Overcoming steric hindrance in aryl-aryl homocoupling via on-surface copolymerization

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On-surface synthesis is a unique tool to grow low-dimensional carbon nanomaterials with precise structural control down to the atomic level. This novel approach relies on carefully designed precursor molecules, which are deposited on suitable substrates and activated to ultimately form the desired nanostructures. One of the most applied reactions to covalently interlink molecular precursors is dehalogenative aryl-aryl coupling. Despite the versatility of this approach, many unsuccessful attempts are also known, most of them associated to the poor capability of the activated precursors to couple to each other. Such failure is often related to the steric hindrance between reactants, which may arise due to their coplanarity upon adsorption on a surface. Here, we propose a copolymerization approach to overcome the limitations that prevent intermolecular homocoupling. We apply the strategy of using suitable linkers as additional reactants to the formation of fully conjugated polycyclic nanowires incorporating non-benzenoid rings.

1. Introduction

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Over the last decades, low-dimensional carbon-based nanomaterials have received significant interest due to their potential use for applications.^[1] Their production via bottom-up processes is preferred to top-down strategies, as the former allows reducing the number of defects of the final products. This advantage permits the fabrication of nanostructures with homogeneous properties throughout the entire sample, without deviations due to defective species. In this context, on-surface synthesis has emerged as a powerful strategy to grow graphene-related nanostructures confined on a solid surface, with exact structural control.^[2,3] Precursor molecules, equipped with specific functional groups, are deposited on a substrate and activated in order to induce their coupling to form one- or two-dimensional (1D or 2D) extended nanostructures. Depending on the type and number of functional groups and chemical reactions employed in the process, different classes of products can be obtained, among which those interlinked via covalent bonds are of particular interest.^[4–7] In fact, covalent 1D and 2D networks are endowed with mechanical and thermal stability, and they allow the extension of π -electron conjugation, relevant for applications in organic electronics.^[8,9]

One of the most used chemical reactions to grow 1D and 2D polymers on metal surfaces is Ullmann coupling.^[10,11] Many studies have given insights into Ullmann-like reactions on various metal substrates,^[12–22] and the ability of synthetic chemists to create all sorts of building blocks has led to the realization of a wide range of graphene-related materials.^[23–27]

However, a careful construction of suitable precursor molecules is not the only requirement for the successful achievement of the targeted product via dehalogenative aryl-aryl coupling. The preferred adsorption geometry and specific molecule-substrate interactions have to be considered as well. Contrary to the approach offered by solution chemistry, on-surface reactions suffer from reduced conformational and orientational degrees of freedom. As a result, a molecule adsorbed on a surface cannot adopt all the geometrical arrangement and spatial orientations that it would adopt in gas phase or in solution. This fact is attributed to the energy gain associated to van der Waals interaction between the molecule and the surface. Thus, a planar molecular orientation upon adsorption on a substrate is usually energetically favored, even if full planarity is not always possible due to intramolecular steric hindrance. In some cases, only a partial planarization of limited regions of a molecular precursor is achieved. Most importantly, planar (or partially planar) molecular conformations and/or equal spatial orientation of reactants considerably reduce the probability that radical sites may approach each other for covalent bond formation.

A clear example of how geometrical constraints affect covalent coupling is given by the case of the 9,10-dibromoanthracene (DBA) molecule. In solution, DBA molecules can approach each other under a large dihedral angle, allowing access to the 9,10-positions for intermolecular C-C coupling. However, when DBA precursors are adsorbed on a solid surface, they adopt a planar adsorption geometry to maximize the van der Waals interaction with the underlying substrate. Homolytic cleavage upon debromination leads to the formation of radicals, the resulting anthracene biradicals diffuse on the surface and can only approach each other in their co-planar spatial orientation. This leads to repulsive interaction between *peri*-hydrogens next to the 9,10 radical positions which prevents the formation of the desired C-C bonds because the system cannot reach a transition state (with the radical positions close enough) suitable for C-C bond formation. Sterically inhibited polymerization may then result in the formation of organometallic chains, as reported for DBA on Ag(111)^[28] or in a slowly progressing hydro-

gen passivation of radicals by hydrogen from the rest gas.^[29] Similar outcomes have been reported for 5,11-dibromo-tetracene^[30] and tetrahydro-5,18:9,14-diethanoheptacene-19,20,21,22-tetraone^[29] on Au(111). Organometallic chains are not the only possible reaction products. In fact, if new intermolecular C-C bonds cannot be achieved, the radical sites may also give rise to intramolecular C-C bond formation, as in the case of 4,10-bis(2'-bromo-4'-methylphenyl)-1,3-dimethylpyrene on Au(111).^[31]

