

Catalytic Action of a Cu(111) Surface on Tetraazaperopyrene Polymerization

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ABSTRACT The polymerization of tetraazaperopyrene molecules on a Cu(111) substrate, as observed in recent scanning tunneling microscopy experiments, has been investigated in detail by first-principles calculations. Tautomerization is the first step required for the formation of molecular dimers and polymers. The substrate has been found to catalyze this tautomerization.

SECTION Surfaces, Interfaces, Catalysis

The ongoing miniaturization of electronic devices drives the search for alternatives to the present approaches of lithographic manufacturing. In this context, the spontaneous ordering and assembly of atoms and molecules on atomically well-defined surfaces, the so-called bottom-up approach, appears to be a very promising way to fabricate functional systems with nanometer dimensions.^{1–3}

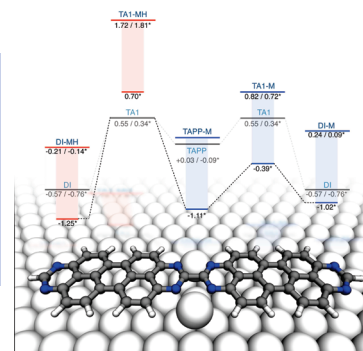
Organic molecules are used as building blocks to construct supramolecular structures for potential applications.^{4,5} During the self-assembling process, the intermolecular interactions ranging from indirect, substrate-mediated interplay,^{6,7} direct Coulomb forces,^{3,8,9} weak dispersion interactions,¹⁰ and metal complexation¹¹ to hydrogen^{12,13} or covalent bonds,^{14,15} set the initial stage for a large number of possibilities to form one- and two-dimensional molecular networks of varying robustness. For applications that require a high thermal and chemical stability, the stabilization through covalent bonds is essential. While it can be expected that the formation of covalent bonds between surface adsorbed molecules is significantly different compared to the corresponding reaction in solution or in bulk films,¹⁶ only little is known in detail about the impact of the surface on the reaction between the adsorbates.

In this article, we present first-principles calculations of the tautomerization reaction of 1,3,8,10-tetraazaperopyrene (TAPP) on a Cu(111) surface. This special system has previously been investigated experimentally by Matena et al.^{17,18} The authors found that the copper substrate is crucial for the formation of the various aggregates they observed, i.e., differently ordered close-packed as well as porous networks on one hand, and covalently bonded linear chains on the other hand. From a surface science point of view, especially the latter are of great interest, since their formation requires a multiple step chemical reaction that does not occur in gas phase. The Cu(111) surface exhibits only a weak interaction with the adsorbed molecules, but obviously is sufficient to change the reaction kinetics. Recent density functional theory (DFT) calculations focused on the energetic stability of the molecular network or the chain, respectively.^{18,19} However,

the detailed mechanism for the tautomerization reaction has not been investigated yet. With the work presented here, we want to close this gap.

Our DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP)²⁰ and the PW91 functional²¹ of the generalized gradient approximation (GGA) to model the electron exchange and correlation. In order to account approximately for the influence of the dispersion interaction, a semiempirical scheme based on the London dispersion formula was used.^{22,23} The electron–ion interaction was described by the projector-augmented wave (PAW) method,²⁴ which allows for an accurate treatment of the first-row elements as well as the Cu 3d electrons with a relatively moderate energy cutoff of 340 eV. The adstructures were modeled in periodically repeated supercells, containing two atomic Cu layers arranged in a $\begin{pmatrix} 14 & 0 \\ 3 & 6 \end{pmatrix}$ translational symmetry, the adsorbed molecules, and a vacuum region of 15 Å. Adsorption energies were calculated with $E_{\text{ads}} = E_{\text{tot}} - E_{\text{sub}} - E_{\text{mol}} - N_{\text{Cu}}\mu_{\text{Cu}} + \frac{1}{2}N_{\text{H}}E_{\text{H}_2}$ with the total energy of the adsystem E_{tot} , the energy of the substrate E_{sub} and the molecule E_{mol} , the number of additional metallic adatoms N_{Cu} and dissociated hydrogens N_{H} , and the chemical potential of copper adatoms μ_{Cu} and molecular hydrogen E_{H_2} . Potential energy surfaces (PES) are calculated by lateral displacement of the molecule followed by a relaxation with a laterally constrained carbon atom (C_c in Figure 1).

