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Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry

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Abstract

A study of the two-dimensional crystallization of rhodizonic acid on the crystalline surfaces of gold and copper is presented. Rhodizonic acid, a cyclic oxocarbon related to the ferroelectric croconic acid and the antiferroelectric squaric acid, has not been synthesized in bulk crystalline form yet. Capitalizing on surface-assisted molecular self-assembly, a two-dimensional analogue to the well-known solution-based coordination chemistry, two-dimensional structures of rhodizonic acid were stabilized under ultrahigh vacuum on Au(111) and Cu(111) surfaces. Scanning tunneling microscopy, coupled with first-principles calculations, reveals that on the less reactive Au surface, extended two-dimensional islands of rhodizonic acid are formed, in which the molecules interact via hydrogen bonding and dispersion forces. However, the rhodizonic acid deprotonates into rhodizonate on Cu substrates upon annealing, forming magic clusters and metal–organic coordination networks with substrate adatoms. The networks show a 2:1 distribution of rhodizonate coordinated with 3 and 6 Cu atoms, respectively. The stabilization of crystalline structures of rhodizonic acid, structures not reported before, and their transition into metal–organic networks demonstrate the potential of surface chemistry to synthesize new and potential useful organic nanomaterials.

Keywords: STM, metal–organic framework, self-assembly, deprotonation, density functional theory, organic ferroelectric, rhodizonic acid, Au(111), Cu(111)

Abbreviations: STM, scanning tunneling microscope; RA, rhodizonic acid; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; DOS, density of states; MOCN, metal–organic coordination network; DFT, density functional theory

The recent discovery of ferroelectricity in crystallized croconic acid¹ has ignited interest in the physical and electronic properties of hydrogen bonded organic ferroelectrics^{2–5} as they potentially offer a path toward molecule-sized electronics. In this context, considerable interest has emerged on the resonance-assisted hydrogen bonding between the keto and enol forms ($-\text{C}=\text{O}\cdots\text{HO}-\text{C}=\leftrightarrow=\text{C}-\text{OH}\cdots\text{O}=\text{C}-$), where the strong coupling between the proton and the π -electron system is essential to the switchable molecular dipole moments.⁶ These β -diketone enol moieties, which are also found in croconic acid, are likely a prototype for many more instances of tautomerism-enabled ferroelectricity, and have inspired interest in related molecules. Croconic acid is a cyclic oxocarbon conjugated system, where other related members are deltic acid, squaric acid and rhodizonic acid (RA), of the form $\text{H}_2\text{C}_n\text{O}_n$ where $n = 3, 4, 6$. Rhodizonic acid differs from ferroelectric croconic acid and antiferroelectric squaric acid simply by the number of carbons in its central ring ($n = 6$), and therefore can be expected to ex-

hibit electronic features similar to either its squaric acid or croconic acid homologues, and potentially ferroelectric behavior. A two-dimensional multiferroic coordination complex consisting of cobalt and RA was recently investigated through first-principles calculations and found to support a large stable electric polarization.⁷ A practical obstacle is that RA is very hygroscopic and typically found in the form of rhodizonic acid dihydrate^{8,9} and, to our knowledge, all attempts to grow crystals of RA have been unsuccessful. On the other hand, growth of various metal–organic frameworks of deprotonated RA, $\text{C}_6\text{O}_6^{2-}$ rhodizonate, have been reported.^{10,11}

Here we present a study of the first two-dimensional crystallization of RA on the crystalline surfaces of gold and copper. Our starting point is the rhodizonic acid dihydrate, which we dehydrate under ultrahigh vacuum to form RA,⁹ followed by thermal evaporation and physical deposition on Au(111) and Cu(111) in vacuum. We capitalize upon surface-assisted molecular self-assembly to build two-dimensional

Figure 1. (a) STM topography of a self-assembled network of RA on Au(111), recorded at 77 K. Tunneling parameters: (i) 1 V, 700 pA; (ii) -1.4 mV, 250 pA. (b) Structure of the molecules discussed in this article: rhodizonate, $C_6O_6^{2-}$ (b-i), anhydrous rhodizonic acid, $H_2C_6O_6$ (b-ii), and dihydrate rhodizonic acid, $H_2C_6O_6 \cdot 2H_2O$ (b-iii). (c) Proposed model of a RA network, where the Au atoms have been removed for clarity. Right: Summed site-projected densities of states of the model network adsorbed over a two layer Au(111) slab over C-O ($-H$) groups on opposite sides of RA. (The two plots correspond to the two molecules with the narrowest and broadest peaks with HOMO/LUMO character. The Fermi energy is set to 0 eV.) Isosurfaces of the LUMO, HOMO, and HOMO-1 of a single gas-phase rhodizonic acid molecule, along with the respective electron density plot, is shown next to the peak which best characterizes them in the two-dimensional structure and the Fermi energy is set to 0 eV.

RA structures. In addition, through controlling the surface chemistry and aided by first principles calculations, we were able to identify a novel surface supported metal coordinated rhodizonate species.

When evaporated under ultrahigh vacuum onto Au(111) at room temperature, RA forms extended molecular networks exhibiting extremely large domains of hexagonal symmetry as illustrated in Figure 1a. The networks grow across the herringbone reconstruction of Au,¹² which is visible as bright ridges below the molecular layer, without lifting this reconstruction. They are limited in size by the coverage alone, meaning that often only one extended island is observed on a terrace. This observation is characteristic of a large mean free path for the molecules upon adsorption and a low diffusion barrier on the Au(111) surface. We also found that annealing the sample even slightly above room temperature results in the gradual decrease in the island size due to desorption of RA from the gold surface, which implies that the molecules are only weakly bound to the surface. No changes in the network architecture itself were observed after annealing. Imaging at certain bias voltages achieved submolecular resolution and reveals an alternating crescent shape pattern, as is illustrated in Figure 1a(ii), which was obtained at -1.4 mV. The calculated spatial distributions of the LUMO (lowest unoccupied molecular orbital), HOMO (highest occupied MO) and HOMO-1 of RA show such a crescent shape as well (see Figure 1c), but those of the deprotonated RA (rhodizonate) $C_6O_6^{2-}$ do not (see the Supporting Information, Figure S12). For example, the HOMO-1 orbital of RA (and therefore its charge density), which is of π -symmetry with respect to the plane of the molecule, is localized mostly on the hydroxyl-side of the carbon ring. The HOMO (σ -symmetry) and LUMO (π -symmetry) are localized on the opposite side of the molecule (Figure 1c).

The summed site-projected densities of states of a model RA monolayer deposited on a two-layer Au(111) slab (Figure 1c) confirms the assignment of select peaks in the densities of states in the periodic, supported system as arising from orbitals that can be correlated to those calculated for the molecule in the gas-phase. The red curves represent the sum of the site-projected densities of states of the carbon and oxygen atoms belonging to the carbonyl groups ($C=O$) opposite the hydroxyls, on which the LUMO and HOMO are localized in the molecule. The black curves represent the sum of the C-O groups belonging to a hydroxyl upon which the HOMO-1 contribution is the strongest. Although scanning tunneling microscope (STM) images cannot be inferred directly from the shape of the frontier orbitals or charge distribution provided in Figure 1c, we attribute the asymmetry of the appearance of the molecules in our STM images to the presence of the two hydroxyl groups, which break the symmetry and give RA the observed orientation in the network.

In spite of the fact that within the computations the RA molecules do not contribute significantly to the occupied densities of states (DOS) within 0.5 eV of the Fermi energy, a region consistent with the conditions used in recording the STM image in Figure 1a(ii), the broken symmetry can be seen in almost every peak in the DOS in Figure 1c. The broken symmetry was also observed in the calculations when a network was formed from RA molecules where one of their hydroxyl groups was rotated 180° about the hydroxyl C-O bond. Such a rotation lowers the total energy of a single isolated molecule by approximately 0.24 eV/molecule in the gas phase, but the simulation cells for the two extended networks adsorbed on a two-layer Au(111) surface have similar energies, within 0.05 eV/molecule of each other. We therefore propose a hydrogen-bonded RA structural model analogous to that presented in Figure 1c, assuming that the molecules are indeed present in the form of RA and alter-

nate in their orientation as seen in the STM images. We note that the alternating orientation scheme is not perfectly repeated over long-range distances, meaning that there is likely a substantial contribution from nondirectional van der Waals forces, which contribute to the observed disorder. Importantly, our computational results illustrate that the presence of RA molecules within hydrogen-bonded networks is consistent with the crescent-shaped images observed by STM. An alternative structural model is discussed further in the Supporting Information.

The hydration of carbonyl groups opposite the hydroxyl groups in RA was established as one of the first controllable and reversible dehydrations of a solid hexol, in this case $\text{H}_8\text{C}_6\text{O}_8$.¹⁰ The bis-hydrated RA rings within the crystallized $\text{H}_8\text{C}_6\text{O}_8$ structure form flat sheets similar to the model of RA shown in Figure 1c, except with different coordination numbers. A viable concern with our proposed structural model of the network imaged in Figure 1 is that the RA molecules deposited on the surface may, in fact, be hydrated. The computed reaction energies of hydrating the RA network shown in Figure 1 are found to favor the hydrated network, just like for an isolated molecule, and are discussed more completely in the Supporting Information. The summed site-projected densities of states of the hydrated surface-adsorbed network are also consistent with the broken-symmetry STM profiles (Supporting Information, Figure S8), meaning the computations cannot ambiguously determine whether the surface-stabilized network is hydrated. The experimental treatment of the RA in this study, however, strictly followed a procedure that has been proven to dehydrate the RA.⁹ Evidence for the presence of anhydrous RA is the characteristic change in color during the dehydration from colorless⁸ to deep orange,¹⁰ which is observed to be reversible after removal of the anhydrous powder from vacuum (see the Supporting Information for further images and discussion). Considering this, it is reasonable to assume that the experimental RA layers consist of the dehydrated species.

When deposited at room temperature on the more reactive Cu(111), RA forms smaller, isolated islands that contain structural defects, with occasional nucleation of a second layer (Figure 2a). Given the identical symmetry of this network and the intermolecular spacing of $0.65 \text{ nm} \pm 0.05 \text{ nm}$ that is within experimental error identical to the spacing of RA on Au(111), we conclude that this network is the same hydrogen-bonded network found earlier on Au(111). Weak annealing of the sample to approximately 360 K, however, results in new structural phases of RA, seen in Figure 2b–e. The annealed islands are more uniform in shape, exhibit fewer defects, and are of single layer height. Characteristic monolayer deep holes in the terraces of the Cu(111) substrates are now observed, along with a roughening of the substrate step edges. Some of the holes in the terraces are filled with molecules, where they form the same network as on top of the terraces. What is striking is that the architecture of the networks has changed drastically, exhibiting a change in the local environment and the apparent height of each molecule. Isolated clusters, which appear to be the basic building blocks of the networks, are frequently observed, such as in Figure 2c,e, and we note that such clusters always appear in groups of 1 or 3 (Figure 2e). The molecules are visible as the bright lobes in the islands, and every third molecule in a row has increased brightness that corresponds to an increased apparent height of $0.2 \text{ \AA}$. There are smaller structures connecting these bright lobes, visible in Figure 2d,e, which we identify below as Cu atoms linking the molecules together. We consider the basic clusters at the top of Figure 2e to be “magic” because they occur only in this particular

Figure 2. STM images, recorded at 77 K, of RA on Cu(111) deposited at room temperature (a) and after annealing (b–e). Note that in b, the step edges are jagged and that holes in the substrate are visible. Image c highlights a 15° orientation relation between the $\langle 101 \rangle$ substrate direction and the symmetry axis of the island. (d) Close up of one island with unit cell highlighted. (e) Magic cluster sizes of RA. Tunneling parameters: (a) 0.6 V, 400 pA; (b–e) 0.08 V, 250 pA.

configuration and size. The concept of magic clusters originates from gas phase cluster physics³⁰ and has been recently applied to surface-supported clusters.²⁹ It refers to particularly stable configurations of atoms or molecules.^{30–32}

