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Frank Palmino, Judicaël Jeannoutot, Vincent Luzet, Alain Rochefort, Frédéric Cherioux. On-Surface Synthesis Guided by Supramolecular Orientation on a Au(111) Surface. *The Journal of Physical Chemistry C*, 2024, 128 (30), pp.12482 - 12487. hal-04776535

**HAL Id: hal-04776535**

**<https://hal.science/hal-04776535v1>**

Submitted on 11 Nov 2024

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# On-Surface Synthesis Guided by Supramolecular Orientation on an Au(111) Surface

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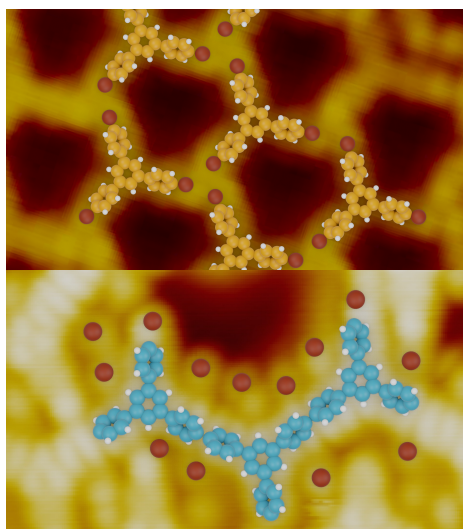
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ABSTRACT. Surface-assisted Ullmann coupling is a very common approach to carry on-surface synthesis. We investigated the deposition of the 1,3,5-tris(4-bromophenyl)benzene molecule on an Au(111) surface at low temperatures. We observed a new supramolecular phase using scanning tunneling microscopy, and we demonstrated that this supramolecular organization promotes the formation of a well-defined 1D-covalent network through thermal annealing.

## TOC GRAPHICS



**KEYWORDS.** STM, Au(111), DFT, on-surface synthesis, Halogen bonding.

On-surface synthesis (OSS), an emerging field at the interface of chemistry and nanotechnology, has garnered significant attention in recent years due to its potential for manipulating and engineering molecular structures directly on solid surfaces.<sup>1,2</sup> This approach offers opportunities for designing materials with tailored electronic, optical, and catalytic properties. OSS also holds an important potential for a plethora of applications ranging from molecular electronics to surface-functionalized nanomaterials.<sup>3</sup> The driving force of OSS is its

ability to assemble, modify, and study molecular architectures with nanometer precision. However, on-surface chemistry confronts several notable limitations that challenge its full realization. These limitations include the complex interplay between reaction kinetics and thermodynamics, the challenges for controlling the reaction conditions at the nanoscale with precision, and the difficulties in the formation of extended 2D-covalent networks.<sup>4,5</sup>

Among all the proposed precursors for creating 2D covalent networks, the molecule 1,3,5-tris(4'-bromophenyl)benzene (TBB, Fig. 1a) stands out as the most extensively examined molecule under ultra-high vacuum conditions using scanning tunneling microscopy (UHV-STM). This star-shaped molecule features three branches, each terminating with a bromine atom, and it serves as the prototype for generating a conjugated 2D network containing hexagonal pores. TBB molecule has been deposited on a variety of surfaces, including Si(111)-B,<sup>6</sup> graphite (HOPG),<sup>7</sup> graphene,<sup>8</sup> Cu(111),<sup>7,9,10</sup> Ag(111),<sup>10,11,12</sup> and Au(111).<sup>13-16</sup> On less reactive surfaces like Si(111)-B,<sup>6</sup> HOPG,<sup>7</sup> or graphene,<sup>8</sup> the deposition of TBB at room temperature leads to the formation of periodic 2D-extended supramolecular networks that desorb upon annealing at temperatures exceeding 400 K. On more reactive surfaces such as Ag(111) or Cu(111), low-temperature depositions (< 80K) result in the formation of 2D-supramolecular networks stabilized by halogen bonds.<sup>10</sup> When TBB molecule is deposited at room temperature on Cu(111), it initiates the formation of a proto-polymer through the oxidative addition of a copper adatom between the terminal phenyl rings of two TBB molecules.<sup>10</sup> On Ag(111), room temperature TBB deposition yields multiple polymorphs, with the primary driving force being

