



## Unexpected Organometallic Intermediate in Surface-confined Ullmann Coupling

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## Unexpected Organometallic Intermediate in Surface-Confined Ullmann Coupling

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Ullmann coupling or, more generally, dehalogenative aryl-aryl coupling, is one of the most widely exploited chemical reactions to obtain one- and two-dimensional polymers on metal surfaces. It is generally described as a two-step reaction: (i) dehalogenation, resulting in the formation of a stable intermediate phase and subsequent (ii) C-C coupling. The topology of the resulting polymer depends on the number and positions of the halogen atoms in the haloaromatic precursor, although its orientation and order are determined by the structure of the intermediate phase. Hitherto, only one intermediate structure, identified as organometallic (OM) phase, has been reported for such reaction. Here we demonstrate the formation of two distinct OM phases during the temperature-induced growth of poly(*para*-phenylene) from 1,4-dibromobenzene precursors on Cu(110). Beyond the already known linear-OM chains, we show that a phase reorganization to a chessboard-like 2D-OM can be activated in a well-defined temperature range. This new intermediate phase, revealed only when the reaction was carried out at low molecular coverages, was characterized by X-ray photoelectron spectroscopy, scanning tunneling microscopy and near-edge X-ray absorption fine structure spectroscopy, and modeled by density functional theory calculations. Our data show that the 2D-OM remains stable after cooling down the sample and is stabilized by four-Cu clusters at each node. The observation of such an unexpected intermediate phase shows the complexity of the mechanisms underlying on-surface synthesis and broadens the understanding of Ullmann coupling, which continues to be astonishing despite its extensive use.

### Introduction

On-surface synthesis is an increasingly exploited bottom-up methodology to grow atomically precise nanostructures from carefully designed molecular precursors.<sup>1, 2</sup> This approach relies on crystalline surfaces to support the low-dimensional growth of desired architectures through catalytically activated chemical reactions, and is capable to produce one- and two-dimensional (1D and 2D) organic arrays that are unlikely to occur naturally.<sup>3-6</sup> The achievement of covalent coupling between the building blocks is desirable, to ensure the mechanical and thermal stability of the atomically thin layer, and allows to extend  $\pi$ -conjugation, which is the key aspect for using these materials in semiconducting devices.<sup>7, 8</sup> In this framework the formation of polymers is initiated by energetic input, either by annealing the surface or by irradiation, according to the specific functional groups involved in the reaction. Changing the precursors, i.e. the building blocks, allows to modify the structure and properties of the polymer.<sup>5</sup> Various chemical reactions have been used in developing on-surface polymerization.<sup>1, 9-13</sup> Among these, Ullmann coupling has been the most successful for its generality, excellent regio- and chemo-selectivity, and convenient activation temperature (in the 100-300 °C range).<sup>1, 2, 12, 14-16</sup> Using different halogens as leaving groups, a hierarchical growth of polymer architectures