The molecule-to-molecule spacing, measured at 77 K increased from $6.5 \pm 0.5 \text{ \AA}$ to $7.3 \pm 0.3 \text{ \AA}$ after annealing at approximately 360 K. Together with the observation of triangular holes in the surface and visibly rough steps, this increased spacing supports the proposal that substrate Cu atoms serve as linkers in the networks, thus enabling the formation of a two-dimensional metal–organic coordination network (MOCN). A computational scan of periodic RA gas-phase networks versus gas-phase networks of rhodizonate with Cu counterions placed in the interstitial sites showed that the molecule-to-molecule spacing (from the center of the C_6 ring of one molecule to that of the next) within the lowest energy planar RA network that we considered was approximately $7.5\text{--}7.6 \text{ \AA}$, while that of the rhodizonate/Cu networks was $7.8\text{--}7.9 \text{ \AA}$. When the planar constraint was released, the rhodizonate networks buckled, and their energy minima were found to occur at approximately $7.2 \text{ \AA}$, a value that which lies curiously close to experiment, and, likewise, the RA networks buckle to form pleated sheets as their energies continue to decrease below $6.9 \text{ \AA}$ intermolecular spacings. The formation of a MOCN under these conditions is not surprising, since Cu atoms are readily available on the surface at sufficiently high temperature, due to continuous evaporation from atomic step edges.¹³ While atomic resolution was

Figure 3. (a) Representations of two coordination environments a dehydrogenated RA molecule may take on in a metal–organic framework of Cu and RA (RA_6 = six-coordinate, RA_3 = three-coordinate). (b) Optimized structure of the model, periodic, dehydrogenated RA network on a fixed-atom two-layer Cu(111) slab. The Cu atoms that are part of the metal–organic framework (purple) are added explicitly to the simulation cell and not extracted from the surface. The C, O, and Cu atoms are colored in black, red, and brown, respectively. The total electronic density of states and the molecule-projected DOS are shown to the right. The Fermi energy is set to 0 eV. (c) A contour plot of a plane of the partial charge density derived from the energy range highlighted in blue in the molecule-projected DOS plot from (b). The plane cuts through the Cu adatoms embedded in the MOCN. The legend shows the charge density in $e/\text{\AA}^3$.

not achieved for the (111) surface of Cu, the $\langle 1\bar{1}0 \rangle$ orientations within the surface plane can be inferred from the orientation of the boundaries of the holes in the substrate. Using this as a guideline, it is noted that the three symmetry directions of the networks are aligned approximately 15° offset to the $\langle 1\bar{1}0 \rangle$ crystallographic directions of the surface, as illustrated in Figure 2c. Thus, two different orientations of molecular islands $\pm 15^\circ$ to the Cu substrate lattice are expected, and both are observed experimentally.

As a starting point for the detailed structural analysis of the MOCN of RA with Cu, we used a molecular first-principles program to calculate the energy of substituting hydrogen atoms in a RA dimer with Cu or Au atoms, $(H_2C_6O_6)_2 + 2M \rightarrow (HC_6O_6)_2M_2 + H_2$, where the metal, M , is either Cu or Au. The right-hand side of the reaction is favored by an additional 1.22 eV when Cu is introduced versus Au, suggesting that the coordination bond of RA with Cu is substantially stronger than with Au. Similar energies were obtained for substituted trimers (the Supporting Information includes a more in-depth discussion of how the reaction energies were computed).

Next, a structural periodic model of the metal–organic frameworks shown in Figure 2 was determined through periodic first-principles calculations of Cu/RA networks on a two-layer Cu(111) slab. This model was then analyzed to determine whether it was consistent with the STM images. In Figure 3a, the coordination environments of the $C_6O_6^{2-}$ (rhodizonate) molecules in the model pictured in Figure 3b are shown, wherein it should be emphasized that if each Cu is assumed to bridge two oxygen atoms, then it is impossible to create a structure in which each $C_6O_6^{2-}$ molecule in the cell has the same coordination environment with respect to the Cu atoms. The formation of this MOCN requires deprotonation of the RA on the surface during annealing. The hexagonal network of $C_6O_6^{2-}$ molecules with Cu atoms interspersed between them is similar to a previously observed bulk crystal structure for $C_6O_6^{2-}$ with Rb counterions.¹⁰ That structure consisted of stacked hexagonal $C_6O_6^{2-}$ sheets wherein each

sheet was offset laterally from the ones above and below. The key difference is that the Rb atoms are coordinated to six nearby oxygen atoms within each sheet instead of two or three, like in the Cu network model considered here. The energy of the analogous 6-fold coordination of the Cu network was found to be higher than the low coordination model.

When the metal–organic framework shown in Figure 3b was optimized in the gas-phase (without the Cu slab), it was found to remain intact in the sense that each Cu atom effectively bridged two nearby carbonyl groups belonging to neighboring molecules, although a third carbonyl group lies at slightly longer distances (~ 0.15 – 0.30 Å longer) to form a three-coordinate Cu environment in the shape shown in Figure 3a; the molecules are labeled either RA_3 or RA_6 to show their symmetries with respect to these “ CuO_3 ” shapes, as depicted in the figure. An alternative arrangement was considered wherein the molecules were rotated slightly to alter the manner in which they coordinated to the neighboring Cu atoms, and although the relative energy of the optimized lattice (see the Supporting Information for details) was found to be ~ 0.2 eV/molecule higher in energy, the networks’ electronic signatures were changed little (as will be discussed below).

The simulation cell of the model structure shown in Figure 3b (outlined by the solid black lines) contains three organic molecules: one sits at the vertex of the surface plane, the cell origin, and the other two take up positions along the long diagonal. The center of the molecule at the origin is situated directly over a surface Cu atom, a top “T” site, and the other two lie over the interstitial region between three neighboring Cu atoms, a hollow “H” site. A lattice constant of 12.78 Å was used to accommodate the lowest energy network in the gas-phase and represent a model with intermolecular spacing of approximately 7.4 Å, close to that determined from the experiments. The RA_6 molecules were favored at the T site by only approximately 0.03 eV/molecule over the H site for this model.

The RA_6 molecules remain almost planar in the relaxed structure, whereas the RA_3 molecules are noticeably either

tilted or buckled, depending upon the manner in which the molecules are oriented with respect to the nearest Cu adatoms and to the surface. Figure 3b suggest the coordination/interaction of the RA₆ molecule with the surrounding Cu adatoms lowers the energy of its LUMO such that, on the surface, there is more charge donated into RA₆ than RA₃. In other words, the highlighted peak just above the Fermi energy in Figure 3b has mostly RA₆ character, corresponding to the RA₆ LUMO, whereas the RA₃ LUMO is found at a slightly higher energy. Note that the lowering in energy of the RA₆ LUMO versus the RA₃ LUMO is also seen in the gas-phase. On the surface, there is more charge transfer into the RA₆ LUMO than that of RA₃; the calculated Bader charges on the molecules are 0.57 *e* higher for RA₆ compared to RA₃. The difference in charge is only 0.08 *e* for the same Cu/RA network when optimized in the gas phase and the charges in both systems (the surface-adsorbed and gas-phase networks) are generally consistent with Cu¹⁺ and C₆O₆²⁻ oxidation states. The computed charges for the surface-adsorbed networks deviate by up to 0.30 *e* from the gas-phase networks, reducing the computed charges on the Cu atoms and RA₃ molecules slightly. Furthermore, the qualitative makeup of the highlighted peak just above the Fermi energy in Figure 3b changes little when the RA₆ is placed over an "H" site. The RA LUMO character also changes little when the network is constrained to be planar and modeled in a cell with 13.525 Å surface vectors to accommodate the lowest energy planar network (see the Supporting Information). In the latter case, the system with RA₆ placed at a hollow site becomes 0.07 eV/molecule lower in energy, but the network itself in this case is stretched out. We note that although our calculations showed only minimal energetic differences of less than 0.05 eV/molecule between both adsorption sites in the closer-packed network, the linker Cu atoms, by contrast, always reside in the hollow sites on the surface, and this has been identified to be energetically favorable in earlier publications.^{14, 15, 33-35} When Cu atoms were manually lifted off the surface above the organic layer, they were always found to migrate back upon geometry optimization.

A contour plot of a plane of the partial charge density for the planar network, derived from the energy window from +0.08 eV to the Fermi energy, is shown in Figure 3c and is qualitatively comparable to the experimentally observed STM images. It can be seen that key features of the STM images, such as those in Figure 2c,d, are reproduced using this proposed structural model, specifically the variation in intensities at the molecular sites and the three- versus six-fold symmetries. This suggests that the intensity variation between the molecules can thus be attributed to the different coordination environments of dehydrogenated RA molecules, where RA₆ appears visibly brighter than RA₃. If the bright spots between molecules in the STM images are assumed to represent the locations of the Cu atoms, then the computational model shown in Figure 3 does not agree in this particular detail with the STM images in the sense that the Cu atoms do not lie directly between the molecular centers as they appear to do in the STM image. This is likely related to the fact that the surface models were built first in the gas phase and then optimized on the surface. Network configurations that are not stable in the gas phase (like molecular rotations which place the Cu in the symmetrical positions) may be stabilized on the surface. There may be other Cu(111) hexagonal simulation cells that give rise to the symmetrical structure, or the Cu atoms that form the MOCN may be extracted from the surface itself and change the RA-Cu-RA geometries accordingly. We reiterate that, in spite of

this discrepancy, the energy of the RA₆ LUMO versus the RA₃ LUMO in both the gas-phase and surface-adsorbed models is consistently lowered. Support of our proposed MOCN structure model comes from its ability to reproduce other key features observed in the STM images: the measured intermolecular distances require that the molecules bind alternately to "T" and "H" sites of the Cu surfaces, thus establishing an epitaxial relationship between the organic adlayer and the substrate. Considering this, the structure model automatically reproduces the observed 15° angle between the rhodizonic acid rows and the principal (11 0) directions of the substrate.

The deprotonation of the RA molecules on the Cu surface upon annealing is analogous to findings for several other classes of molecules on Cu.¹⁵⁻¹⁸ Notably, a wide variety of different molecules, including 1,3,5-tris(4-mercaptophenyl)benzene (TMB), 1,3,8,10-tetrazaperopyrene (TAPP), oxalic acid, among many others deprotonate upon adsorption to crystalline Cu, which for carboxyl groups is known to be catalyzed by the lattice gas of Cu adatoms.¹⁹⁻²¹ Once deprotonated, molecules often form metal coordination bonds with the present Cu adatoms, which was demonstrated conclusively for trimesic acid (TMA).¹⁵ Some of these molecules require thermal activation in order to deprotonate. The temperature at which deprotonation occurs depends not only on the type of molecule used, but also on which crystal face of Cu is exposed, since the density of adatoms evaporating from Cu is higher for the (110) facet than the (111) facet.²² What is of practical importance is that the properties of surface-supported metal coordination networks are often different than their traditional solution or crystalline counterparts. Two-dimensional metal-coordination networks can exhibit nontraditional electronic properties, such as charge-donating metal linkers that are directly attributable to the influence of the surface.²³ This surface hybridization makes determining unambiguously the oxidation state of the metal coordinating atoms impossible.

In conclusion, the self-assembled structures formed by rhodizonic acid are strongly dependent on the chemical nature of the surface. The hydrogen-bonded networks of RA on Au described herein represent the first reported example of a crystalline phase of RA. Our ability to crystallize molecular RA on surfaces, considering that RA is unstable in the bulk, demonstrates the potential of surface-assisted molecular self-assembly. Because RA retains its hydrogen, molecular self-assemblies maintain the possibility for proton transfer ferroelectricity as seen in the related compound croconic acid.³ Deprotonation on Cu(111), upon annealing and reaction with Cu atoms provided by the surface, yielded a complex MOCN with stoichiometric arrangement of 3-fold and 6-fold copper-coordinated rhodizonates. Those networks could be the starting point for future studies of useful properties of MOCN, such as nanocatalytic properties and magnetism of organics-coordinated metal centers.

Experimental Methods

An Omicron low-temperature STM with an electrochemically etched W tip was used for all images. The microscope was run in the ultrahigh vacuum regime with a base pressure of <3 × 10⁻¹⁰ Torr. Cu(111) and Au(111) single crystals were purchased from Princeton Scientific and cleaned through repeated cycles of Ar⁺ sputtering and annealing. Cleanliness of crystals was checked by STM imaging. Rhodizonic acid was synthesized from glyoxal in two steps according to the method of Fatiadi.²⁴ RA was thermally evaporated

onto the surfaces held at room temperature in a home-built Knudsen cell evaporator.