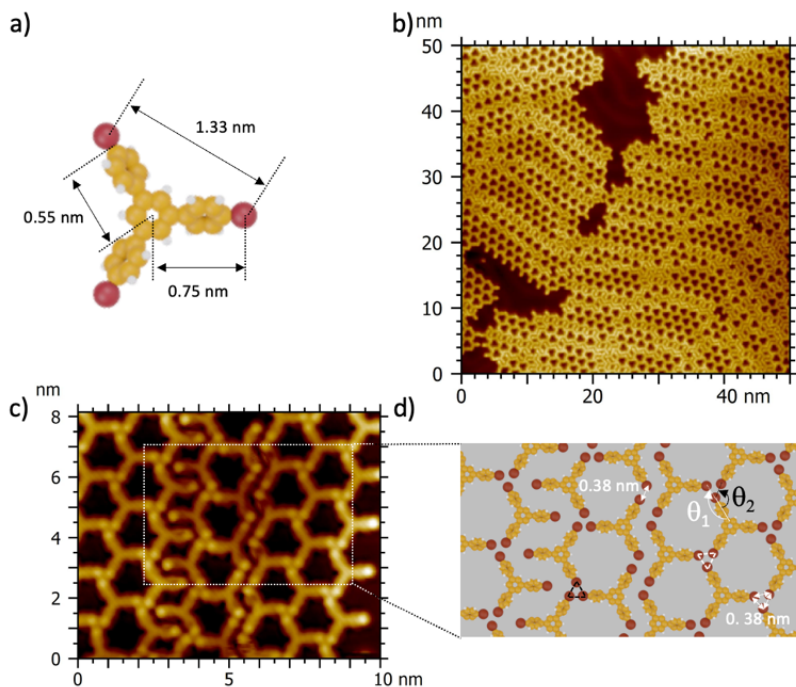
halogen bonds.<sup>10</sup> On Cu(111)<sup>7,9,10</sup> or Ag(111)<sup>10-12</sup> surfaces, supramolecular networks or proto-polymers polymerize when heated above 400 K, induced by thermally activated carbon-carbon bond formation. The resulting polymers comprise a variety of interconnected polygons and exhibit numerous structural defects.

The deposition of TBB molecule on the Au(111) surface has been a subject of extensive investigation.<sup>13-16</sup> At room temperature, this leads to the formation of a highly compact network stabilized by both hydrogen and halogen bonds.<sup>13</sup> Upon annealing above 400 K, this network forms a periodic array of TBB dimers along with some oligomerized motifs resembling to those observed after annealing on Ag(111) or Cu(111).<sup>13</sup> This dimer formation is attributed to the reduced mobility of TBB molecule associated to the initial network's compactness. This result is corroborated by depositions on an Au(111) surface preheated to 430 K. In this case, 2D-extended but highly disordered covalent networks are formed.<sup>13-16</sup> On the Au(111) surface, the polymerization of TBB molecule is under thermodynamic control.<sup>15</sup> Specifically, the radicals generated by the homolytic cleavage of C-Br bonds exhibit an extended lifetime. Consequently, given this extended lifetime, we aim to address the following question: Can an ordered covalent network be established by heating an initially porous supramolecular structure that might facilitate the diffusion of TBB molecules on the Au(111) surface? To address this question, we conducted a study involving the deposition of TBB molecules onto the Au(111) surface at low temperatures and the impact of thermal annealing using UHV-STM. Our findings revealed an improved stability of the supramolecular network through

triple halogen bonding, within the temperature range of 10 K to 400 K on Au(111). Additionally, the geometry of this supramolecular network promotes the creation of well-ordered 1D covalent networks through thermal annealing, above 400 K.

