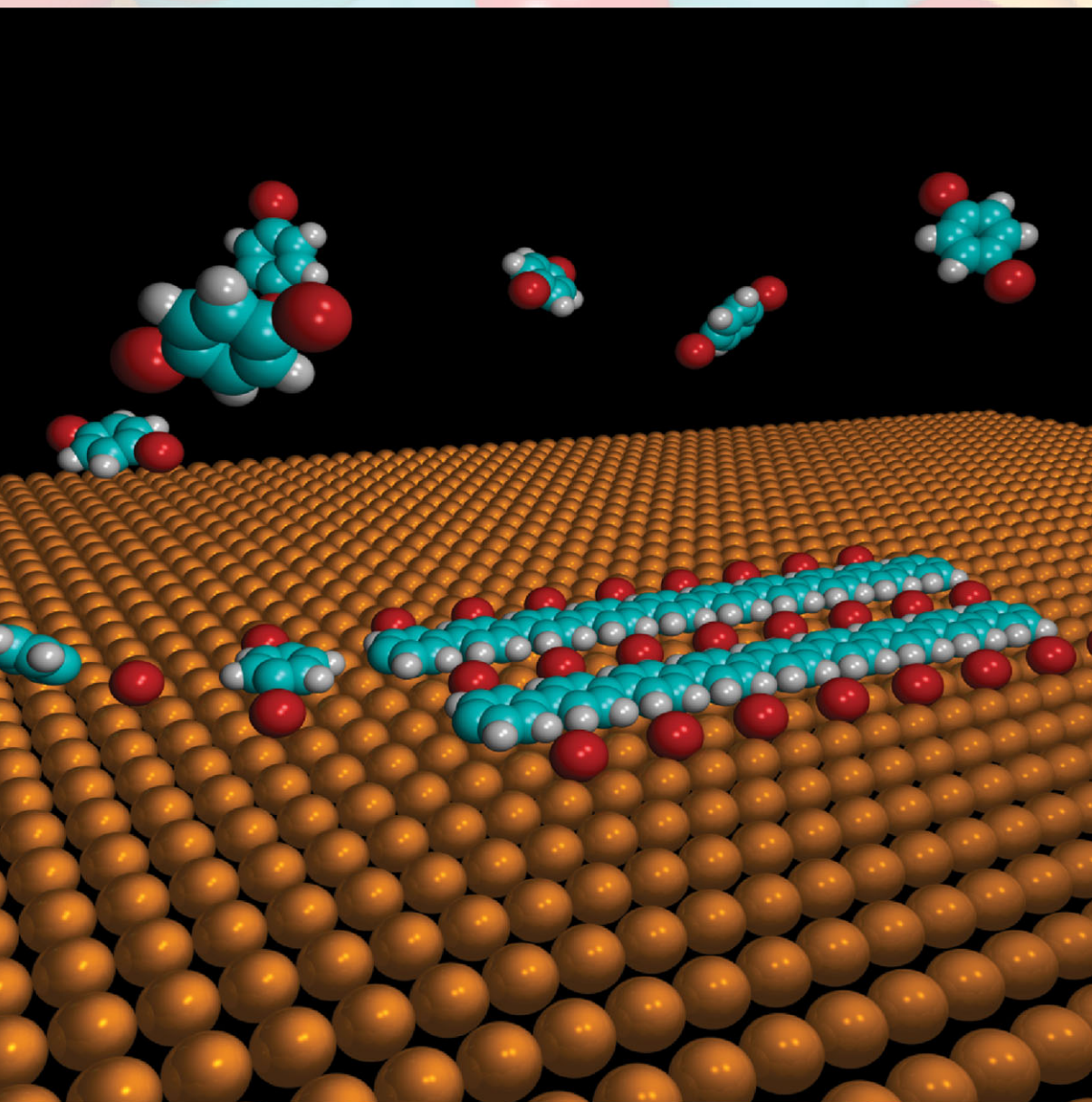


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Synthesis of Polyphenylene Molecular Wires by Surface-Confined Polymerization