The density functional theory (DFT) calculations (geometry optimizations and electronic densities of states) were performed using the Vienna Ab-initio Simulation Package (VASP) version 5.2.11.²⁵ The projector augmented wave (PAW) method²⁶ was used to treat the core states along with a plane-wave energy cutoff of 500 eV, and the C/O 2s/2p, H 1s Cu 4s/3d, and Au 6s/5d electrons were treated explicitly. The non-local correlation functional of Langreth and Lundqvist (vdW-DF2)²⁷ was employed to account for the dispersion interactions of the Au-containing slab models, while DFT-D2²⁸ was used for the Cu-containing systems. Further information concerning *k*-point meshes, structure comparisons, and gas-phase model calculations can be found in the Supporting Information.

Supporting Information regarding experimental dehydration, further details on the computational settings and the structural models, structural coordinates of Figure 1 and Figure 3 models, binding energies of various RA monomers to Cu(111) and Au(111) surfaces, canonical molecular orbitals of various RA monomers and $\text{C}_6\text{O}_6^{2-}$, the Cartesian coordinates of the gas-phase clusters models for substituted RA clusters, and the summed site-projected densities of states of the various RA-based networks described in the text. This material is presented following the References.

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Supplemental Information follows.

Supplemental Information for:

Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry

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Vacuum Dehydration Procedure

Figure S1. (a) Dihydrate rhodizonic acid, image taken before vacuum dehydration procedure. (b) Rhodizonic acid after heating the molecules shown to approximately 140°C for six hours in ultra high vacuum. (c) 90 minutes after being removed from vacuum the rhodizonic acid is transforming back into dihydrate rhodizonic acid, with concomitant color change.

We monitored the color of the rhodizonic acid powder carefully, to compare with colors reported in the literature (Figure S1). The color of the dihydrate RA, which is typically present under ambient conditions, has been described in the literature as colorless [s1]. De-hydration of the dihydrate rhodizonic acid has been reported to occur upon heating the molecules to approximately 140°C for six hours in vacuum. Characteristic for the dehydrated form of RA is a deep orange hue, as reported in [s2]. The image in figure S1b was taken promptly after being removed from the vacuum chamber. After being removed from vacuum the rhodizonic acid is transforming back into dihydrate rhodizonic acid by adsorbing water vapor from the atmosphere. Concomittantly, the orange tone fades slowly back to colorless. The picture in figure S1c has been taken 90 minutes after removal from vacuum. The rhodizonate ion, discussed in the main article, has a reported deep yellow color [s3].

[s1] Patton, E.; West, R. New Aromatic Anions. VIII. Acidity Constants of Rhodizonic Acid. *J. Phys. Chem.* **1970**, 74 (12), 2512-2518.

[s2] Braga, D.; Cojazzi, G.; Maini, L.; Greponi, F. Reversible Solid-State Interconversion of Rhodizonic Acid $\text{H}_2\text{C}_6\text{O}_6$ into $\text{H}_6\text{C}_6\text{O}_8$ and the Solid-State Structure of the Rhodizonate Dianion $\text{C}_6\text{O}_6^{2-}$ (Aromatic or Non-aromatic?), *New J. Chem.* **2001**, 25, 1221-1223.

[s3] Preisler, P. W.; Berger, L.; Hill, E. S. Oxidation-Reduction Potentials of Thiol-Dithio Systems: Thiourea-Formamidine Disulfide, *J. Am. Chem. Soc.* **1947**, 69 (2), 326-329.

Computational Details

All of the results reported in the main text were obtained from surface models which used two-layer 2D Cu(111) or Au(111) slab models with the organic network adsorbed onto only one face, the other face is left exposed to a vacuum measuring at least 20 Å. All of the cells were hexagonal and a dipole correction was applied along the direction perpendicular to the metal surface (using the IDIPOL tag in VASP). Preliminary calculations using four-layer slabs were performed with RA monomers and are reported in this SI. All of the Cu slabs on which the MOCN networks were adsorbed were built from a bulk fcc lattice with the experimental 3.61 Å lattice constant. For the Au slabs, both the experimental lattice constant (4.08 Å) and the optimal vdW-DF2 lattice constant (4.35 Å) were used with the RA networks and their corresponding hydrated networks. Although the changes in binding energies and slight shifts in some peaks of their site-projected densities of state are to be expected, the asymmetric profile of the PDOS peaks as discussed in the main text and the computed hydration reaction energies were unaffected.

From the main text:

(Periodic) “Density Functional Theory (DFT) calculations (geometry optimizations, electronic densities of states, charge densities) were performed using the Vienna Ab-initio Simulation Package (VASP) version 5.2.11. The projector augmented wave (PAW) method was used to treat the core states along with a plane-wave energy cutoff of 500 eV, and the C/N/O 2s/2p, H 1s and Au 6s/5d electrons were treated explicitly. The non-local correlation functional of Langreth and Lundqvist (vdW-DF2) was employed to account for the dispersion interactions.”

The G-centered Monkhorst-Pack scheme was used to generate k-point grids for various RA networks. A 3x3x1 grid was used for the gas-phase optimizations/scans (reported in this SI and referenced in the main text) and 7x7x1 grids were used to produce all of the DOS/PDOS plots and charge densities. The PDOS curves were smoothed slightly by applying running averages over 0.003 eV energy windows to improve visibility. In cases where relative energies were reported, they were compared with the results from 5x5x1 grids and found to vary by less than 2 meV/atom. The surface-adsorbed RA network geometries were initially converged using a 3x3x1 k-point grid and then raised to 5x5x1 and 7x7x1 grids. In the optimized structures, the magnitude of the largest force acting on the optimized atoms was less than 0.05 eV/Å.

The molecular calculations performed on the Cu-/Au- substituted molecular fragments (RA dimers and trimers) were performed using the ADF molecular program [s4]. The revPBE functional with the Grimme DFT-D3 dispersion correction were used with the TZP basis set from the ADF basis set library; the frozen core approximation was used for the Cu and Au atoms with the Cu.3p and Au.4f entries in the library. Scalar relativistic effects (using ZORA) [s5] were included.

[s4] ADF2012, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>

[s5] van Lenthe, E.; Baerends, E. J.; Snijders, J. G. Relativistic Regular Two-component Hamiltonians. *J. Chem. Phys.* **1993**, 99, 4597.

RA monomers

Rhodizonic acid (RA) has three possible conformers when considering the rotation of the hydroxyl groups (Figure S2). Using DFT-D3, it was determined that the relative energy of the monomers, in the gas phase, was 0, 5.5, and 20.4 kcal/mol for monomer i, monomer ii, and monomer iii.

Figure S2: Conformers of rhodizonic acid.

Frontier Orbitals of Various RA Species

The calculated spatial distribution of the frontier orbitals of the RA molecules in three different conformations (Monomers i-iii) and a deprotonated RA molecule (Monomer iv). The MOs of monomer iv no longer has a “crescent shaped” topology, like that of monomers i and ii.

Figure S3: The frontier orbitals of the difference RA monomers and the dehydrogenated RA molecule (Monomer iv in the figure). Isovalue = ± 0.03 au.

Alternative RA network on Au (111)

An alternative RA network to that shown in figure 1 of the main text is shown in Figure S4(a). The network is constructed from a different monomer, monomer i from Figure S2 instead of monomer ii, and the dipole moments of each molecule are aligned. This network is 0.030 eV/molecule higher in energy than the figure 1 model when placed on the two layer Au(111) slab built with 13.40 Å lattice vectors (4.35 Å bulk lattice constant).

Figure S4: (a) An alternative RA network to the one shown in figure 1 of the main text. In addition, the top layer of Au is shown as well. (b) The summed site-projected densities are similar to what is shown in figure 1 of the main text. All three molecules in the simulation cell are shown. Unlike the model from the main text, all three molecules are symmetrically equivalent with respect to the organic network and this symmetry is broken slightly by the Au surface (eg. “T” site or “H” site).

Gas Phase Reactions : Hydrates

Bulk rhodizonic acid is hydroscopic. The dihydrated form of RA has been crystallized in bulk, as cited in the main text. In this section we investigate the relative stabilities of the dihydrate RA (1) with respect to the mono-hydrate RA (2) and unadulterated RA (3) via various density functionals (Figure S5).

Figure S5: A partial sketch of the potential energy landscape of the dehydration of the dihydrated RA (1) to mono-hydrate RA (2) to RA (3).

Functional	ΔE_1	ΔE_2	ΔE_{total}
DFT-D3	0.49	1.40	1.90
revPBE	0.24	0.60	0.84
PBE	0.52	1.14	1.67
B3LYP	0.46	1.05	1.51

Table S1: The change in energy to go from the dihydrate RA to the mono-hydrate RA (ΔE_1) and the energy to go from the mono-hydrate RA to RA (ΔE_2), along with the energy to go from the dihydrate RA to RA (ΔE_{total}), as calculated by revPBE-D3, revPBE, PBE and B3LYP functionals (in ADF). The reaction energies are given in eV.

For the hydration of the network shown in figure 1 of the main text (the hydrated networks are shown further down in Figures S7 and S9 of this SI) the $\Delta E_1 / \Delta E_2$ reaction energies were calculated (with VASP) as 0.67/0.75 eV/molecule and 0.26/0.43 eV/molecule using the DFT-D2 and vdW-DF2 functionals, respectively. When optimized over the Au(111) surface and the vdW-DF2 functional, the ratio becomes 0.07/0.44. The reduction of ΔE_1 is the result of the “RA sheets” lying further from the surface in the dihydrated species, due to the presence of the extra hydroxyl group between them.

Figure S6 : A partial sketch of the potential energy landscape of the dehydration of the dihydrated RA-2Cu (1) to mono-hydrate RA-2Cu (2) to RA-2Cu (3).

Functional	ΔE_1	ΔE_2	ΔE_{total}
DFT-D3	0.16	0.27	0.43
PBE	0.18	0.55	0.73
B3LYP	0.15	0.46	0.60

Table S2: The change in energy to go from the dihydrate RA-2Cu to the mono-hydrate RA-2Cu (ΔE_1) and the energy to go from the mono-hydrate RA-2Cu to RA-2Cu (ΔE_2), along with the energy to go from the di-hydrate RA to RA (ΔE_{total}), as calculated by revPBE-D3, revPBE, PBE and B3LYP functionals (in ADF). The reaction energies are given eV.

Hydrated RA Sheet - Structure Model

Figure S7: The mono-hydrated RA molecule and the extended structure of a sheet of hydrated RA molecules.

Figure S7 shows a planar hydrated network of RA constructed from the RA network in figure 1a of the main text; the hydration of a carbonyl yields two hydroxyl groups, one participates in a hydrogen bond within a layer and the other would connect molecules between layers in the 3D solid. In the gas-phase, periodic computations suggest that this network is energetically favored by 0.400, 0.630, and 0.750 eV/molecule with respect to decomposition into the RA network illustrated in figure 1a and molecular H₂O using the vdW-DF2, PBE, and DFT-D2 functionals, respectively. The vdW-DF2 value is only slightly larger than the 0.360 eV/molecule reaction energy computed for the hydration of a single RA molecule. When modeled over a two-layer Au(111) slab with 13.4 Å lattice vectors (4.35 Å bulk lattice constant), the hydrated network is favored by 0.440 eV/molecule.

Frontier Orbitals of Hydrate RA

Figure S8: Frontier Orbitals of mono-hydrated RA.

The frontier orbitals of the hydrated RA molecule were calculated using ADF, the revPBE functional, and the Grimme3 empirical dispersion correction.

Hydrated RA networks on a Au(111) surface

Figure S9 : (a) The overhead view of the hydrated RA network (one H₂O added per molecule) shown in figure S7. The summed site-projected densities are shown to the right, wherein the assymetric profiles of the peaks can still be seen and, in addition, there are considerable differences between molecules due to the presence of different configurational isomers. Note that only two of the three molecules are shown, the third indeed represents a different isomer but behaves similarly to the right plot. (b) The overhead view of a further hydrated RA network (two H₂O's per molecule). The top layer of Au atoms are also shown. The summed site-projected densities are shown to the right, Note that the underlying “RA sheet” is further off the surface because there is now a second set of hydroxyl groups attached to the molecules which lie between them and the surface.