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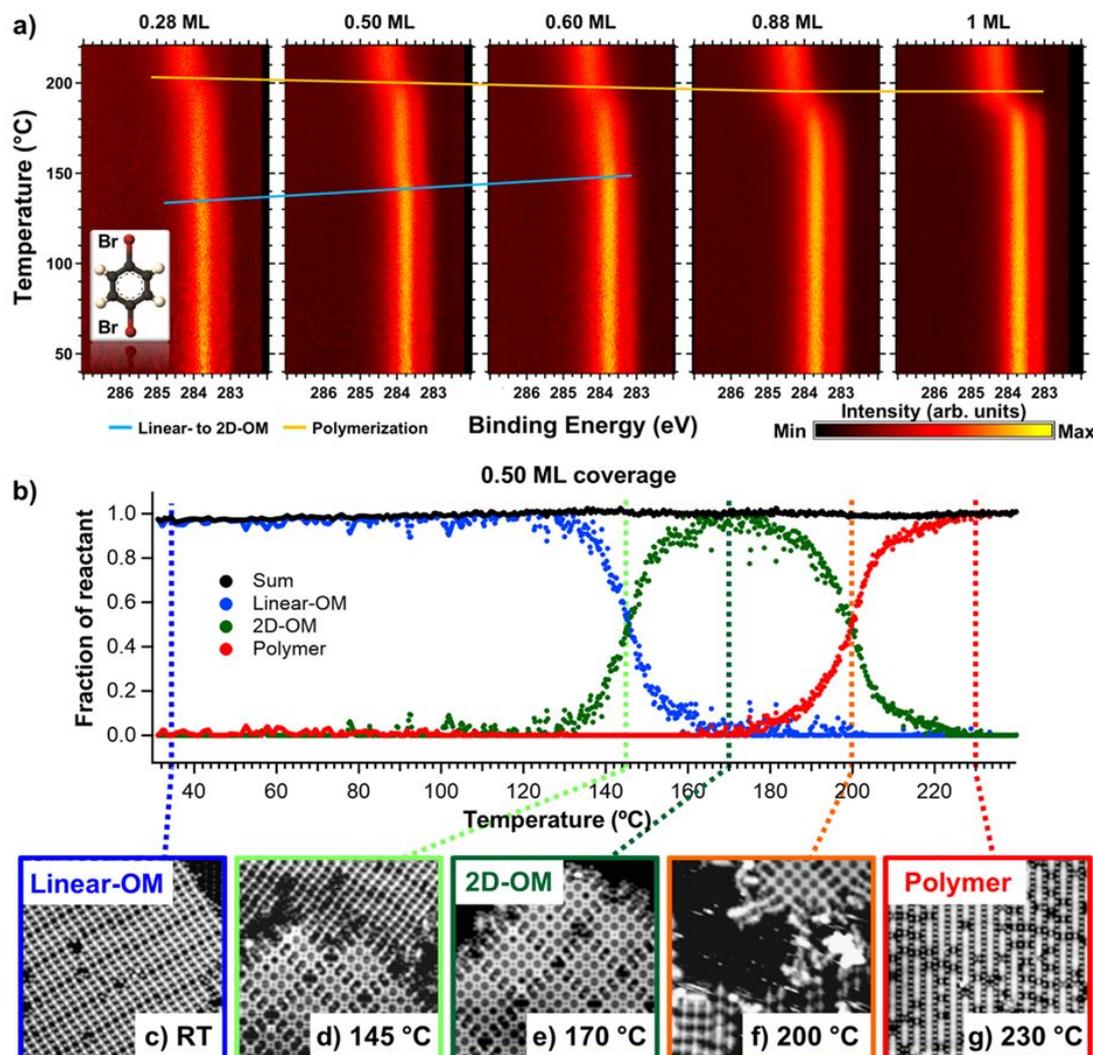


Figure 1. a) C 1s fast-XPS maps of dBB on Cu(110) at different molecular coverages, from 0.28 ML to 1 ML. b) Kinetic curves extracted from the fast-XPS map at 0.5 ML coverage according to a previously reported fitting procedure.<sup>24</sup> These curves represent the surface density of the different phases present on the surface as a function of temperature (see Section 1 of the SI). c-g) STM images (18x18 nm<sup>2</sup>) of the sample with 0.5 ML coverage annealed at different temperatures, showing the phase evolution from linear-OM, to 2D-OM, to polymer.

of increased complexity and/or enhanced order can be achieved.<sup>12, 14, 17</sup>

Ullmann coupling<sup>18</sup> is generally understood as a two-step reaction, involving the formation of organo-cuprate intermediates (R-Cu-R) in the first step, with subsequent ejection of the metal to form covalently linked products in the second step.<sup>19-21</sup> On crystalline metal surfaces, the reaction has been proven to proceed in a similar manner.<sup>9, 15, 22-25</sup> Aside from the classical case of copper substrates,<sup>26-28</sup> on-surface coupling of aryl-halides has also been demonstrated on Ag and Au surfaces.<sup>29-31</sup> Stable organometallic (OM) phases are commonly observed on Cu and Ag,<sup>28, 32, 33</sup> while they are less frequent – but still reported – on Au.<sup>34-38</sup> Extensive studies of on-surface Ullmann coupling have been performed, exploring the effects of the detached halogen atoms,<sup>25</sup> the underlying surface,<sup>29</sup> and other reaction parameters,<sup>17, 32, 39, 40</sup> although most focused on the final product (the polymer). However, the reaction pathways may proceed through the formation of