An elegant solution to overcome the steric repulsion issue discussed above was demonstrated for the on-surface synthesis of 7-AGNRs, where a precursor molecule composed of two anthracene units (10,10'-dibromo-9,9'-bianthryl, DBBA) was used.^[32] After its deposition on the Au(111) surface, DBBA largely retains its twisted gas phase conformation. The anthracene subunits of DBBA cannot be planar due to steric repulsion between their inner *peri*-hydrogens and maintain a dihedral angle of 54°. After debromination, the biradical molecules can thus approach each other to distances suitable for the C-C intermolecular coupling because the outer *peri*-hydrogens of each monomer are oriented in different spatial positions.

While this strategy was successfully used for anthracene-based precursors, it cannot generally be applied to all other systems. In fact, the sublimation temperature of a molecule increases with its mass, and it can reach values which are able to induce molecular dissociation or intramolecular cyclization and planarization upon sublimation. Therefore, alternative approaches are required. In this work, we propose the use of suitable linker precursors that undergo dehalogenative aryl-aryl coupling with selected building block precursors which cannot homocouple (Scheme 1). The selection of an appropriate linker unit is based on its ability to access the radical positions of the molecular building blocks, which often implies that the linker precursors can also undergo homocoupling.

We report herein two examples, with experiments performed on Au(111) under ultrahigh vacuum (UHV) conditions, demonstrating the versatility of our approach. The same linker (**3** in Scheme 1) is used to grow 1D polymers incorporating two building blocks (**1** and **2** in Scheme 1) that were initially designed for the on-surface synthesis of graphene nanoribbons (GNRs) (see Scheme 1 and Figure S1 in Supporting Information for further details) but for which it turned out that homocoupling is sterically inhibited. After a first copolymerization step, the copolymer subunits undergo further thermally induced chemical transformations (described below), finally affording fully conjugated polycyclic nanowires **4** and **5** incorporating non-benzenoid rings (Scheme 1). The resulting compounds are characterized by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM), which reveal the presence of newly formed five-membered rings. This strategy can in principle be employed in a wide variety of cases where homocoupling of molecular precursors is sterically restricted, permitting to access novel architectures of potential interest for organic electronics.

Scheme 1. Molecular schemes of the precursors and products discussed in this work. The building block precursors **1** and **2** are unable to undergo aryl-aryl homocoupling, and cannot be used to form GNRs. If suitable linker precursors (e.g. **3**) are used, a successful dehalogenative aryl-aryl coupling is achieved. The resulting copolymers are then converted into the fully conjugated polycyclic nanowires **4** and **5** upon further chemical transformations. See Figures S1, S3 and S6 for the complete reaction pathways.

2. Results and Discussion

In a first step, we have characterized the two systems composed of solely precursor **1** or **2**, respectively. As discussed above, homocoupling toward the formation of the targeted GNRs did not take place in either of the two cases due to steric repulsion between the planar molecular subunits when attempting the aryl-aryl coupling. Annealing of **1** to 535 K onto an Au(111) substrate results in the sequential dehalogenation and cleavage of the α -diketone moieties from the molecular backbone, as previously reported.^[29,33] Figure 1a,b shows constant-current STM images where Au-heptacene organometallic complexes coexisting with sporadic individual heptacene molecules (**1'**) are observed. Thus, the resulting radical sites that emerge from the dehalogenation are frequently quenched by the residual hydrogen gas present in the vacuum chamber or stabilized by Au complexation. The formation of **1'** is further confirmed by nc-AFM measurements using a CO-functionalized tip (see Figures 1c,d for the nc-AFM image and the corresponding chemical structure). The study of precursor **2** shows comparable results in terms of unsuccessful dehalogenative aryl-aryl coupling. After annealing of **2** to 640 K onto the Au(111) substrate, dehalogenation and subsequent cyclodehydrogenation of the molecular species are achieved. Figure 1e-h presents STM, nc-AFM images and the corresponding chemical structure of individual trapezoidal-shaped species, attributed to cyclohepta[4,5]fluoreno[3,2,1-de:6,7,8-d'e']dianthracene molecules (**2'**).