Gas Phase Substitution Reactions

RA dimer and trimer models were used to preliminarily assess trends in substituting hydrogen bonding bridges with Cu bridges. This was done to help explore why MOCN's are thought to form on the Cu (111) surface but not the Au(111) surface. A number of Cu-containing monomer and dimer geometries were initially considered, encompassing different interactions between the Cu atom and the RA monomers/dimers, and it was found that it was preferable for the Cu atom to bridge a pair of nearby carbonyl groups.

Figure S10(a) shows the reaction discussed in the main text, wherein the condition for the reaction being exothermic (where E is the internal electronic energy) or spontaneous (where E is the Gibbs Free energy) is outlined in part (b). The values of the right hand side (R.H.S.) of the inequality for both the electronic energy and the computed Gibbs Free energy at zero pressure are also given in part (b). The trend shows that the reaction is stable for a wider range of values for the Cu reference state than Ag or Au, suggesting the reaction itself is more likely.

Figure S10. (a) Schematic illustration of a simple substitution reaction of hydrogen with Cu within an RA dimer. For the purposes of this study, the reference state of the Cu is treated as arbitrary, but the picture shows one model of removing the Cu atoms from the surface. (b) The condition for spontaneity of the reaction shown in part (a). The table shows the computed values for the right hand side (R.H.S.) of the inequality.

The metal atom is in an unspecified reference state, M_{ref} (specifically, the default reference state which the ADF program uses). It would be reasonable to define a reference state which could, for example, be related to the atom's binding energy to the surface or to the surface's vacancy formation energy, but here we only comment on the trend in going from Cu to Au. In order for the right hand side of the above reaction to be favored, M_{ref} must be $> -2.10/-0.86/-0.88$ eV for Cu/Ag/Au. The trend suggests that Cu favors the substituted dimer in contrast to what is found for Ag and Au. Similar energies were seen for substituted trimers (see Figure S11).

Figure S11 (a) shows a related reaction with an RA trimer. The trends agree with those shown in Figure S10, again suggesting the reaction is more likely with Cu than with Ag or Au.

Figure S11. (a) Schematic illustration of a simple substitution reaction of hydrogen with Cu within an RA trimer. For the purposes of this study, the reference state of the Cu (Cu_{ref}) is treated as arbitrary. (b) The condition for spontaneity of the reaction shown in part (a). The table shows the values of the right hand side (R.H.S.) of the inequality.

Molecular Orbital Level Diagram of $\text{C}_6\text{O}_6^{2-}$

The frontier molecular orbitals of rhodizonate were calculated using revPBE+D3. It is noted that the molecule retains D_{6h} symmetry, similar to benzene. The LUMO and LUMO+1 are degenerate in energy.

Figure S12: Schematic level diagram of the rhodizonate anion. An isovalue of ± 0.03 au was used to generate the isosurfaces.

Gas Phase MOCN Networks

A number of plausible MOCN structures were modeled in the gas phase, constructed by effectively substituting each H atom for a Cu atom. The specifics of all these structures is outside the scope of this study, but the two structures shown in figure S13 (a) were the focus.

Figure S13: (a) Two model gas-phase MOCN networks; network I is what was initially placed on the model Cu (111) slab and optimized to what is shown in Figure 3 of the main text. The relative energies of the two are shown in (b), where zero is referenced to the absolute electronic energy of I when it crosses the dashed line in the plot. (c) The same as (b) except the energies of network I when constrained to be planar are added as well.

Note that these energies are taken from a rough scan of the cells' lattice constant as it is incrementally decreased. When intermolecular RA-RA spacings of ~ 7 Å or less are reached, the sheets can buckle somewhat to lower the energy further and create a myriad of structures which are subtly different but comparable in energy. However, our focus here was not on the precise atomic structure but more on the influence the surrounding Cu atoms can have on the molecules' electronic structure.

Figure S14 shows the summed site-projected densities of states over each molecule in structures I and II from figure S13. The qualitative behavior of the peak near the Fermi energy (outlined by a thick yellow line) is similar to what is discussed in the main text concerning the surface-adsorbed networks.

Figure S14: (top) Extended representations of structures I and II from Figure S13; the molecules are labeled according to how they are coordinated to the Cu motifs around them, similar to what is described for figure 3 of the main text. (bottom) The summed site-projected densities of states over molecules in the two structures; the enhanced RA₆ character near the Fermi energy is highlighted.

MOCN adsorbed on Cu(111): “T” vs. “H” site

Figure S15 expands upon figure 3 from the main text. In addition to figure 3, it shows the summed site-projected densities of states over all three molecules in the simulation cell when the RA₆ molecule is placed over an “H” site instead of a “T” site.

Figure S15: The total and summed site-projected densities of states over RA molecules in an MOCN network adsorbed on a two-layer Cu(111) slab (12.77 Å lattice vectors). The top and bottom plots represent model where the RA₆ molecule is placed over (top) the “T” site or (bottom) the “H” site.

The similarities between the two sites reflects how the organic layer itself in these models is lifted slightly off the surface compared to how it would sit in the absence of Cu adatoms; the Cu adatoms lie mostly underneath them. The top plot was also computed using the vdW-DF2 functional and found to behave quite similarly.

Simulated STM image of Benzene on Pd(111)

To complement the MOCN image in Figure 3c of the main text, we computed a similar image of benzene on a Pd(111) surface to compare with the previous literature.

Figure S16: Simulated STM image of Benzene adsorbed on the Pd(111) surface in the B30 binding configuration. The legend shows the density in $\text{e}/\text{\AA}^3$.

Using VASP, the adsorption of benzene was simulated on a four layer Pd(111) slab comprised of 100 atoms. The Grimme2 semi-empirical dispersion correction was used to account for van der Waals forces. The bottom two layers of the slab were fixed at the experimental lattice constant, while the top two layers were permitted to relax.

The STM image was simulated using the Tersoff-Hamann approximation, representing a plane of the charge density generated from bands within 0.08 eV of the Fermi energy. The plane is approximately 4 $\text{\AA}$ from the metal surface. This is in good agreement with previously observed/calculated STM images.[s6,s7,s8]

[s6] Futaba, D. N.; Chiang, S. Calculations of Scanning Tunneling Microscopic Images of Benzene on Pt(111) and Pd(111), and Thophene on Pd(111). *Jpn. J. Appl. Phys.* **1999**, *38*, 3809-3812.

[s7] Weiss, P. S.; Eigler, D. M. Site dependence of the apparent shape of a molecule in scanning tunneling microscope images: Benzene on Pt(111). *Phys. Rev. Lett.*, **1993**, *71*, 3139-3142.

[s8] Javier, A.; Li, D.; Balbuena, P. B.; Soriaga, M. P. Simulation of scanning tunneling microscope image of benzene chemisorbed on Pd(111) electrode surface by density functional theory. *Reports in Electrochemistry*, **2013**, *3*, 1-5.

Monomers on Cu(111) and Au(111)

The adsorption of four different monomers on Cu(111) and Au(111) was modelled using VASP. The DFT-D2 dispersion correction parameter set does not include the required parameters for Au, so vdW-DF2 was used to account for dispersion in Au-containing systems. The relative energies of the adsorbed monomers i and ii, as computed by DFT-D2, are reversed from what they are the gas phase and monomer iii was unstable upon geometry optimization. In contrast, the vdW-DF2 numbers retain the same approximate energy ranking as the gas phase calculations. This is similar to what we found for CA monomers [*Phys. Rev. B*, 87 (2013) 041402] and is likely related to how DFT-D2 is known to overbind adsorbates at the surface-adsorbate interface and vdW-DF2 tends to underbind.

Figure S17: Structures of monomers on Cu(111) as obtained using first-principles calculations. Note that in monomer iv the H atoms are removed from RA to form an H₂ molecule in the simulation cell; its energy was always found to be higher than the other monomers.

Monomer	E_{rel} Gas (revPBE)	E_{rel} Gas (DFT-D3)	E_{rel} Cu (vdW-DF2)	E_{rel} Cu (DFT-D2)	E_{rel} Au (vdW-DF2)
i	0.0	0.0	0.0	3.9	0.0
ii	5.5	5.2	3.8	0.0	3.9
iii	20.4	19.9	16.5	- ^A	26.0

Table S3: Relative energies (E_{rel}) of RA monomers in the gas phase, on Cu(111), and on Au(111). The values are reported in kcal/mol.

^A Monomer iii optimized to monomer ii on the Cu(111) and Au(111) surface

Coordinates

Slab model from Figure 1b of the main text – RA on Au(111)

POSCAR format

C O H Au
1.0000000000000000
13.407600000000000 0.000000000000000 0.000000000000000
-6.703800000000000 11.611321999999999 0.000000000000000
0.000000000000000 0.000000000000000 25.000000000000000
18 18 6 38
Direct
0.4443763214459153 0.8151543373968977 0.2443112775694729
0.2611993402582087 0.5717530070612113 0.2421226806891497
0.3890850511122679 0.6063565672682145 0.2443241014072370
0.4757034387567742 0.7298158230403189 0.2449780128864703
0.3240376808561223 0.7910289976966070 0.2415416797007808
0.2284951124136683 0.6657696237770594 0.2339176633861442
0.0946939451236517 0.1529771550734225 0.2446242650243846
0.9786706256081743 0.1237235846349520 0.2458675977598190
0.8834447408731663 0.0043600811316438 0.2435074799398151
0.9107812114449416 0.9088493871893775 0.2314282395656733
0.0378052838838272 0.9397067361345179 0.2298534285159590
0.1312025009940001 0.0662785505771026 0.2382645641065935
0.5531852570261222 0.3214688937928045 0.2435496169858524
0.5764899002144617 0.2259427047885154 0.2424408833076086
0.7014498867658929 0.2540832020261163 0.2450527317638347
0.7969181280051316 0.3796285161832316 0.2544595769859583
0.7649373648587598 0.4748485570445169 0.2516834484304340
0.6402760293527052 0.4376820339928926 0.2466427648457312
0.1851153262388863 0.4704808069358535 0.2463715374608100
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0.1308188110855895 0.6408781708062534 0.2210353325928409
0.1822165339071873 0.2612333712658241 0.2471300739953222
0.9566699520955382 0.2107892683274031 0.2488567905643961
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0.2340945947300526 0.0936489728678609 0.2364807528720050
0.5291435830271425 0.9250080777520751 0.2447743450565270
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0.8946896417475401 0.4011325668795394 0.2648792898155605
0.8392987652479249 0.5766804894276376 0.2547857754109515
0.6191519918121671 0.5244581509364110 0.2461324671699217
0.1612567509558644 0.3226187993907104 0.2489203108729328
0.6446486426365681 0.8368494368022183 0.2459625966658336
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0.5367328467313328 0.5039500173549669 0.2442836084423803
0.5005901188789892 0.9812135938343545 0.2430360937765101
0.8728941707007962 0.1855492166632402 0.2480247335447601
0.0000000000000000 0.0000000000000000 0.1004590000000007
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0.5263160000000013 0.3157890000000023 0.1004590000000007

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0.5614040000000031 0.0701749999999990 0.0000000000000000
0.7368420000000029 0.8421049999999966 0.1004590000000007
0.4561399999999978 0.8070179999999993 0.0000000000000000
0.7719299999999976 0.5964910000000003 0.0000000000000000
0.0526320000000027 0.6315790000000021 0.1004590000000007
0.3684209999999979 0.4210530000000006 0.1004590000000007
0.0877189999999999 0.3859649999999988 0.0000000000000000
0.6842109999999977 0.2105260000000015 0.1004590000000007
0.4035089999999997 0.1754389999999972 0.0000000000000000
0.5789469999999994 0.9473679999999973 0.1004590000000007
0.2982459999999989 0.9122810000000001 0.0000000000000000
0.8947369999999992 0.7368420000000029 0.1004590000000007
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0.9298250000000010 0.4912279999999996 0.0000000000000000
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0.1578950000000034 0.8947369999999992 0.1004590000000007
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0.1403510000000026 0.0175440000000009 0.0000000000000000
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0.6315790000000021 0.5789469999999994 0.1004590000000007
0.3508769999999970 0.5438600000000022 0.0000000000000000
0.9473679999999973 0.3684209999999979 0.1004590000000007
0.6666669999999968 0.3333330000000032 0.0000000000000000
0.9824559999999991 0.1228070000000017 0.0000000000000000
0.8771929999999983 0.8596489999999974 0.0000000000000000