Atomically clean Au(111) surface was prepared by standard procedure (See Fig. S1). TBB molecule was sublimated and deposited under ultra-high vacuum conditions onto an Au(111) substrate maintained at a temperature below 80 K (see ESI for experimental details). STM images were acquired using a low-temperature STM operating at 10 K in constant current mode. The STM images obtained after the deposition of TBB, with a coverage ranging from 0.3 to 0.9 monolayer, on the Au(111) surface reveal the formation of large 2D-extended supramolecular islands composed of several domains separated by grain boundaries (Fig. 1b). Each periodic domain consists of a network containing hexagonal pores (Fig. 1c). These pores are bounded by three star-shaped structures, where each end of the three arms is brighter than the rest. The length of each arm is  $0.80 \pm 0.08$  nm. Each of these arms points towards the end of two other branches from two stars. The three bright ends of three different stars form an equilateral triangle measuring  $0.38 \pm 0.03$  nm on each side. The grain boundaries consist of two different star-shaped features, each pointing one of their bright ends towards the end of another star. The distance between the two ends is consistently  $0.38 \pm 0.03$  nm. The influence of temperature was subsequently examined. Firstly, the supramolecular network was annealed either at room temperature for 12 hours or at 100°C for 30 minutes. In both cases, no modification of the network occurred, as only the porous network was observed in the STM

images (Fig. S2-4). These results reveal that the initial supramolecular network remained unchanged after such thermal treatments. Finally, we have deposited TBB molecules on a Au(111) surface held at room temperature. In this case, only a highly compact network was observed, as reported in the literature.<sup>13</sup>



**Figure 1.** Porous supramolecular networks were obtained after depositing 0.8 monolayers of TBB molecule onto an Au(111) surface at 80 K. a) CPK model of the 1,3,5-tris(4'-bromophenyl)benzene (TBB) molecule. b) A large-scale STM image ( $50 \times 50 \text{ nm}^2$ ,  $V_s = -1.37 \text{ V}$ ,  $I_t = 400 \text{ pA}$ , 10 K) reveals the porous supramolecular structure consisting of fused porous periodic domains bordered by grain boundaries. c) High-resolution STM image ( $10 \times 8 \text{ nm}^2$ ,  $V_s = -0.01 \text{ V}$ ,  $I_t = 440 \text{ pA}$ , 10 K) of the TBB/Au(111) interface. Each arm of the star-shaped features ends with a bright protrusion. d) Model of the supramolecular network corresponding to the white-dashed rectangle in the STM image shown in c). The porous

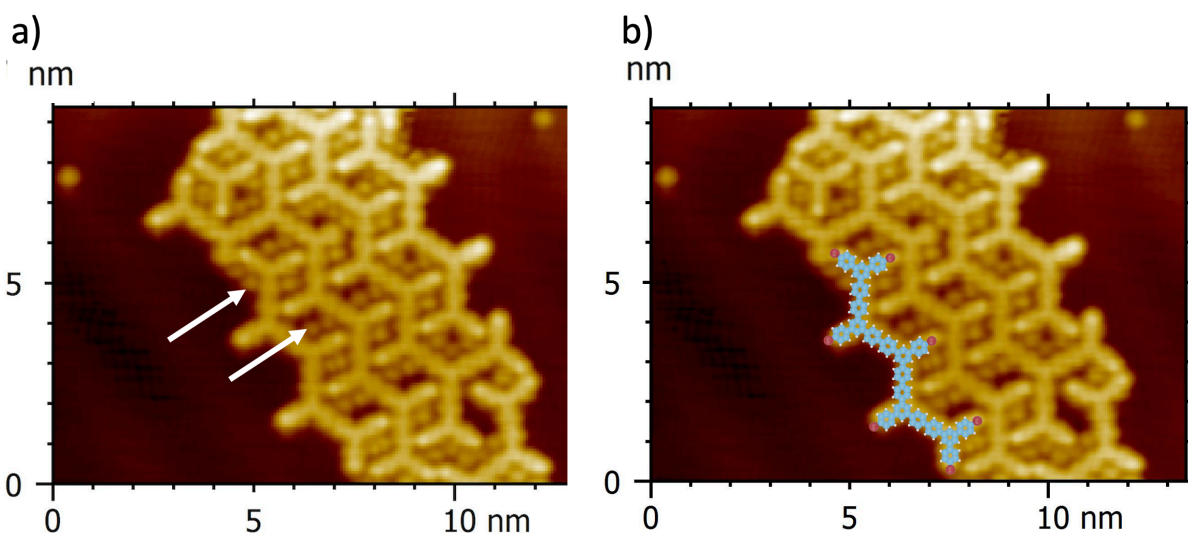
network is formed by three TBB molecules that interact through three halogen bonds in a  $X_3$ -synthon geometry ( $\theta_1 = 180^\circ$  and  $\theta_2 = 120^\circ$ ), as highlighted by the dashed white triangle. The grain boundaries are stabilized by two halogen bonds between two TBB molecules (white arrows). The distance between bromine atoms involved in all halogen bonds is  $0.38 \pm 0.04$  nm. The two enantiomeric  $X_3$ -synthons are depicted, respectively with white and black dashed triangle.

