Roles of Precursor Conformation and Adatoms in Ullmann Coupling: An Inverted Porphyrin on Cu(111)

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Supporting Information

ABSTRACT: Surface diffusion, molecular conformation, and on-surface coupling reactions are key processes for building tailored molecular nanostructures such as graphene nanoribbons, polycyclic aromatic hydrocarbons, and one-dimensional/two-dimensional (2D) polymers. Here, we study the surface diffusion and coupling in situ of a chlorinated porphyrin, namely 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (Cl4TPP), using a combined scanning tunneling microscopy (STM), density functional theory (DFT), and X-ray photoelectron spectroscopy approach. Using STM, we obtain surface migration and rotation barriers ΔE of 0.77 ± 0.09 and 0.93 ± 0.28 eV, respectively, indicative of covalent binding to the surface. In fact, we find that the precursors as well as all the reaction species exclusively (≈100%) adopt a peculiar “inverted” conformation covalently bonded to Cu(111). Using DFT, we have mapped two coupling reaction pathways: direct dechlorination and Cu adatom-mediated Ullmann coupling. We find that the latter is essentially barrierless, whereas the former faces a barrier of about 0.9 eV for inverted Cl4TPP on Cu(111). Our STM measurements show that C–Cu–C organometallic species are the main final products in the presence of Cu adatoms, which is explained by our DFT reaction profile when heat dissipation to the substrate is taken into account. This work not only highlights the relevance of surface adatoms in selecting the reaction pathway but also opens the possibility of precisely tailoring 2D molecular assemblies by controlling the supply of Cu adatoms.

On-surface synthesis has become one of the most interesting approaches to building complex molecular nanostructures, generally under ultra-high vacuum conditions. Typically, the molecular precursors are sublimated onto a well-defined substrate and subsequently, via the stabilization of transition states by a catalyst, the chemical reaction takes place. Even though multiple on-surface reactions are achievable, Ullmann coupling reactions have been shown to be among the most effective ways to build promising covalently bonded nanostructures. For example, this approach has recently been used to synthesize one-dimensional (1D) polymers, polycyclic aromatic hydrocarbons, two-dimensional (2D) conjugated aromatic polymers, which can be exfoliated into micrometer-sized 2D sheets, and to precisely synthesize graphene nanoribbons, among others. In general, an Ullmann coupling reaction begins with the cleavage of the halogens on the molecular precursors, proceeds via organometallic intermediates, and terminates with the formation of C–C covalent bonds. Depending on the molecular precursor, substrate, coverage, and annealing temperature and time, it may be possible to observe the precursors, organometallic intermediate species, C–C bonded species, radicals, etc. To obtain a deeper insight into the Ullmann coupling on-surface reaction, it is necessary to characterize the precursor’s conformation and the chemical intermediates formed, as well as the most stable final product of the reaction.

Herein, we have studied the molecular self-assembly of a chlorinated porphyrin, 5,10,15,20-tetrakis(4-chlorophenyl)-6-porphyrin (Cl4TPP), depicted in Figure 1, on Cu(111). By means of a combined experimental and computational study using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT), we are able to image and unequivocally characterize the initial, intermediate, and final species after the deposition of Cl4TPP on Cu(111). Moreover, by comparing the calculated energy barriers for a Cu adatom-assisted Ullmann coupling reaction and a direct dechlorination of the molecule, we are able to determine the preferred pathway for this reaction. These calculations, in agreement with our experimen-
In Figure 2, we analyze the surface diffusion behavior of Cl₄TPP on Cu(111) via an Arrhenius plot of the temperature-dependent rates. Similar to other tetraphenylporphyrins, Cl₄TPP deposition on Cu(111), the adsorbed isolated species rotated around the C₄ bonds, as indicated in Figure 1. After Cl₄TPP deposition on Cu(111), the adsorbed isolated species are mobile on the surface, whereas linear chains are less mobile, at room temperature (Figure S1 in the Supporting Information (SI)). By cooling the samples down to 233 K, we drastically reduce the mobility and are able to precisely resolve individual molecules. This already indicates that there is a high activation barrier for surface migration.