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Synthesis of Polyphenylene Molecular Wires by Surface-Confined Polymerization

J. A. Lipton-Duffin, O. Ivasenko, D. F. Perepichka,* and F. Rosei*

*The surface-mediated synthesis of epitaxially aligned and separated polyphenylene lines on Cu(110) by exploiting the Ullmann dehalogenation reaction is reported. Scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) show that the C-I bonds of 1,4-diiodobenzene and 1,3-diiodobenzene (C₆H₄I₂) are catalytically cleaved when dosed onto the surface. Subsequent annealing transforms the copper-bound phenylene intermediates into covalent conjugated structures: linear chains of poly(*p*-phenylene) for 1,4-diiodobenzene and zigzag chains of poly(*m*-phenylene) as well as macrocyclic oligomers in the case of 1,3-diiodobenzene. The chains are strongly bound to the surface (likely through C–Cu bonds at the chain-ends) while the macrocycles are very mobile and can only be imaged by STM at low temperature. The detached halogens adsorb on the surface and separate the polymer chains from each other.*

Keywords:

- catalysis
- conjugated polymers
- STM
- surface science
- Ullmann coupling

1. Introduction

Conjugated polymers constitute a class of low-dimensional materials of broad scientific interest.^[1] Despite several decades of research, surface-confined polymerization^[2] has only recently been recognized as a route to synthesize aligned conducting nanostructures, opening new opportunities in nanoelectronics. Surface-confined epitaxial growth of individual conjugated polymer wires in ambient conditions has been directly observed on Au^[3] and graphite surfaces.^[4,5] In these studies, the reaction was induced electrochemically,^[3] photo-

chemically,^[4] or by a voltage pulse from the tip of a scanning tunneling microscope (STM).^[5] By contrast, producing polymers in an ultrahigh vacuum (UHV) environment gives enhanced control of cleanliness and coverage,^[6] and facilitates low-temperature studies. Recent UHV work has successfully demonstrated surface polymerization using heating as the activation mechanism.^[7] However, the use of the surface itself as a catalyst for the surface-confined polymerization reaction has not yet been explored.^[8]

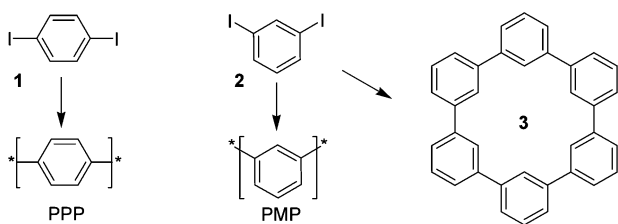
The Ullmann reaction is one of the oldest known ways to couple aromatic units through a C–C bond.^[9] Heating an iodoaromatic compound with copper powder cleaves the C–I bond to form an aromatic dimer with copper iodide as a byproduct.^[10] The reaction was used to synthesize conjugated aromatic polymers,^[11] although homogeneous transition metal catalysis methods dominate the field.

Recently, modern UHV and scanning probe techniques were used to revisit the mechanism of the Ullmann reaction. For iodobenzene (C₆H₅I), cleavage of the C–I bond was shown to occur on Cu(111) at temperatures as low as 200 K. However, temperatures above 300 K are required to couple the resulting copper-bound phenyl radicals in a biphenyl molecule.^[12] Dehalogenation and coupling can also be achieved at much lower temperatures (20 K) on individual molecules by using a voltage pulse from an STM tip.^[13] Performing the reaction

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Scheme 1. Ullmann coupling of diiodobenzene molecules.

with a bifunctional monomer on an atomically flat surface in UHV should lead to individual strands of conjugated aromatic polymers, which can be imaged with an STM tip. The first studies using this approach employed 1,4-diiodobenzene on Cu(111).^[14,15] The monomer was dosed at room temperature (RT); the products were imaged at 77 K. Under these conditions the dissociated phenyl biradicals assemble into so-called “protopolymer” chains at the surface, which are not linked by covalent C–C bonds. The expected conjugated polymer poly-*p*-phenylene (PPP) was not formed.