A single TAPP molecule adsorbs completely flat on the Cu(111) surface. The adsorption geometry can be seen in the top left part of Figure 1. The molecule–substrate interaction is weak and dominated by dispersion forces. The molecule's center ring is located on top of a copper atom as energetically most favorable adsorption position. In this minimum energy position, the adsorption energy amounts to -2.55 eV. However, due to the weak interaction with the substrate and its



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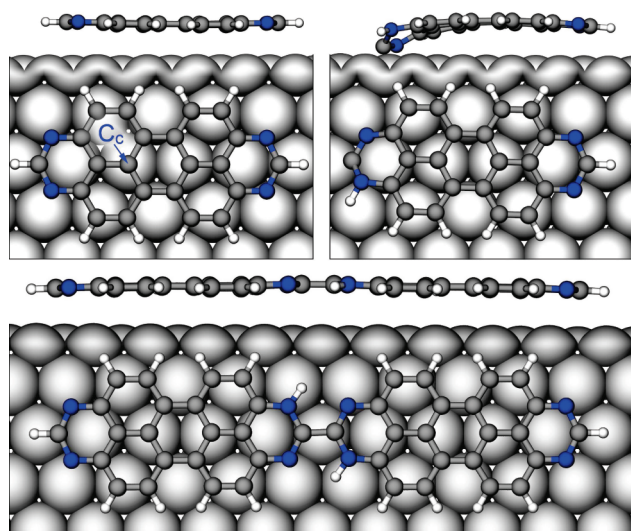


Figure 1. Molecular model for the single TAPP molecule (left), the first tautomer TA1 (right), and the dimer adsorbed on the Cu(111) surface (bottom).

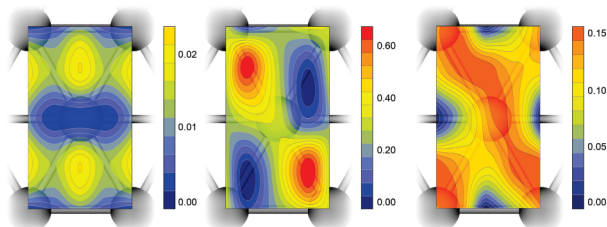


Figure 2. PES (including dispersion corrections) for a single TAPP molecule, the first tautomer TA1, and the metal-coordinated tautomer TA1-M (reference point is the center of the molecule). All values are in electron volts.

mainly dispersive character, the molecule can be expected to be rather mobile, which is crucial for the polymerization reactions discussed in the following. The calculated PES shown in Figure 2 shows the energy barriers for the molecule to move around at the surface. The center ring of the molecule moved to a bridge site increases the energy by less than 0.01 eV, and even the most unfavorable hollow site is only by 0.02 eV less favorable in energy than the top site.

The important prerequisite for chain and network formation of the molecules is their tautomerization. The hydrogen atom at the central edge carbon has to move to one of the adjacent nitrogen atoms in order to form the first tautomer (TA1, cf. Figure 1). In this configuration, the central carbon is left with only two bonds to the neighboring nitrogen atoms and a free electron pair. The same reaction happens for the second tautomer (TA2) at the central edge carbon at the opposite side of the molecule. With an energy difference of 2.09 eV between TAPP and TA1, the described tautomerization process is unfavorable in the gas phase (see Figure 3 for an overview of the energetics). Analogously, the same holds for the formation of TA2. In the gas phase, the polymerization is hindered due to this costly removal of the hydrogen atom.