other phases, i.e. intermediate products, with unique chemical and structural features. A successful case-study of the on-surface Ullmann reaction is the coupling of *para*-dihalobenzenes, characterized by linear-OM chains of substrate-stabilized phenyls, which shrink to poly(*para*-phenylene) (PPP) polymers after annealing.<sup>15, 24, 25, 33, 41-43</sup> Here we report the observation of an additional intermediate phase characterized by a 2D chessboard-like appearance during the Ullmann coupling of 1,4-dibromobenzene (dBB) on Cu(110). Using scanning tunneling microscopy (STM) and photoelectron spectroscopies, complemented with density functional theory (DFT) calculations we show that this structure is formed at an intermediate temperature range between the previously known linear-OM and polymer phase, and is observed only for sub-monolayer surface coverage ( $\leq 0.6$  ML) of the starting precursor.

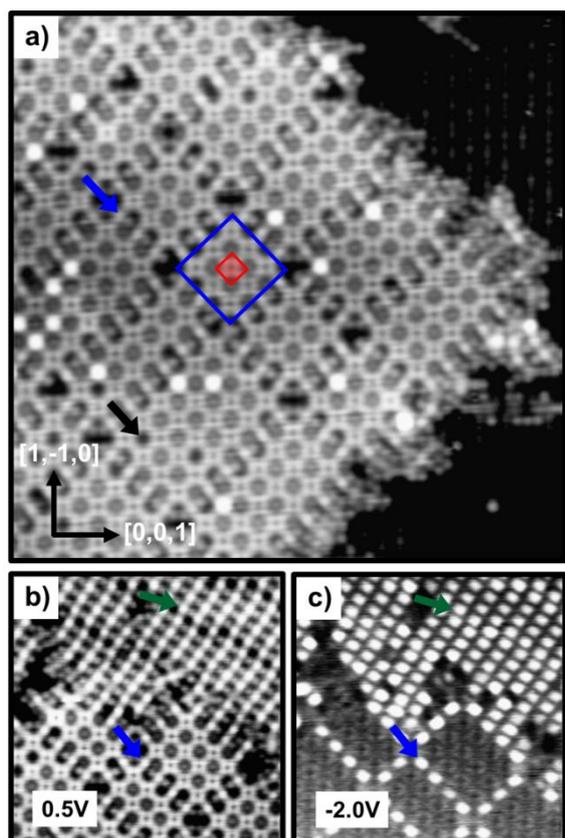


Figure 2. a) STM image ( $22 \times 22 \text{ nm}^2$ ) of the 2D-OM phase at 0.5ML coverage of dBB on Cu(110) after annealing at  $170 \text{ }^\circ\text{C}$ . The red box indicates the unit cell of a 2D-OM domain (blue box). The linear structures along the  $[1,-1,0]$  direction are Br atoms adsorbed on the substrate. b, c) STM image ( $14 \times 14 \text{ nm}^2$ ) and corresponding conductance map (acquired at  $V_b = -2.0 \text{ eV}$ ) of coexisting linear- and 2D-OM phases, showing the same spectroscopic features characterizing the 2D-OM domain boundaries and the linear-OM phase.

## Results

When deposited on Cu(110) at room temperature (RT) in ultra-high vacuum (UHV) conditions, dBB molecules dehalogenate and form linear-OM chains that can be subsequently converted into a 1D polymer upon further annealing.<sup>15</sup> Fast-X-ray photoelectron spectroscopy (fast-XPS) maps at the C 1s core level acquired during temperature ramping of samples with different initial molecular coverage are reported in Figure 1a. The chemical shift associated with the polymerization transition is observed in all the maps in the  $190\text{--}200 \text{ }^\circ\text{C}$  range, where the C-C covalent coupling takes place (yellow line in Figure 1a).<sup>15, 16, 25</sup> However, an additional shift is also present at lower temperature in the maps with initial coverage up to 0.6 ML (cyan line in Figure 1a). To understand the origin of this unexpected reaction, we focused on the sample with initial molecular coverage of 0.5 ML. Here, the two observed chemical shifts give rise to three distinct spectral features of the corresponding fast-XPS, each arising from the dominant phase in distinct temperature ranges (Figure S1 and discussion).<sup>15, 24</sup> The first phase is dominant in the RT- $145 \text{ }^\circ\text{C}$  range, the second in the  $145\text{--}200 \text{ }^\circ\text{C}$  range, and the third above  $200 \text{ }^\circ\text{C}$  (Figure 1b). STM after sequential annealing steps at increasing temperatures reveals that the spectral features