Here we describe the *first successful* surface-confined synthesis of individual conjugated polyphenylene chains by depositing and annealing 1,4- and 1,3-diiodobenzene (**1** and **2**) on the 110 surface of copper. We demonstrate that the lines can be grown perfectly straight (for **1**), or with kinks (for **2**) as defined by molecular geometry (Scheme 1).

2. Results

Figure 1 shows an STM image of a Cu(110) surface dosed with 0.2 L of **1** at RT. The molecules arrange themselves on the surface in long continuous lines, similar to those observed by McCarty and Weiss on Cu(111).^[15] The lines grow preferentially along the $\langle 11 \rangle$ and $\langle 1-1 \rangle$ surface lattice directions. They are mostly packed in dense groups that are commensurate with the substrate, although we seldom observed isolated, non-commensurate lines.

Between groups of lines, the substrate predominantly exhibits a $c(2 \times 2)$ symmetry, the expected reconstruction for iodine on Cu(110).^[16] X-ray photoelectron spectroscopy (XPS: Figure 2) of the I_{3d} core levels reveals two sharp and well-resolved peaks, corresponding to $3d_{5/2}$ and $3d_{3/2}$ spin-orbit split levels. The full width at half-maximum (FWHM) of each peak is approximately 1.5 eV, which is roughly the overall

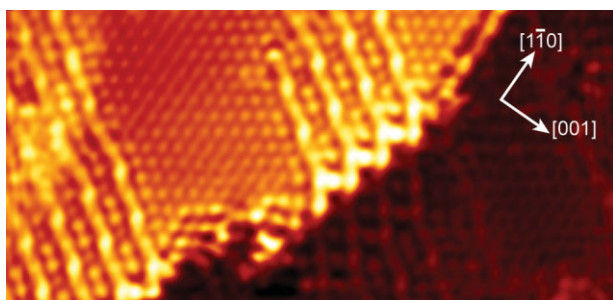


Figure 1. STM image of 1,4-diiodobenzene lines grown on Cu(110) at RT ($16.5 \times 8.0 \text{ nm}^2$, $V_s = -0.77 \text{ V}$, $I_t = 1.02 \text{ nA}$).

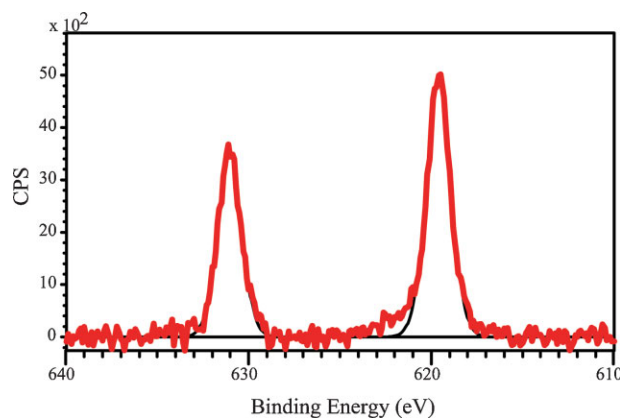


Figure 2. XPS spectra of I_{3d} core levels of the Cu(110) surface after depositing a submonolayer of 1,4-diiodobenzene at RT.

resolution of the XPS system. The peak centroid for the $3d_{5/2}$ is at 619.5 eV, in agreement with previous studies for Cu–I compounds.^[17,18] Previous works indicate that iodine bound to hydrocarbon compounds exhibits a core level shift of the $3d_{5/2}$ level to larger binding energies by approximately 1 eV.^[19] Since there is no indication of a peak at higher energies we can conclude that the dehalogenation is complete at RT, and that all the diiodobenzene is converted to phenyl biradicals. Together, these sets of data confirm that the first step of a reaction (cleavage of the C–I bond) has occurred at RT.