For the molecules being adsorbed on the Cu(111) substrate, energetics change significantly. However, since the

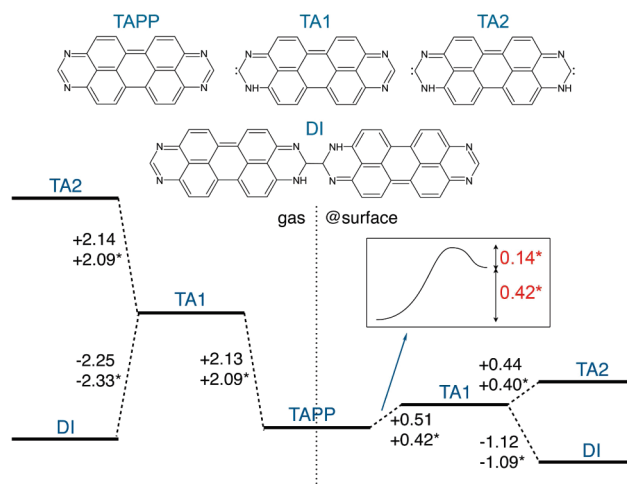


Figure 3. Energetics of the reaction. Toward the left, results for the gas phase are shown. Toward the right, the reaction on the substrate is shown. All values are in electron volts per molecule. Energies including dispersion corrections are marked with an asterisk. See text for details.

polymerization process is preceded by a copper coordination network, additional surface adatoms can also modify the reaction kinetics. To get a clear idea of the different influences, we start with the discussion of the clean unperturbed surface followed by the inclusion of copper adatoms later.

Since the TA1 tautomer can deform after desorption and bind covalently to a Cu atom, the adsorbate system can remain in an energetically more favorable geometry than in the gas phase. Thus, the energetic difference between TAPP and TA1 (in the adsorbed geometry) decreases by a factor of 5 to 0.42 eV. Figure 1 shows the adsorption geometries for TAPP (top left part of the figure) and TA1 (top right part).

The diffusion barrier of the tautomer TA1 (TA2) is higher than that of TAPP and amounts to 0.5 eV (0.7 eV). Also the energetically favored bonding position for both tautomers is shifted toward the bridge side with respect to the central ring of the molecule. Therefore, the mobility of the tautomers is reduced compared to the TAPP molecule, suggesting covalent bonding to the substrate. This is supported by the calculated charge density differences revealing that the free electron pair of the central carbon atom of the TA1 tautomer binds to the substrate. Additionally, the nitrogen lone pair interacts weakly with the surface. At this point, the catalyzing effect of the surface can to some extent already be understood.

While the total energy differences between the tautomers explain the relative stabilities, the activation energies for the tautomerization reactions have to be calculated in order to understand the reaction kinetics.

We have calculated the PES for the moving hydrogen both for the molecule in the gas phase and in the adsorbed state (Figure 4). The barrier for the first tautomerization (TAPP→TA1) has been calculated to be significantly smaller in the adsorbed state (0.56 eV) than in the gas phase (2.10 eV). Figure 4 shows the path taken by the H-atom during the tautomerization process in the adsorbate state and reveals that the final state is a local energy minimum. An energy

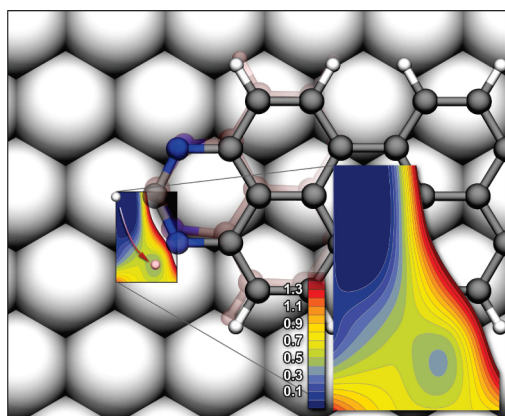


Figure 4. PES (including dispersion corrections) of the tautomerization process from TAPP toward TA1 (one hydrogen moves from the carbon to the nitrogen). All values are in electron volts.

