from metallic substrate (cf. Figure SI9).

Spatially resolved scanning tunneling spectra were recorded over the molecular wires simultaneously with spectra on the clean Au(111) surface. As illustrated in Figure 2b, two frontier resonances are distinguished at -0.6 eV (green curve) and 0.9 eV (red curve), which are tentatively assigned to the valence (VB) and conduction (CB) band edges, respectively. Notice that the VB and CB edges are not located in the same position in space, the VB edge appearing in between anthracene moieties, and the CB edge on top of them. Within the bandgap the downshifted surface state convoluted with tip states is observed. In agreement with the point spectra, the dI/dV map at the VB edge (cf. Figure 2d) does not show maxima over the anthracene moieties, but it has states over the bridges and, remarkably, also on the voids adjacent to the links. The dI/dV map of CB, on the contrary, exhibits states located over the edges of the anthracene moieties (cf. Figure 2f). The calculated dI/dV maps (cf. Figure 2c,g) match very well with the experimental evidence, validating the character of band structure predicted by DFT calculations.

The analysis of experimental STS spectra reveals a band gap of 1.5 eV. The polymer shows a band gap *circa* 2 eV smaller than the 3.6 eV value recently reported for the HOMO-LUMO gap of a pure anthracene monomer on Au(111).[26] Notably, our results highlight the versatility of on-surface synthesis for designing polymers with varied bandgaps going from large values in the case of PMP (3.7 eV)[27] or PPP (3.2 eV)[28] to small quantities (1.5 eV) as reported here.

Finally, we studied the reaction pathway for the homocoupling of **4BrAn** on Au(111) with DFT-based transition state theory. The most favorable mechanism is shown in Figure 3 in which complete dehalogenation of the molecule initiates the reaction. An alternative reaction pathway is illustrated in Figure SI10 and discarded due to higher activation barriers. Removal of the third bromine has the highest activation energy (0.82 eV), and the full dehalogenation is highly exothermic with a reaction energy of -1.80 eV. The dehalogenated species (S_{deBr4}) can then diffuse along two of the main directions of the substrate (Fig. 3b) with a barrier of 0.53 eV. Finally, the activation energy for two molecules to come together and couple (Figure 3c) is 0.93 eV, similar to the dehalogenation step with highest barrier. The coupling is a second-order process and one may expect the occurrence of non-coupled S_{deBr4} species. However, this would require sufficient time for thermally equilibration of S_{deBr4} while avoiding coupling, *i.e.* the excess heat released during dehalogenation could explain the absence of monomers following the initial annealing. Notably, the coupling between two molecules is highly exothermic, as expected for the linking between two surface-stabilized carbenes.[24]

In conclusion, we report a strategy to on-surface synthesize ethynylene bridged anthracene π-conjugated polymers. To this aim, we rely on the combination of scanning tunneling microscopy and non-contact atomic force microscopy, complemented with state-of-the-art density functional theory.

The deposition of quinoid moieties equipped with =CB₂ termini on Au(111) and subsequent annealing enable a unique reaction pathway. A first annealing step to 400 K results in the

detachment of the bromine atoms and the diffusion of the resulting surface-stabilized carbenes till they homocouple forming high quality 1-D molecular wires. Non-contact atomic force microscopy combined with simulations elucidate the structure of such ribbons as unprecedented ethynylene bridged anthracene polymers. A second annealing step to 500 K enables desorption of bromine, giving rise to long flexible polymers, preserving the integrity of the ethynylene bridge. Importantly, such a polymer exhibits a low experimental bandgap of 1.5 eV.
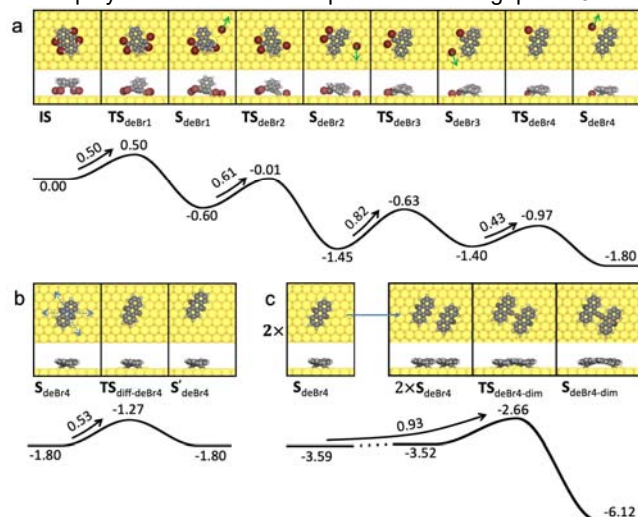
Figure 3. a-c) Energetically most favorable reaction pathway for the dehalogenative homo-coupling of **4BrAn** precursors on Au(111), depicting top and side views of local minima (**S**$_x$) and transition states (**TS**$_x$) with corresponding energy profile with respect to the initial state (**IS**): (a) initial dehalogenation cascade, (b) diffusion of dehalogenated molecule, and (c) coupling of two dehalogenated molecules. Units in eV.

Our results herald novel pathways to engineer π-conjugated polymers on surfaces, addressing the relevant family of acenes, and thus contribute to develop the field of on-surface chemistry and to steer the design of modern low bandgap polymers.

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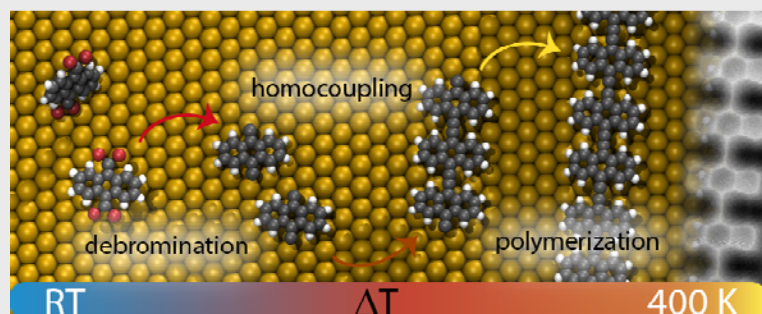
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Page No. – Page No.

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On-surface synthesis of ethynylene bridged anthracene polymers on Au(111) by debromination, homocoupling and aromatizacion of quinoid precursors endowed with =CBr_2 moieties.