In Figure 2, we analyze the surface diffusion behavior of Cl₄TPP on Cu(111) via an Arrhenius plot of the temperature-dependent rates. Similar to other tetraphenylporphyrins, Cl₄TPP moves only along the three main (110) directions and exhibits discrete rotations of ±60°. The data exhibits a clear linear dependence, consistent with the Arrhenius equation for surface diffusion

\[
\nu \exp\left(\frac{-\Delta E}{k_B T}\right)
\]

where \(\nu\) is the attempt frequency and \(\Delta E\) is the activation barrier. From the slope, we obtain the migration barrier for unidirectional diffusion of \(\Delta E = 0.77 \pm 0.09\) eV, and from the intercept an attempt frequency of \(\nu = 10^{15.2} \text{ s}^{-1}\). These values are comparable to \(\Delta E = 0.71 \pm 0.08\) eV and \(\nu = 10^{18.1} \text{ s}^{-1}\) for 2H-tetraphenylporphyrin (2HTPP). The slightly higher migration barrier suggests a stronger molecule—substrate interaction for Cl₄TPP compared to 2HTPP. Similarly, from the linear fit to the surface rotation data, we determine the rotation barrier \(\Delta E = 0.93 \pm 0.28\) eV and the corresponding attempt frequency \(\nu = 10^{15.6} \text{ s}^{-1}\). The higher barrier for rotation compared to migration is already suggestive of a covalent interaction between Cl₄TPP and Cu(111).

Our STM measurements of Cl₄TPP deposited on Cu(111) show individual molecules with a “rectangular” symmetry characterized by four bright protrusions at the corners of the molecule and two bright central ovals (Figure 3a). To precisely measure individual molecules, we have performed statistical analysis of several STM images, including atomically resolved images, where porphyrin molecules are imaged simultaneously with Cu surface atoms (Figure S2 in the SI). From this analysis, the dimensions of a single molecule are determined to be \(a = 1.47 \pm 0.05\) nm and \(b = 1.11 \pm 0.05\) nm with a separation between the two bright central ovals of \(d = 0.46 \pm 0.05\) nm (Figure 3a). This indicates that surface adsorption on Cu(111) elongates the porphyrin, reducing the symmetry from square to rectangular.

Since STM measurements only provide geometrical information indirectly via the local electronic density of states, often their interpretation is not straightforward. To obtain deeper insight into the molecular conformation, we have performed structural relaxations of an individual Cl₄TPP molecule on Cu(111) for the two main conformations of surface-adsorbed porphyrins. Cl₄TPP moves only along the three main (110) directions and exhibits discrete rotations of ±60°. The data exhibits a clear linear dependence, consistent with the Arrhenius equation for surface diffusion

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rotation arising from chemisorption rather than physisorption (Figure 2). Moreover, the separation between the rotated pyrrole rings \(d = 0.52 \text{ nm}\) is commensurate with \(\text{Cu}(111)\), i.e., the next nearest neighbor separation of 0.51 \text{ nm} along the \(\langle 110 \rangle\) directions. This differs from the other coinage metals, where the next nearest neighbor separation of 0.58 \text{ nm} would require further rotation leading to steric hindrance between the rotated pyrrole rings.

Lepper et al. recently reported this extremely distorted configuration for CN and H terminated porphyrins,\(^26\)\(^{−}\)\(^28\) as seen previously by Albrecht et al.\(^32\) This configuration was named the inverted structure by Lepper et al., and from here on, we will use their nomenclature. In previous works,\(^26\)\(^{−}\)\(^28\) the most commonly reported configuration of surface-adsorbed porphyrins was the so-called saddle structure.\(^33\)\(^{−}\)\(^35\) To check this possibility, in Figure 3c, we show our relaxed DFT structure (wire-frame model) and the resulting STM simulation for Cl\(_4\)TPP adsorbed on \(\text{Cu}(111)\) in the saddle conformation. Comparing Figure 3a−c, we find that the STM simulation for the inverted conformation is in better agreement with the measurement than for the saddle conformation. In particular, Figure 3a does not feature the central gap, two opposing “banana” structures, and more squarish shape of Figure 3c, which are, however, in excellent agreement with the saddle configuration rarely observed here (Figure S3 in SI) but frequently reported for similar molecules.\(^33\)\(^{−}\)\(^35\) Moreover, our DFT calculations show that Cl\(_4\)TPP is physisorbed on \(\text{Cu}(111)\) when in the saddle conformation, with a N−Cu separation of 3.0 Å. This physisorption is inconsistent with the high activation barriers we observe for surface migration and rotation (Figure 2).

