Cleaning up after the Party: Removing the Byproducts of On-Surface Ullmann Coupling

Maryam Abyazisani, Jennifer M. MacLeod* and Josh Lipton-Duffin*

Abstract

Ullmann coupling is one of the most frequently employed methodologies for producing π-conjugated surface-confined polymers. One unfortunate side product of the reaction is the creation of metal halide islands formed from liberated halogen atoms. Following the coupling reaction, these halide islands can account for a large proportion of the substrate surface area and thus inhibit domain growth and effectively poison the catalyst. Here, we describe an efficient and reliable methodology for removing the halogen byproduct at room temperature by exposure to a beam of atomic hydrogen; this action removes the halogen atoms in a matter of minutes, with minimal impact to the polymer structure. We also find that it is possible under certain circumstances to preserve the pre-exposure epitaxy after removal of the halogen. This finding provides a convenient and straightforward technique for addressing the most often-cited drawback of the on-surface Ullman coupling methodology and provides access to a previously inaccessible parameter space for these types of experiments.

Introduction

Surface-confined polymerization has been the subject of intense study for the last 10 years since its inception in the mid to late 2000s. The concept of building materials from the bottom up, using rationally designed building blocks, is an alluring approach to generate materials that address challenges in electronics, sensing, energy storage, and other areas. The use of a flat surface as a template for the material bypasses the entropic penalties against forming planar materials that are inherent in solution synthesis. A wide variety of coupling methodologies have been studied in this context, including Glaser–Hay coupling, Sonogashira coupling, Bergman cyclization, Schiff base coupling, and decarboxylative coupling, all of which have been demonstrated to produce 1D or 2D materials on surfaces. However, the most popular methodology to date has been on-surface Ullmann coupling (Scheme 1).

Ullmann coupling is a particularly attractive approach as the substrate acts as a catalyst for the coupling reaction, meaning that only moderate thermal inputs are required to initiate the reaction. The reactants and products are readily identifiable both by morphological characterizations by scanning tunneling microscopy (STM) as well as chemical characterizations like X-ray photoelectron spectroscopy (XPS).

Scheme 1. On-Surface Ullmann Coupling of Dibromobenzene and Subsequent Removal of Bromine by Exposure to Atomic Hydrogen

\*Empirically determined temperatures are as follows: for both Cu(111) and Cu(110), \( T_1 < 25 \, ^\circ\text{C} \); for Cu(110), \( T_2 \geq 220 \, ^\circ\text{C} \); for Cu(111), \( T_2 \geq 275 \, ^\circ\text{C} \).

One drawback of the surface-confined Ullmann reaction is that the byproducts, halogen atoms abstracted from the aryl-containing building blocks, remain on the surface after the reaction.
These halogen atoms are often chemisorbed to the surface where they inhibit the diffusion of radicals,\(^{(16−19)}\) which in turn inhibits polymer growth.\(^{(20)}\) The polymers grow surrounded by halogens\(^{(21)}\) which effectively block catalytic sites of the surface,\(^{(22)}\) preventing additional dehalogenation and coupling events.\(^{(18,20)}\) This problem is often exacerbated by the tendency of small building blocks to undergo dehalogenative desorption during the deposition process,\(^{(23)}\) leaving a surface that is far richer in halogen content than would be suggested purely by the stoichiometry of the precursors.

There is, therefore, a concerted effort to either identify “clean” methodologies for producing surface-confined polymers\(^{(13,14,24)}\) or to find reliable procedures for removing the adsorbed halogen atoms from the substrate. A recent publication by Stöhr and co-workers\(^{(25)}\) demonstrated the effect of annealing Ullmann-coupled systems in a molecular hydrogen background: after a \(~2\) h annealing in a background of \(10^{-7}\) mbar H\(_2\) the halogen content of this surface was significantly reduced. The most likely mechanism is that the halogen is removed by splitting of the hydrogen molecule to form and subsequently desorbs as HBr.\(^{(26)}\) Here, we report on a significantly more efficient method of using a beam of atomic hydrogen to achieve halogen-free poly paraphenylene (PPP) from 1,4-dibromobenzene (dBB) on both Cu(111) and (110) after Ullmann coupling. Notably, the procedure may be performed at room temperature with a light annealing subsequent to halogen removal to improve ordering on the surface.