Due to their size and symmetry, the three-fold bright features observed in STM images are assigned to single pristine TBB molecule. On the basis of the high-resolution STM images, a model of adsorption is proposed in Fig. 1d. In this model, Br–Br distances are all equal to  $0.38 \pm 0.03$  nm and the  $\theta_1$  and  $\theta_2$  angles are of  $180^\circ$  and  $120^\circ$ , respectively. These features correspond to a  $X_3$ -synthon geometry that is based on three halogen-bonds of the type II (See Fig. S5).<sup>17,18</sup> These types of  $X_3$ -synthons have been observed for the deposition TBB molecule onto Ag(111)<sup>10,11</sup> and Cu(111)<sup>10</sup> at low temperature (<80 K). However, a deposition of TBB molecules on Ag(111)<sup>10,11</sup>, Cu(111)<sup>10</sup> or Au(111)<sup>13</sup> surface at room temperature led to the formation of compact networks instead of  $X_3$ -synthons. This discrepancy can be clarified by considering polymorphisms influenced by the interplay of kinetics and thermodynamics.<sup>19,20</sup> In the case of TBB, we used a lower molecular coverage than the 1 monolayer reported in the literature, along with a deposition temperature below 80 K. These two conditions support the formation of  $X_3$ -synthons on Au(111) surface and maintain their stability at temperatures up to 373 K. Finally, a close examination of the STM images shows that the supramolecular organization is



chiral due to the geometry of the X<sub>3</sub>-synthons.<sup>11</sup> The two enantiomers are highlighted by respectively a black and a white triangle in Fig. 1d (enlarged in Fig. S6). Each periodic domains observed in large-scale STM images (Fig. 1b and Fig. S7) is constituted by a single enantiomer. Then, we have investigated the thermal-induced reactivity of this new supramolecular phase on the Au(111) surface. The X<sub>3</sub>-synthon based supramolecular network was heated to 383 K for 30 minutes. The large 2D islands disappeared, giving way to smaller islands (Fig. 2a and Fig. S8) containing parallel sawtooth-like lines. These lines are separated by lozenge-shaped pores containing well-defined single spots (white arrow in Fig. 2a). Annealing was conducted for 30 minutes at temperatures above 383 K. Between 383 K and 483 K, the annealing process led to increasingly interconnected networks, with the formation of more and more polygons with 5, 6, or 7 edges, while the number of sawtooth lines gradually decreased until they completely vanished. The number of single protrusions within the pores or polygons remained constant over this temperature range (See Fig. S9a and S10a-c). Starting from a temperature of 483 K, the number of interconnected polygons no longer changed, but the number of single protrusions decreased significantly, nearly disappearing from the surface at 526 K (See Fig. S10d). The lines and polygons observed in the STM images following thermal annealing at temperatures above 383 K correspond to the formation of polymers through an Ullmann-type coupling between TBB molecules.<sup>13-16</sup> The single protrusions correspond to bromine atoms adsorbed on the surface,<sup>21,22</sup> which are generated through thermally-induced debromination of the TBB molecules. The polymerization of TBB molecules on an Au(111) surface leads to

