

Two-Dimensional Polymer Formation on Surfaces: Insight into the Roles of Precursor Mobility and Reactivity

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Abstract: We report on a combined scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) study on the surface-assisted assembly of the hexaiodo-substituted macrocycle cyclohexa-*m*-phenylene (CHP) toward covalently bonded polyphenylene networks on Cu(111), Au(111), and Ag(111) surfaces. STM and XPS indicate room temperature dehalogenation of CHP on either surface, leading to surface-stabilized CHP radicals (CHPRs) and coadsorbed iodine. Subsequent covalent intermolecular bond formation between CHPRs is thermally activated and is found to proceed at different temperatures on the three coinage metals. The resulting polyphenylene networks differ significantly in morphology on the three substrates: On Cu, the networks are dominated by "open" branched structures, on the Au surface a mixture of branched and small domains of compact network clusters are observed, and highly ordered and dense polyphenylene networks form on the Ag surface. Ab initio DFT calculations allow one to elucidate the diffusion and coupling mechanisms of CHPRs on the Cu(111) and Ag(111) surfaces. On Cu, the energy barrier for diffusion is significantly higher than the one for covalent intermolecular bond formation, whereas on Ag the reverse relation holds. By using a Monte Carlo simulation, we show that different balances between diffusion and intermolecular coupling determine the observed branched and compact polyphenylene networks on the Cu and Ag surface, respectively, demonstrating that the choice of the substrate plays a crucial role in the formation of two-dimensional polymers.

Introduction

Supramolecular structures formed by the surface-confined self-assembly of functional molecular building blocks are a promising class of materials for future technologies.^{1–3} Particularly efficient for their fabrication is hydrogen bonding, which provides both high selectivity and directionality: highly ordered hydrogen-bonded porous molecular networks have been fabricated on well-defined surfaces under ultrahigh vacuum (UHV) conditions.^{4–6} Other promising strategies for the self-organized growth of regular supramolecular structures rely on surface metal coordination^{7–9} or aromatic coupling motifs.¹⁰ However, a common feature of these nanostructures is, due to

the comparably weak interaction energies, the poor thermal and chemical stability that limits their use in potential applications. The obvious requirement for more stable structures has recently led to great interest in covalently bonded two-dimensional molecular networks.^{11,12} Various proof-of-principle studies have demonstrated that different reactions readily proceed on surfaces, even though the reactants are confined to two dimensions (2D).^{13–22} However, despite the recent progress, the self-

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organized growth toward extended and regular 2D covalent networks still defines one of the major challenges in surface chemistry.²³

A partial explanation for this situation is related to the fact that the formation of covalent intermolecular bonds, in contrast to noncovalent bonding, is usually an irreversible process; therefore, molecules confined to covalent structures on surfaces are firmly anchored, and postcorrection of defects or modification of morphology is usually not possible. Thus, to minimize defects in covalent networks and to steer the on-surface synthesis toward desired structures, a detailed understanding of the influence of adsorption energies, diffusion barriers, and lateral interactions of molecular precursors, all of which depend on the substrate atomic environment, symmetry, and chemical nature, is required. Up to the present day, however, there exists little experimental and computational insight into the role of the substrate in on-surface chemical routes toward two-dimensional covalent networks.

Here, we present a combined experimental and computational study of the impact of the substrate on the formation and connectivity of a two-dimensional polymer. We use a prototypical multidentate molecular precursor, the hexaiodo-substituted macrocycle cyclohexa-*m*-phenylene (CHP) (Figure 1),²⁴ and exploit covalent intermolecular bond formation on the coinage metal surfaces Cu(111), Au(111), and Ag(111). On either surface, the adsorption of CHP at RT results in C–I bond cleavage, giving rise to the formation of surface-stabilized CHP radicals (CHPRs) and coadsorbed iodine. Thermally activated CHPR addition is found to proceed at different temperatures on the three metals, notably at about 475 K (Cu), 525 K (Au), and 575 K (Ag). The morphology of the resulting polyphenylene networks differs significantly: On Cu, the growth of dendritic network structures with single-molecule-wide branches prevails; the Au surface promotes the evolution of small 2D network domains, and on the Ag surface extended and well-ordered 2D networks emerge as we have reported recently.^{25,26} With the aid of density functional theory (DFT) calculations, the nature of the surface-stabilized CHPRs, as well as the details of diffusion and reaction pathways, are elucidated. We find that on Cu, diffusion of CHPR is hindered, while the coupling step is significantly promoted. On Ag, on the other hand, the CHPRs

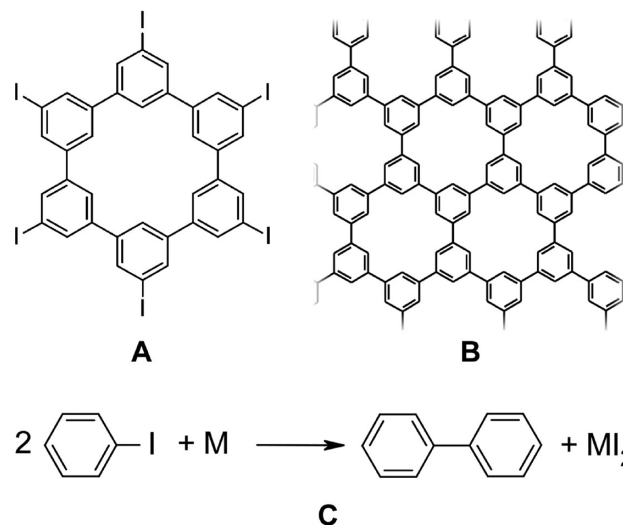


Figure 1. (A) Chemical structure of hexaiodo-substituted CHP. (B) Chemical structure of a fraction of the polyphenylene network. (C) Mechanism of the surface-assisted aryl–aryl coupling of iodobenzene to biphenyl (here, M represents Cu, Au, or Ag).

retain a high surface mobility but exhibit a low coupling affinity. We demonstrate that these differences are responsible for the formation of dendritic and 2D polyphenylene networks as observed on Cu and Ag surfaces, respectively.

Results and Discussion

Adsorption of CHP on Cu(111), Au(111), and Ag(111): Evolution of Surface-Stabilized Radicals and Coadsorbed Iodine. Figure 2A shows an overview STM image of CHP molecules adsorbed on Cu(111) that was held at room temperature during deposition (see the Supporting Information for experimental details). CHP agglomerates to small islands of a few molecules, which are distributed over the terraces. Individual molecules can only be spotted along the step edge. Figure 2B shows a high-resolution STM image of two CHPs overlaid with the optimized structure of the molecule derived from DFT calculations (drawn to scale). Line profile analysis across the molecules yields a center-to-center distance of about 1.6 nm, which indicates that the CHPs are not covalently bonded under the applied experimental conditions. Around the CHPs, bright spherical features can be discerned, which are distributed evenly around the molecules. The distance between these features is about 1.8 nm, which is significantly more than the value of the distance between two diametrically opposite CHP iodine atoms (1.5 nm). Furthermore, careful inspection of Figure 2A shows that not all molecules are surrounded by such features and that some of the latter are “shared” by multiple molecules (see, e.g., the three islands marked by white circles). The position as well as the distribution of the spherical features thus suggest C–I bond cleavage upon adsorption of CHP on Cu(111) at room temperature.