## Results and Discussion

### Cu(110)

Figure 1 shows an STM image of dBB deposited on Cu(110) held at 200 °C. The molecule dehalogenates upon adsorption and forms arrays of organometallic (OM) chains. The structure depicted is well-known from previous work; the phase appearing in Figure 1 corresponds to a saturated single monolayer of dBB OM assemblies.\(^{(27,28)}\) The bright features in these arrays correspond to the metal atoms separating each phenyl ring, and the smaller features are halogen atoms. Chemically similar but structurally distinct features are observed when the experiment is repeated using Cu(111) as the substrate (see below).
Annealing to 275 °C converts the OM chains to PPP. On Cu(110) this results in ordered arrays of PPP, with each polymer strand interdigitated with a row of bromine. The polymers are epitaxially matched to the substrate, running along \( \langle 1-1 2 \rangle \) (a subset of polymers may also run along \( \langle 1-1 0 \rangle \), which has been correlated with lower starting coverages).\(^{(27,29)}\)

Exposing the surface to a flux of atomic hydrogen at room temperature for sufficient time completely removes the bromine from the surface, as seen in the photoelectron spectra in Figure 2. The removal rate follows first-order kinetics, as evident from the logarithmic decrease of the ratio of the Br 3p signal to C 1s with respect to dosing time, presented in Figure 3. No substantive change in the intensity of the C 1s core level is observed after hydrogen dosing, but a progressively increasing shift toward higher binding energy is observed as the exposure continues. We presume that the removal rate is tied both to the binding energy of the bromine to the metal surface as well as the interaction between bromine and the organic species themselves. Since there appears to be a higher cohesive interaction between polymers and bromine on Cu(110) we expect the time required to remove Br to be substantially shorter on Cu(111), due to the absence of forces associated with halogen-polymer interaction. This is consistent with the results from our single exposure experiments where all of the Br was removed on Cu(111) after just 5 min (see below).
Figure 2. Photoelectron spectroscopy of (a) the C 1s and (b) the Br 3p core levels of PPP grown on Cu(110) (275 °C anneal for 5 min of dBB monolayer, cf. Figure 1), stacked as a function of atomic hydrogen exposure. Sample is held at room temperature throughout. Hydrogen cracker operated at 40 W in a background pressure of $5 \times 10^{-7}$ mbar.

Figure 3. Evolution of Br 3p:C 1s and C 1s:Cu 2p XPS intensity ratios of PPP grown on Cu(110) as a function of hydrogen exposure.

The removal of a substantial amount of Br from Cu(110) is correlated with a dramatic change in the surface morphology, as summarized in Figure 4. STM images collected from successively
hydrogen-exposed surfaces show polymer features with a progressively fuzzier appearance and a reduction in lateral cohesion and epitaxial alignment. While pristine polymer surfaces (Figure 4a–c) show short oligomers aligned either along surface (1 0) or (1 ±1) azimuths, this ordering is progressively lifted as the hydrogen exposure continues. By the time that all of the bromine has been removed from the surface (corresponding to a dose time of 960 s) the surface is nearly impossible to image with STM, with substantial tip-fouling and diffusion present at room temperature and an apparent loss of ordering in regions where imaging was previously possible (see Figure 4d–f). We also note a progressive up-shifting in binding energy of the C 1s core level with hydrogen exposure, suggesting that sp3-type defects are introduced to the polymer framework by superhydrogenation. We anticipate that this induces an upward shift of the binding energy for those affected carbons, e.g., cyclohexene manifests a higher binding energy (284.8 eV) than benzene (284.5 eV) on the same Pt(111) surface. The original position of the carbon core level is restored by annealing for 5 min at 275 °C. This change is accompanied by a ~20% reduction of intensity in the C/Cu ratio, a sharpened appearance of features in the STM images, and a reorientation of the polymers to lie along the surface ⟨1 0⟩ azimuth (Figure 4g–i). This suggests desorption of the sp3-like carbon species that may have arisen from interaction with the atomic hydrogen (or conversion of sp3 carbons to sp2), leaving only well-formed PPP structures on the surface. This intuitive description is supported by deconvolution of the C 1s core level in Figure 5 (details of the fitting procedure are found in SI), where an sp3-like component (blue, BE = 285.2 eV) is found to grow as a function of exposure to hydrogen and is subsequently removed by annealing leaving only the original sp2-like component (yellow, BE = 284.8 eV). This spectroscopic interpretation along with the appearance of the STM images postannealing (Figure 4g–i) suggests that the polymers are mostly left intact by the hydrogen-dosing treatment. The overall decrease in intensity of the C 1s peak after annealing implies that the rehybridized carbon species formed during the removal of the bromine are desorbed but the majority of the surface sp2 carbon character is recovered subsequent to heating at the synthesis temperature.