Moreover, according to the Sabatier principle of heterogeneous catalysis, the binding of the reagents must be neither too strong nor too weak, but “just right”.\(^36\) On the one hand, this implies that when Cl\(_4\)TPP is physisorbed in the rarely observed saddle conformation it is probably too weakly bound to have significant reactivity at low coverage. On the other hand, it also implies that when Cl\(_4\)TPP is covalently bound in the inverted conformation it is both mobile enough for species to meet and sufficiently bound for species to react, as seen in our STM measurements. This underscores the important role played by the adsorption conformation in determining a precursor’s reactivity.

Finally, careful observation of Figure 3a finds a brighter STM contrast in the diagonally opposite Cl atoms. To explain this observation, we have performed DFT calculations for Cl\(_4\)TPP on \(\text{Cu}(111)\) with Cu adatoms underneath the Cl atoms which exhibit a brighter contrast. The resulting STM simulation is shown in Figure 3d, with top and side views of the structure shown in Figure 3e,\(f\) respectively. Moreover, the presence of the 2 anchoring Cu adatoms explains why this particular molecule was stationary during 20 consecutive STM measurements. Note that a variety of contrasts were observed, e.g., one, two, three, or four bright spots, consistent with a corresponding number of Cu adatoms underneath the Cl terminations. However, our STM measurements of Cl\(_4\)TPP deposited on \(\text{Cu}(111)\) most commonly exhibited a uniform contrast between the Cl terminating groups, resembling Figure 3b.

Overviews of the samples show that Cl\(_4\)TPP molecules are oriented in three equivalent crystallographic directions with their long axis oriented along the \(\langle 110 \rangle\) main directions of the substrate (Figure 4a). To obtain a deeper insight into the molecule−molecule interactions, we have analyzed the main bonding motifs observed between neighboring molecules.

On one hand, some molecules are bonded via single side-on interactions (Figure 4b). In this configuration, the Cl atoms of neighboring molecules are placed beside each other. This configuration is consistent with a noncovalent type I van der Waals (vdW) halogen−halogen interaction, where the C−Cl···Cl angles are approximately equal \(\theta_1 \approx \theta_2\), as depicted in Figure 4c.\(^37\)\(^,\)\(^38\) For our relaxed DFT structure, we obtain \(\theta_1 = 217\)
Figure 4. (a) STM measurement after deposition of Cl₄TPP on Cu(111) \((T = 300 \text{ K}, A = 7.0 \times 7.0 \text{ nm}², U = -1.5 \text{ V}, I = 130 \text{ pA})\). van der Waals (vdW) (dotted oval) and covalent (dashed oval) single “head-on” interactions and a single “side-on” (dashed rectangle) interaction are marked. (b) STM simulation of the latter (dashed rectangle in (a)), a type I van der Waals interaction \( (θ_1 \approx θ_2) \), as shown in (c). The white arrows shown in (a) indicate the \((110)\) crystallographic directions of Cu(111).

At this stage, the isolated molecules are extremely difficult to observe and almost all \((\sim 99\%\)) of the molecules are involved in head-on interactions, with a majority being covalent in nature. This result suggests that after deposition at room temperature some molecules undergo cleavage of the C-Cl bonds as part of the on-surface Ullmann coupling reaction.

Moreover, our STM simulation\(^{40}\) (Figure 4b) is in excellent agreement with our STM measurement (dashed rectangle of Figure 4a), both in the dimensions and in the overall appearance.

On the other hand, some molecules are bonded via single head-on interactions (dotted and dashed ovals). In these configurations, the “arms” of neighboring molecules are collinear, that is, directly facing each other. From the STM measurements, two different kinds of single head-on interactions can be clearly distinguished, with one (dotted oval) \(0.54 \text{ nm}\) longer than the other (dashed oval). The longer single head-on interaction (dotted oval) is consistent with a noncovalent type I vDW Cl--Cl interaction \( (θ_1 \approx θ_2 \approx 180°) \), whereas the shorter single head-on interaction is covalent in nature. This result suggests that after deposition at room temperature some molecules undergo cleavage of the C-Cl bond as part of the on-surface Ullmann coupling reaction.

As we mentioned before, remarkably, even at room temperature, some molecules indicate cleavage of Cl atoms, whereas after annealing at 400 K for 30 min other molecules are still intact. This result might suggest that the rate-limiting step for cleavage of the Cl atoms is a limiting reactant (e.g., Cu adatoms) rather than a kinetic activation barrier.