To confirm this conclusion, XPS experiments were performed. Figure 2C shows XPS spectra of the I 3d core levels. The red trace refers to the spectrum that was recorded after depositing a submonolayer of CHP on Cu(111) at room temperature. The spectrum reveals two narrow peaks at 630.6 and 619.1 eV binding energy, which correspond to the I 3d_{3/2} and I 3d_{5/2} spin–orbit split levels. The reference spectrum represented by the green trace corresponds to Cu–I, which was obtained after depositing a submonolayer of iodine on Cu(111) at room

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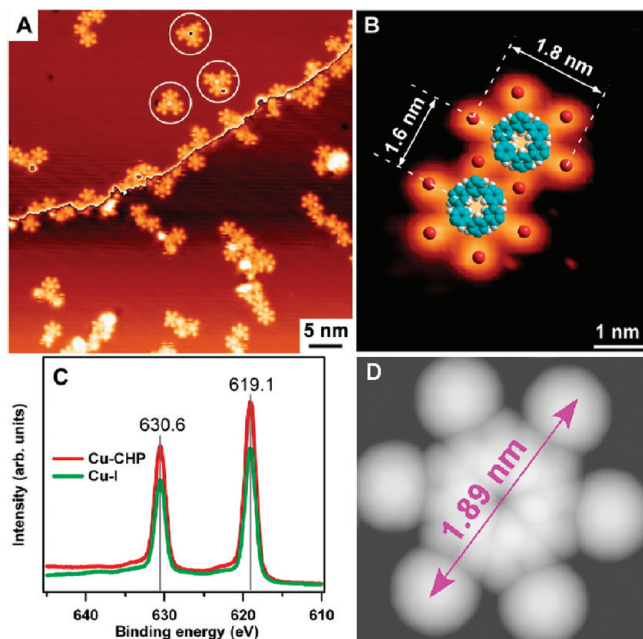


Figure 2. (A) STM image⁴³ (−2 V, 20 pA) of CHP adsorbed on Cu(111) held at room temperature. Full color contrast has been applied individually to both terraces visible in the image. (B) STM image (−2 V, 20 pA) of two CHP molecules on Cu(111). A model of the molecule is overlaid and drawn to scale. Detached iodine atoms that assemble around the surface-stabilized CHP radicals are indicated as red spheres. (C) XPS spectra of the I 3d core level. The red trace refers to a spectrum that was recorded after depositing a submonolayer of CHP on Cu(111). The green trace was obtained after adsorbing a submonolayer of iodine on Cu(111). Both spectra were recorded at room temperature. (D) STM simulation⁴⁴ of a molecule radical encircled by coadsorbed iodine atoms on Cu(111).

temperature. As is obvious, both spectra are in excellent agreement, and no shifts of the core level peaks are detectable, which indicates the presence of Cu–I (and the absence of C–I) species after adsorbing CHP on Cu(111). Furthermore, the peak position of I 3d_{5/2} at 619.1 eV agrees well with previous studies for Cu–I compounds.^{19,27–29} Peak shifts between Cu–I and Cu–CHP were not observed for the I 4d and I 4s core levels (data not shown). Our conclusion on C–I bond scission is further supported by XPS investigations by Zhou and White on the thermal decomposition of C₂H₅I on Ag(111).³⁰ In this study, it was shown that the dissociation of the C–I bond is manifested by a significant shift of the I 3d_{5/2} peak to lower binding energies, indicating that metal–I and C–I species are readily distinguishable in XPS spectra. On the basis of the STM and XPS results, we thus conclude that the CHP molecule readily dehalogenates upon adsorption on Cu(111), leaving surface-stabilized CHP radicals (CHPRs) and coadsorbed iodine on the surface. The evolution of CHPRs was also observed on Au(111) and Ag(111) at room temperature (data not shown). These findings are in agreement with previous studies reporting on the dissociative adsorption of small alkyl or aryl halides on metal surfaces.³¹ Specifically, the C–I bond in iodobenzene, which can be regarded as a subunit of CHP, has been reported

to dissociate below room temperature on Cu(111),^{32–34} Au(111),³⁵ and Ag(111),³⁶ resulting in adsorbed phenyl and iodine.

The notion “surface-stabilized radical” requires some further explanation. Because of their unpaired electrons, radicals are usually associated with high chemical reactivity and short lifetime. However, this picture does obviously not hold for radicals adsorbed on a metal surface under UHV conditions. In this case, the free electrons of the metal surface readily couple to the unpaired electrons of the radical. Plots of the calculated charge density for CHPR located in energetically favorable on-top configurations confirm that the radical strongly binds via six covalent bonds to both the Cu(111) and the Ag(111) surface atomic lattices. The corresponding projected density of states (PDOS) diagrams, shown in Figure S3 of the Supporting Information, confirm a modification of the d electronic band for the involved metal atoms due to the bonding to the dehalogenated carbon atoms. Strictly speaking, the term “radical” is thus not quite correct, but for simplicity we use this terminology to refer to the dehalogenated, surface-stabilized CHP species. STM delivers further experimental evidence for a strong surface interaction: The CHPR species is easily imaged at room temperature even at very low surface coverage (Figure 2A), whereas the structurally similar polyaromatic hydrocarbon hexa-*peri*-hexabenzocoronene (HBC) is highly mobile under similar experimental conditions.³⁷ In fact, calculated adsorption energies are −15 eV for CHPR/Cu(111) and −11 eV for CHPR/Ag(111) (see the Supporting Information for discussion and analysis of various adsorption geometries for CHPR on Cu and Ag). We note that the adsorption energy is calculated as the energy difference between the most stable atop orientation of the radical on the metal surface and the total energy of the two individual systems, that is, the surface-mimicking slab and CHPR held in the middle of the vacuum region. The considerable energy of adsorption is thus related to the high energy of the radical in vacuum.

So far, it has been implied that the bright spherical features around CHPR refer to iodine atoms. However, in earlier work by Xi and Bent, these authors proposed two different potential bonding geometries for phenyl on Cu(111), notably a phenyl-induced elevation of a surface metal atom to achieve both σ - and π -interactions, and flat-laying phenyl groups bound as anions.³² On the other hand, the preferential allocation of halogens around surface-stabilized radicals has been observed for diiodobenzene on Cu(110).¹⁹ From our DFT calculations (see the Supporting Information), we find that the observed structures in the STM images (Figure 2B) are in excellent agreement with iodine occupying hollow sites adjacent to CHPR, as is evident by inspecting the STM simulation in Figure 2D. Furthermore, the calculated iodine–iodine distance (1.89 nm) agrees very well with observation (1.8 nm). In contrast, assuming Cu adatoms binding to CHPR, DFT predicts a distance of only 1.54 nm, which is significantly shorter than the experimental value (Supporting Information, Figure S1).

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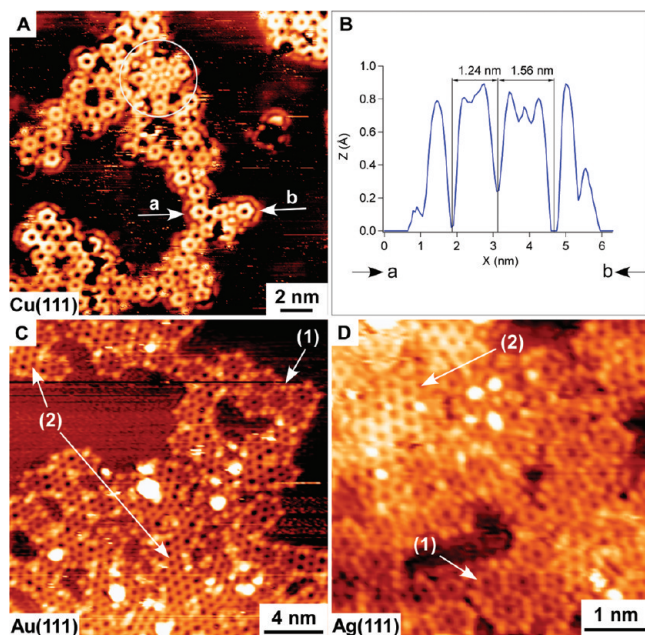


Figure 3. Set of STM images showing the onset of the thermally activated CHP radical addition reaction on the coin metal surfaces Cu(111) (A,B), Au(111) (C), and Ag(111) (D). (A) STM image (-1 V, 200 pA) recorded after CHP deposition on Cu(111) held at RT and postannealing the sample at 475 K for 5 min. The white circle highlights radicals surrounded by iodine atoms. (B) Line profile along arrows a,b shown in (A) with the black vertical lines denoting the center of the CHP species. (C) STM image (-0.8 V, 20 pA) recorded after CHP deposition on Au(111) held at room temperature and postannealing the sample at 525 K for 5 min. (D) STM image (-1.5 V, 30 pA) recorded after CHP deposition on Ag(111) held at room temperature and postannealing the surface at 575 K for 5 min. In (C,D), arrows (1) point to areas of unreacted molecules, and arrows (2) mark covalently interlinked species.