Figure 4. (a–c) STM images of Cu(110) surface after growth of PPP from dBB precursor by a 275 °C anneal for 5 min, subsequent to deposition. (d–f) Images of the same surface after exposure to atomic hydrogen at room temperature. (h–j) Images of the hydrogen-treated surface after 5 min
anneal to 275 °C. Image dimensions are identical by column, and a z-height colorscale is given beside each image. (a, c) $I = 630 \text{ pA}, U = -1.26 \text{ V}$, (b) $I = 630 \text{ pA}, U = -280 \text{ mV}$, (d) $I = 50 \text{ pA}, U = -1.14 \text{ V}$, (e, f) $I = 100 \text{ pA}, U = -180 \text{ mV}$, (g, i) $I = 20 \text{ pA}, U = -980 \text{ mV}$, (h) $I = 100 \text{ pA}, U = -300 \text{ mV}$.

Figure 5. Evolution of C 1s XPS line shape in PPP on Cu(110) as a function of atomic hydrogen exposure: (a) As-grown, (b) after H-exposure for 16 min, (c) after annealing to 275 °C.

On surfaces with saturated monolayer coverage we find that after etching the PPP lines predominantly run along $\langle 1 -1 0 \rangle$, the close-packing orientation of the Cu atoms on the 110 surface, which is generally known to be the more facile direction for diffusion of surface species. The surface maintains this preferential direction over large regions exceeding 2500 nm$^2$, which is a substantial departure from the starting geometry of short segments running along $\langle 1 -1 2 \rangle$ and $\langle 1 -1 1 \rangle$ in Figure 4a–c. This implies that the epitaxy observed upon growth may in some part be driven by a cooperative assembly in which the halogens play a critical role in positioning and aligning the polymers. Cu(110) surfaces with submonolayer starting coverage show a preferential orientation of the polymers along $\langle 1 -1 0 \rangle$, but the dense arraying observed for the monolayer surfaces is not present, and in certain cases entire islands of polymer are observed to exhibit a diffusive motion (see the SI).

**Cu(111)**

As with Cu(110), the organometallic assembly on Cu(111) grows epitaxially in very large defect-free domains. It consists of bright chains spaced by 6.78 ± 0.05 Å along $\langle 3 -2 -1 \rangle$ (substrate $\langle 1 2 1 \rangle$), which corresponds to an epitaxial spacing of $\sqrt{7}a = 6.773$ Å where $a = 2.56$ Å is the nearest-neighbor spacing on Cu(111). This provides a reasonably close match to the expected gas-phase dimension of the OM structure (6.74 Å) and is qualitatively similar to arrays of OM chains on Cu(110) at ~0.5 ML coverage. On Cu(110) the chains kink every five units to relieve internal strain
caused by the epitaxial mismatch. By contrast no kinking is observed on Cu(111), consistent with adsorption along a substrate direction that yields a periodicity very close to that predicted for the gas phase. The chains on Cu(111) pack into dense arrays described by epitaxy matrices of the form \( \begin{pmatrix} -\frac{1}{5} & \frac{2}{5} \\
\end{pmatrix} \) with very large domains reflecting mirror symmetry along sample \( \langle 110 \rangle \) azimuths simultaneously present on the surface. Next to the arrays of OM lines we observe regions bearing a \( (\sqrt{3} \times \sqrt{3})R30^\circ \) reconstruction (left of Figure 6c), which is the expected arrangement for Br on Cu(111). As on Cu(110), we also observe features consistent with Br atoms between every OM chain (see the SI), though these are not visible at all STM biases. Together these regions of Br amount to substantially more Br on the surface than would be expected by the stoichiometry of the molecule, supporting the hypothesis of dehalogenative desorption during the preparation of the surface.

Figure 6. STM images of organometallic chains of dBB on Cu(111) immediately after deposition (30 s, \( 2 \times 10^{-8} \) mbar, \( T = 150 \) °C) ((a) \( 100 \times 100 \) nm\(^2\), \( I = 10 \) pA, \( U = -0.5 \) V, (b) \( 39 \times 39 \) nm\(^2\), \( I = 5 \) pA, \( U = -100 \) mV, (c) \( 10 \times 10 \) nm\(^2\), \( I = 20 \) pA, \( U = -1.0 \) V).