correspond to three morphologically distinct phases. At RT the known linear-OM phase is present on the Cu(110) surface (Figure 1c).<sup>15</sup> After annealing at  $170 \text{ }^\circ\text{C}$ , a new phase is observed, characterized by rectangular symmetry, which we identify as the 2D-OM phase (Figure 1e). The 2D-OM is converted into 1D polymers after annealing at  $230 \text{ }^\circ\text{C}$  (Figure 1g). Figure 1d and 1f show the STM images of the surface after annealing to  $145 \text{ }^\circ\text{C}$  and  $200 \text{ }^\circ\text{C}$  respectively, where the coexistence of two phases is observed. The 2D-OM phase is stable when the sample is cooled down to 5 K, as observed in STM images (Figure 1d-f).

STM images of the 2D-OM phase reveal a chessboard-like motif forming distinct domains (e.g. blue box in Figure 2a), separated by domain boundaries (blue arrow in Figure 2a). The domain unit cell is described by the epitaxy matrix  $(3, 2 \mid -3, 2)$  (red box in Figure 2a). The average domain size obtained from large-area STM images is  $3 \times 4$  unit cells, with maximum observed size of  $6 \times 6$ . Performing dI/dV conductance mapping of a region where both linear- (green arrow in Figure 2b,c) and 2D-OM phases are observed unveils that the domain boundaries (blue arrow in Figure 2) exhibit spectroscopic characteristics identical to those of the linear-OM phase (Figure 2c). As previously reported,<sup>15</sup> the linear-OM phase consists of phenyl rings anchored on either side to Cu atoms, which appear significantly brighter than the phenyls when imaged by STM. In the 2D-OM domain boundaries we observe the same morphology, and as such we ascribe the bright

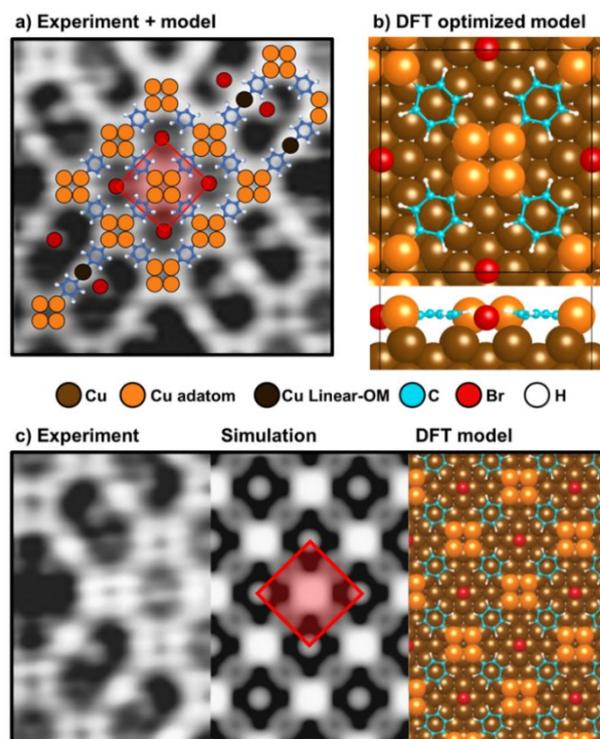


Figure 3. a) STM image ( $5 \times 5 \text{ nm}^2$ ) superimposed with the proposed structure of the 2D-OM phase and the domain boundary region. b) Top and side view of DFT optimization of the 2D-OM structure. c) Side-by-side view of experimental ( $4 \times 3 \text{ nm}^2$ ), DFT simulated STM images at  $-2.0 \text{ V}$  bias and DFT model. The red boxes in panels a) and c) indicate the unit cell of the 2D-OM network.

protrusions to Cu atoms bridging phenyls (dark brown circles in Figure 3a).