Figure 1. Unsuccessful aryl-aryl coupling of **1** and **2** on Au(111). (a,e) Large-scale STM images of samples obtained after depositing **1** (a) or **2** (e) on Au(111) at RT, and subsequent annealing to 533 K (a) and 643 K (e). Scale bars: 2 nm. (b,f) High-resolution STM images of **1'** and **2'**. Scale bars: 1 nm. (c,g) Laplace-filtered constant-height frequency-shift nc-AFM images acquired with a CO-functionalized tip. Scale bars: 1 nm (c) and 0.5 nm (g), respectively. (d,h) Chemical structure of **1'** (d) and **2'** (h). Scanning parameters: $V_b = -1.5$ V, $I_t = 100$ pA (a); $V_b = -1.5$ V, $I_t = 20$ pA (b); Z offset is -171 pm below STM setpoint: $V_b = 5$ mV, $I_t = 10$ pA (c); $V_b = -0.5$ V, $I_t = 10$ pA (d); $V_b = 5$ mV, $I_t = 2$ pA (e); Z offset is -100 pm below STM setpoint: $V_b = 5$ mV, $I_t = 2$ pA (f).

Next, the tendency of **3** toward homocoupling has been explored. Annealing of **3** to 625 K on the Au(111) substrate confirms the successful aryl-aryl coupling and subsequent cyclization of the methyl groups to form five-membered rings. These processes lead to the formation of 1D polymers (*poly-3'*) consisting of indeno[1,2-*b*]fluorene (**3'**) units (see Figure S2 for a detailed STM characterization of the room temperature and annealed phases), as previously reported by employing a similar molecular precursor.^[34]

In order to form polymers embedding the building blocks (B) **1'** or **2'** arising from **1** or **2**, respectively, we have performed codeposition experiments. For both systems, the same linker (L) was used, obtained from precursor **3**. First, **1** and **3** were deposited on Au(111) at RT with a ~1.8:1 stoichiometric ratio. Annealing the substrate to 543 K promotes the formation of the fully conjugated polycyclic nanowire **4**. The reaction steps leading to **4** – dehalogenation of both precursors, aryl-aryl coupling, cleavage of the α -diketone moieties from **1**, cyclization of the methyl groups of **3** toward five-membered rings, and further CH activation and ring closure – are known to occur at different temperatures^[29,34] and thus to proceed in a sequential fashion (see Figure S3 for the reaction pathway).

STM of the resulting surface reveals the presence of polymeric chains coexisting with some isolated molecules (Figure 2a). We attribute the isolated molecules to **1'** and broken species, while the observed chains are assigned to the successful formation of **4** (Figure 2d). Figure 2b,c report the STM and constant-height frequency-shift image of **4** where features assigned to the seven benzene rings of each heptacene molecule fused to **3'** units are clearly resolved. The junction between **1'** and **3'** is characterized by an extra five-membered ring, formed via CH activation in a similar temperature range as the cyclization of the methyl groups. It is worth mentioning that nanowires with a sequential alternation of the two molecular precursors were not the only obtained product, due to the capability of **3** to homocouple. Interestingly,

we did not observe the formation of heptacene organometallic complexes, as previously reported when **1** is annealed on Au(111) without the presence of a linker precursor.^[29] We attribute this behavior to the more energetically favored formation of the covalent nanowire in contrast to the organometallic structure. The observed nanowires are always terminated with **1**. This might be related to several aspects, such as (i) the high reactivity of the indenofluorene units, (ii) the ratio of precursors, and (iii) the hindered homocoupling of heptacenes, which increase the probability of hydrogen passivation.