The constituents of the bright lines are spaced by 5.5 \AA , which is 30% larger than the expected periodicity of PPP, yet is close to the expected periodicity of a metal-organic polymer (e.g., $[-\text{Ph-Cu-}]_n$); this is likely to be the protopolymer observed by McCarty and Weiss.^[15] The lines comprise rounded elements of two distinct sizes. Extrapolating from the iodine atoms’ known position, we find that the smaller elements occupy long bridge sites on the Cu(110) lattice, whereas the larger ones sit on the short bridge sites. For comparison, benzene (C_6H_6) adsorbs on the long bridge site on Cu(110),^[20] while dehalogenated phenyl rings (from $\text{C}_6\text{H}_5\text{I}$) reside on four-fold hollow (H4) sites.^[17]

Heating to $\approx 500 \text{ K}$ for 5–10 minutes subsequent to dosing transforms the protopolymer structures into clusters of lines oriented along $[1-10]$, that is, parallel to the Cu substrate rows. These clusters consist of alternating rows of bright and dim lines, with the brightest ones consisting of discrete circular elements (Figure 3). At the top left we observe furrows of the underlying substrate lattice. While we do not attain atomic resolution in the $[1-10]$ direction, a line section along the $[001]$ direction (blue in Figure 3) shows that the bright components of the lines sit between the furrows, because these lines are always spaced by an odd number of half-unit cells from the substrate furrows.^[21]

In the perpendicular $[1-10]$ direction the bright lines appear as solid streaks, or as a series of discrete elements. A line section through one of the discrete structures (green in Figure 3) shows that the constituents are separated by 5.12 \AA (or $2a_2$, where $a_2 = 2.56 \text{ \AA}$ is the short substrate lattice constant). We conclude that the bright lines are rows of iodine atoms, which are known to favor H4 sites.

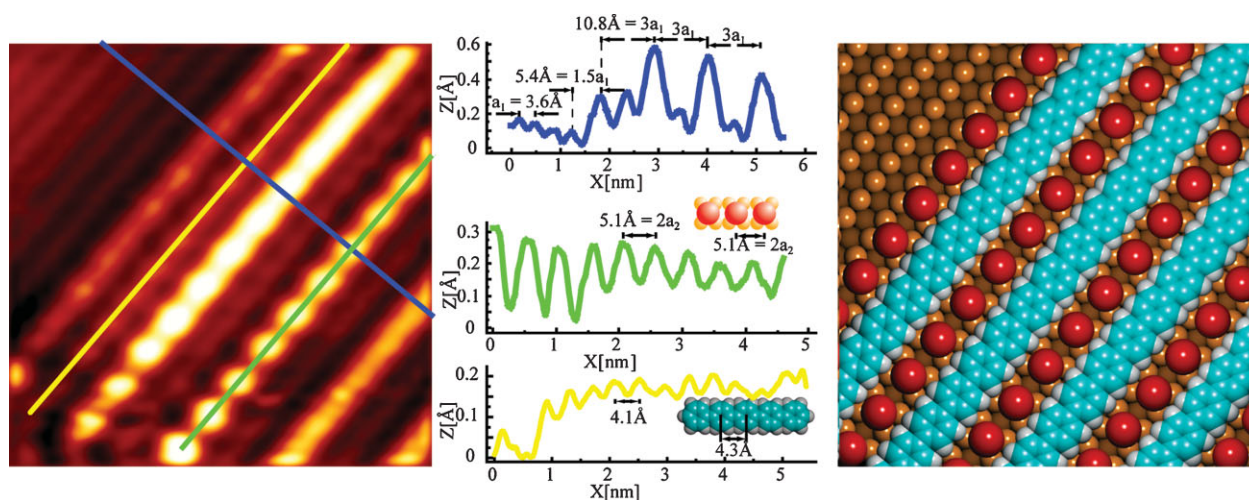


Figure 3. STM image of 1,4-diiodobenzene lines after annealing at 500 K on Cu(110). The line profiles indicate the registry of the lines with respect to the substrate furrows (blue line), the spacing of the bright features (green profile), and the spacing of the dim lines (yellow profile). At the right is a molecular model corresponding to the STM image at the left ($6.4 \times 6.4 \text{ nm}^2$, $V_s = -1.93 \text{ V}$, $I_t = 0.93 \text{ nA}$).