To understand the structure of the chessboard-like domains, we performed DFT calculations of several possible models (a detailed discussion is reported in Section 2 of Supporting Information). Figure 3 shows the structure whose Tersoff-Hamann<sup>44</sup> STM simulation best matches the experimental data. This model comprises an array of four Cu adatoms at the nodes (Figure 3a, orange circles) and phenyls as linkers, with Cu-Ph-Cu connections oriented along the  $[1,-1,\pm 1]$  directions. The distance between two copper atoms bridged by a phenyl is 0.7 nm. This value makes the Cu adatom clusters preferred anchoring sites for phenyl biradicals in the 2D-OM phase. In the 2D-OM phase each Cu atom is linked to just one phenyl, rather than two as in the linear-OM, which plausibly explains the spectral differences observed in Figure 2c. The features observed at the vertices of the unit cell are ascribed to Br

black arrow in Figure 2a. Cartoon models of the 2D-OM phase including the domain boundaries are shown in Figure S4 and S5, showing that Br atoms in the domain boundaries are located in the short-bridge position (Figure S5), in agreement with the linear-OM phase.<sup>15, 25</sup>

As mentioned, we do not observe the 2D-OM phase for coverages greater than 0.6 ML (Figure 1a). Based on the proposed model, the areal density of aromatic rings in the linear-OM, 2D-OM, and polymer phase is 2.0, 1.8, and 2.3 phenyls/nm<sup>2</sup>, respectively (see Figure S6), and notably the density of the 2D-OM phase is lower than that of the linear-OM. If the coverage is close to 1 ML (above 0.90 ML for a 10% change in density, in agreement with the 0.88 ML experimental point) there is insufficient space on the surface for the expansion required for transformation into 2D-OM domains, and thus the conversion to polymer occurs directly. The linear- to 2D-OM transition temperature increases as a