To gain additional insight into the chemical environment of the Cl atoms as a function of the annealing temperature, we have performed XPS measurements. Figure 6 shows a summary of the dependence on annealing temperature of the XPS data for Cl atoms. XPS measurements of a freshly\(^{41}\) deposited sample of Cl₄TPP on Cu(111) show a main set of two peaks in the Cl region, which represent \(~61\%\) of the total integrated area (blue fitting, Cl(1)). These peaks have a binding energy of 200.2(5) and 201.9(5) eV for the Cl 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks, in excellent agreement with the reference values for Cl atoms in chlorobenzene \((C₆H₅Cl)\).\(^{47}\) This allows us to assign the Cl(1) peaks to Cl atoms bonded to the molecules. As we increase the annealing temperature of the samples, the Cl(1) peaks start to decrease, whereas the Cl(2) peaks (orange peaks in Figure 6) increase in magnitude. The binding energies of the Cl(2) peaks are 198.2(5) and 199.7(5) eV for the 2p\(_{3/2}\) and 2p\(_{1/2}\) components, respectively, in quantitative agreement with the reference values for CuCl₂.\(^{42}\)

Based on this, we can attribute the Cl(2) peaks to Cl atoms that are cleaved from the molecule and are strongly interacting with the Cu substrate. XPS shows that, as the samples are annealed, various 1D chains. A double head-on configuration is shown in Figure 5b, where a small gap in the charge density between the molecules is clearly observed. For this arrangement, the distance between the closest pyrrole rings of neighboring molecules is \(L = 1.51 \pm 0.05 \text{ nm}\), following the procedure described in Figure S5 of the SI. Figure 5c shows our STM simulation,\(^{40,43}\) where the distance between the neighboring pyrrole rings \((L = 1.52 \text{ nm})\), the small gap in the charge density, and the overall structure of the molecules is consistent with our experimental results. From our relaxed DFT structure (Figure 5c), we obtain intermolecular Cl--Cl separations \(\sim 4.6 \text{ Å}\), which is much larger than the sum of their vDW radii \(2.35 \text{ Å}^{40}\) and a negligible binding energy between species.

These results are in agreement with the observed instability of this structure in consecutive STM images acquired at 274 K (Video 1 in SI). For these reasons, we attribute the double head-on structure to confinement effects.

At this point, it is worth highlighting the different behavior we have observed in the cleavage of the Cl atoms on the molecules. As we mentioned before, remarkably, even at room temperature, some molecules indicate cleavage of Cl atoms, whereas after annealing at 400 K for 30 min other molecules are still intact. This result might suggest that the rate-limiting step for cleavage of the Cl atoms is a limiting reactant (e.g., Cu adatoms) rather than a kinetic activation barrier.

Figure 5. (a) STM measurement after annealing of Cl₄TPP deposited on Cu(111) \((T = 350 \text{ K} \text{ for } t = 30 \text{ min}, A = 30.0 \times 30.0 \text{ nm}², U = -2.0 \text{ V}, I = 200 \text{ pA})\). A double head-on configuration is marked (dashed rectangle). Direct comparison of STM (b) measurement (A = 3.0 \times 3.5 \text{ nm}²) and (c) simulation of the double head-on configuration (dashed rectangle in (a)), with a distance between pyrrole rings of \(L = 1.51 \text{ and } 1.52 \text{ nm}\), respectively.
In a organometallic bond see Figure S8. For a three-dimensional high-resolution image of a structure containing a C−C organometallic bond and the C−C organometallic bonds shows a bright protrusion in the bond between the molecules and a distance between the two pyrrole rings of neighbor molecules of L = 1.54 nm (Figure 7b), the STM simulation of C−C organometallic bonds is characterized by a uniform STM contrast in the bond with a distance between the two neighboring pyrrole rings of L = 1.33 nm (Figure 7c). The better agreement between Figure 7a,b allows us to assign the covalent single head-on interaction to a C−C organometallic bond. For a comparison between the C−C organometallic bond and the C−Cl−C configuration, see Figure S7 in the SI. For a three-dimensional high-resolution image of a structure containing a C−C organometallic bond see Figure S8.

In a final effort to shed light on the kinetics and thermodynamics of the processes, we performed DFT energy calculations for the relevant chemical species following two different reaction pathways: direct dechlorination (red lines) and Cu adatom-mediated Ullmann coupling (blue lines), as shown in Figure 8. Here, we reference all energies to that of Cl4TPP adsorbed on Cu(111) in the inverted conformation.