To understand if the electronic properties of **4** differ from those of the isolated systems, we performed DFT calculations of a finite nanowire segment (see Figure S4). The density of states of **4** adsorbed on Au(111) has been projected onto its frontier orbitals in gas phase. The projection reveals that on the substrate, its HOMO-LUMO gap (identified to be 0.25 eV) is lower than the gaps of isolated *poly-3'* (1.20 eV)^[34] and **1'** molecules (0.50 eV, Figure S5). Indeed, experimental *dI/dV* spectra of **4** on Au(111) show peaks in the density of states at -0.60 V and $+0.20$ V, resulting in a band gap of 0.80 eV, smaller than the experimentally measured gaps of *poly-3'* (2.30 eV)^[34] and **1'** (1.50 eV)^[33] on Au(111). This band gap reduction can be attributed to the extension of the conjugation in **4**. Moreover, experimental *dI/dV* maps acquired at bias voltages corresponding to the maximum of the conduction and the minimum of the valence bands display features resembling the lobes observed at the heptacene periphery in DFT calculated HOMO and LUMO orbitals of a finite nanowire **4** in gas phase, confirming our results. Finally, the band structure of a periodic nanowire **4** in gas phase, calculated by DFT, reveals significant dispersion of the electronic states (Figure S6).

Figure 2. Nanowire **4** on Au(111). (a,b) High-resolution STM images of samples obtained after depositing **1** and **3** on Au(111) at RT, and subsequent annealing of the surface to 543 K. B and L designate the building block (**1'**) and the linker (**3'**), respectively. Scanning parameters: $V_b = -1.0$ V, $I_t = 10$ pA. Scale bars: 2 nm (a) and 1 nm (b), respectively. c) Laplace-filtered constant-height frequency-shift nc-AFM image of the polymer segment in (b)

acquired with a CO-functionalized tip. Scanning parameters: Z offset is 185 pm above STM setpoint: $V_b = 5$ mV, $I_t = 4$ pA. Scale bar: 1 nm. d) Chemical structure of the nanowire **4** observed in (c).

We have also investigated the propensity of **2** towards copolymerization with **3** using a similar stoichiometric ratio as the one employed for the formation of the nanowire **4**. Annealing the substrate to 600 K promotes the formation of chains, composed of trapezoidal-shaped motifs linked by linear units (Figure 3a), which are attributed to the fully conjugated polycyclic nanowire **5**. This product is achieved via the sequence of dehalogenation of both precursors, aryl-aryl coupling, cyclization of the methyl groups of **3** toward five-membered rings, further CH activation and cyclization (see Figure S7 for the reaction pathway). Figures 3b,c depict the STM and the constant-height frequency-shift image of the resulting nanowire **5**.

Figure 3. Nanowire **5** on Au(111). (a,b) High-resolution STM images of samples obtained after depositing **2** and **3** on Au(111) at RT, and subsequent annealing the surface to 600 K. Scanning parameters: $V_b = -1.0$ V, $I_t = 10$ pA. Scale bar: 2 nm. B and L designate the building block (**2'**) and the linker (**3'**), respectively. Scanning parameters: $V_b = -0.2$ V, $I_t = 10$ pA. Scale bar: 2 nm. (c) Laplace-filtered constant-height frequency-shift nc-AFM image of the copolymer strand highlighted in panel (b) acquired with a CO-functionalized tip. Scanning parameters: Z offset is -10 pm below STM setpoint: $V_b = 5$ mV, $I_t = 3$ pA. Scale bar: 1 nm. (d) Chemical structure of the nanowire **5** observed in (c).

To obtain more information regarding the length and the alternation of the B-L units in the two types of nanowires reported above, we have carried out a sequence analysis. Codeposition of B and L precursors was performed with a stoichiometric ratio of $\sim 1.8:1$. An excess of the building block precursors with respect to the linker precursor was required to reduce the chances of L precursors toward homopolymerization. Representative large scale STM images are reported in Figure S8. In the case of **4**, we found that 78% of **1'** molecules are incorporated in nanowires, while the remaining ones appear isolated on the surface. Conversely, all the linker units (**3'**) are embedded in nanowires. The histogram in Figure 4a shows the number of **3'** observed in between two **1'** units, i.e. the occurrence of n in $B-(L)_n-B$ segments. The distributions reveal that most of the **1'** species involved in a copolymer chain are separated by only one **3'** unit (69%), representing the targeted $---B-L-B-L-B-L---$ type of nanowire. The number m of repeating pairs in such $B-(L-B)_m$ coupling scheme is reported in the histogram in Figure 4b, which reveals a majority of short segments (similar to the number of heptacenes that form organometallic complexes in absence of any linker, probably due to hydrogen passivation),^[29] but also a few rather long nanowires, with a maximum m value of 10 (corresponding to 20.2 nm).