From Surface-Stabilized CHP Radicals to Covalently Bonded Polyphenylene Networks. The STM, XPS, and DFT results discussed in the previous section clearly demonstrate dissociative adsorption of CHP on Cu, Au, and Ag. The subsequent formation of covalently bonded networks is based on thermally activated aryl–aryl homocoupling (see scheme in Figure 1C). The STM images in Figure 3 summarize the experimental findings, which give strong evidence for covalent intermolecular bond formation. Figure 3A shows coupled and uncoupled CHP species as well as iodine atoms on the Cu(111) surface. A prominent domain of uncoupled radicals surrounded by iodine atoms is highlighted in the image (white circle). A line profile analysis (Figure 3B) of adjacent species reveals CHP–CHP distances of 1.24 and 1.56 nm. The former value is in excellent agreement with DFT calculations of covalently bonded molecules, whereas the latter clearly indicates uncoupled radicals (e.g., shown in Figure 2B). Figure 3C and D displays the evolution of covalently bonded species on Au and Ag, respectively. Prominent domains of iodine-surrounded radicals and domains of polymerized radicals are highlighted by arrows (1) and (2). The observed CHPR polymerization is consistent with previous reports on iodobenzene coupling on Cu(111),^{32,33} Au(111),³⁵ and Ag(111).^{38,39} However, we find significantly different annealing temperatures to initiate intermolecular bonding on the three coinage metal surfaces, notably Cu (~ 475 K)

$< \text{Au} (\sim 525 \text{ K}) < \text{Ag} (\sim 575 \text{ K})$, which implies that the nature of the surface plays an important role in intermolecular coupling.

Figure 4 shows STM images of fully polymerized polyphenylene networks supported on Cu(111), Au(111), and Ag(111). Below each overview image, the structures are resolved in more detail. The network morphologies differ significantly on the three substrates. On Cu(111) (Figure 4A,B), branched low-density clusters with single-molecule-wide branches prevail. Careful inspection further reveals the presence of iodine atoms along the border of the structures (Figure 4B, experimental condition: 5 min postannealing step at 675 K). On the other hand, on Au(111) the homocoupling of CHP leads to a mixture of branched and denser polyphenylene clusters as can be identified in Figure 4C,D. No iodine is discerned because the polymerization was performed during a 5 min postannealing step at 745 K. Figure 4E,F eventually shows that dense and highly ordered networks extend on the silver surface. No residual iodine can be identified after performing the polymerization at 825 K for 5 min (Figure 4F).

Monte Carlo Simulations of Covalent Network Growth. To better understand the origin of the significantly different network morphologies, we used a generic Monte Carlo process to simulate the diffusion and assembly of molecules on a hexagonal surface lattice (see the Supporting Information for a detailed model description). Briefly, a seed molecule fixed to the center of the lattice serves as nucleation site, and the subsequent growth of network clusters is based on iterative addition of molecules. The molecules are free to perform a random walk on the simulation grid; when they reach a possible binding site, their affinity to join the seed or a cluster is given by the coupling probability P , which can be interpreted as the ratio between the reaction rate of the coupling step and the total number of events, that is, coupling and diffusion, according to

$$P = \frac{\nu_{\text{coupl}}}{\nu_{\text{coupl}} + \nu_{\text{diff}}} \text{ with } 0 \leq P \leq 1 \quad (1)$$

where ν_{coupl} and ν_{diff} denote the reaction rates for the coupling and diffusion steps, respectively. Very high or low coupling probabilities readily allow the following inference on the reaction rates for coupling and diffusion:

$$P \approx 1, \text{ if } \nu_{\text{coupl}} \gg \nu_{\text{diff}}, \text{ and } P \approx 0, \text{ if } \nu_{\text{diff}} \gg \nu_{\text{coupl}} \quad (2)$$

Figure 5 displays simulated network clusters of 400 molecules by using coupling probabilities $P = 1$, 0.1 , and 0.01 , respectively. For a more quantitative description, a histogram showing the coordination number distribution of the molecules is appended below each cluster. In the growth regime corresponding to $P = 1$, a diffusing molecule immediately sticks to the cluster when and where it hits the cluster. Note that this condition is equivalent to the classical diffusion-limited aggregation (DLA) model⁴⁰ that was applied to study metal–particle aggregation processes. As a consequence, characteristic branched “fractal-like” polyphenylene network structures with single-molecule-wide branches develop (Figure 5A). By lowering the coupling probability by 1 order of magnitude, the evolution of denser network domains can be discerned (Figure 5B). Eventually, compact network formation occurs for $P = 0.01$ (Figure 5C). Thus, by gradually increasing ν_{diff} and reducing ν_{coupl} , denser network clusters emerge. This can readily be understood

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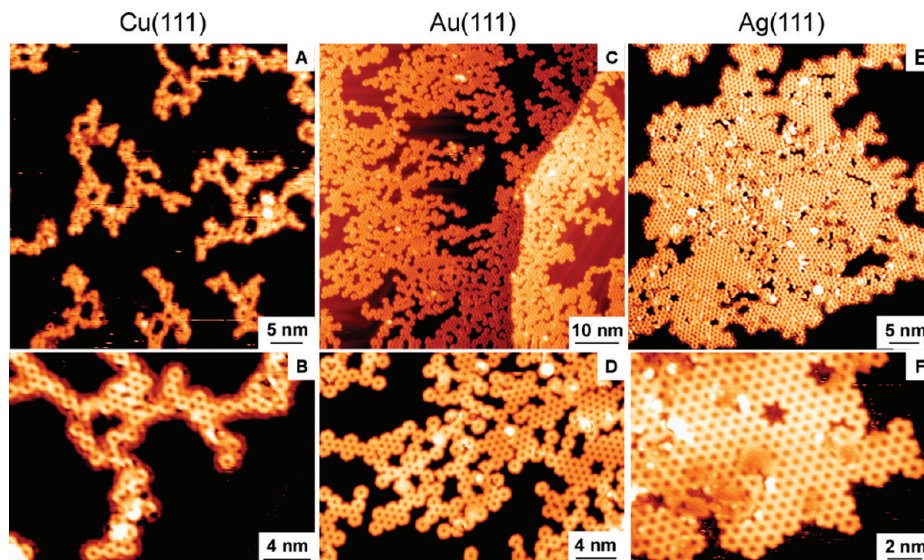


Figure 4. Top panels: Overview STM images of polyphenylene networks on Cu(111), Au(111), and Ag(111). Bottom panels: High-resolution STM images of the polyphenylene networks shown above. Tunneling parameters are (−2 V, 20 pA) (A), (1.5 V, 300 pA) (B), (−1 V, 50 pA) (C), (−1 V, 50 pA) (D), (−0.8 V, 50 pA) (E), and (−1 V, 50 pA) (F). STM topographs shown in panels (E) and (F) are related to the images reported in ref 25.

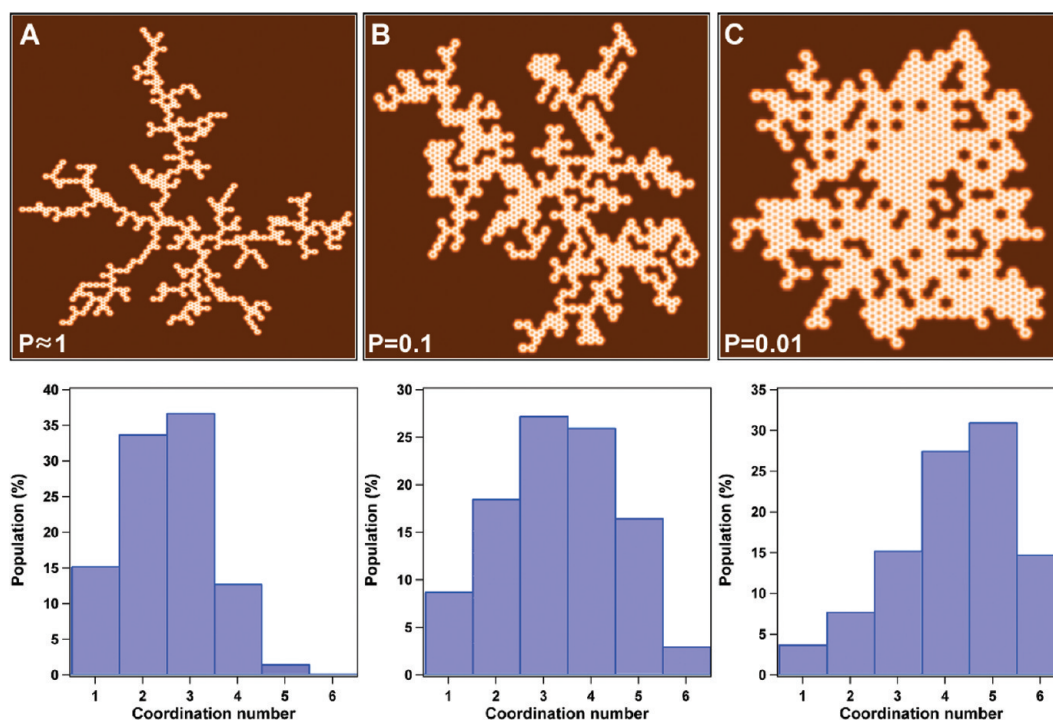


Figure 5. Monte Carlo simulations of molecular network growth. For the networks shown in panels A–C, coupling probabilities of $P = 1$, 0.1, and 0.01, respectively, were used for the growth of clusters consisting of 400 molecules. Below each simulation, the corresponding coordination number distribution of the molecules in the cluster is given.

with simple reasoning: To promote the formation of compact structures, molecules must diffuse along the borders of islands and eventually occupy higher coordinated sites, a process that requires a high mobility and/or low coupling affinity of the reactants. However, it is equally important to notice that even under favorable growth conditions, defects discernible as “holes” in the clusters (Figure 5B,C) occur. These defects arise when six CHP units join at their meta positions to a circle. Because molecules are not allowed to cross over island borders, these defects persist in the clusters. These theoretical findings are in excellent agreement with experiment; “holes” with a characteristic star-shape pattern can easily be spotted within domains

of the polyphenylene networks grown on Au(111) and Ag(111) (Figure 4D, F). More importantly, the sequence of the presented cluster simulations is in excellent agreement with the polyphenylene networks grown on Cu(111), Au(111), and Ag(111) (compare Figures 4 and 5), which clearly points to different growth regimes for the covalent assembly of CHP on these surfaces.