The relative stability of saddle versus inverted conformations of Cl4TPP (Figure 8ii) is highly sensitive to the choice of exchange and correlation (xc) functional. When vdW interactions are neglected (PBE4 solid lines in Figure 8), inverted and saddle conformations are isoenergetic, whereas, if vdW interactions are included at the Grimme’s D3 level (PBE-D345 dashed lines in Figure 8), the inverted conformation is 0.6 eV more stable than saddle configuration, as expected. If instead, vdW interactions are included at the self-consistent level (vdW-DF246 dotted lines of Figure 8), we find the opposite behavior.49 This suggests that PBE-D3 is the more robust xc functional for describing porphyrins on metal surfaces.26,27 Nonetheless, the remainder of the pathway, referenced to the experimentally observed inverted configuration of Cl4TPP, is in semi-quantitative agreement amongst all three xc functionals. This suggests that our vdW-DF2 calculations benefit from an error cancellation between the various inverted structures in the pathway, and we may have confidence in all these results. From here on, we shall refer specifically to PBE-D3 energy values.

To form a stable C−C covalent bond between molecules via the direct dechlorination path (Figure 8a), two isolated molecules (2Cl4TPP) first find a slightly more stable configuration interacting via a single side-on Cl−Cl interaction (Cl4TPP)2 (Figure 8a,iii). Then, after overcoming an energy barrier of 0.9 eV, a Cl atom is cleaved from one molecule to form the complex Cl4TPP−Cl4TPP (Figure 8a,v). Finally, after overcoming a similar barrier, the second Cl atom is also cleaved from the other molecule and the final C−C covalent bond is formed between molecules (Cl4TPP)2 with a binding energy of 2.8 eV (Figure 8a,v). This C−C covalent bond is the energetically most favorable structure in a direct dechlorination process.

In contrast, the reaction pathway to form a stable C−C covalent bond via a Cu adatom (Cuad)-mediated Ullmann coupling reaction is facile with no overall barrier (Figure 8b). In this case, one of the two isolated molecules first interacts with a Cu adatom (Figure 8b,iii), spontaneously forming a
Finally, it is important to highlight that the behavior of Cl₄TPP on Cu(111) is a quite rich process that cannot be fully understood without considering the two reaction pathways described herein. Since the Cu₄ad-mediated Ullmann coupling reaction is a facile and thermodynamically most stable process, the direct dechlorination process will only take place when no Cu adatoms are available. However, heating the Cu(111) surface naturally produces more Cu adatoms, so that the Cu₄ad-mediated Ullmann process remains facile even under conditions where the barrier for direct dechlorination could be overcome. For this reason, we do not expect the direct dechlorination pathway to play a major role under ordinary conditions.

## CONCLUSIONS

We have studied the surface migration, conformation, and Ullmann coupling reaction profile for 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin deposited on Cu(111). We obtain significant surface migration and rotation barriers of 0.77 ± 0.09 and 0.93 ± 0.28 eV, respectively, indicative of covalent binding to the surface. Surprisingly, we find that all adsorbates exclusively (∼100%) adopt a highly distorted molecular configuration where the pyrrole rings of the molecules are rotated ∼100°, the so-called inverted structure. Moreover, based on this conformation, we are able to unequivocally identify the bonding motifs: vdW single head-on and side-on Cl−−Cl interactions, and Cu−−Cl species; and the product: the organometallic C−−Cu−−C species, by our combined STM-DFT study. Finally, by simulating two different chemical reaction pathways, we have shown that a Cu adatom-mediated Ullmann coupling reaction is essentially barrierless, and the organometallic C−−Cu−−C species is the final product of the reaction under mild conditions when heat dissipation to the Cu(111) surface is taken into account.

To summarize, we report (1) the first system to have chlorinated TPP molecules as building blocks for on-surface synthesis; (2) the first system to adsorb almost 100% in the...
inverted structure conformation; (3) the first system to remain exclusively in the inverted conformation throughout the Ullmann reaction pathway, (4) the first elucidation of the Ullmann coupling reaction profile for inverted porphyrins, and (5) the first measurements of surface mobility of an inverted porphyrin. Altogether, these results blaze the trail toward the production of precisely tailored 2D molecular assemblies via the controlled application of Cu adatoms to the molecular precursors.