Slab model from Figure 1c of the main text – hydrated RA on Au(111)

POSCAR format

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1.0000000000000000
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-6.7038000000000002 11.6113219999999995 0.0000000000000000
0.0000000000000000 0.0000000000000000 25.0000000000000000
18 21 12 38
Direct
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0.2552554589487883 0.5680484340888299 0.2435932932921006
0.3828870883093032 0.6043077168689308 0.2430112044899815
0.4666227064016297 0.7273014887808955 0.2421989840111181
0.3133340186318634 0.7871728335994135 0.2536298975028402
0.2207952233623587 0.6617071165472836 0.2405593633242162
0.1024505115514529 0.1475323431627089 0.2421337002801422
0.9862662118702588 0.1153174105754502 0.2417304450143405
0.8917848951924370 0.9948828944049026 0.2431694857230227
0.9200554320172500 0.8983882533976342 0.2556341839296792
0.0472767063778505 0.9335941502541090 0.2434990253038265
0.1396859709007003 0.0616627934661906 0.2414804384730544
0.5571741994859707 0.3261399724346958 0.2426656540475207
0.5830849256217121 0.2322989198354719 0.2427875147815470
0.7096775243641318 0.2624679458109753 0.2433425655650936
0.8028048379369963 0.3880889804918368 0.2558728079212145
0.7662634979130942 0.4793019126701665 0.2444581979347831
0.6426060619121259 0.4422263143664225 0.2424803905263744
0.1790866229249701 0.4661591478244347 0.2458976992952486
0.4099076602392273 0.5278018462206546 0.2412141721955194
0.5778078743532120 0.7526405452103049 0.2381935366825161
0.2999545494111757 0.8694003069426870 0.2247070110538161
0.1211770250010673 0.6376181941104662 0.2314649119718197
0.1889772825487768 0.2571843733157095 0.2400108331462789
0.9605096396003958 0.2003613357933318 0.2388611462330914
0.7909062741216104 0.9740505974472597 0.2385126881503510
0.8401268931191836 0.7995117762612267 0.2285607081982022
0.0734964103793416 0.8589279442016959 0.2369856455483514
0.2424091629888565 0.0877163343830958 0.2383849939549734
0.5202579766842277 0.9213017494196905 0.2383434569185852
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0.5041840385344898 0.1297342221153457 0.2411959828161372
0.7336795657466055 0.1857450337165716 0.2380430245294320
0.9036517641946347 0.4109855597885783 0.2293284690796042
0.8424372441153096 0.5810376220450948 0.2389284042179156
0.6206493537538478 0.5291517432306136 0.2390084727843629
0.3046531373395069 0.7976088779016308 0.3117331316334102
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0.9136290951331674 0.8839314092388761 0.3136939881801766
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0.4958011682437800 0.9804444285956677 0.2390960369634243
0.8763865872096233 0.1713181471879537 0.2365050848737695

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0.4561399999999978 0.8070179999999993 0.0000000000000000
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0.0526320000000027 0.6315790000000021 0.1004590000000007
0.3684209999999979 0.4210530000000006 0.1004590000000007
0.0877189999999999 0.3859649999999988 0.0000000000000000
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0.5789469999999994 0.9473679999999973 0.1004590000000007
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0.1929820000000007 0.6491230000000030 0.0000000000000000
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0.5087720000000004 0.4385970000000015 0.0000000000000000
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0.6315790000000021 0.5789469999999994 0.1004590000000007
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0.9473679999999973 0.3684209999999979 0.1004590000000007
0.6666669999999968 0.3333330000000032 0.0000000000000000
0.9824559999999991 0.1228070000000017 0.0000000000000000
0.8771929999999983 0.8596489999999974 0.0000000000000000

Slab model from Figure 3b of the main text – MOCN on Cu(111)