The streaking in the bright lines is consistent with their constituents being highly mobile at RT; lines consisting of discrete elements may have their geometries stabilized by external factors (e.g., surface defects). To test this hypothesis, we cooled the surface to 115 K, so as to “freeze out” thermal motion. Figure 4 displays a cluster of lines in which every bright line consists of discrete circular elements separated by 2.56 \AA . The bright elements of adjacent lines are often shifted by one lattice constant along $[1-10]$.

The dim regions between bright lines are also composed of discrete elements, though they are much more difficult to resolve. A profile along a dim line (yellow; Figure 3) shows that the separation between the elements is approximately 4.1 \AA , which agrees within experimental uncertainty with the Ph–Ph separation in the crystal phase (4.32 \AA , measured for *p*-septiphenyl^[22]) and gas phase (4.33 \AA by DFT calculations; see Supporting Information) of PPP. Thus, dosing 1,4-diiodobenzene on Cu(110) followed by annealing at 500 K

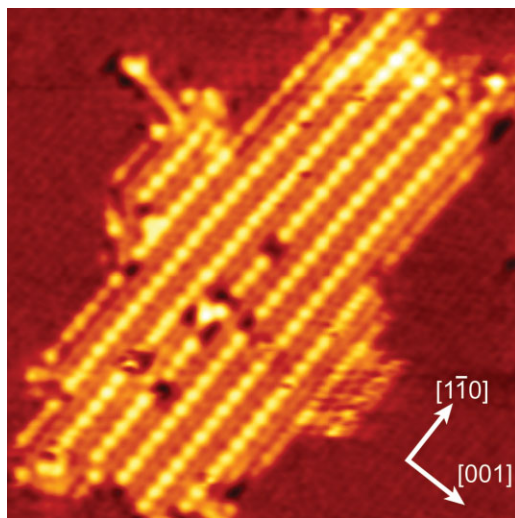


Figure 4. An annealed 1,4-diiodobenzene surface imaged at $T = 115 \text{ K}$ ($19 \times 19 \text{ nm}^2$, $V_s = -1.93 \text{ V}$, $I_t = 1.06 \text{ nA}$).

produces PPP chains epitaxially aligned on the surface and separated from each other by a row of iodine atoms. In preliminary experiments, qualitatively identical PPP lines were produced by dosing and annealing 1,4-dibromobenzene on Cu(110).

To further investigate the applicability of the surface-confined Ullmann reaction to build complex polymer architectures of different symmetry, we performed additional experiments using 1,3-diiodobenzene (**2**). In contrast to the rigid 180° linking geometry of PPP produced from **1**, polymerization of **2** at 500 K produces lines with zig-zag structures at $\approx 120^\circ$, giving a convincing signature of the formation of the poly(*m*-phenylene) (PMP) polymer (Figure 5).^[23] The zig-zag polymer chains grow principally along the $\langle 21 \rangle$ and $\langle 2-1 \rangle$ surface vectors. They are flanked by discrete circular satellites that occupy H4 substrate lattice sites, and by analogy with 1,4-diiodobenzene results we infer these are iodine atoms. Figure 5 shows an overlaid scale model of a PMP oligomer; its vertex-vertex periodicity (7.37 \AA from single-crystal X-ray analysis for *m*-quinquephenyl^[24]) matches the structures observed in our experiment (7.1 \AA). Chains with more than 30 repeated *m*-phenylene units were observed. The bottom-right inset in Figure 5 shows a scale image of a protopolymer line, which forms when depositing **2** at RT (i.e. without annealing). As with the protopolymer of **1**, the structure qualitatively resembles PMP, but exhibits a very large intrachain spacing (11.8 \AA vertex-vertex periodicity).