DFT Calculations on CHPR Diffusion and Reaction Pathways on Cu(111) and Ag(111). To gain deeper insight into the energetics of the surface-confined polymerization of CHP, we performed extensive *ab initio* DFT calculations. We focused on CHP/Cu(111) and CHP/Ag(111) because the assembled

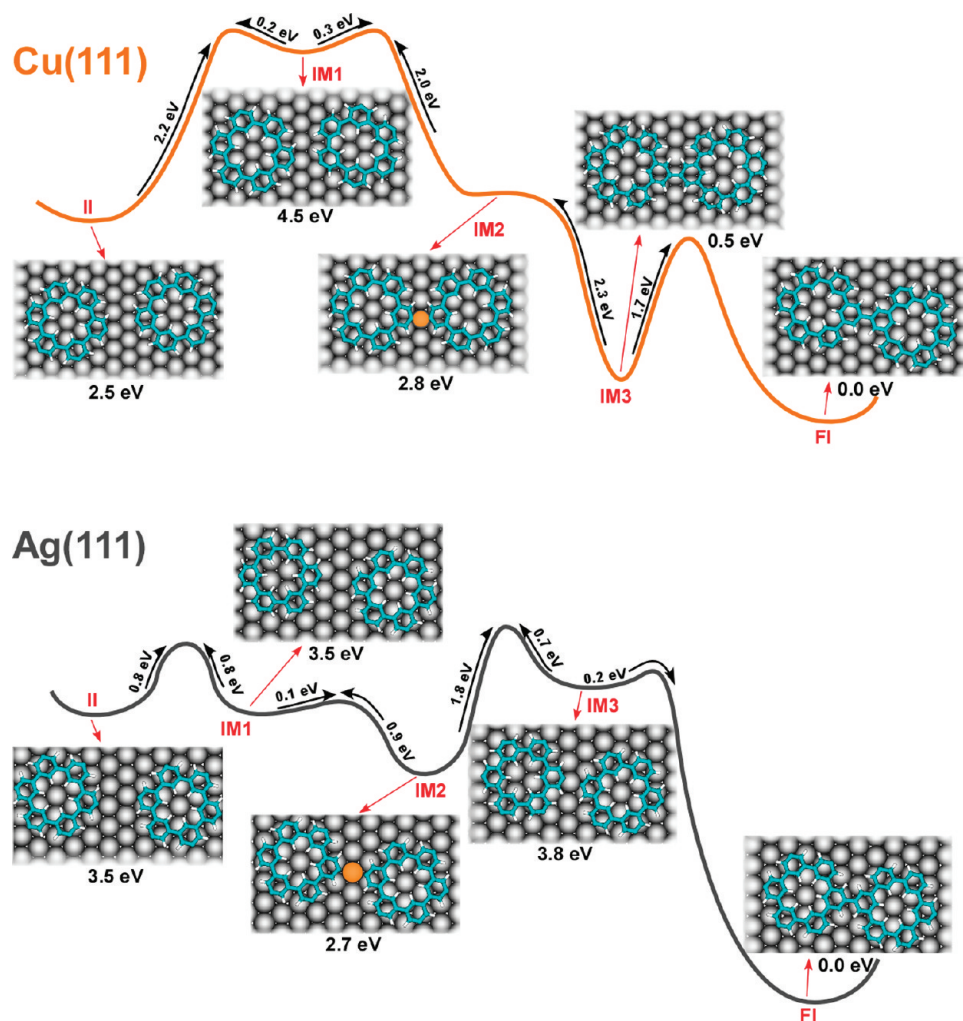


Figure 6. Energy diagrams of the reaction pathways for CHPR–CHPR coupling on Cu(111) (top) and Ag(111) (bottom) elucidated via NEB calculations. Pictorial representations (top views) of the molecule–surface configuration are given for the initial (II), intermediate (IM), and final (FI) states, respectively. The energies below each configuration are given with respect to the total energy of the final state. On both surfaces, the orange sphere indicates the central metal atom bonded to both CHPRs prior to intermolecular bond formation.

polymer networks are found to differ most significantly in structure and morphology on these two substrates. In a first step, the diffusion pathway of a “free”, single CHPR on the Cu(111) and Ag(111) surface lattices is investigated via nudged elastic band (NEB) calculations (a detailed discussion of the calculation methods is provided in the Supporting Information). We find that on both substrates the molecule performs a rotational movement (see Supporting Information, Figure S4) between energetically favorable atop positions and that the corresponding diffusion barrier is higher on Cu(111) (2.2 eV) than on Ag(111) (0.8 eV). The difference in the diffusion barrier is related to the strength of the metal–CHPR bond, which is consistent with the reported higher chemical activity of Cu(111) as compared to Ag(111).⁴¹ In particular, the induced charges and projected density of states (see Supporting Information, Figure S3) indicate that CHPR forms a stronger bond to Cu(111) than to Ag(111). Because the diffusion process of a surface-confined CHPR involves bond breaking and reforming, this difference in bond strength explains the trend in the diffusion barrier.

In a next step, we investigate covalent intermolecular bond formation between two CHPRs on Cu(111) and Ag(111). To

do so, the proper definition of the starting configuration is crucial. The initial (II) state is shown in Figure 6 (left panels), where two CHPRs are anchored to atop sites and separated by two atomic rows of the metal substrate. After collecting several possible reaction pathways, we find that the system always passes through intermediate (IM) states in which the two CHPRs bind to a common surface metal atom. The final step of the reaction is given by covalent bond formation between the CHPRs. Note that in this final (FI) state the macrocycles of the CHP–CHP pair are both located on energetically favorable atop sites (Figure 6, right panels). The NEB calculations reveal that intermolecular CHPR coupling follows similar reaction pathways on Cu(111) and Ag(111), including diffusion steps toward IM states, and final covalent bond formation toward the (FI) state. However, inspection of the corresponding configurations and the energy diagrams of the reaction pathways depicted in Figure 6 reveals striking differences between the two substrates. These differences, as discussed in the following, are related to a radical-induced surface reconstruction and the matching of CHPR with respect to the metal surface lattice.

Along the path from II to FI, one radical performs a rotation around one unbroken CHPR–surface bond, while the other one is fixed to the surface atomic lattice. In our NEB procedure,

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only the initial (II) and final (FI) images are fixed, while all intermediate images are allowed to fully relax. This particular choice of II and FI states, in which one of the two molecules maintains its original atop site whereas the other one approaches, mimics a diffusing molecule encountering and eventually binding to an “immobilized” network cluster (which, in this case, is represented by a single molecule).

The initial step of the overall coupling process is determined by the diffusion of a “free” radical toward the first IM1 state (see the Supporting Information) and is activated by significantly different energies, notably 2.2 eV on Cu(111) and 0.8 eV on Ag(111). Further diffusion with small activation energies of 0.3 eV (Cu) and 0.1 eV (Ag) transfers the system toward the IM2 state. On Ag, the IM2 state is considerably more stable than the II state, where the two CHPRs are well separated. The energy difference between these two states can be explained by the rearrangement of atoms in the metal surface layer when the two CHPRs bind to a common surface atom (highlighted in orange in Figure 6): On Ag(111), this radical-induced surface reconstruction is significant, and an elevation of 1.7 Å is predicted for the central surface atom and of 0.7 Å for the other Ag atoms binding to the CHPRs. The significantly elevated central Ag atom is thus less coordinated to neighboring metal atoms, which eventually contributes to a stronger CHPR–Ag bond. On Cu(111), the geometry of the surface–CHPR complex is nearly unaffected upon the transition from the II to the IM2 state. Moreover, because of the calculated distance between CHPR hydrogen atoms of only 1.8 Å, intermolecular H···H repulsion results in a slightly higher energy of the IM2 (2.8 eV) as compared to the II state (2.5 eV).