Unlike on the 110 surface (see prior work), the polymers on Cu(111) are generally not ordered on the surface. After heating to 275 °C disordered aggregates of “spaghetti” are found, with patches of organometallic chains still present on the surface, as shown in Figure 7a. In close vicinity of the OM island edges we find morphologies similar to those in Figure 7b, where individual polymers nucleate from the ends of OM lines and split off from the edge of the islands, leading to partially converted OM chains, and regions of Br-\( (\sqrt{3} \times \sqrt{3}) \) between the polymer and OM regions. This image suggests that the conversion of organometallic to polymer is nondissociative, with the reaction progressing stepwise from the end of the OM, ejecting the metal atoms from the OM without significantly disrupting the chains. In this localized region the conversion to polymer is accompanied by a reorientation along a new surface direction.
Figure 7. STM images of dBB on Cu(111) (cf. Figure 6) subsequent to annealing for 5 min at 275 °C: (a) $I = 10$ pA, $U = -300$ mV, $200 \times 200$ nm$^2$, (b) $I = 0.1$ nA, $U = -250$ mV, $7.2 \times 7.2$ nm$^2$, (c) $I = 0.2$ pA, $U = -710$ mV, $50 \times 50$ nm$^2$.

However, most of the non-OM surface comprises disordered and meandering polymers with no evidence of ordering, as shown in Figure 7c, with the localized regions of order between Br, OM, and polymer presented in Figure 7b being the exception rather than the norm. This suggests that once polymers are formed, the mediating action of bromine atoms found on Cu(110) plays no significant role on Cu(111).

The removal rate of halogen from Cu(111) is substantially faster than on Cu(110), with complete removal of the bromine occurring after just 5 min of atomic hydrogen dosing, as shown in the XPS spectra in Figure 8. We note slight offsets in both the Br 3p and C 1s core levels when comparing spectra taken on the two different surfaces, which are summarized in Table 1. In the case of C 1s, this can plausibly correspond to differences in workfunction between the 110 and 111 surfaces; the 110 surface is known to have a $\sim 400$ meV shallower work function,(37) which should correspond to higher observed binding energies for a physisorbed species.
Figure 8. Evolution of (a) C 1s and (b) Br 3p core levels during atomic hydrogen dosing of 275 °C annealed dBB on Cu(111) surface, stacked as a function of exposure time. Sample is held at room temperature throughout. Hydrogen cracker operated at 40 W in a background pressure of $5 \times 10^{-7}$ mbar.

Table 1. Summary of Binding Energies of Carbon and Bromine Core Levels on Cu(110) and Cu(111) Surfaces

|                  | binding energy on Cu(111) (eV) | binding energy on Cu(110) (eV) |
|------------------|---------------------------------|--------------------------------|
| C 1s (sp3)       | 285.0                           | 285.2                          |
| C 1s (sp2)       | 284.6                           | 284.8                          |
| Br 3p 3/2        | 182.3                           | 182.2                          |

The surface morphology is largely unchanged from the as-polymerized sample, with strings of PPP following random directions on the surface with no sign of epitaxial ordering. Further images of the polymer-phase post-hydrogen exposure can be found in the SI. We also note that there is no apparent shifting of the C 1s core level after complete removal of the bromine from the 111 surface. We presume that the exposure time is not long enough to induce defects on the scale of those observed on Cu(110), and as such, the perceived change to the PPP on the surface is vanishingly small.