barrier of 0.14 eV separates this state from the initial configuration (TAPP). In the gas phase, in contrast, TA1 is not stable, since the energy barrier for the reverse reaction (TA1→TAPP) is with 0.01 eV negligible, even within the error bar of our calculations. Thus, on the substrate, TA1 can be viewed as a meta stable state. This fact, together with the total energy differences discussed above, enhances the tautomerization and makes the reaction, contrary to the gas phase, likely to occur at the substrate.

The tautomerization is the first step toward chain or network formation. The second step toward the formation of longer polymers is the dimerization of two tautomers. The formation of a dimer (DI) consisting of two TA1 tautomers is highly favored at the substrate as well as in the gas phase. The energy gain has been calculated to be by a factor of 2 higher in the gas phase (−2.33 eV) than at the substrate (−1.09 eV). One reason for this is that the isolated TA1 tautomer is unstable in the gas phase; another reason is the covalent bonding of TA1 to the substrate, which has to be lifted for the dimer bond formation. Since the dimer has a flat adsorption geometry (see bottom part of Figure 1), the molecule–substrate bonds of TA1 must be broken. Nevertheless, there is an overall energy gain due to the formation of a C=C double bond between the two TA1. Comparing DI with the originating TAPP, this energy gain is by a factor of 2 higher for the molecules adsorbed on the Cu-surface than in gas phase. Figure 3 summarizes the results of our calculations in a reaction diagram. Starting from the TAPP molecule in the center, the two-step process via TA1 to DI is shown for the gas phase (toward the left) or for the adsorbate (toward the right), respectively. Values marked with an asterisk include dispersion interactions, while those without are DFT-GGA values. Although the dispersive interaction is the main contribution to the binding energy of TAPP to the substrate, it does not change the reactions qualitatively, as could have been expected based on our previous experiences with comparable systems.^{10,25,26} An explanation for this finding might be the crucial role of the formation of covalent bonds for TA1. From TA1, the second tautomerization step to TA2 is in both cases unlikely. For chain formation, however, it is not needed. The deformation of the adsorbed TA1 due to the bond to the substrate does not affect

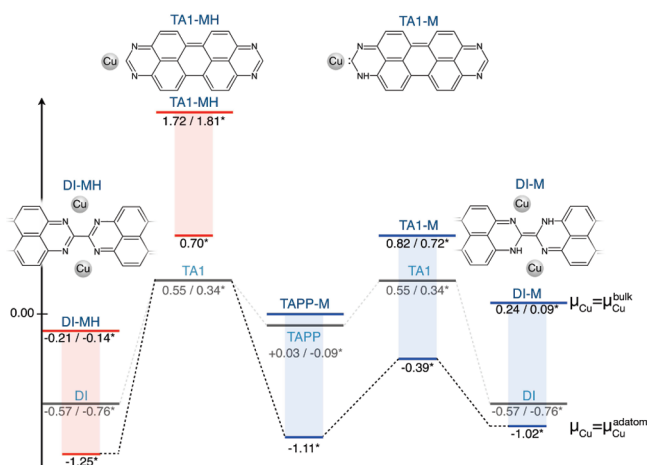


Figure 5. Energetics of the reaction with coordination adatoms (right) and an additional dehydrogenation (left). The corresponding molecular structures are visualized as well. The ranges of the chemical potentials of copper are marked with shaded areas for metal-coordinated structures (ranging from $\mu_{\text{Cu}}^{\text{bulk}}$ to $\mu_{\text{Cu}}^{\text{adatom}}$ as indicated). All values are in electron volts per molecule. Energies including dispersion corrections are marked with an asterisk. See text for details.

more than half of the molecule. The other end of the molecule remains approximately flat. In DI, the situation is similar, thus deformation is not hindered, and the mechanism of the repositioning of the hydrogen atom at the DI central C can occur completely analogously to the reaction from TAPP to TA1. Likewise, a third and any further TA1 can be added, resulting in linear molecular chains.