The following two steps toward radical addition again reveal important differences on the two surfaces: On Cu(111), intermolecular bond formation is essentially barrierless and readily occurs from IM2 to IM3, which reflects a favorable configuration and intermolecular distance for bond formation (see insets of IM2 and IM3, where the orange sphere indicates the central atom binding to both CHPRs). However, inspection of the IM3 state shows that there is substantial stress on the CHP–CHP bond, and the system thus relaxes toward the favorable atop configuration in the FI state with an activation energy of 1.7 eV. On Ag(111), on the other hand, the configuration and intermolecular distance between the two CHPRs in the IM2 state are obviously less favorable for intermolecular coupling. During the transition from the IM2 to the IM3 state, one CHPR rotates about the central surface atom from the energetically favorable atop to a bridge site, which requires a significant amount of energy (1.8 eV). Eventually, bond formation and relaxation to atop sites in the FI state proceed readily with a barrier of 0.2 eV. The calculations thus strongly indicate that the difference between the two substrates with respect to 2D polymer formation is related to the favorable and less favorable matching of CHPR to the Cu and Ag surface lattice, respectively, as well as to the different chemical activities of Cu and Ag.

These findings have striking implications on the energy diagram of the overall reaction pathway. On Cu(111), the initial diffusion process (2.2 eV) is the rate-limiting step. Once this barrier is overcome, the reaction is predicted to proceed spontaneously because the path toward intermolecular bond formation (IM3 state) is essentially barrierless and the 1.7 eV required to relax the system is significantly lower than bond breaking (2.3 eV for IM3 to IM2) and backward diffusion (2.0 eV for IM2 to IM1). Thus, the surface-mediated polymerization on Cu with hindered diffusion and favored coupling corresponds

ideally to the regime of diffusion-limited network formation, which explains why the branched clusters predicted by Monte Carlo simulations for this growth regime (Figure 5A) are in excellent agreement with experimental observations on Cu(111) (Figure 4A). Conversely, on Ag(111) the energy diagram shows that CHPR coupling is the rate-limiting step: Once the initial diffusion barrier of 0.8 eV is overcome, the system readily reaches the IM2 state, and backward diffusion with individual barriers of 0.9 (IM2 to IM1) and 0.8 eV (IM1 to II) is favored over covalent bond formation (1.8 eV), leading to an overall increased mobility of the molecules.

Here, a few more comments on the experimental conditions are required. The discussed formation of polyphenylene networks is obviously based on the self-assembly of molecules deposited on a surface. For metal aggregation processes, it was shown that the growth conditions and thus the morphology of the resulting clusters can be addressed by varying the deposition rate and substrate temperature. Thus, to have unbiased conditions, we used an identical and low deposition rate for all experiments reported here. Concerning temperature effects, we find no significant modifications of the network morphologies after performing the polymerization at different annealing temperatures. On the basis of the calculated energy diagram for CHPR/Cu(111), network growth is diffusion-limited and is thus not expected to change at higher temperatures. On the Ag surface, only at very high temperatures will the coupling probability increase. The barriers resulting from DFT reveal that diffusion-limited growth cannot be promoted by temperature.

A final important point in this discussion is the effect of coadsorbed iodine on the reaction mechanism. For verification, different sample preparation procedures were applied, in particular inducing the polymerization in a postannealing step or by immediately preparing the sample above the desorption temperature of iodine (not possible on Cu without the risk of surface degradation). Briefly, we find no evidence for iodine-induced network modification. This is consistent with previous findings on methyl radical coupling where the reaction pathways in the presence and absence of iodine remained unchanged.⁴² These and our results thus suggest that the predominant effect of the halogen is to block surface sites and not to participate chemically in the coupling reaction. Collective electrostatic or indirect interaction effects mediated by the substrate might, however, contribute in reducing reaction barriers, which would require further theoretical investigation.

Conclusions

We investigated the adsorption and self-assembly of the hexaiodo-substituted macrocycle CHP on well-defined (111) surfaces of the coinage metals Cu, Au, and Ag. STM analysis shows that on either surface the adsorption of CHP follows a dissociative pathway with selective C–I bond cleavage, resulting in coadsorbed iodine and the evolution of surface-stabilized CHP radicals. Subsequent covalent intermolecular bond formation between CHP radicals toward covalently bonded polyphenylene networks is thermally activated by annealing the corresponding substrate to temperatures of about 475 K (Cu), 525 K (Au), and 575 K (Ag). The polymer networks show significantly different morphologies on the three substrates, ranging from branched, fractal-like structures

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on Cu(111) to extended, regular 2D networks on Ag(111). DFT analysis of the diffusion and coupling pathways on Cu and Ag reveals that the balance between the diffusion and coupling steps is significantly different on the two substrates. On Cu, the radicals spontaneously form covalent intermolecular bonds once the initial diffusion barrier is overcome. Conversely, on the Ag surface, diffusion clearly prevails over intermolecular coupling, which results in an overall increased mobility of the radicals on the surface and in regular 2D network formation. With the aid of generic Monte Carlo simulations, we have shown that a high mobility (or low coupling affinity of the reactants) is a prerequisite for the growth of dense 2D polymer networks. However, the simulations also clearly indicate that even under favorable growth conditions defects in the network clusters have to be expected, demonstrating that surface-supported two-dimensional polymers based on irreversible reactions are inherently limited with respect to their structural perfection. Our results demonstrate that the substrate not only acts as a static support

but that it is actively involved in all reaction steps and significantly influences the morphology of self-assembled covalently bonded nanostructures.

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Supporting Information Available: Experimental details, description of DFT calculation methods, considerations of the diffusion pathway and reaction mechanism of CHP on Cu(111) and Ag(111), and description of the Monte Carlo process for network growth simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Two-dimensional polymer formation on surfaces: Insight into the roles of precursor mobility and reactivity

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Experimental Section

Sample preparation, scanning tunnelling microscopy, and X-ray photoelectron spectroscopy

Detailed information on the synthesis and characterization of the molecular precursor used in this study, the hexaiodo-substituted macrocycle cyclohexa-*m*-phenylene (CHP), can be found elsewhere.¹ The CHP molecule is deposited on the Cu(111), Au(111), and Ag(111) single crystal surfaces from resistively heated quartz crucibles held at 745 K, resulting in deposition rates of about 0.02 monolayer per minute, as monitored by a quartz crystal microbalance. The surface-assisted coupling of CHP towards covalently bonded polyphenylene networks is activated by annealing the corresponding sample to temperatures above 475 K (Cu), 525 K (Au), and 575 K (Ag). STM analysis shows that co-adsorbed iodine, the byproduct of the coupling reaction, desorbs at 745 K from the gold and at 825 K from the silver surface, which agrees well

with previous reports.²⁻⁴ Desorption of iodine from the Cu surface is not feasible since the halogen was reported to desorb at 900 K,^{5,6} which is above the roughening transition temperature of Cu(111).

All experiments reported here were performed in a UHV system with a base pressure below 2×10^{-10} mbar. Prior to each experiment, the single crystal surfaces were cleaned by Ar⁺ sputtering (1 kV) for 30 min followed by annealing at 725 K for 15 min. The sample was then transferred to the analysis chamber equipped with an Omicron variable-temperature STM that was operated at RT. STM images were acquired in the constant-current mode with the stated voltage referring to the electric potential of the sample with respect to the STM tip.

XPS experiments were performed at the near-node endstation UHV system of the X11MA-SIM beamline at the Swiss Light Source (SLS). Iodine (99.99+%) was received from Sigma-Aldrich and was used for reference experiments. Prior to use, iodine was subjected to several freeze-pump-thaw cycles to remove impurities, and was afterwards dosed into the UHV system by means of a leak valve. All XPS spectra were recorded with a pass energy of 20 eV and averaged over 25 scans for the I 3*d*, and 100 scans for the I 4*s* and I 4*d* core levels.