Our STM images reveal that the PPP chains show a strong degree of epitaxial alignment to $(1\overline{1}0)$ (surface $(1\overline{1}0)$) on Cu(110) subsequent to bromine removal and annealing. This suggests that the domain orientations along $(1\overline{1}0)$ (surface $(1\overline{1}0)$) observed for monolayer surfaces subsequent to deposition are driven largely by coordinated assembly with halogen atoms and that the ordering observed in arrays of products produced by Ullmann coupling is significantly influenced by the interaction of the halogen byproducts with the polymers. This phenomenon has been implied by previous works where the species of halogen (i.e., iodine, bromine, chlorine) is found to have a direct relation to the topology of the resultant surfaces. However, it is clear that this is not a result of chemical bonding, as the XPS signature of each of the polymers produced by this method is identical; no halogen–carbon association is discernible in the C 1s or Br 3p core levels. As such, we propose that the interaction proceeds via a modulation of the local potential energy landscape surrounding the surface containing each halogen-monomer triplet: as nucleation and growth of the organometallics proceeds, there is apparently a net attraction between the detached halogen atoms and their parent molecule that drives the assembly based on the preferred adsorption site for each species. This produces a cooperative assembly effect that drives self-assembly of the islands of alternating organometallic chains and rows of bromine. This effect must persist during the conversion to polymer, which as illustrated above, is nucleated at the end of organometallic chains and proceeds step-by-step down each of the rows, with surrounding halogens driving the epitaxy into the new energetic minimum for the PPP and Br system. The complete removal of the bromine from the surface suppresses the attractive interactions between adjacent chains and releases the PPP from its epitaxial constraints, and the alignment observed on Cu(110) is likely driven by diffusion considerations. Furthermore, it appears that the energetic input required to remove the halogen from the 110 surface is larger than for the 111 surface, implying local increase of adsorption energy between halide and substrate that is enhanced by the presence of the polymer.

Conclusions

In conclusion, we found that room-temperature exposure to atomic hydrogen effectively removes the byproduct of Ullmann dehalogenation of dBB, surface-bound bromine. Prior to exposure to
atomic hydrogen, the bromine aligns in interstitial rows between the PPP lines. The pre-exposure surface is highly ordered and clearly adheres to epitaxy. Following hydrogen exposure, when no trace of Br can be detected on the surface, the PPP polymers are observed to exist in disordered clumps. These results suggest that the surface-bound bromine drives the ordering of the PPP polymer, and that this ordering is compromised by removal of the bromine. Further studies into the applicability of this method to other halogen/substrate combinations are underway.

**Experimental Methods**

All experiments were performed in an ultrahigh vacuum chamber with a base pressure of $10^{-11}$ mbar (Scienta-Omicron GmbH). The system consists of two chambers, the first containing a dual-anode X-ray lamp (DAR 400) and a hemispherical electron energy analyzer (iSphera). The second chamber contains a scanning tunneling microscope (VT-AFM/XA), which was operated at room temperature for this study. High-resolution XPS core level spectra were collected in fixed analyzer transmission mode using Al K-α radiation with a pass energy of 20 eV and a step size of 0.1 eV. Intensity ratios were computed using the area beneath full entire core level regions (both peaks in the case of doublets), with Scofield sensitivity factors and the empirically determined transmission function for the analyzer. STM measurements were acquired in constant current mode, with the quoted bias voltages measured with respect to the tip.

**Sample Preparation**

111- and 110-oriented single crystals of copper (Mateck GmbH and SPL, respectively) were cleaned by repeated cycles of Ar⁺ sputtering (1 keV) and annealing (450 °C) until no carbon or oxygen surface contaminants were detectable by XPS. The 1,4-dibromobenzene (98%, Sigma-Aldrich Corp) was deposited by allowing a room temperature vapor of the molecules to leak into the chamber via a drift tube pointed at the sample. Typical apparent pressures were in the mid $10^{-8}$ mbar range, with depositions lasting 1–5 min. This corresponds to an estimated coverage of 1–10 Langmuir, though the ion gauge is calibrated for nitrogen and likely does not read a true pressure of dibromobenzene. The substrates were annealed with a resistive element embedded in the sample manipulator, and temperatures were controlled via a Eurotherm 2048 PID controller feeding back on a k-type thermocouple mounted on the manipulator in proximity to the sample. Atomic hydrogen dosing was achieved with a hot-capillary-type thermal H₂ cracker (EFM-H, Focus GmbH) operated at 40 W, with an inlet pressure of approximately 1 bar and an in-vacuum pressure reading of $5 \times 10^{-7}$ mBar (equivalent N₂ pressure as read by an ionization gauge). The source was mounted at an angle of 52° with respect to the sample normal at a working distance of 62.5 mm. The flux of hydrogen on the surface was estimated to be $(6 \pm 3) \times 10^{17}$/s/m² based on the erosion rate of an amorphous carbon film (see the SI).

**Notes**

The authors declare no competing financial interest.