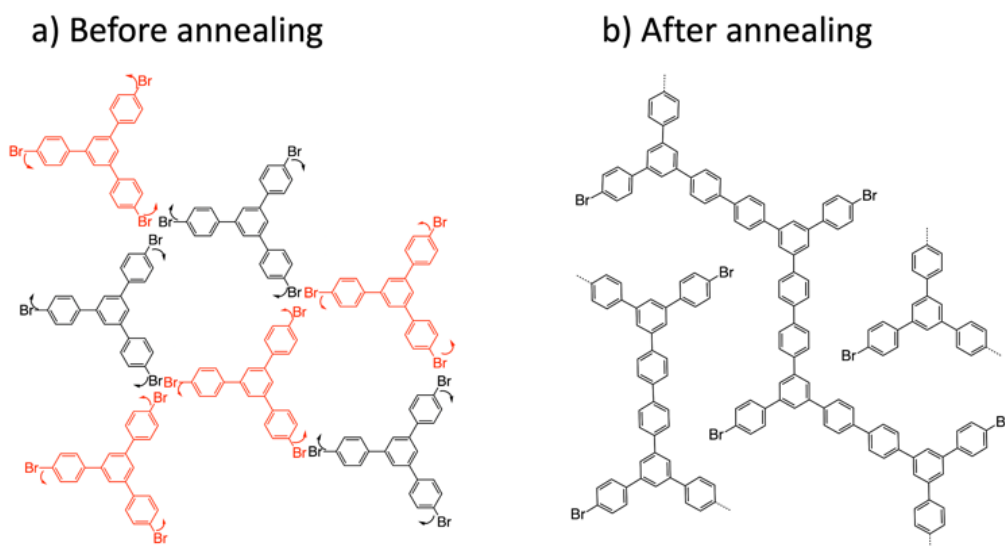
the formation of disordered polygon networks when heated to temperatures exceeding 413 K,<sup>14-16</sup> despite the homolytic cleavage of C-Br bonds in TBB molecules initiated at 325 K.<sup>15</sup> This phenomenon is attributed to the thermodynamic control of the Ullmann coupling on the Au(111) surface. The two critical factors contributing to this phenomenon are the reversibility of debromination on Au(111) and the stabilization of radicals formed by the homolytic cleavage of C-Br bonds through interactions with surface Au atoms.<sup>15</sup>



**Figure 2.** The evolution of the porous supramolecular network obtained after deposition of 0.8 monolayer of TBB molecule onto an Au(111) surface at 80 K. a) STM image ( $13.5 \times 9.5 \text{ nm}^2$ ,  $V_s = -2.20 \text{ V}$ ,  $I_t = 214 \text{ pA}$ , 10 K) after thermal annealing at 383 K for 30 minutes. A covalent network is composed of parallel interdigitated saw-tooth lines that surround individual protrusions (highlighted by white arrows). Only a few lines are interconnected. b) Covalently-bounded network superimposed on STM image shown in a).