Density functional theory calculations

Calculation methods

To gain detailed insight into the surface-assisted coupling of cyclohexa-*m*-phenylene radicals (CHPRs) on Cu(111) and Ag(111) we perform several ab initio simulations based on density functional theory (DFT). We use the CP2K code within the mixed Gaussians and plane waves scheme (GPW).⁷ The exchange-correlation functional adopted is based on the local density approximation (LDA).⁸ The atomic potentials are represented via norm-conserving pseudo-potentials of the Goedecker-Teter-Hutter (GTH) type⁸ and the electronic states are expanded in localized Gaussian basis sets (DZVP for surface metal and iodine atoms, and TZV2P for hydrogen and carbon atoms). The cutoff for the plane wave expansion of the total electronic charge density is 280 Ry.

To model the metal surfaces, we use the repeated slab scheme: a unit cell with periodic boundary conditions contains three M(111) layers (M = Cu, Ag) and 30 Å of vacuum mimicking a slab with infinite 2D extension. The procedure of the DFT analysis can be outlined in three steps: i) determination of adsorption geometries and energies of CHPR on M(111); ii) identification of diffusion pathways and diffusion barriers; iii) identification of reaction barriers for CHPR–CHPR coupling. Reaction barriers are calculated with the nudged elastic band method (NEB) in the “climbing-image” scheme.⁹

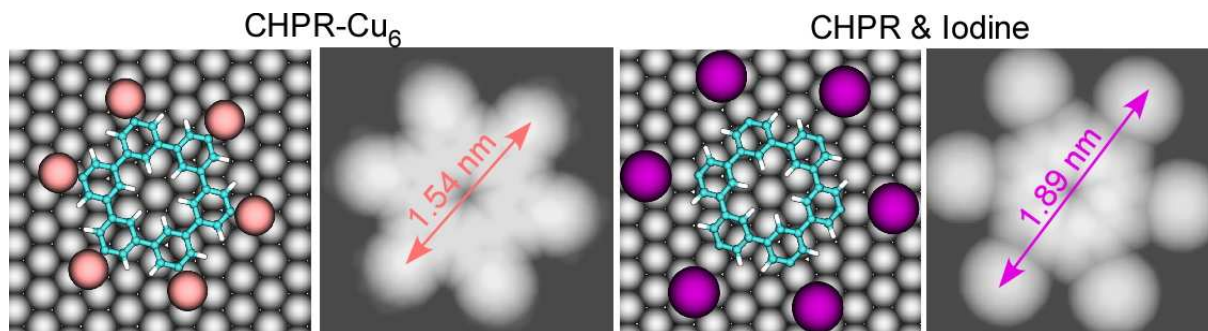


Figure S1. Left panel: CHPR adsorbed on Cu(111) with Cu adatoms (highlighted in brown color) binding to the radical. The corresponding STM simulation is shown to the right. Right panel: CHPR with co-adsorbed iodine atoms (shown in purple color) occupying threefold hollow sites adjacent to the radical. The corresponding STM simulation is shown on the right side.

When CHP is adsorbed on Cu(111), C–I bonds are spontaneously broken which results in the evolution of CHPRs and co-adsorbed iodine. Ab initio DFT calculations are performed in order to better understand whether the bright protrusions discerned in the STM images (Figs. 2A and 2B) originate from Cu adatoms or iodine atoms located around the CHPRs. We simulate STM images within the Tersoff–Hamann approximation.¹⁰

Since dehalogenation of CHP is strongly indicated by STM and XPS, the dissociative adsorption pathway is not further studied here. Thus, a single CHPR adsorbed on the Cu surface is used as the starting point for the calculations. In a next step, Cu adatoms are added in close proximity (resulting in a hollow site) to the phenyls of CHP and the system is allowed to reach the configuration of lowest energy. The model of the optimized structure with Cu adatoms (shown in brown color) binding to the CHP phenyls is shown in Fig. S1, left panel, and the corresponding STM simulation is shown to the right. A distance of 1.54 nm emerges between the protrusions referring to the Cu adatoms. The procedure for the calculations for co-adsorbed iodine is analogous. For the starting geometry, iodine atoms are added at the same initial positions than for the Cu adatoms and a structure optimization of the system is performed. The most stable configuration is shown in Fig. S1, right panel (iodine is highlighted in purple color). The iodine atoms allocate in hollow sites where the distance to the closest carbon atom of CHP is 3.96 Å, reflecting that the halogen is not covalently bonded to the CHPR. In the corresponding STM simulation (shown to the right) a distance of 1.89 nm is found between the protrusions, in excellent agreement with experiment (Fig. 2B). The allocation of iodine (or halogen atoms in general) close to surface-stabilized radicals is frequently observed in the surface-assisted Ullmann reaction¹¹ and has been reported elsewhere.¹²

Geometric considerations of CHPR on Cu(111) and Ag(111)

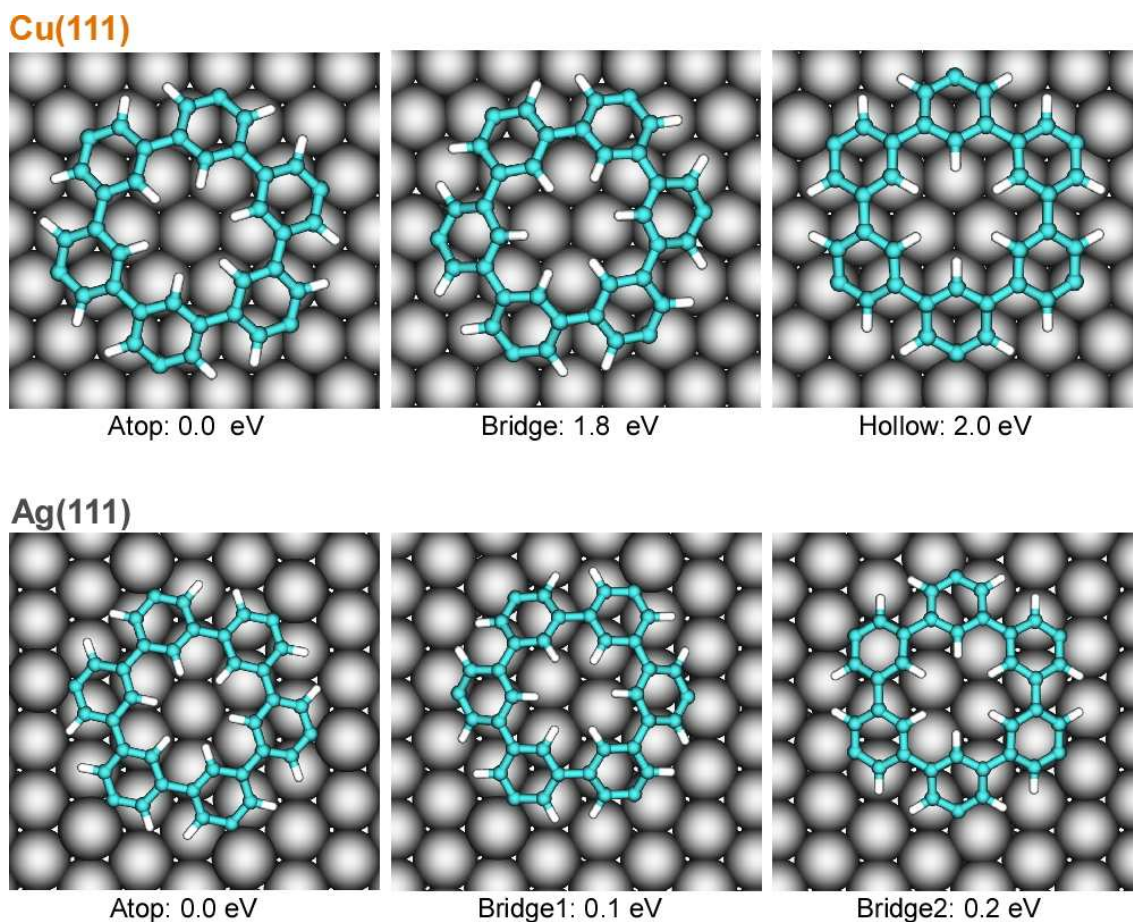


Figure S2. Pictorial representation of some calculated adsorption geometries for CHPR/Cu(111) and CHPR/Ag(111). For each configuration, the corresponding energy is given. Reference energy is the most stable “atop” configuration.