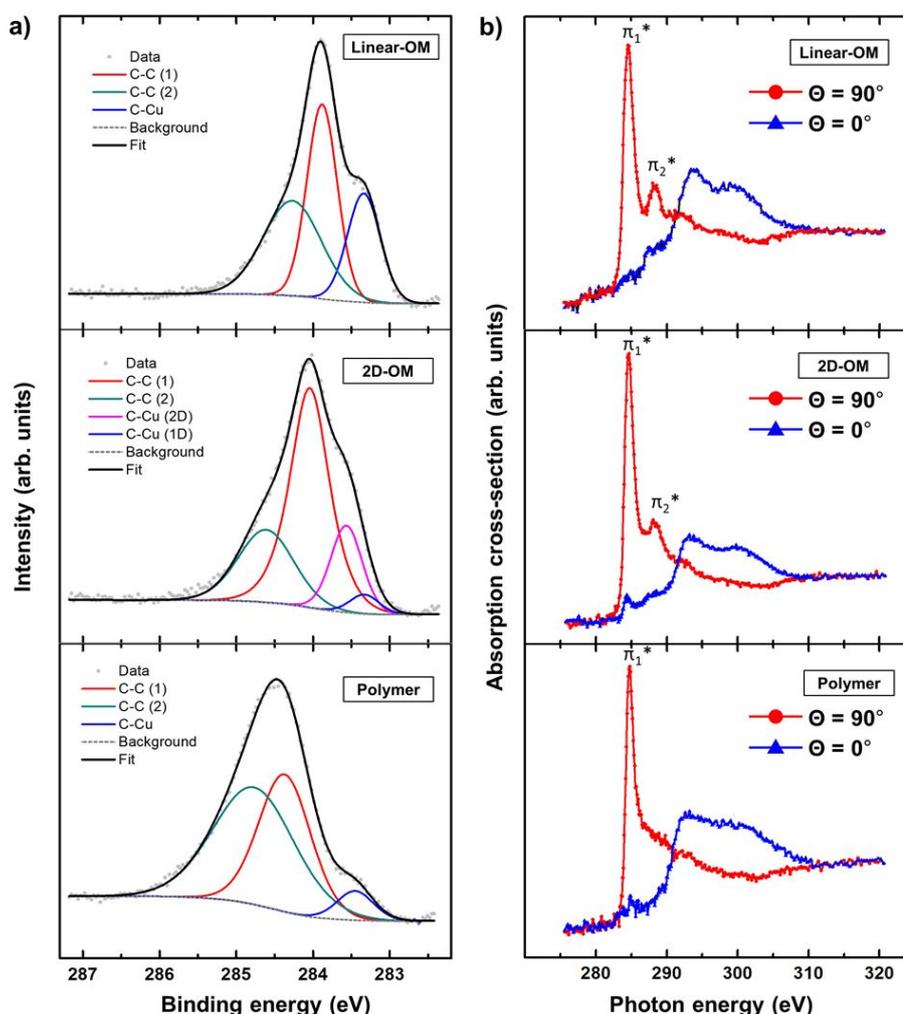


Figure 4. a) Spectral deconvolution of C 1s XPS spectra of the three phases: linear-OM, 2D-OM and polymer. b) Polarization-dependent C K-edge NEXAFS spectra for the linear-OM, 2D-OM and polymer phases measured at  $\theta = 0^\circ$  (s-polarization) and  $\theta = 90^\circ$  (p-polarization), respectively. For  $\theta = 0^\circ$  the polarization vector of the incident polarized photons is on the surface along the  $[001]$  direction, while for  $\theta = 90^\circ$  the polarization vector is almost perpendicular to the surface.

atoms (Figure 3a, red circles).<sup>15, 25</sup> These bromine atoms do not always fill the empty space of the network, as indicated by the

function of initial coverage, while the 2D-OM to polymer transition temperature decreases; these trends can probably

be connected to the different surface mobility of the phenyls in the linear-OM and 2D-OM phases. A higher surface temperature is needed to obtain the 2D-OM from the linear-OM. This can presumably be ascribed to (i) a higher surface density of Cu adatoms and (ii) their lower diffusion barrier, explaining the easier access to the 2D-OM phase, bearing a larger adatom-to-phenyl ratio. The fast-XPS shows that the 2D-OM phase is the most favorable phase at about 170 °C, while the STM shows that is thermodynamically stable even at RT or at 5K. In fact, we never observed a spontaneous reversion over a period of 3 days. To further characterize the newly observed 2D-OM phase, we performed spectroscopic investigation of the surfaces prepared at RT, and annealed to 170 °C and 230 °C, *via* XPS and C K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (**Figure 4**). XPS spectra acquired at the C 1s core level for the linear-OM and polymer phases (at RT and 230 °C, respectively) show the same line shapes as previously reported.<sup>15</sup> The red and green components correspond to the four hydrogen terminated carbons, with the splitting probably being linked to either a different position of the C-H bonds relative to the Cu lattice sites, or to vibrational modes, due to stretching type vibrations along C-H bonds.<sup>15, 16</sup> The blue component at 283.3 eV is due to Ph-Cu-Ph type of linkage, typical of the linear-OM phase.<sup>15, 25</sup> The small shoulder at low BE observed for the polymer phase arises from the C-Cu connections at the polymer endpoints, suggesting a predominance of short polymers. The C 1s spectrum of the 2D-OM phase (middle panel of Figure 4a) shows a new feature that is not observed in neither the linear-OM nor the polymer spectra. While the red and green components likely have the same origin described above, the component at 283.6 eV (magenta) can be assigned to phenyls linked to Cu adatoms clusters (Ph-Cu) as proposed in the model (Figure 3). The ratio 1:5 between the components at 283.3 eV and 283.6 eV in the XPS spectrum of the 2D-OM phase agrees with the average number of Ph-Cu-Ph and Ph-Cu linkages observed by STM, with the relative abundance of Ph-Cu-Ph being substantially reduced from linear-OM to 2D-OM, as in the latter case it only arises from the domain boundaries. The peaks positions, full width at half maximum (FWHM), and percentage for the three phases are reported in Table S1 of the SI.