**Acknowledgments**

This work was enabled by use of the Central Analytical Research Facility hosted by the Institute for Future Environments at QUT. J.M.M. acknowledges support from the Australian Research Council (ARC) through DE170101170. J.L.-D. acknowledges support from the ARC through DP160103116.
References

1. McCarty, G. S.; Weiss, P. S. Formation and Manipulation of Protopolymer Chains. J. Am. Chem. Soc. 2004, 126, 16772–16776, DOI: 10.1021/ja038930g

2. Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. Nano-Architectures by Covalent Assembly of Molecular Building Blocks. Nat. Nanotechnol. 2007, 2, 687–691, DOI: 10.1038/nnano.2007.346

3. Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Fagot-Revurat, Y.; Cossaro, A.; Verdini, A.; Perepichka, D. F.; Rosei, F.; Contini, G. Insight into Organometallic Intermediate and Its Evolution to Covalent Bonding in Surface-Confined Ullmann Polymerization. ACSNano 2013, 7, 8190–8198, DOI: 10.1021/nn4035684

4. Lackinger, M. On-Surface Polymerization—a Versatile Synthetic Route to Two-Dimensional Polymers. Polym. Int. 2015, 64, 1073–1078, DOI: 10.1002/pi.4943

5. Franc, G.; Gourdon, A. Covalent Networks through on-Surface Chemistry in Ultra-High Vacuum: State-of-the-Art and Recent Developments. Phys. Chem. Chem. Phys. 2011, 13, 14283–14292, DOI: 10.1039/c1cp20700h

6. Abyazisani, M.; Jayalatharachchi, V.; MacLeod, J., Directed on-Surface Growth of Covalently-Bonded Molecular Nanostructures. In Comprehensive Nanoscience and Nanotechnology, 2nd ed.; Elsevier Academic Press: London, 2019; Vol. 2, pp 299–326.

7. Colson, J. W.; Dichtel, W. R. Rationally Synthesized Two-Dimensional Polymers. Nat. Chem. 2013, 5, 453, DOI: 10.1038/nchem.1628

8. Zhang, Y.-Q.; Kepčija, N.; Kleinschrodt, M.; Diller, K.; Fischer, S.; Papageorgiou, A. C.; Allegretti, F.; Björk, J.; Klyatskaya, S.; Klappenberger, F.; Ruben, M.; Barth, J. V. Homo-Coupling of Terminal Alkynes on a Noble Metal Surface. Nat. Commun. 2012, 3, 1286, DOI: 10.1038/ncomms2291

9. Bakker, A.; Gao, H. Y.; Fuchs, H., Glaser–Hay Coupling on Surfaces A2 - Wandelt, Klaus. In Encyclopedia of Interfacial Chemistry; Elsevier: Oxford, 2018; pp 272–284.

10. Sanchez-Sanchez, C.; Orozco, N.; Holgado, J. P.; Beaumont, S. K.; Kyriakou, G.; Watson, D. J.; Gonzalez-Elipe, A. R.; Feria, L.; Fernández Sanz, J.; Lambert, R. M. Sonogashira Cross-Coupling and Homocoupling on a Silver Surface: Chlorobenzene and Phenylacetylene on Ag(100). J. Am. Chem. Soc. 2015, 137, 940–947, DOI: 10.1021/ja5115584

11. de Oteyza, D. G.; Gorman, P.; Chen, Y.-C.; Wickenburg, S.; Riss, A.; Mowbray, D. J.; Etkin, G.; Pedramrazi, Z.; Tsai, H.-Z.; Rubio, A. Direct Imaging of Covalent Bond Structure in Single-Molecule Chemical Reactions. Science 2013, 340, 1238187, DOI: 10.1126/science.1238187

12. Weigelt, S.; Busse, C.; Bombis, C.; Knudsen, M. M.; Gothelf, K. V.; Strunskus, T.; Wöll, C.; Dahlbom, M.; Hammer, B.; Lægsgaard, E. Covalent Interlinking of an Aldehyde and an Amine on a Au (111) Surface in Ultrahigh Vacuum. Angew. Chem. 2007, 119, 9387–9390, DOI: 10.1002/ange.200702859
13. Gao, H.-Y.; Held, P. A.; Knor, M.; Mück-Lichtenfeld, C.; Neugebauer, J.; Studer, A.; Fuchs, H. Decarboxylative Polymerization of 2,6-Naphthalenedicarboxylic Acid at Surfaces. J. Am. Chem. Soc. 2014, 136, 9658–9663, DOI: 10.1021/ja5033875