In Figure S2 we present some of the stable adsorption geometries for CHPR on Cu(111) and Ag(111). It is found that the energetically most favorable orientation of CHPR both on Cu(111) and Ag(111) corresponds to the one with the center of CHPR coinciding with an atop site and the CHP phenyls binding to a surface metal atom (“atop” positions in Fig. S2). The conformation of adsorbed CHPR resulting from calculations is essentially planar, in agreement with the STM experiments (Fig. 2B). In Fig. S3 we depict iso-surfaces of the induced charges, defined as the difference in electron density between the bound system and its components. These difference charge density plots reveal that the CHPR strongly binds to the surface via six covalent bonds. The corresponding density of states projected on the involved atoms indicates a saturation of the C unpaired electron via a metal surface atom. The average height of the phenyl carbon atoms with respect to the first surface atomic plane is 2.3 Å (Cu) and 2.5 Å (Ag). This height difference can be explained in terms of the surface reactivity and the matching of the CHPR with respect to the surface lattice, as discussed below.

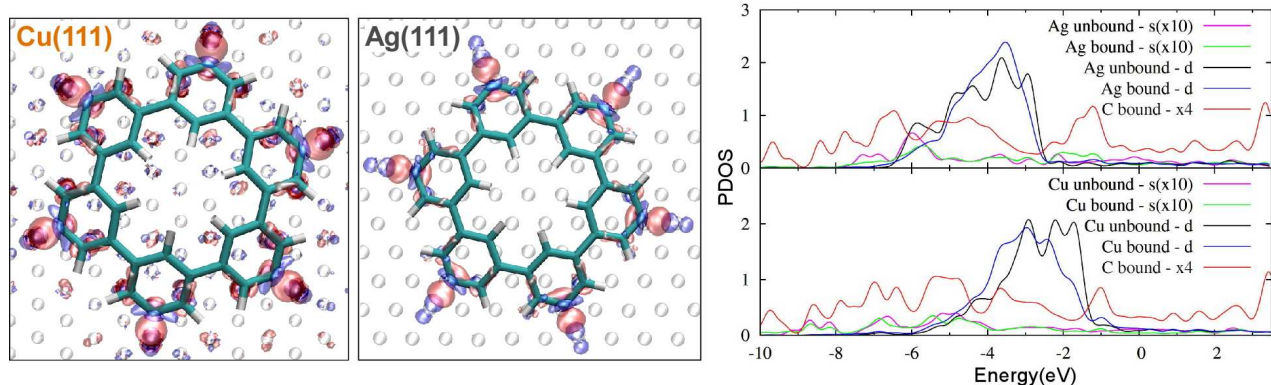


Figure S3. Induced charge (difference charge density) in the lowest-energy geometry of CHPR/Ag and CHPR/Cu: iso-surface at 0.005 a.u with accumulation (red) and depletion charge (blue). Right panel: projected density of states (PDOS) on the dehalogenated carbon atoms (red line) and on a bound and unbound metal atom (*s* and *d* states). Particularly in the case of Cu, a modification of the *d* states with resonance at about -3 eV (the zero is fixed at the system Fermi energy) is observed, indicating a chemical bond between C and the metal atom.

We calculate the adsorption energy of the CHPR on the metal surface as the energy difference $E_{\text{ads}} = E_{\text{bound}} - E_{\text{separated}}$, where E_{bound} is the total energy calculated for the most stable orientation (atop) of the CHPR on M(111), $E_{\text{separated}}$ is the total energy of the two individual systems, i.e. the surface-mimicking slab and the CHPR held in the middle of the vacuum region; and we find -15 eV and -11 eV for CHPR/Cu(111) and CHPR/Ag(111), respectively. The difference in adsorption energy is mainly related to the nature of chemical bonding and can be understood with a simple reasoning: The unpaired electrons of CHPR couple to the metal *s* and *d* states. Contribution from the former to the molecule–surface bonding is similar for the different coin metals whereas coupling to *d* states becomes weaker for the sequence Cu to Au.¹³

Diffusion pathway of CHPR on Cu(111) and Ag(111)

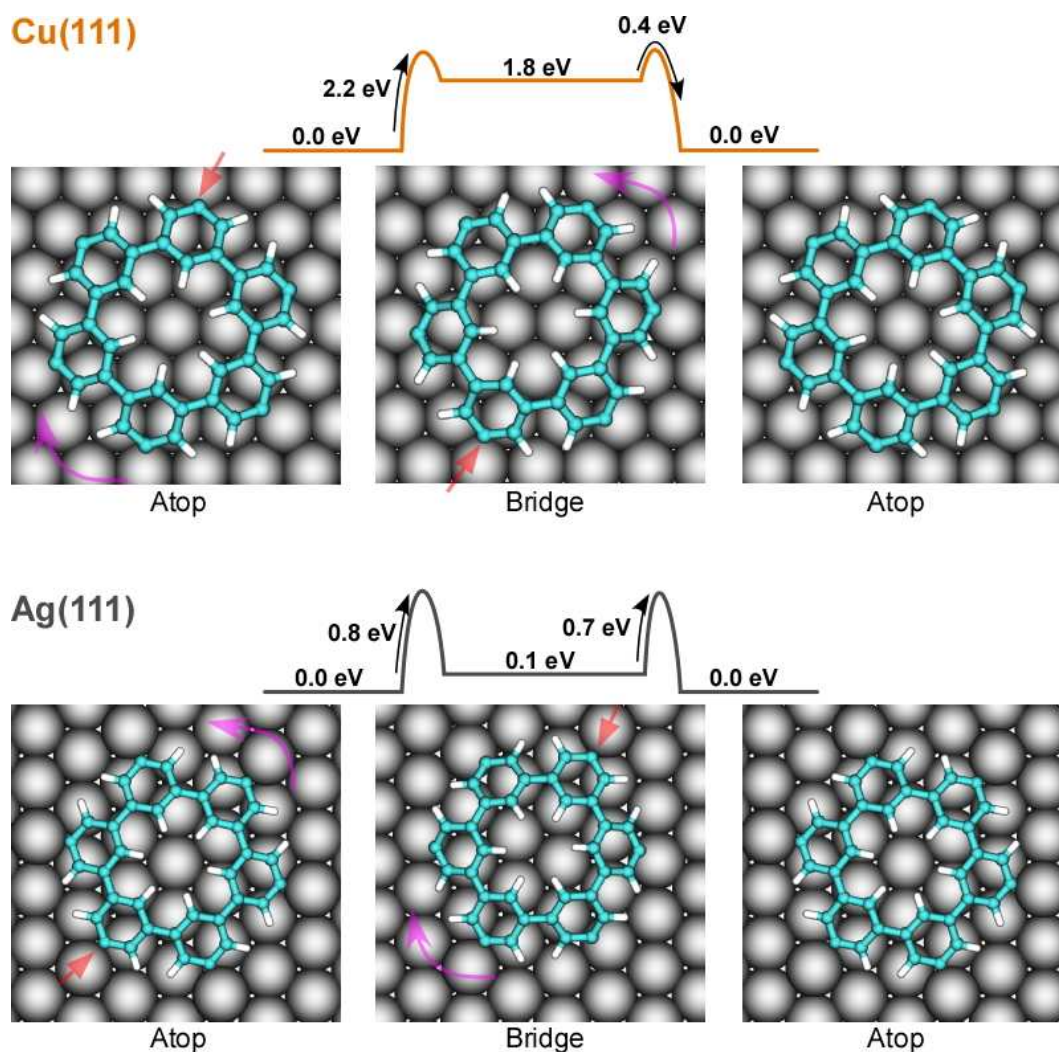


Figure S4. Graphical illustration of the CHPR diffusion pathway on Cu(111) and Ag(111). During displacement, the molecule rotates (purple arrow) around one unbroken CHPR–surface bond (red arrow) from an atop via a bridge to a new atop site. Above each image, the corresponding energy is given with respect to the atop configuration.

To elucidate the diffusion pathways of CHPR on the copper and silver surfaces we calculate the energy barriers that have to be overcome to move the molecule between two atop positions. CHPR can either undergo a direct translation (involving a single barrier) or diffuse through intermediate equilibrium states (such as, e.g. the “bridge” configuration shown in Fig. S2).

On both Cu(111) and Ag(111) we find similar pathways for the diffusion of CHPR (Fig. S4): The center of the molecule rotates about one unbroken C–M bond from an atop via a bridge to a new atop site. Following Fig. S4, the corresponding diffusion barriers are 2.2 eV and 0.8 eV on Cu and Ag, respectively.

For the NEB calculations we use a slab with lateral dimension of $19.7 \times 19.9 \text{ \AA}^2$ for Ag(111) and $17.5 \times 7.3 \text{ \AA}^2$ for Cu(111). Twelve system images are used to sample each diffusion pathway.