However, additional adatoms can also play a crucial role during the covalent synthesis. Figure 5 summarizes the potential influence of Cu adatoms on the reaction process. Hereby, the energy levels depend on the chemical potential of the adatoms μ_{Cu} ranging from the energy of copper bulk $\mu_{\text{Cu}}^{\text{bulk}}$ up to the adsorption energy of a single isolated adatom $\mu_{\text{Cu}}^{\text{adatom}}$ as shown in Figure 5 with shaded areas. The discussion will start with the case that the system is in equilibrium with the copper bulk reservoir.

For the single TAPP, one molecular nitrogen is coordinated to the metal, and the energy difference of 0.09 eV compared to the clean surface shows a slight preference of the non-coordinated geometry for lower coverages. After the first tautomerization, the total energy difference between coordinated and noncoordinated TA1 increases to 0.38 eV. Now, the central carbon is bonded to the additional metal atom resulting in just a small deviation from the planar structure, which reduces the strain of the molecule compared to the uncoordinated case. The corrugation of the PES shown in Figure 2 also decreases for the TA1-M tautomer compared to the uncoordinated case from 0.6 to 0.15 eV. Thus, the metal coordination reduces the diffusion hindrance of the tautomer while it is still possible for both configurations (TA1 and TA1-M) to diffuse at the experimental temperatures above 250°. Another possibility to form the TA1 state is indeed the diffusion of hydrogen to the substrate, which may be assisted by the metal adatom. The resulting molecule is now partially dehydrogenated and bonds to the coordination atom.

However, this increases the energy by 1.81 eV and is thus not likely. The dimerization of two TA1 tautomers results in an energy gain for all three possibilities: DI with metal coordination (-0.25 eV), DI with metal coordination and hydrogen loss (-0.48 eV), as well as DI (-1.09 eV). The dehydrogenated state DI-MH is now more stable than the solely coordinated dimer (DI-M). Nevertheless, for the upper limit of the chemical potential, the uncoordinated reaction pathway as described above is preferred.

Indeed, at high temperatures there are additional adatoms available as a result of thermal degradation from step edges shifting the chemical potential to lower values and increasing the probability of metal-coordinated molecules at the surface. This situation is reflected by the lower limit of the chemical potential. For constant temperature, the shaded area in Figure 5 can be interpreted as the partial pressure of available adatoms. The stability of the copper-coordinated molecular dimerization can be favorable depending on the adatoms available. In this case, the dehydrogenated, metal-coordinated dimer is more stable than the hydrogenated one in contrast to the tautomer case where the hydrogenated TA1-M is more stable. Thus, the preferred reaction pathway starts with a metal-coordinated TAPP molecule followed by a tautomerization step without losing the coordination to the adatom. Now, tautomers can dimerize, but an additional dehydrogenation is preferred (energy gain compared to TAPP just with dehydrogenation). Likewise, more tautomers can be added, resulting in metal-coordinated, linear molecular chains. In the end, the preferred reaction pathway depends on the number of adatoms available ranging from an uncoordinated to a metal-coordinated polymerization.

Summarizing, we presented detailed first-principles investigations of the polymerization process of TAPP molecules on a Cu(111) surface. We have identified the mechanisms that lead to the tautomerization of molecules as a necessary first step (formation of TA1) and the dimer (DI) formation as a second step in the reaction. A catalyzing effect could be attributed to the Cu(111) substrate, which is crucial for the stability of the tautomer TA1, the formation of which is required for the polymerization. We find that metal-coordinated (provided the process is accompanied by a dehydrogenation) as well as uncoordinated polymerization processes are possible. Therefore, the catalytic effect of metallic surfaces can help to build new covalent networks that are not producible in the gas phase or in solution.

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