METHODS

Experimental Setup. The experiments were performed in two connected chambers. One chamber was equipped with an STM and the other one with an XPS, low energy electron diffraction, home-made Knudsen cell for molecule sublimation, and standard cleaning facilities. The base pressure in the XPS chamber was in the low 10⁻¹⁰ mbar range and in the STM in the middle 10⁻¹¹ mbar range. The STM microscope used was a SPECS Aarhus 150 equipped with a SPECS SPC 260 controller. The STM measurements were performed in a constant current mode with a tungsten tip cleaned in situ at Ar⁺ sputtering. XPS was performed with a SPECS Phoibos 150 hemispherical analyzer with multi-channeltron detection. The photons employed in XPS were obtained from an Al Kα anode. The Cu(111) single crystal was prepared by several cycles of Ar⁺ sputtering (1000 V @ ~5 μA cm⁻²) for 30 min with subsequent annealing at 850 K for 20 min following a slow cooling ramp to ensure large and well-ordered terraces. Cl₄TPP molecules (5,10,15,20-tetrakis(4-chlorophenyl)porphyrin) were sublimed in situ using a home-made Knudsen cell from a quartz crucible at a temperature of ∼850 K for 20 min following a slow cooling ramp to ensure coverage was maintained on the surface to avoid molecule exclusion when molecules were already trapped, e.g., at step-edges.

Coverage was determined using STM images. STM bias voltages are performed in the tunneling resistance range of 1.5 V, I ≈ 0.2 Å and τ = 0.03 eV/Å was obtained. To model the Cu(111) surface, we have employed a 15 × 14 × 3 supercell of 5823.59095 × 2.417 nm³, frozen to the experimental coordinates (a = 0.361 nm), with more than 1.5 nm of vacuum between repeated images. STM simulations have employed the Tersoff–Hamann functional in a constant current mode with a bias of ~1.5 V relative to the Fermi level as implemented in the code ASE. To estimate the C–Cl and C–C bond distances in the transition states during direct dechlorination and a Cu adatom-mediated coupling reaction, we have performed nudged elastic band calculations for a chlorinated benzene with the anchoring C atom constrained to the same height and/or position as the relevant atom in Cl₄TPP above the Cu(111) surface. The transition state energy for Cl₄TPP was then estimated by fixing either the C–Cl or C–C bond distance and performing an otherwise unconstrained surface relaxation on the frozen Cu(111) surface slab.

Computational Details. All DFT calculations were performed using linear combinations of atomic orbitals within the projector-augmented wave method code GPAW. For the adsorbed species, we employed a double-ζ-polarized basis set and a single-ζ-polarized basis set for the Cu(111) surface. We employed three different types of xc functionals: the generalized gradient approximation for the exchange and correlation (xc) functional as implemented by Perdew, Burke, and Ernzerhof (PBE), including vdW interactions at the Grimme’s D3 level (PBE-D3), and including vdW interactions self-consistently (vdW-DF2). We used a grid spacing of h ≈ 0.2 Å and performed structural relaxation of the relevant species until a maximum force of ≤ 0.03 eV/Å was obtained. To model the Cu(111) surface, we have employed a 15 × 14 × 3 supercell of 3823.59095 × 2.417 nm³, frozen to the experimental coordinates (a = 0.361 nm), with more than 1.5 nm of vacuum between repeated images. STM simulations have employed the Tersoff–Hamann approximation in a constant current mode with a bias of ~1.5 V relative to the Fermi level as implemented in the code ASE. To estimate the C–Cl and C–C bond distances in the transition states during direct dechlorination and a Cu adatom-mediated coupling reaction, we have performed nudged elastic band calculations for a chlorinated benzene with the anchoring C atom constrained to the same height and/or position as the relevant atom in Cl₄TPP above the Cu(111) surface. The transition state energy for Cl₄TPP was then estimated by fixing either the C–Cl or C–C bond distance and performing an otherwise unconstrained surface relaxation on the frozen Cu(111) surface slab.

ASSOCIATED CONTENT

Supporting Information

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Notes

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(40) In this DFT analysis, two Cl₃TPP molecules were placed on a Cu(111) surface where they were brought close together to form the desired bond and then allowed to relax.

(41) We defined a freshly sample as a sample in which the deposition was done a maximum of 6 h before the measurement.


(49) We attribute this opposite relative stability to our use of PAW pseudopotentials that are not norm-conserving, something which is assumed by the vD-W-DF2 implementation, but are currently unavailable for the GPAW code. This leads to an overestimation of metallic bond lengths with vD-W-DF2 and an underestimation of the N−Cu bond energy in the inverted configuration (see pyrrole tests in Table S1 of Supporting Information). Although correcting this issue is beyond the scope of this article, we believe that it is important to show this discrepancy.

(50) We use Cl₃TPP to denote a Cl₃TPP molecule which has lost one Cl atom.