Interactions between two CHPRs on the Cu(111) and Ag(111) surfaces

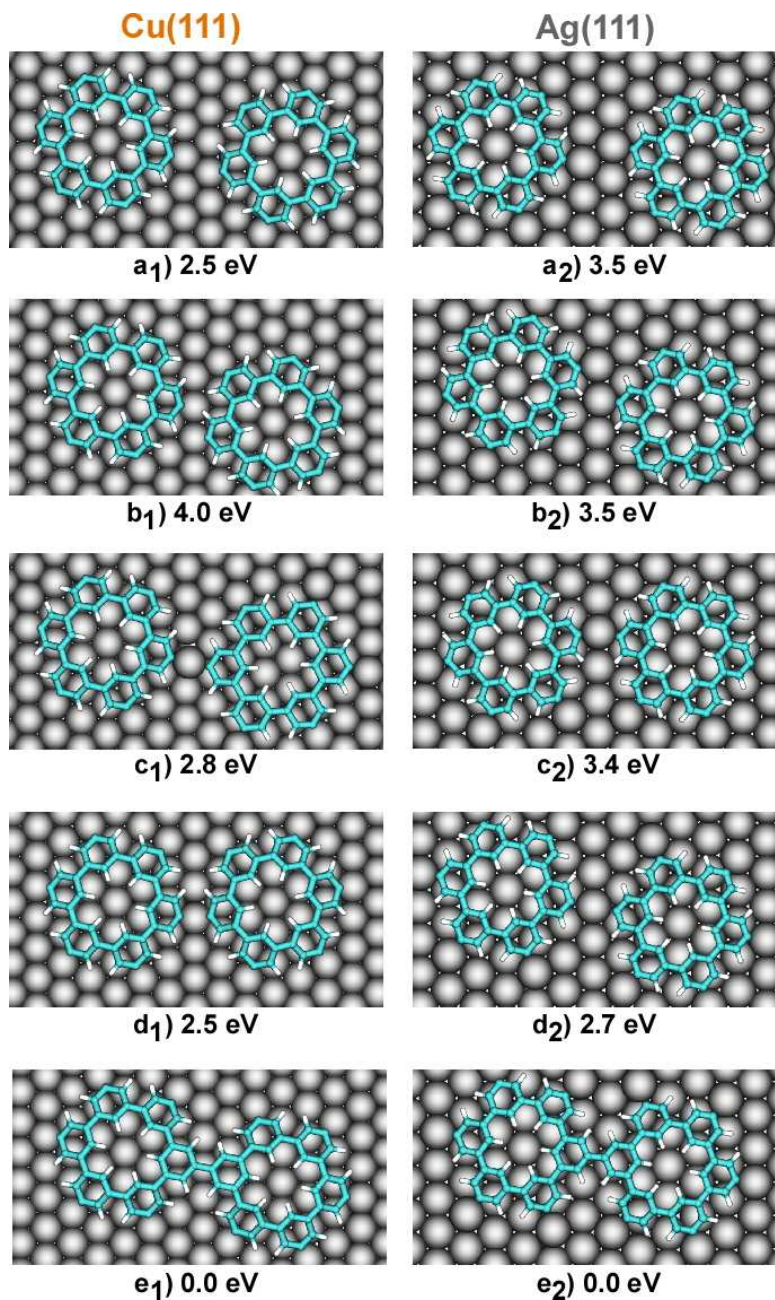


Figure S5. CHPR dimers on Cu(111) and Ag(111) for different configurations. Radicals binding to two different surface atoms (panels $a_{1,2}$ and $b_{1,2}$), CHPRs binding to a same surface metal atom (panels $c_{1,2}$ and $d_{1,2}$, with the latter for the lowest energy configuration), and CHP–CHP located on atop sites (panels $e_{1,2}$). Total energies are given with respect to the latter state.

The elucidation of the reaction pathway for CHPR coupling is not trivial and also involves diffusion steps. For the reaction pathway, the configuration in which two CHPRs bind to two neighbouring surface atoms is considered as the initial state (II, panels a_{1,2} and b_{1,2} in Fig. S5). The system then evolves to a state where the two CHPRs bind to a same surface metal atom (panels c_{1,2} and d_{1,2} in Fig. S5 show different configurations). As can be seen, the total energy for these configurations critically depends on the orientation of the individual CHPRs with respect to the surface lattice, with the lowest energy configurations shown in panels d_{1,2}. Panels e_{1,2} show CHP–CHP in the most stable atop configuration on the two surfaces.

For the calculations, slabs with a size 34.5×17.1 Å² and 34.7×17.5 Å², containing 360 and 444 atoms, respectively, are used to represent the Ag(111) and Cu(111) substrate, respectively. Twelve to sixteen images are used to sample the pathways.

Monte Carlo simulations of covalent network growth

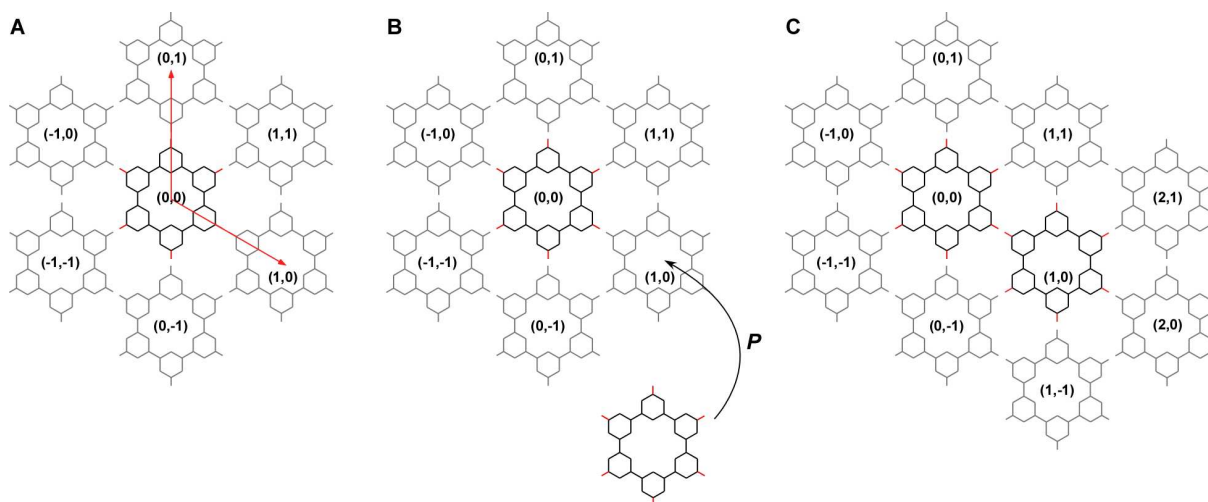


Figure S6. Illustration of the Monte Carlo process used for network growth simulations. (A) A seed molecule is fixed at the center of a hexagonal lattice (the arbitrarily defined (0,0) site) of a rhombic super cell. At the vertices of the seed, six equivalent coupling sites (shown in grey) are defined. (B) After performing a random walk a second molecule visits the seed and binds to the latter with the coupling probability P . (C) Once a molecule couples to the seed (in this example at the (1,0) site) new occupation sites at the (2,1), (2,0), and (1,-1) grid points become available.

Here we present a model that is used to simulate the assembly of CHPRs towards covalent networks. The simulations are based on a hexagonal lattice where the possible adsorption sites for the molecules are arranged in an ($n \times n$) rhombic super cell with periodic boundary conditions. The model is initialized by placing a seed molecule at the center of the hexagonal lattice (Fig. S6A). Then, a second molecule is added at the border of the super cell far away from the seed. This molecule walks randomly until it visits a site

adjacent to the seed. The probability that it couples to the seed (or otherwise diffuses further) is defined as the coupling probability P . Once the molecule joins the seed a further molecule is introduced at a random distant point and the described procedure repeats. With this iterative process the simulation is terminated when a pre-defined number of molecules forms a network cluster (note that “free”, i.e. uncoupled molecules are not allowed to exist). The model does not include temperature and energy explicitly to define the coupling probability P of the Monte Carlo process. Therefore, the kinetics, i.e. the rate at which the network clusters grow, is not captured by the model. The coupling probability P is defined *ad hoc* and can be regarded as the ratio between the reaction rates of the coupling process and the total number of events, i.e. the reaction rates for coupling (v_{coupl}) and diffusion (v_{diff}), according to

$$P = \frac{v_{\text{coupl}}}{v_{\text{coupl}} + v_{\text{diff}}} \quad (1)$$

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