A similar outcome is observed for **5**, where 86% of the **2'** species are embedded in nanowires. Here, the number of **3'** observed in between two **2'**, i.e. the occurrence of n in $B-(L)_n-B$ segments, is shown in Figure 4c. As for the previous case, we find a majority of **2'** separated by only one **3'** unit (65%). Again, the strands of $B-(L-B)_m$ type are usually short, but we could identify a few long ones with a maximum m value of 5 (Figure 4d), corresponding to 13.8 nm long nanowires.

Both systems thus present a significant number of the targeted fully conjugated polycyclic nanowires with alternating units, even if the undesired motifs (L-L connections) could not be fully suppressed, as expected. To gain better control over the reactant sequence and to avoid undesired linkages further investigations will be carried out, based on an alternative design of the precursor molecules.

Figure 4. Length histograms of $B-(L)_n-B$ and $B-(L-B)_m$ segments of nanowires **4** (a,b) and **5** (c,d), respectively.

3. Conclusions

We have demonstrated a novel strategy for the dehalogenative aryl-aryl coupling of molecular building blocks unable to undergo homocoupling into extended architectures. The steric repulsion that prevents C-C bond formation between radical sites of identical molecules is circumvented by the use of suitable linkers. We have shown that such a copolymerization approach allows the on-surface synthesis of covalently linked chains with alternating building blocks, which are converted into fully conjugated polycyclic nanowires by a further annealing step. The two examples of nanowire formation on Au(111) reported in this work suggest the general efficacy of our approach. Due to the ability of the linker precursors to homocouple, complete control over the sequence of building blocks in the copolymers (and subsequent nanowires) could not be achieved. By careful design of the molecular precursors and the reaction pathways, in combination with specific substrates, it should, however, be possible to gain full control over the repeating sequence. In addition, the combination of different building blocks and linkers will allow the fine tuning of the electronic properties of the nanowires pro-

duced. These aspects will open new perspectives for the realization of relevant materials in organic electronics.

Methods Section

The experiments were performed in ultrahigh vacuum (UHV) with base pressure below 2×10^{-10} mbar. Au(111) (MaTeck GmbH) substrates were cleaned by repeated cycles of Ar^+ sputtering (1 keV) and annealing (740 K). The precursor molecules were thermally evaporated onto the clean Au(111) surface held at RT from quartz crucibles heated at the sublimation temperature of each precursor (633 K for **1**, 413 K for **2**, and 353 K for **3**), using a deposition rate of about $0.5 \text{ \AA} \cdot \text{min}^{-1}$. Subsequent thermal treatments were performed using a resistive element to anneal the sample with heating rate of about 1 K/s to the temperature reported in the image captions, which was held for 10 min before cooling down the sample. STM images were acquired with a low-temperature scanning tunneling microscope (Scienta Omicron) operated at 4.7 K in constant-current mode using an etched tungsten tip. Bias voltages indicated in each image refer to the sample (so that empty states are imaged at positive bias). The stoichiometric ratio of the co-deposited monomers has been determined by counting the absolute number of monomers belonging to the two molecular species, over more than 1000 molecules. Non-contact AFM measurements were performed with a tungsten tip placed on a QPlus tuning fork sensor.^[35] The tip was functionalized with a single CO molecule at the tip apex picked up from the previously CO-dosed surface.^[36] The functionalized tip enables the imaging of the intramolecular structure of organic molecules (see Figure S9 where the raw constant-height frequency-shift nc-AFM images together with their corresponding Laplace-filtered images acquired with a CO-functionalized tip are shown).^[37] The sensor was driven at its resonance frequency (22500 Hz) with a constant amplitude of 70 pm. The frequency shift from resonance of the tuning fork was recorded in constant-height mode using Omicron Matrix electronics and HF2Li PLL by Zurich Instruments.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Copolymerization, covalent coupling, on-surface synthesis, scanning probe microscopy

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On-surface synthesis can lead to the formation of novel carbon-based materials. Here, a copolymerization strategy circumventing the unsuccessful homocoupling of sterically hindered precursor molecules is presented.