Such high annealing temperatures may also result into a substantial diffusion of species on the surface, leading to the disordered and highly connected covalent networks. However, the first instance of Ullmann coupling with TBB molecules on an Au(111) surface was observed solely through thermal annealing at 383 K, but it lead only to the formation of an ordered supramolecular network built exclusively from TBB dimers, without polygons. The formation of dimers is attributed to the constrained mobility of molecules at 383 K, resulting from the initial compactness and stability of the supramolecular network.<sup>11</sup> In addition, the deposition of 0.25 monolayer of TBB molecules onto an Au(111) surface held at 413 K leads only to the formation of 2D-interconnected polygons.<sup>13</sup> Based on our experimental results and a thorough analysis of the literature, the formation of unexpected 1D-sawtooth-like polymer lines is clearly governed by the initial supramolecular network, which is centered around an X<sub>3</sub>-synthon. Indeed, when the TBB molecules do not self-assemble in this X<sub>3</sub>-synthon arrangement, thermal annealing only results in 2D-interconnected polygons.<sup>13</sup> However, when TBB molecules adopt the X<sub>3</sub>-synthon arrangement, three bromine atoms come into close proximity (See Figure 1d). Consequently, thermal activation at 383 K triggers the cleavage of C-Br bonds, leading to the generation of radicals with a sufficiently extended lifetime on the Au(111) surface. Since the initial bromine atoms are closely positioned due to the X<sub>3</sub>-synthon arrangement, aligning phenyl groups carrying a radical only requires half of them to rotate by -30° (i.e.,  $-(180-\theta_2)/2$ , clockwise, highlighted in black), while the remaining half rotates by +30° (i.e.,  $(180-\theta_2)/2$ , anticlockwise, in red, Fig. 3a). In addition, the formation of C-C bonds also requires a translation of approximately half the distance between two bromine atoms, which

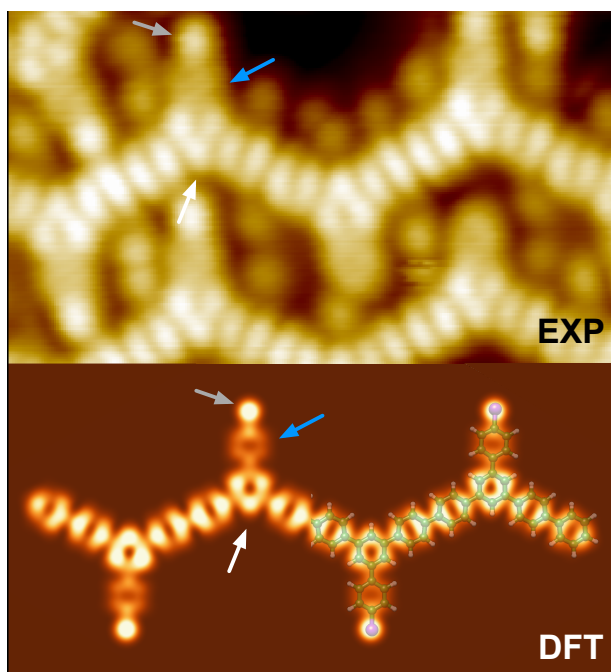
is approximately 0.19 nm (See supplementary video). Due to the limited rotation and diffusion, minimal energy is required for these processes. Therefore, annealing at 383 K is sufficient to initiate C-Br bond cleavage and reorganize the molecules into a 1D-sawtooth-like covalent network, unlike the case of a compact supramolecular network, which requires higher energy for reorganization.<sup>13</sup> The formation of covalent bonds between adjacent TBB molecules, forming an X<sub>3</sub>-synthon, leaves one bromine end per molecule, as rotations are opposite (+30° and -30°) between neighboring molecules (Fig 3). As a result, only a limited number of cross-linking nodes between chains have been observed, leading to the formation of exclusively sawtooth-like polymer lines (Fig. 2a-b and supplementary video). A similar polymer has been observed as a minor side-product after polymerization of 1,3,5-tris(4'-iodophenyl)benzene on an Au(111) surface at the solid-liquid interface.<sup>23</sup> However, the presence of bromine atoms adsorbed on the surface, in close proximity to the sawtooth-like polymer lines, can explain the limited length (<20 nm) of these 1D polymers as observed during the growth of polyphenylene on copper surfaces.<sup>24</sup>



**Figure 3.** Supramolecular network reorganization a) supramolecular network: TBB molecules rotate by  $-30^\circ$  (in black) or  $+30^\circ$  (in red) to align aromatic cycles. b) Sawtooth-like covalent network.