POSCAR format

```
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1.000000000000000
12.779999999999994 0.000000000000000 0.000000000000000
6.389999999999997 11.067804999999999 0.000000000000000
0.000000000000000 0.000000000000000 30.000000000000000
18 18 56
Direct
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0.9517588444560587 0.1300266578172042 0.1705875400201009
0.0780488862107234 0.0426353631917706 0.1715610359236805
0.1161000345570571 0.9153028787280633 0.1705787651144064
0.0272158265438378 0.8772754866039136 0.1678305692592303
0.9015916325238038 0.9645488153041555 0.1669612043020834
0.2129600374809115 0.4687221730873077 0.1893558573079019
0.3377612772562344 0.4486719001937729 0.1816139401827499
0.4420725118167752 0.3232506687452386 0.1867983055042330
0.4181312985410344 0.2286415749257031 0.1693454584756680
0.2962831339659004 0.2590225475968779 0.1573677437418155
0.1925700297462498 0.3706675007807689 0.1724074105517275
0.5522621201321627 0.8063044177120844 0.1727338734616097
0.5360653829578368 0.7073181955404024 0.1575029525864480
0.6335309582532247 0.5821178538223748 0.1622874117657531
0.7544018517109521 0.5656674065893270 0.1590995817942584
0.7767692111781983 0.6600123812206817 0.1747790524299546
0.6733843261496233 0.7796639918873183 0.1897033012833873
0.3568750970532051 0.5334759375250542 0.1730116667517052
0.5418608111566030 0.3024806215256888 0.2001763417482181
0.5035200794550860 0.1238095199228511 0.1595048815054838
0.2805985430927151 0.1833798015693375 0.1337111909282882
0.0855899619685019 0.3910356471110248 0.1678232888596582
0.1338668450703224 0.5625356046351797 0.2064952047978110
0.4679370277660198 0.9148735118160829 0.1696236428463038
0.4408974705017030 0.7289538362732628 0.1361303642121356
0.6104157732083593 0.4971685951992555 0.1564968623609744
0.8340774285302146 0.4763452714721126 0.1360490696168952
0.8814178233061938 0.6457502712574126 0.1712895693873193
0.6894002822605714 0.8557306481457303 0.2086079186206149
0.9144339512608255 0.2438204793099956 0.1653301934614078
0.1551624795180686 0.0788986451520302 0.1672366731578094
0.2272993173560636 0.8370705736779982 0.1655798746619155
0.0643534108595674 0.7652234556051312 0.1588838274778297
0.8239220832652023 0.9305867355336872 0.1578291587498768
0.7528862416781408 0.1679998739824171 0.1592237983122473
0.0236293899062900 0.2951613509685060 0.1411320287433853
0.6634793979744416 0.0612886783244520 0.1376598628780812
0.2594508105929236 0.6769241241351907 0.1363713200774299
0.9376131054486407 0.7304878653432425 0.1353269393097492
0.7107463784879613 0.3306112213286525 0.1397250079823493
0.3131851111017241 0.9787625131373900 0.1405347260769574
0.000000000000000 0.000000000000000 0.0695649999999972
0.000000000000000 0.2000000000000028 0.0695649999999972
0.000000000000000 0.3999999999999986 0.0695649999999972
0.000000000000000 0.6000000000000014 0.0695649999999972
0.000000000000000 0.7999999999999972 0.0695649999999972
0.2000000000000028 0.000000000000000 0.0695649999999972
0.2000000000000028 0.2000000000000028 0.0695649999999972
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Slab model from Figure 3c of the main text – MOCN on Cu(111)

POSCAR format

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-6.762500000000000 11.712994000000000 0.000000000000000
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0.1055562527996443 0.0078089184614569 0.1947730459067429
0.0068132854591667 0.8944281261376688 0.1950458507251227
0.8934139141778203 0.8797178348071597 0.1952335673544923
0.8787465844194671 0.9784037065344506 0.1949595094247627
0.6875130053582978 0.4473780831915306 0.1959539035682383
0.7780344939696278 0.4171840654522683 0.1957448808374593
0.7506089962598850 0.2978825319954197 0.1957170280257614
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0.5380056436889404 0.2346758175164609 0.1953497938270203
0.5682558073932640 0.3554257824375071 0.1953283994647776
0.3539994440945122 0.7789334382884618 0.1960312399325801
0.2332972937481088 0.6883150885752158 0.1961419480369386
0.2061894250414937 0.5690720117737911 0.1956367359693090
0.2967925181556552 0.5390028408047414 0.1960122737223031
0.4160171258768628 0.6309826589953857 0.1960115527828705
0.4460022179237271 0.7516616250202404 0.1963447777801974
0.8825526006136215 0.4965927011386384 0.1922719197158500
0.8260882216444045 0.2694826728558155 0.1926373782911526
0.6051271754184455 0.1028572876100355 0.1914489965058337
0.4340787155891448 0.1592831453921804 0.1923222006860144
0.4888209706485398 0.3804982470980178 0.1914712427696230
0.7158907070046965 0.5512559580543410 0.1933471989755660
0.3791536538777933 0.8834372090075533 0.1921043396754456
0.1577022396284917 0.7164849290509068 0.1931357262615307
0.1018045190531254 0.4894537456581887 0.1914384258999604
0.2684404739346533 0.4351610860700532 0.1925788488260025
0.4955790498943742 0.6061309023409223 0.1922260609224367
0.5497824625639893 0.8272401540150227 0.1930524663241613
0.1759615815948052 0.2093574380257763 0.1920049486017774
0.2084295095779751 0.0255409590613240 0.1926014936925284
0.0244360746306000 0.8092407300354694 0.1931565421736323
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0.7759581325543365 0.9608881891034216 0.1928069979409130
0.9597267682531694 0.1768644840361802 0.1922425671091545
0.3328088481558638 0.2721571227168980 0.1696025236999787
0.7144050850534214 0.0561458316413308 0.1707658906222846
0.9301432142348389 0.6524836823661744 0.1725798499016662
0.6514783401220114 0.7145027389985188 0.1723817317294731
0.0545615206707595 0.3335270700084649 0.1697846864183319
0.2719750032806445 0.9322916431757662 0.1713517904762654
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0.000000000000000 0.500000000000000 0.0834779999999995
0.500000000000000 0.000000000000000 0.0834779999999995
0.500000000000000 0.500000000000000 0.0834779999999995
0.142856999999999 0.428570499999999 0.0834779999999995
0.142856999999999 0.928570499999999 0.0834779999999995
0.642856999999999 0.428570499999999 0.0834779999999995
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0.9285704999999993 0.2857135000000000 0.0834779999999995
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0.2857135000000000 0.8571420000000032 0.0834779999999995
0.7857135000000000 0.3571420000000032 0.0834779999999995
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0.2142849999999967 0.6428569999999993 0.0834779999999995
0.7142849999999967 0.1428569999999993 0.0834779999999995
0.7142849999999967 0.6428569999999993 0.0834779999999995
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0.0714285000000032 0.7142849999999967 0.0834779999999995
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0.5714285000000032 0.7142849999999967 0.0834779999999995
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0.3571420000000032 0.5714285000000032 0.0834779999999995
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0.8571420000000032 0.5714285000000032 0.0834779999999995
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0.1904759999999968 0.7380945000000025 0.0000000000000000
0.6904759999999968 0.2380945000000025 0.0000000000000000
0.6904759999999968 0.7380945000000025 0.0000000000000000
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0.0476189999999974 0.8095229999999987 0.0000000000000000
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0.3333324999999974 0.6666664999999981 0.0000000000000000
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0.1190475000000006 0.5238094999999987 0.0000000000000000
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0.7619040000000012 0.9523799999999980 0.0000000000000000

Gas-Phase Models for Substitution Reaction – RA dimer

XYZ format

28

C	14.296116	6.867626	5.902752
C	15.833100	6.786423	5.864487
C	16.496817	5.377459	5.858945
C	15.586892	4.125020	5.962393
C	14.122495	4.360131	6.001770
C	13.536176	5.624961	5.957698
O	16.504089	7.800272	5.843289
O	17.702460	5.261409	5.780055
O	16.060219	2.997761	6.004492
O	13.357969	3.261145	6.078547
O	12.193030	5.652163	5.990658
O	13.724963	7.969417	5.891568
O	10.525981	7.801408	5.855315
C	9.959958	8.905775	5.871275
C	8.427451	8.997551	5.756034
C	7.761982	10.401793	5.859046
C	8.674120	11.651597	5.954238
C	10.135687	11.409865	6.033952
C	10.719818	10.143938	5.992817
O	7.760201	7.995742	5.586274
O	6.553417	10.514997	5.864002
O	8.205477	12.781911	5.962576
O	10.900870	12.504348	6.150228
O	12.061314	10.114331	6.067802
H	12.418613	9.186477	6.000659
H	11.837787	12.209808	6.191019
H	11.836411	6.581788	5.945322
H	12.418997	3.551759	6.085630

XYZ format

28

C	14.819896885	6.640232308	5.970618933
C	16.336309472	6.439944304	5.979353104
C	16.911780448	5.023607792	5.729636460
C	15.939995369	3.835187679	5.792871063
C	14.503039021	4.178770873	5.848546276
C	13.938551849	5.485942244	5.895909859
O	17.078068496	7.389578522	6.168269804
O	18.096621755	4.866411126	5.505234797
O	16.331647405	2.672405577	5.784999259
O	13.650517291	3.156535997	5.819460878
O	12.627646405	5.509071259	5.905446171
O	14.441287433	7.847801080	6.036554054
O	9.753227414	7.881168273	6.005554313
C	9.382906247	9.093397801	5.976988058
C	7.868812788	9.305234585	5.963627212
C	7.315936271	10.717326508	5.647694309
C	8.280744257	11.905411366	5.782378426
C	9.710114434	11.557409176	5.919176670
C	10.268068987	10.247427115	5.968194533
O	7.112782439	8.372766087	6.180133849
O	6.154827775	10.870782834	5.320838985
O	7.889539139	13.068577926	5.766177191
O	10.567245014	12.576137548	5.946203163
O	11.576876733	10.222236997	6.044779911
Cu	12.879183392	8.873122542	6.030154117
H	11.459101685	12.144401075	6.002590761
Cu	11.318915134	6.856394466	5.953750284
H	12.754319868	3.582875477	5.839322463

Gas-Phase Models for Substitution Reaction – Au-substituted RA dimer

XYZ format

28

TIME: 1.02000

C	14.907415373	6.521717971	6.163186581
C	16.394607260	6.237028417	6.417769223
C	17.027233740	4.983435461	5.770198459
C	16.081574718	3.819055916	5.464788821
C	14.637537363	4.139717598	5.525433211
C	14.038372414	5.406584599	5.811153272
O	17.066508736	7.008539119	7.078213221
O	18.220285301	4.936684816	5.542568865
O	16.489524621	2.691346911	5.206170155
O	13.814148094	3.146567163	5.202142396
O	12.725221737	5.368057010	5.737039966
O	14.611268318	7.744659743	6.332156326
O	9.579105834	7.978396242	6.250098590
C	9.287793137	9.205174558	6.097633815
C	7.787977466	9.479811315	6.287945003
C	7.189770487	10.784108943	5.710859110
C	8.153470802	11.958742435	5.524417121
C	9.591472857	11.616525472	5.587277536
C	10.170473725	10.326960600	5.804378221
O	7.078595596	8.664435011	6.849301224
O	6.005426362	10.862613537	5.449493042
O	7.763028513	13.107802863	5.346433721
O	10.432497025	12.617918791	5.345402574
O	11.484233629	10.355487443	5.738425020
Au	12.961816076	8.948316955	6.035987698
H	11.333144009	12.200416885	5.388731110
Au	11.237508436	6.774127249	6.005896509
H	12.907112937	3.547825747	5.259147954

Optimized Monomers Adsorbed to Cu(111)/Au(111) surfaces

POSCAR format

Monomer i on Cu(111) -DFT-D2

Cu O C H

1.0000000000000000

12.7810000000000006 0.0000000000000000 0.0000000000000000

6.3905000000000003 11.0686699999999991 0.0000000000000000

0.0000000000000000 0.0000000000000000 40.0000000000000000

100 6 6 2

Direct

0.8008127847410684 0.8007077725762377 0.1546228984433817

0.4045666159519344 0.7976326915392286 0.1544762208006889

0.7973799723540553 0.4045821558629951 0.1544230971291763

0.6020915084153259 0.8002604836883862 0.1544257485582362

0.8003115223348179 0.6019893713815018 0.1544256332759013

0.6006662538540152 0.6007182466181862 0.1544246305922634

0.9995693080983339 0.8003264414483904 0.1543709890565424

0.4003296382012997 0.4003406275316412 0.1543828063178355

0.2053040223032948 0.7926868997342539 0.1564940140031432

0.4025090269376389 0.5980890841930930 0.1542851382505721

0.2005122564841558 0.5985284129774017 0.1544830536830882

0.8005095220097118 0.9992276527222188 0.1543143756213308

0.5982031541142615 0.4023503608607882 0.1542766060498474

0.7927516172006557 0.2047380168245203 0.1565836878185426

0.5984562989318619 0.2004305486871319 0.1544899323535846

0.0002923158528443 0.4055296738131860 0.1539011991170525

0.0006547757543540 0.6019021202757824 0.1545306918088530

0.4056302685713933 0.0003262980865450 0.1538849254407836

0.2008672435378165 0.4012316068953615 0.1543581693706739

0.4011797453286332 0.2008881215030870 0.1543472245726673

0.2024953227864608 0.2027245568027246 0.1540493575352928

0.6019694654342177 0.0005635559943436 0.1545055119024007

0.0009103963246676 0.9999378857441802 0.1551495224350336

0.9995404316355354 0.2093399047172870 0.1547271395913473

0.2093361544497089 0.9999752882837000 0.1546698363924854

0.8673546784807982 0.8672517981697820 0.1030601019616434

0.6670059948147543 0.6670065383327785 0.1031218819380892

0.6672517360287801 0.8669210308938423 0.1031634759370913

0.4667917596059412 0.8668066763773794 0.1031858330032387

0.8669569907786469 0.6671964958489798 0.1031735078498815

0.8667928211593020 0.4667595200051651 0.1031829224694812

0.2664307632031015 0.6679438117180130 0.1035114906255699

0.2659153240819067 0.8672969131503251 0.1041071408188445

0.0683845685020696 0.8676845052466692 0.1041523260330083

0.6680552047386300 0.2663390685590374 0.1035432682319370

0.4665434335894442 0.6670448389804763 0.1031292378163584

0.6669395372355734 0.4666206496345192 0.1031074588541295

0.4667595848266684 0.4667431729308710 0.1029218804729015

0.8671917082046964 0.2658852290713530 0.1041028178566963

0.8678522335278906 0.0682866358438672 0.1041717608132692

0.2671002365069462 0.2671218608036185 0.1030404692702910

0.0672304690075874 0.6675117105177116 0.1031487237273749

0.2671765151228118 0.4673420294815345 0.1030057183377779

0.0672999634467513 0.4673597406326746 0.1029548755853177

0.4673944327573964 0.2671634170443471 0.1030078261215919

0.6675945322321601 0.0672053090909851 0.1031393460895740

0.4674095684388819 0.0673151016541407 0.1029439311805967