The NEXAFS spectra acquired from surfaces prepared at RT and 230 °C are in agreement with previously reported measurements for the linear-OM and polymer phase.<sup>15, 25</sup> The spectrum acquired on the 2D-OM phase (middle panel in Figure 4b), exhibits a  $\pi_1^*$  intensity for s- and p-polarization ( $\theta = 0^\circ$  and  $\theta = 90^\circ$ , respectively) which is essentially unchanged from that of the RT structure, and reflects the mostly planar adsorption geometry of the aromatic rings with respect to the surface. The split of the  $\pi^*$  transition into two components ( $\pi_1^*$  and  $\pi_2^*$ ) is attributed to symmetry breaking in the ring (due to geometrical distortions) and/or to newly formed electronic state composed of  $\pi$  electron orbitals of the adsorbate and the 3d electronic states of the substrate, as observed for the RT phase.<sup>45, 46</sup> In the case of the 2D-OM the character of the  $\pi_2^*$  state is likely very similar to that of the

linear-OM, and geometric distortions of the phenyl ring are present in both calculated geometries.

## Discussion

Despite the large number of published studies on surface-confined Ullmann polymerization, our findings show that the complexity of its mechanistic pathways is not yet fully understood, even for the simplest reactive monomers. In particular, the observation of two distinct and stable OM phases (linear- and 2D-OM) is unusual given that no such result has yet been reported for this system<sup>15, 16, 24, 25, 41</sup> nor for systems using similar precursors.<sup>25, 26, 28, 33, 42</sup> To date, only linear (1D) OM phases have been reported for bidentate monomers, probably due to the narrow temperature and coverage ranges where additional 2D-OM phases might exist. Only a systematic study exploring the entire temperature range of interest and different starting molecular coverage is able to capture phases existing in a limited parameter space. Therefore, we do not exclude that similar additional phases exist also in other systems. Another key aspect that characterizes our system is the presence of Cu clusters which stabilize the 2D-OM phase. Although the role of Cu clusters in homogenous catalysis is well established,<sup>47</sup> in on-surface Ullmann coupling the stabilization of OM intermediates by metal clusters instead of single atoms has only been shown once, by Zhou et al.<sup>48</sup> Similarly to our case, they observed molecular aggregates where each (monoradical) molecule is stabilized by one metal atom.<sup>48</sup> However, these clusters were observed only for extremely low concentrations (0.1 ML of coverage), and, due to the mono-radical nature of the used precursor, did not yield an assembled structure. Differently, our 2D-OM phase represents an exceptional example of extended ordered network.

Being able to control the self-assembly ordering and tessellation is a crucial aspect of supramolecular chemistry, which requires a deep understanding of molecular interactions for driving the system towards the wanted structure. It has been shown that the molecular ordering of intact halogenated molecules can be controlled by the temperature,<sup>49, 50</sup> and that the tessellation of metal-organic self-assemblies can be controlled by changing the type of the metal.<sup>51-54</sup> However, the present work represents the first case of on-surface transition between two isomeric OM phases, driven solely by temperature. The behavior described herein could be of general interest: additional stable ordered intermediates could also exist in the case of other reactions and systems, maybe in a short range of temperatures or for a precise set of parameters, and not experimentally observed so far. While enriching the fundamental understanding of the mechanism of the most important on-surface coupling reaction, our finding of multiple intermediates, with different molecular density and dimensionality, could also have implications for the structural quality of the final polymers.<sup>41</sup> In fact, the presence of intermediate phases is an essential feature for design of hierarchical on-surface polymerization, which is the key tool for increasing the order and control dimensionality of the final

polymer.<sup>14, 17, 55</sup> These later examples emphasize the importance of understanding the mechanisms of on-surface synthesis for the rational design of surface confined conjugated structures.

## Conclusion and perspectives

We report the observation of two structurally distinct intermediate phases in the Ullmann polymerization of dBB on Cu(110), created within well-defined temperature ranges. The already known linear-OM is converted into a 2D-OM chessboard-like structure. This phase has been observed during the annealing of the surface at a temperature between 145 °C and 200 °C for sub-monolayer surface coverage ( $\leq 0.6$  ML) and remains stable after cooling down the sample to RT or below. Combining STM observations with DFT calculations, we have described the structural details of the 2D-OM phase, comprising phenyls bridging four-atom clusters of Cu adatoms. Investigations *via* XPS and NEXAFS support our findings and show that the presence of the 2D-OM phase, and its evolution as function of initial coverage, causes slight differences in the polymerization temperature.