14. Morchutt, C.; Björk, J.; Straßer, C.; Starke, U.; Gutzler, R.; Kern, K. Interplay of Chemical and Electronic Structure on the Single-Molecule Level in 2d Polymerization. ACS Nano 2016, 10, 11511–11518, DOI: 10.1021/acsnano.6b07314

15. Lackinger, M. Surface-Assisted Ullmann Coupling. Chem. Commun. 2017, 53, 7872–7885, DOI: 10.1039/C7CC03402D

16. Bieri, M.; Nguyen, M.-T.; Gröning, O.; Cai, J.; Treier, M.; Aît-Mansour, K.; Ruffieux, P.; Pignedoli, C. A.; Passerone, D.; Kastler, M.; Müllen, K.; Fasel, R. Two-Dimensional Polymer Formation on Surfaces: Insight into the Roles of Precursor Mobility and Reactivity. J. Am. Chem. Soc. 2010, 132, 16669–16676, DOI: 10.1021/ja107947z

17. Batra, A.; Cvetko, D.; Kladnik, G.; Adak, O.; Cardoso, C.; Ferretti, A.; Prezzi, D.; Molinari, E.; Morgante, A.; Venkataraman, L. Probing the Mechanism for Graphene Nanoribbon Formation on Gold Surfaces through X-Ray Spectroscopy. Chem. Sci. 2014, 5, 4419–4423, DOI: 10.1039/C4SC01584C

18. Fan, Q.; Wang, T.; Liu, L.; Zhao, J.; Zhu, J.; Gottfried, J. M. Tribromobenzene on Cu (111): Temperature-Dependent Formation of Halogen-Bonded, Organometallic, and Covalent Nanostructures. J. Chem. Phys. 2015, 142, 101906, DOI: 10.1063/1.4906214

19. Björk, J.; Hanke, F.; Stafström, S. Mechanisms of Halogen-Based Covalent Self-Assembly on Metal Surfaces. J. Am. Chem. Soc. 2013, 135, 5768–5775, DOI: 10.1021/ja400304b

20. Fan, Q.; Wang, C.; Liu, L.; Han, Y.; Zhao, J.; Zhu, J.; Kuttner, J.; Hilt, G.; Gottfried, J. M. Covalent, Organometallic, and Halogen-Bonded Nanomeshes from Tetrabromo-Terphenyl by Surface-Assisted Synthesis on Cu (111). J. Phys. Chem. C 2014, 118, 13018–13025, DOI: 10.1021/jp5037475

21. Di Giovannantonio, M.; Deniz, O.; Urgel, J. I.; Widmer, R.; Dienel, T.; Stolz, S.; Sánchez-Sánchez, C.; Muntwiler, M.; Dumslafl, T.; Berger, R. On-Surface Growth Dynamics of Graphene Nanoribbons: The Role of Halogen Functionalization. ACS Nano 2018, 12, 74–81, DOI: 10.1021/acsnano.7b07077

22. Pham, T. A.; Song, F.; Nguyen, M.-T.; Li, Z.; Studener, F.; Stöhr, M. Comparing Ullmann Coupling on Noble Metal Surfaces: On-Surface Polymerization of 1,3,6,8-Tetrabromoopyrene on Cu(111) and Au(111). Chem. - Eur. J. 2016, 22, 5937–5944, DOI: 10.1002/chem.201504946

23. Schlögl, S.; Heckl, W. M.; Lackinger, M. On-Surface Radical Addition of Triply Iodinated Monomers on Au (111)—the Influence of Monomer Size and Thermal Post-Processing. Surf. Sci. 2012, 606, 999–1004, DOI: 10.1016/j.susc.2012.02.011

24. Abyazisani, M.; Bradford, J.; Motta, N.; Lipton-Duffin, J.; MacLeod, J. Adsorption and Reactivity of Pyridine Dicarboxylic Acid on Cu (111). J. Phys. Chem. C 2018, 122, 17836–17845, DOI: 10.1021/acs.jpcc.8b04858
25. Tran, B. V.; Pham, T. A.; Grunst, M.; Kivala, M.; Stöhr, M. Surface-Confined $[2+2]$ Cycloaddition Towards One-Dimensional Polymers Featuring Cyclobutadiene Units. *Nanoscale* **2017**, *9*, 18305–18310, DOI: 10.1039/C7NR06187K

26. Bronner, C.; Björk, J.; Tegeder, P. Tracking and Removing Br During the on-Surface Synthesis of a Graphene Nanoribbon. *J. Phys. Chem. C* **2015**, *119*, 486–493, DOI: 10.1021/jp5106218