0.0667379985222682 0.2669143307256042 0.1032135426789086

0.2670078079185019	0.0668518209442473	0.1031716446470778
0.0677793545174337	0.0677182303009322	0.1043307706482950
0.9333200000000019	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.9333200000000019	0.0521799999999999
0.9333200000000019	0.5333299999999994	0.0521799999999999
0.7333199999999991	0.9333200000000019	0.0521799999999999
0.9333200000000019	0.7333199999999991	0.0521799999999999
0.7333199999999991	0.7333199999999991	0.0521799999999999
0.1333300000000008	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.5333299999999994	0.0521799999999999
0.3333299999999966	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.7333199999999991	0.0521799999999999
0.3333299999999966	0.7333199999999991	0.0521799999999999
0.9333200000000019	0.1333300000000008	0.0521799999999999
0.7333199999999991	0.5333299999999994	0.0521799999999999
0.9333200000000019	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.3333299999999966	0.0521799999999999
0.1333300000000008	0.5333299999999994	0.0521799999999999
0.1333300000000008	0.7333199999999991	0.0521799999999999
0.5333299999999994	0.1333300000000008	0.0521799999999999
0.3333299999999966	0.5333299999999994	0.0521799999999999
0.5333299999999994	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.1333300000000008	0.0521799999999999
0.7999900000000011	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.3999900000000025	0.0000000000000000
0.5999899999999982	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.5999899999999982	0.0000000000000000
0.5999899999999982	0.5999899999999982	0.0000000000000000
0.0000000000000000	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.3999900000000025	0.0000000000000000
0.2000000000000028	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.5999899999999982	0.0000000000000000
0.2000000000000028	0.5999899999999982	0.0000000000000000
0.7999900000000011	0.0000000000000000	0.0000000000000000
0.5999899999999982	0.3999900000000025	0.0000000000000000
0.7999900000000011	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.2000000000000028	0.0000000000000000
0.0000000000000000	0.3999900000000025	0.0000000000000000
0.0000000000000000	0.5999899999999982	0.0000000000000000
0.3999900000000025	0.0000000000000000	0.0000000000000000
0.2000000000000028	0.3999900000000025	0.0000000000000000
0.3999900000000025	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.0000000000000000	0.0000000000000000
0.2102601842370520	0.9899937080016065	0.2033164330704350
0.2025106931474471	0.7790338068914318	0.2147801996684059
0.0154920472345369	0.7783209870801067	0.2442487630989822
0.7897403987055981	0.9978740915583203	0.2442448611156453
0.7800828168030581	0.1901872000399290	0.2148838323337886
0.9844895900976428	0.2095983856176135	0.2031930775649921
0.1082102485148889	0.9946837606850839	0.2107368415407849
0.1099219673295296	0.8820167382964292	0.2201578241511519
0.0031760519756163	0.8851893850636391	0.2347206815461252
0.8942561681614132	0.9911264049101697	0.2347057536507149

0.8851828633487048 0.1006675396674131 0.2201385921385703
 0.9946531291380675 0.1049897613928324 0.2106544288956974
 0.1006189074523850 0.7180893136547155 0.2391844582112729
 0.7265521167369192 0.0817580734917384 0.2392266701005140

Monomer ii on Cu(111) -DFT-D2

Cu O C H

1.0000000000000000
 12.7810000000000006 0.0000000000000000 0.0000000000000000
 6.3905000000000003 11.0686699999999991 0.0000000000000000
 0.0000000000000000 0.0000000000000000 40.0000000000000000
 100 6 6 2

Direct

0.8007501556083627 0.8005229239044892 0.1548752568395629
 0.3989477612536516 0.8002571656778702 0.1547870351684750
 0.8006277738646583 0.3987699220195552 0.1549009759775590
 0.6001144345306827 0.8007109330210309 0.1544454718167534
 0.8008114160816224 0.5995501818103227 0.1543429609193348
 0.6000534281057052 0.5992067261483622 0.1543192866842444
 0.0000903272226685 0.8014939018222419 0.1550170554401940
 0.3999511898323623 0.4000872244490184 0.1545273693851305
 0.1973440683572498 0.8004857117871280 0.1549825319264171
 0.3998097509137572 0.5987892168111028 0.1545877096472600
 0.1991993887873321 0.6002100490219949 0.1550578043089465
 0.8022531673188020 -0.0009245941615469 0.1548693753529942
 0.5998277275234952 0.3992008368566493 0.1544051706533827
 0.8010776871755119 0.1975374376385657 0.1554761890673246
 0.6003183660455484 0.1991359855304577 0.1550403523163550
 0.0009218166318258 0.3984114198397356 0.1544893307008328
 0.0006541387188236 0.5996116936196929 0.1547557380451649
 0.3990587953042967 0.0009487450697155 0.1546401553756990
 0.1994224081617465 0.4001706588095384 0.1546275567432891
 0.4001587699416548 0.1994846883606461 0.1544508768507767
 0.1998040560159159 0.1997382641734209 0.1553029083486827
 0.6002258945211553 0.0000119149441309 0.1546502864495129
 0.0004821423646843 0.9995668857085750 0.1538352189041532
 0.0006954193501182 0.1963524295173248 0.1552476227892127
 0.1968820090408722 0.0006004947479051 0.1555903476017092
 0.8652463687813787 0.8643094834101680 0.1053787801640726
 0.6663342110259306 0.6667998290949861 0.1048238892734860
 0.6664458355412468 0.8655026039419680 0.1049797263325578
 0.4686880048109469 0.8657605515542496 0.1050455317299627
 0.8660226111432737 0.6660386467923568 0.1050141543050953
 0.8657350035184086 0.4686635965696389 0.1050219508031841
 0.2681213334055729 0.6635948188058000 0.1051418422523306
 0.2691220975977622 0.8646228499125050 0.1055272627855034
 0.0669032534177559 0.8638270842709626 0.1045526506031441
 0.6640646187516500 0.2674932731189142 0.1052271813599146
 0.4679926492019743 0.6655927598132462 0.1050891127910969
 0.6660979089166560 0.4680367610371067 0.1050299970722313
 0.4666056432566951 0.4661454075230952 0.1048054298947052
 0.8646401148664670 0.2691546693152480 0.1055995409218114
 0.8636039276712886 0.0671971640944633 0.1047883603730765
 0.2669340047314023 0.2672170150246208 0.1050428321367915
 0.0676016535195394 0.6647178996220270 0.1051557747324221
 0.2664963038079869 0.4660082695348964 0.1050740238445507
 0.0662523068139217 0.4673618984260354 0.1048767337340807
 0.4658371446528371 0.2668158561115656 0.1051017596942343
 0.6649169515723943 0.0672446770436040 0.1051459994378292
 0.4675427878773751 0.0665008154962318 0.1048412746474697
 0.0677689295644646 0.2677195586542078 0.1052673189584755
 0.2685106512821858 0.0669883379968652 0.1053518382841664

0.0678199672302558	0.0675821763608407	0.1044772582053470
0.9333200000000019	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.9333200000000019	0.0521799999999999
0.9333200000000019	0.5333299999999994	0.0521799999999999
0.7333199999999991	0.9333200000000019	0.0521799999999999
0.9333200000000019	0.7333199999999991	0.0521799999999999
0.7333199999999991	0.7333199999999991	0.0521799999999999
0.1333300000000008	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.5333299999999994	0.0521799999999999
0.3333299999999966	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.7333199999999991	0.0521799999999999
0.3333299999999966	0.7333199999999991	0.0521799999999999
0.9333200000000019	0.1333300000000008	0.0521799999999999
0.7333199999999991	0.5333299999999994	0.0521799999999999
0.9333200000000019	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.3333299999999966	0.0521799999999999
0.1333300000000008	0.5333299999999994	0.0521799999999999
0.1333300000000008	0.7333199999999991	0.0521799999999999
0.5333299999999994	0.1333300000000008	0.0521799999999999
0.3333299999999966	0.5333299999999994	0.0521799999999999
0.5333299999999994	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.1333300000000008	0.0521799999999999
0.7999900000000011	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.3999900000000025	0.0000000000000000
0.5999899999999982	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.5999899999999982	0.0000000000000000
0.5999899999999982	0.5999899999999982	0.0000000000000000
0.0000000000000000	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.3999900000000025	0.0000000000000000
0.2000000000000028	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.5999899999999982	0.0000000000000000
0.2000000000000028	0.5999899999999982	0.0000000000000000
0.7999900000000011	0.0000000000000000	0.0000000000000000
0.5999899999999982	0.3999900000000025	0.0000000000000000
0.7999900000000011	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.2000000000000028	0.0000000000000000
0.0000000000000000	0.3999900000000025	0.0000000000000000
0.0000000000000000	0.5999899999999982	0.0000000000000000
0.3999900000000025	0.0000000000000000	0.0000000000000000
0.2000000000000028	0.3999900000000025	0.0000000000000000
0.3999900000000025	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.0000000000000000	0.0000000000000000
0.995118406922653	0.2127902061434796	0.2095290810968127
0.7881157768013355	0.1976098780027169	0.2094771448178180
0.7814537915453725	0.9947694963704421	0.2338623637845311
0.0085102922388988	0.7841595077462827	0.2371924837116901
0.2206796124012179	0.7824269499756238	0.2202504360279655
0.2224293889115088	0.0017391918800241	0.2038292062451185
0.0061922691108413	0.1114320492947199	0.2127677998140792
0.8872481689364773	0.1044122545772618	0.2168041960105484
0.8893617921614284	0.9953332880505618	0.2291016763068130
0.0040225107184211	0.8928264918962723	0.2310280764578105
0.1273117581333502	0.8834143067175555	0.2211250782501520

0.1255167328557818 -0.0005799490620670 0.2122822196236620
0.8117156500985336 0.9089393578315039 0.2411380211785014
0.0954572268567551 0.7330077580760661 0.2374029425866215

Monomer iii on Cu(111) -DFT-D2

Cu O C H

1.000000000000000
12.7810000000000006 0.000000000000000 0.000000000000000
6.3905000000000003 11.068669999999991 0.000000000000000
0.000000000000000 0.000000000000000 40.000000000000000
100 6 6 2

Direct

0.8004093480688567 0.7995921711419287 0.1542947959166878
0.4049164258899600 0.7979098968002148 0.1547550972736923
0.7972858232835178 0.4042807810941827 0.1546195928558374
0.6021988242387564 0.7997916115577129 0.1543134324862501
0.8005331195314606 0.6012682222686092 0.1543376141897681
0.6010580274695023 0.6004731915365157 0.1544188036128594
0.9986858589433448 0.7993029631831162 0.1532988155409630
0.4002434185632656 0.3999207503173178 0.1540922994612696
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0.7294013081207172 0.0382313115620109 0.2213715611698112

Monomer iv on Cu(111) -DFT-D2

Cu O C H

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100 6 6 2

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Monomer i on Cu(111) -vdW-DF2

Cu O C H

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100 6 6 2

Direct

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0.3999900000000025	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.0000000000000000	0.0000000000000000
0.2187520352165749	0.0133380207767751	0.2060365668275000
0.2232446767826674	0.7956184001448341	0.2057602656582518
0.0099837405871183	0.7908819231969311	0.2057206214627311
0.7922155819720432	0.0038422422656104	0.2057332139657719
0.7875185653493433	0.2218984577992100	0.2055302705074545
0.0005938232523135	0.2267328974720387	0.2057508295809390
0.1198663303243803	0.0112388440778039	0.2099701422186282
0.1221530663225382	0.8945142176389359	0.2097868398747333
0.0078580204150340	0.8921559135031563	0.2095846928318691
0.8912954349112541	0.0061435568295852	0.2095508749474669
0.8885967996388007	0.1229945129988759	0.2096002987559918
0.0028016489103905	0.1257399582831277	0.2098107147000429
0.8061558013273350	0.7089831505850457	0.2615095833436326
0.7944512134471161	0.7683035857147840	0.2544259306433823

Monomer ii on Cu(111) -vdW-DF2

Cu O C H

1.0000000000000000

12.7810000000000000 0.0000000000000000 0.0000000000000000

6.3905000000000000 11.068669999999999 0.0000000000000000

0.0000000000000000 0.0000000000000000 40.0000000000000000

100 6 6 2

Direct

0.7999647818459525 0.7999345595242519 0.1635314152795916

0.4001351657207248 0.7999518576844356 0.1636671763076643

0.7999794240681548 0.4001074679584999 0.1636703003441196

0.6000673605573995 0.8001160608548856 0.1635906514515084

0.8001543615527161 0.6000311209789541 0.1635803290941763

0.5999706213818622 0.5999836417473533 0.1635523440578293

0.9999077066758031 0.7997821436201422 0.1631812638372241

0.3999491425215670 0.4000993828840284 0.1636374170926839

0.2000697458580785 0.7997596132281939 0.1634452692348061

0.4001065400503976 0.5998298340797261 0.1636623788232590

0.1999825036977062 0.5999116715432894 0.1635982314645259

0.7999533254309120 0.9997276282821647 0.1632414960276132

0.5997758682141863 0.4002168246587476 0.1636406624327218

0.7998416749773218 0.1999787413613848 0.1635130403051376

0.5998667160964359 0.2000061149082456 0.1636952647289368

0.0000061745365825 0.4001283175094317 0.1636726933296846

-0.0000129013244835 0.5998169728290867 0.1636052401289923

0.4000913521269617 0.9999759018608255 0.1637021558422160

0.1998618912540031 0.4001815389425733 0.1636449284416695

0.4000857934166543 0.1998785560401888 0.1636184286446280

0.2000802940237754 0.2000861796274003 0.1637650467333583

0.5998587755400215 0.9998517195308392 0.1635906155349574

0.0001586380006840 0.9998708995158748 0.1632245870475592

-0.0000278255014667 0.1999399186018300 0.1635747984534510

0.1999581289683882 0.9999309058518313 0.1636040105873773

0.8666291274312695 0.8666227756850038 0.1075252087907925

0.6666673151556144 0.6666620039627702 0.1076843446306657

0.6666117426772564 0.8666243571493113 0.1075970871625528

0.4666812561929444 0.8666352594171253 0.1076842265387636

0.8666568162186001 0.6665972043146609 0.1076081408243378

0.8666379630833155 0.4666834678404572 0.1076809735997496

0.2666144829120279 0.6665531770196278 0.1076849823437960

0.2667147042380466 0.8666486819507329 0.1076865457945825

0.0667823691020370 0.8664439236754652 0.1075072634449928

0.6665603859378364 0.2665983439011879 0.1077529198341130

0.4666808212072881 0.6666632412361033 0.1076907428271152

0.6666604236423721 0.4666993677947274 0.1076885599107983