These results demonstrate that even for simple molecules, on-surface Ullmann coupling may follow multiple pathways. The observation of two stable OM phases, with distinct morphologies and spectroscopic fingerprints, shows the complexity of on-surface mechanisms, offering the opportunity of fine tuning the growth of specific structures through the design of different synthetic routes.

## Experimental Section

All the experiments have been performed under UHV conditions (base pressures below  $2 \times 10^{-10}$  mbar). The dBB precursor molecule (Sigma-Aldrich, 98% purity) is shown in Figure 1 and was deposited onto Cu(110) (MaTeck GmbH) through a leak valve, while the substrate was held at RT. The Cu(110) surface was prepared before dosing by multiple cycles of Ar<sup>+</sup> sputtering (0.8–1.2 keV) followed by annealing (480 °C). The surface coverage was evaluated by comparing the XPS C 1s/Cu 2p peak intensity ratio, imposing 1ML in the case of saturated coverage.

STM was performed with an Omicron LT-STM at 5 K, using constant tunneling current (0.2 nA) and constant bias voltage measured from the tip to the sample (0.5 V, unless stated otherwise), at various surface coverages calibrated with an XPS spectrometer hosted in the same UHV chamber. The reported STM images correspond to 0.5 ML coverage, for a better comparison with the fast-XPS experiments. The dI/dV maps were recorded in the open feedback loop mode ( $V = 2$  V) using a lock-in amplifier (peak to peak modulated voltage of 30 mV,  $f = 1100$  Hz). STM images were analyzed using WSxM,<sup>56</sup> and treated for line-by-line flattening, plane subtraction and contrast enhancement.

XPS, fast-XPS and NEXAFS were performed at the ALOISA beamline at the Elettra synchrotron radiation facility in Trieste

(Italy). For XPS and fast-XPS experiments a normal electron emission geometry was used, with the linearly polarized radiation having a 4° grazing incidence, by using a home-built hemispherical electron analyzer equipped with a multichannel plate (MCP) detector. The C 1s core level fast-XPS maps have been acquired, using 390 eV of photon energy, while rising the temperature of Cu(110) from RT to 230 °C (0.2 °C/s), by using a heating element located behind the sample. Every line of the fast-XPS map is obtained from snapshots of the C 1s peak (one spectrum per second) at the reported temperature, with a 30 eV PE and overall energy resolution of 350 meV. A partial electron yield, obtained by a channeltron with a -240 V biased filtering grid, was used to record the NEXAFS C K-edge spectra with a photon energy resolution of 100 meV. The photon energy was calibrated by measuring the drain current on the last refocusing mirror of the beamline simultaneously with the C K-edge. The C K-edge spectrum acquired from the clean Cu(110) was used to normalize the spectra. Rotating the sample along the beam axis allowed to perform polarization dependent measurements. The surface angle ( $\theta$ ) was changed from transverse electric (TE, s-polarization) to transverse magnetic (TM, almost p-polarization) with respect to the polarization vector with the grazing photon angle of incidence fixed at 6° (for details about photon energy calibration and NEXAFS geometry see Floreano *et al.*).<sup>57</sup>

DFT calculations were performed using the Vienna *Ab initio* Simulation Package (VASP).<sup>58</sup> To include non-local interactions (in particular between the Cu surface and the carbon structure) the optB86b-vdW exchange correlation functional was implemented.<sup>59–61</sup> An energy cutoff of 400 eV was used with projector-augmented wave pseudopotentials.<sup>62</sup> Given the large size of the unit cell, a gamma-point k-point sampling was set for all calculations. A vacuum spacing of  $\sim 15$  Å was used to prevent interactions between periodic images. Atomic coordinates were relaxed to a force cutoff of 0.01 eV/Å. The Cu(110) substrate was represented by six layers, with the bottom four layers fixed. The STM image simulations were carried out within the Tersoff-Hamann approximation.<sup>44</sup> Atomic models were visualized with VESTA.<sup>63</sup> For the case reported in Figure S2a, the PBE functional<sup>64</sup> was used with the D3 method to include van der Waals interactions,<sup>65</sup> and the Cu(110) substrate consisted of nine layers with the bottom five fixed in the calculations.

## Conflicts of interest

There are no conflicts to declare.

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