27. Lipton-Duffin, J.; Ivasenko, O.; Perepichka, D.; Rosei, F. Synthesis of Polyphenylene Molecular Wires by Surface-Confined Polymerization. *Small* **2009**, *5*, 592–597, DOI: 10.1002/smll.200801943

28. Vasseur, G.; Fagot-Revurat, Y.; Sicot, M.; Kierren, B.; Moreau, L.; Malterre, D.; Cardenas, L.; Galeotti, G.; Lipton-Duffin, J.; Rosei, F. Quasi One-Dimensional Band Dispersion and Surface Metallization in Long-Range Ordered Polymeric Wires. *Nat. Commun.* **2016**, *7*, 10235, DOI: 10.1038/ncomms10235

29. Vasseur, G.; Fagot-Revurat, Y.; Sicot, M.; Kierren, B.; Moreau, L.; Malterre, D.; Cardenas, L.; Galeotti, G.; Lipton-Duffin, J.; Rosei, F.; Di Giovannantonio, M.; Contini, G.; Le Fevre, P.; Bertran, F.; Liang, L. B.; Meunier, V.; Perepichka, D. F. Quasi One-Dimensional Band Dispersion and Surface Metallization in Long-Range Ordered Polymeric Wires. *Nat. Commun.* **2016**, *7*, 10235, DOI: 10.1038/ncomms10235

30. Galeotti, G.; Di Giovannantonio, M.; Lipton-Duffin, J.; Ebrahimi, M.; Tebi, S.; Verdini, A.; Floreano, L.; Fagot-Revurat, Y.; Perepichka, D. F.; Rosei, F.; Contini, G. The Role of Halogens in on-Surface Ullmann Polymerization. *Faraday Discuss.* **2017**, *204*, 453–469, DOI: 10.1039/C7FD00099E

31. Rauls, E.; Hornekær, L. Catalyzed Routes to Molecular Hydrogen Formation and Hydrogen Addition Reactions on Neutral Polycyclic Aromatic Hydrocarbons under Interstellar Conditions. *Astrophys. J.* **2008**, *679*, 531, DOI: 10.1086/587614

32. Skov, A. W.; Andersen, M.; Thrower, J. D.; Jørgensen, B.; Hammer, B.; Hornekær, L. The Influence of Coronene Super-Hydrogenation on the Coronene-Graphite Interaction. *J. Chem. Phys.* **2016**, *145*, 174708, DOI: 10.1063/1.4966259

33. Sanchez-Sanchez, C.; Martinez, J. I.; del Arbó, N. R.; Ruffieux, P.; Fasel, R.; Lopez, M. F.; de Andres, P. L.; Martin-Gago, J. A. On-Surface Hydrogen-Induced Covalent Coupling of Polycyclic Aromatic Hydrocarbons Via a Superhydrogenated Intermediate. *J. Am. Chem. Soc.* **2019**, *141*, 3550–3557, DOI: 10.1021/jacs.8b12239

34. Rodriguez, J.; Campbell, C. T. Cyclohexene Adsorption and Reactions on Clean and Bismuth-Covered Pt (111). *J. Catal.* **1989**, *115*, 500–520, DOI: 10.1016/0021-9517(89)90053-5

35. Zhang, R.; Hensley, A. J.; McEwen, J.-S.; Wickert, S.; Darlatt, E.; Fischer, K.; Schöppke, M.; Denecke, R.; Streber, R.; Lorenz, M. Integrated X-Ray Photoelectron Spectroscopy and Dft Characterization of Benzene Adsorption on Pt (111), Pt (355) and Pt (322) Surfaces. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20662–20671, DOI: 10.1039/c3cp53127a

36. Inukai, J.; Osawa, Y.; Itaya, K. Adlayer Structures of Chlorine, Bromine, and Iodine on Cu(111) Electrode in Solution: *In-Situ* STM and *Ex-Situ* LEED Studies. *J. Phys. Chem. B* **1998**, *102*, 10034–10040, DOI: 10.1021/jp982952I
37. Gartland, P.; Berge, S.; Slagsvold, B. Photoelectric Work Function of a Copper Single Crystal for the (100), (110), (111), and (112) Faces. *Phys. Rev. Lett.* **1972**, *28*, 738, DOI: 10.1103/PhysRevLett.28.738