The PMP structures contain kinks due to the symmetry of 1,3-diiodobenzene. Flipping around a single C–C bond changes the chain-substrate alignment, yet the latter is always maintained by a second flip (Figure 4 top inset). The kinked portion of the oligomer is $7.5 \pm 0.5 \text{ \AA}$ in length (i.e., two phenylenes). The majority of the observed chains (85%) contain one or more kinks; those that do not contain kinks are rarely longer than 10 *m*-phenylene units.^[25]

Low-temperature scanning of the PMP-modified surfaces elucidates the source of the streaking observed in RT images: in addition to the PMP chains, ring structures also form in this

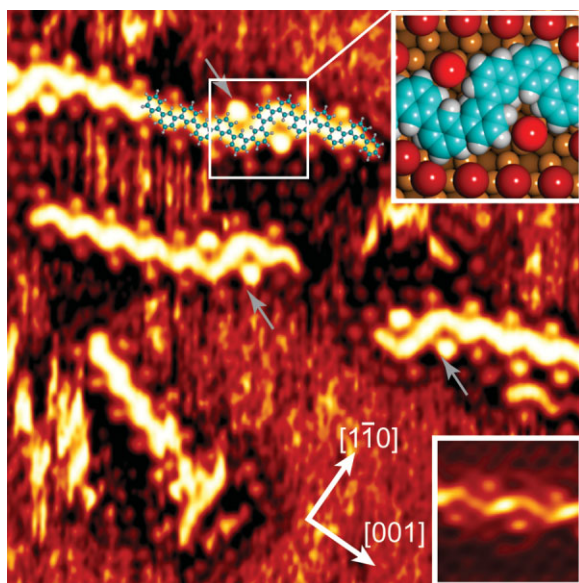


Figure 5. Cu(110) with 0.2 L of 1,3-diiodobenzene, dosed with the substrate held at 500 K. A model of PMP is overlaid on one of the oligomer branches ($11.3 \times 11.3 \text{ nm}^2$, $V_s = -0.57 \text{ V}$, $I_t = 0.82 \text{ nA}$). Top-right inset: a force field relaxed model of PMP chain in the iodine matrix on a slab of Cu corresponding to the marked region in the STM image. Bottom right inset: a scale portion of the RT deposited surface, showing a protopolymer of **2**.

reaction (Figure 6).^[26] The measured sizes of these structures scanned at high resolution ($8.3 \pm 0.8 \text{ \AA}$ diameter) are in agreement with the known X-ray structure of sexiphenylene macrocycle **3**.^[27] Some, but not all, ring structures do not display a hexagonal symmetry but rather appear as pentagons or squares. This is not surprising since oligophenylene macrocycles are not flat, due to the torsion around the Ph-Ph bond. Their appearance will depend on a) their conformation and b) their orientation on the surface, as has