Regarding this sawtooth-like polymer, a STM image of a short polymeric chain is shown at Fig. 4 in comparison to a simulated STM image obtained from DFT calculations of a  $(\text{TBB})_4$  oligomer adsorbed on Au(111). The unit cell used in the DFT calculations is reported at Fig. S11. Although the gas phase geometry of both TBB molecule and  $(\text{TBB})_4$  oligomer exhibit a non-planar structure, where the benzene rings are mutually rotated, adsorbed  $(\text{TBB})_4$  becomes completely flat on the Au(111) surface. Moreover, the observed STM contrasts are perfectly reproduced through the DFT simulation. More specifically, the higher intensity of Br atoms (grey arrows), the fainted benzene ring in the unreacted branch (blue arrows), and the three-dots protrusion structure of the most central ring (white arrows). These STM features are in

very good agreement with the nature of molecular orbitals of 1,3,5-triphenylbenzene.<sup>25</sup> Moreover, the topology observed for the polymeric backbone is also quite nicely reproduced through STM simulation from DFT calculations. Upon heating to higher temperatures, TBB molecules exhibit increased surface diffusion, leading to the formation of more highly crosslinked 2D polymers. Due to this enhanced molecular diffusion, the polymer chains are more disordered than those formed at 383 K. Notably, STM images reveal that debromination is not complete even after annealing at temperatures exceeding 483 K, as some branches of TBB molecules retain their initial length ( $0.80 \pm 0.05$  nm), while others are shorter ( $0.6 \pm 0.05$  nm, see Fig. 1a and S7b in ESI). Moreover, bromine atoms are still adsorbed on the Au(111) as they are visible on STM images (See Fig. S8 in ESI) after a thermal annealing at 526 K. In contrast, XPS analyses have demonstrated complete debromination beyond 460 K and complete desorption of bromine atoms at 500 K.<sup>15</sup> This discrepancy can be attributed to the localized nature of the information obtained by STM compared to that derived from XPS analysis.



**Figure 4.** Expanded STM images of a small sawtooth-like polymer that emphasize the similitude between the experimental (EXP) and the calculated (DFT) electronic structure properties. The main STM contrasts are identified by the colored arrows, gray arrow identifies the presence of Br, the blue arrow shows a fainted benzene ring, and the white arrow points toward the three-dots protrusion associated to the central ring. The observed STM contrasts among the ring backbone is quite similar to the nature of molecular orbitals calculated for an adsorbed (TBB)<sub>4</sub> oligomer on Au(111). (EXP:  $V_s = -2.20$  V,  $I_t = 214$  pA, 10 K, DFT:  $V_s = -2.30$  V, 0 K)

We have demonstrated the existence of a novel supramolecular self-assembly resulting from the deposition of TBB molecules on the Au(111) surface. This self-assembly is guided by a triple halogen bond, locally forming an X<sub>3</sub>-synthon. Halogen interactions are exceptionally

strong, and the network remains stable up to temperatures of 373 K. By adjusting the annealing temperature to 383 K, we have demonstrated the formation of 1D sawtooth-like polymers through an Ullmann-like cross-coupling process. These 1D covalent networks are highly ordered and nearly defect-free, thanks to the initial supramolecular network geometry, which promotes the propagation of polymerization at low temperatures to limit excessive precursor diffusion. This result highlights the potential for controlling surface polymerization and achieving defect-free conjugated nanostructures guided by supramolecular orientation. Ongoing work is focused on optimizing polymerization conditions to produce longer polymer chains.

#### ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures and additional STM images. The following files are available free of charge.

#### ACKNOWLEDGMENT



This work is supported by the French National Agency through the project HITS (ANR-20-CE09-0016) and Pays de Montbéliard Agglomération. A.R. thanks the Alliance and Calcul Québec for providing computational resources and support.

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