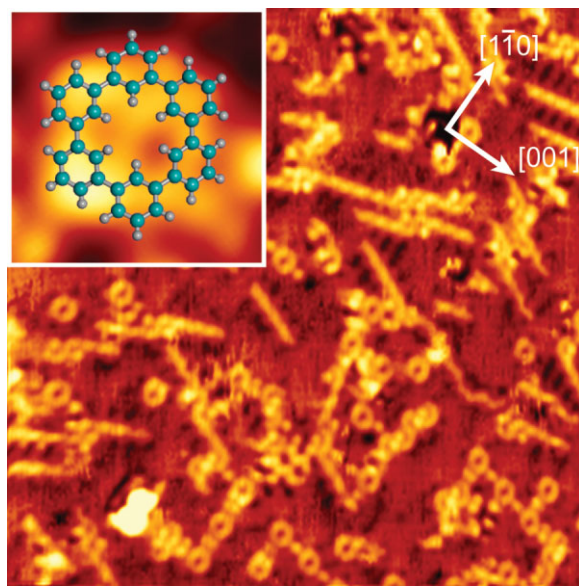


Figure 6. STM image of PMP oligomers, scanned at 102 K; inset: a high-resolution image of a macrocycle, overlaid with a model of a sexiphenylene ^[27] ($30 \times 30 \text{ nm}^2$, $V_s = -1.61 \text{ V}$, $I_t = 0.66 \text{ nA}$).

been demonstrated for other conformationally labile aromatic molecules.^[28] Also, we cannot rule out possible formation of smaller (quinquephenylene) and large (heptaphenylene) rings. In fact, 5- and 6-membered macrocycles can be produced in bulk by Ullmann coupling of **2**.^[29,30] The macrocycles' high mobility on the surface at RT is ascribed to relatively weak interaction with the copper surface as a result of their small size (as observed for other polyaromatics deposited on metals).^[31] By contrast, the larger open-chain (zigzag) oligomers are immobilized on the surface through a large number of $\pi \dots \text{Cu}$ contacts and also, most likely, covalent C-Cu bonds at the chain termini.^[32]

3. Conclusions

In summary, we demonstrated the epitaxial Ullmann polymerization of diiodobenzene isomers on Cu(110), by using the substrate simultaneously as a template and a catalyst. Aligned and separated PPP and PMP wires are generated from 1,4- and 1,3-diiodobenzene, respectively, by annealing during sample preparation. 1,3-Diiodobenzene also produces macrocyclic oligomer that have high surface mobility at RT. This catalytic method can now be extended to other halogenated monomers, opening the possibility of producing individual conjugated aromatic polymers with complex structure and tailored functionality. The method can be potentially extended to the synthesis of more complex architectures (including 2D polymers), to be used, for example, in nanoelectronic circuits.

4. Experimental Section

A single-crystal copper specimen was cleaned by repeated cycles of ion bombardment (Ar+ at 600 eV) and annealing to $\approx 800 \text{ K}$. After cooling to room temperature, 1,4-diiodobenzene and 1,3-diiodobenzene (Aldrich/99%) were dosed through a leak valve. Coverages in Langmuir were estimated from the ion gauge reading but were not adjusted by the unknown correction factor for diiodobenzene. During dosing a 200 a.m.u. quadrupole mass spectrometer (MKS Vacscan) indicated mass peaks at 74 a.m.u. (C_6H_4) in the 10^{-11} Torr range, and at 126 and 127 a.m.u. (atomic iodine) in the 10^{-12} Torr range. All measurements were collected using a commercial UHV system with a variable temperature (VT) scanning tunneling microscope (Omicron GmbH, Germany). The bias voltages are quoted from the tip to the sample. The system has a base pressure of $< 2 \times 10^{-11}$ mbar. Unless stated otherwise the sizes measured by the STM are accurate to within 5% of the quoted values, with the uncertainties arising from thermal drift and/or piezo creep. Where possible, the data have been corrected to reflect the known lattice spacing of the Cu(110)l-c(2×2) reconstruction. All image analysis was performed using the free WSxM software,^[33] with analyses typically involving plane-flattening and smoothing to enhance critical details.

XPS spectra were acquired with VG ESCALab 220i XL instrument, using a MgK_{α} source.

The Force field calculations were performed on a two-layer Cu432 slab by relaxation of the tetradecameric PMP oligomer placed within predefined (according to STM results) iodine matrix using the default MM+ force field implemented in the HyperChem package. Periodic boundary conditions (PBC) calculations of poly-*p*-phenylene were performed with density functional theory at B3LYP/6-31G(d) level implemented in GAUSSIAN 03 (see details in Supporting Information).^[34]

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