0.4666229067871764 0.4666478308974555 0.1076720087057274

0.8666444143196731 0.2666995964375748 0.1077045564209537

0.8664630837044163 0.0667620732813419 0.1075723053970323

0.2666140221049242 0.2666399153606613 0.1077010328762022

0.0668708409037364 0.6664585367640153 0.1075825769720760

0.2666590965125513 0.4666630259858462 0.1076439093256235

0.0667124598922214 0.4666242489342375 0.1076524707834979

0.4666790023558964 0.2666560942576989 0.1077009036101022

0.6664557325291642 0.0668835820541170 0.1076516995599078

0.4666159494291481 0.0667064299174867 0.1076687222411407

0.0668379445015878 0.2665873471212653 0.1077781885889958

0.2665956711634409 0.0668291618006408 0.1077858411518065

0.0667783527591844 0.0667597924981162 0.1076130889092784

0.9333200000000019 0.9333200000000019 0.0521799999999999

0.5333299999999994 0.9333200000000019 0.0521799999999999

0.9333200000000019 0.5333299999999994 0.0521799999999999

0.7333199999999991	0.9333200000000019	0.0521799999999999
0.9333200000000019	0.7333199999999991	0.0521799999999999
0.7333199999999991	0.7333199999999991	0.0521799999999999
0.1333300000000008	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.5333299999999994	0.0521799999999999
0.3333299999999996	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.7333199999999991	0.0521799999999999
0.3333299999999996	0.7333199999999991	0.0521799999999999
0.9333200000000019	0.1333300000000008	0.0521799999999999
0.7333199999999991	0.5333299999999994	0.0521799999999999
0.9333200000000019	0.3333299999999996	0.0521799999999999
0.7333199999999991	0.3333299999999996	0.0521799999999999
0.1333300000000008	0.5333299999999994	0.0521799999999999
0.1333300000000008	0.7333199999999991	0.0521799999999999
0.5333299999999994	0.1333300000000008	0.0521799999999999
0.3333299999999996	0.5333299999999994	0.0521799999999999
0.5333299999999994	0.3333299999999996	0.0521799999999999
0.3333299999999996	0.3333299999999996	0.0521799999999999
0.7333199999999991	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.3333299999999996	0.0521799999999999
0.3333299999999996	0.1333300000000008	0.0521799999999999
0.7999900000000011	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.3999900000000025	0.0000000000000000
0.5999899999999982	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.5999899999999982	0.0000000000000000
0.5999899999999982	0.5999899999999982	0.0000000000000000
0.0000000000000000	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.3999900000000025	0.0000000000000000
0.2000000000000028	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.5999899999999982	0.0000000000000000
0.2000000000000028	0.5999899999999982	0.0000000000000000
0.7999900000000011	0.0000000000000000	0.0000000000000000
0.5999899999999982	0.3999900000000025	0.0000000000000000
0.7999900000000011	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.2000000000000028	0.0000000000000000
0.0000000000000000	0.3999900000000025	0.0000000000000000
0.0000000000000000	0.5999899999999982	0.0000000000000000
0.3999900000000025	0.0000000000000000	0.0000000000000000
0.2000000000000028	0.3999900000000025	0.0000000000000000
0.3999900000000025	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.0000000000000000	0.0000000000000000
0.9934792819496966	0.2184611359401609	0.2491779516586259
0.7823092966419674	0.2042477248569879	0.2489263756208565
0.7907727871212222	0.9868111449236271	0.2500266530215509
0.0114593877044682	0.7775969189674585	0.2503085447212658
0.2174301798415704	0.7824141438024055	0.2492758744803151
0.2186696560364060	0.0040583605094323	0.2490903229354767
0.9998004436489617	0.1197146935774704	0.2497944508515393
0.8820777048808860	0.1119784823197689	0.2500813335506680
0.8952956409586574	0.9901889118811245	0.2508090469469355
0.0068046674971256	0.8863769962251266	0.2508990162716505
0.1234606024344480	0.8827413238393260	0.2501699291197318
0.1236908603686577	0.0019429961233783	0.2497440440146526
0.8088879322258926	0.9027413717858452	0.2498352585056217
0.0980905668600823	0.7153630818973832	0.2498514908524087

Monomer iii on Cu(111) -vdW-DF2

Cu O C H

1.0000000000000000

12.7810000000000006 0.0000000000000000 0.0000000000000000

6.3905000000000003 11.068669999999999 0.0000000000000000

0.0000000000000000 0.0000000000000000 40.0000000000000000

100 6 6 2

Direct

0.8000764778646540 0.7999286241806879 0.1638161971263025

0.4001661674759750 0.7999751093750395 0.1636726044584075

0.7999791180331695 0.4001340810759249 0.1636709457754643

0.6001713185824736 0.8001163937075609 0.1636271061829444

0.8001426449367505 0.6001396421856470 0.1636391524837008

0.6000185754712908 0.6000008418729000 0.1635366236355734

0.9996930623782142 0.7998850331535085 0.1631661401863516

0.4000138878335274 0.4000291996711017 0.1635945582389547

0.2000303968006672 0.7998398869011953 0.1634271982504698

0.4001962876125217 0.5998091491248738 0.1636450978200583

0.1999110408146675 0.5999362953063943 0.1636764924889853

0.7999698843234155 0.9995917698260209 0.1632221086931995

0.5998318758502502 0.4001823133988639 0.1636348915211474

0.7998371565255649 0.1999470010645638 0.1635290556302514

0.5999252425973793 0.1999194042793602 0.1636808500826356

0.9999521917874765 0.4001558019682865 0.1636875222535202

0.9997298082547839 0.5999758441183354 0.1636469613005801

0.4001409658453121 0.9999539068320642 0.1636900301109335

0.1997972687541212 0.4001636781238478 0.1635959137427055

0.4001254439054837 0.1998243668695365 0.1635904892257452

0.2000645587871476 0.2000880553141037 0.1637587637504881

0.5999541789357079 0.9997337616183150 0.1636128237415525

0.0000677388800911 0.9999215511620989 0.1631664224273255

0.9999299689523788 0.1999635117978001 0.1636306726438863

0.1999355053922156 -0.0000104894434209 0.1635954318584560

0.8665751724012311 0.8665822105549029 0.1074745722911669

0.6666992126420613 0.6666829604135995 0.1076923551690874

0.6666883696224815 0.8665751419434071 0.1076084696510438

0.4667390349113106 0.8666140944507160 0.1076862139900455

0.8665922476799718 0.6666596996472702 0.1075885843005931

0.8666122875538925 0.4667368918262361 0.1076848032590748

0.2665851771318699 0.6665554623529044 0.1077507351783951

0.2667308662088155 0.8666535685745144 0.1076893366502041

0.0667488845314547 0.8664254714291499 0.1075061780608836

0.66658039861113765 0.2665771645054636 0.1077615732465405

0.4667047718498708 0.6666710336923631 0.1076845675737330

0.6666748427889092 0.4667049064750723 0.1076786989641318

0.4666484736956616 0.4666433730373998 0.1076663924475519

0.8666396636174664 0.2667155633802382 0.1077102638826829

0.8664270537625377 0.0667521267914799 0.1075491426932881

0.2666092524071526 0.2666236692301203 0.1076801956524447

0.0668580476318466 0.6664421868508954 0.1076143788909248

0.2666308345838275 0.4666840236808309 0.1076818724508963

0.0666459038881266 0.4666771140690840 0.1076708310147767

0.4666939861113765 0.2666311429867314 0.1076818181524119

0.6664715774755514 0.0668472467773120 0.1076457732127361

0.4666677714489232 0.0666560417140709 0.1076670915912475

0.0668063626537014 0.2666014162953193 0.1077904088802593

0.2665997159845251 0.0668278874964076 0.1077848131140633

0.0667559766410533 0.0667792503619626 0.1076077325594198

0.9333200000000019 0.9333200000000019 0.0521799999999999

0.5333299999999994 0.9333200000000019 0.0521799999999999

0.9333200000000019 0.5333299999999994 0.0521799999999999

0.7333199999999991 0.9333200000000019 0.0521799999999999

0.9333200000000019	0.7333199999999991	0.0521799999999999
0.7333199999999991	0.7333199999999991	0.0521799999999999
0.1333300000000008	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.5333299999999994	0.0521799999999999
0.3333299999999966	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.7333199999999991	0.0521799999999999
0.3333299999999966	0.7333199999999991	0.0521799999999999
0.9333200000000019	0.1333300000000008	0.0521799999999999
0.7333199999999991	0.5333299999999994	0.0521799999999999
0.9333200000000019	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.3333299999999966	0.0521799999999999
0.1333300000000008	0.5333299999999994	0.0521799999999999
0.1333300000000008	0.7333199999999991	0.0521799999999999
0.5333299999999994	0.1333300000000008	0.0521799999999999
0.3333299999999966	0.5333299999999994	0.0521799999999999
0.5333299999999994	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.3333299999999966	0.0521799999999999
0.7333199999999991	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.1333300000000008	0.0521799999999999
0.1333300000000008	0.3333299999999966	0.0521799999999999
0.3333299999999966	0.1333300000000008	0.0521799999999999
0.7999900000000011	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.3999900000000025	0.0000000000000000
0.5999899999999982	0.7999900000000011	0.0000000000000000
0.7999900000000011	0.5999899999999982	0.0000000000000000
0.5999899999999982	0.5999899999999982	0.0000000000000000
0.0000000000000000	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.3999900000000025	0.0000000000000000
0.2000000000000028	0.7999900000000011	0.0000000000000000
0.3999900000000025	0.5999899999999982	0.0000000000000000
0.2000000000000028	0.5999899999999982	0.0000000000000000
0.7999900000000011	0.0000000000000000	0.0000000000000000
0.5999899999999982	0.3999900000000025	0.0000000000000000
0.7999900000000011	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.2000000000000028	0.0000000000000000
0.0000000000000000	0.3999900000000025	0.0000000000000000
0.0000000000000000	0.5999899999999982	0.0000000000000000
0.3999900000000025	0.0000000000000000	0.0000000000000000
0.2000000000000028	0.3999900000000025	0.0000000000000000
0.3999900000000025	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.2000000000000028	0.0000000000000000
0.5999899999999982	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.0000000000000000	0.0000000000000000
0.0000000000000000	0.2000000000000028	0.0000000000000000
0.2000000000000028	0.0000000000000000	0.0000000000000000
0.2164658463333731	0.0027626688727221	0.2489526662580838
0.2203323174711699	0.7826517227127827	0.2487945309543622
0.0219339181606854	0.7665777711607215	0.2504339959358485
0.7864569431102062	0.9909401356220296	0.2503757393296715
0.7825099759949105	0.1997667694534256	0.2487997820307468
0.9914947680552859	0.2170720402044608	0.2489722583893291
0.1217270326277131	0.0005467944794954	0.2497206615394252
0.1238539739169684	0.8786432847914840	0.2500521479561882
0.0065274515097226	0.8805888269048747	0.2509254504399661
0.8960420659712611	0.9858583574354630	0.2509103071500124
0.8828374648054718	0.1082568522057832	0.2500485397977198
0.9985989946251919	0.1178075451857335	0.2497265535440399
0.9463824407047551	0.7652639138663688	0.2492401143972317
0.7925386583650615	0.9118592948213715	0.2491994076169751

Monomer iv on Cu(111) -vdW-DF2

Cu O C H

1.000000000000000
12.781000000000000 0.000000000000000 0.000000000000000
6.390500000000000 11.068669999999999 0.000000000000000
0.000000000000000 0.000000000000000 40.000000000000000
100 6 6 2

Direct

0.7977608097424104 0.7968327618880485 0.1624802285259039
0.4007064893092180 0.7991424581614044 0.1638004862734654
0.7998817539107794 0.4001935221176079 0.1636947190036759
0.5991055201885214 0.7989393311315015 0.1636305796861179
0.7995292905248149 0.5984643853201468 0.1636569771153520
0.6000261361644194 0.5993676385408307 0.1635141126951738
0.9997116917497587 0.7952898119714522 0.1641866342171021
0.4006616642415491 0.3983759138215748 0.1634774119699896
0.2040168681381880 0.7967646814268194 0.1620670143333928
0.4014237147682139 0.5981888448153523 0.1635440769589360
0.2035024297865035 0.5946534161432021 0.1623361986224598
0.7968316430174023 0.0005366881616362 0.1653812403042731
0.5993745311695349 0.4003542817846744 0.1636252719921522
0.7978304204385783 0.2031937902542897 0.1626501031705498
0.5980046141679675 0.2010183148905111 0.1632074542189147
0.0003092726091551 0.3985687177915239 0.1636560738821486
0.9997254306036455 0.5959260384155289 0.1623634022635529
0.3995200951549238 0.9994072298119886 0.1636525213492509
0.2004368603085376 0.3981857442930899 0.1632766527932601
0.3998174043905132 0.1991763451586351 0.1632999857238404
0.2004928783267269 0.1994101969588549 0.1635690323628177
0.5973539323223095 0.9989789270789110 0.1625855194216038
0.0022765114337220 0.0029677417925884 0.1595407323899379
0.0004561728793369 0.2007948675845384 0.1626643413377548
0.2011796004705204 0.9999403221871057 0.1624104792845218
0.8674279507392303 0.8665309583520158 0.1091993772582194
0.6666803019414176 0.6662466401454723 0.1075883804026738
0.6668436574271585 0.8662228027865581 0.1072605609798875
0.4667234110596167 0.8662313858860989 0.1076322365756448
0.8666537067432826 0.6662533282149006 0.1072134268936836
0.8667395734720280 0.4662779215854948 0.1076324913183720
0.2669693331577584 0.6656708188463084 0.1073909991057373
0.2668013521902019 0.8660201336189197 0.1074795553236281
0.0665803346648376 0.8651916570511909 0.1075410712342349
0.6663179408090170 0.2664159616030327 0.1075098326743307
0.4668481309634488 0.6662133107977301 0.1076393459637485
0.6667289952768368 0.4663163245734415 0.1076690206220415
0.4668552572915274 0.4660672916830164 0.1075105426019679
0.8665373432795346 0.2664305424562193 0.1074396919334770
0.8654274402737261 0.0661313471744077 0.1077257497310075
0.2670443279667902 0.2660853618609623 0.1074337594397872
0.0661101969058885 0.6670213605514592 0.1080775788710197
0.2668480972678082 0.4658103297054909 0.1071993527774097
0.0670104016072054 0.4658955661373072 0.1071776642853285
0.4671069914420845 0.2657667021360070 0.1073678508617432
0.6682571766360554 0.0651851039318849 0.1085246659843655
0.4668524691881837 0.0662755905177909 0.1072276125786922
0.0670532482635730 0.2665582219202796 0.1074473782626292
0.2672717505464164 0.0664580371841338 0.1073578985809276
0.0671345242552448 0.0667589856663640 0.1063606987195042
0.9333200000000019 0.9333200000000019 0.0521799999999999
0.5333299999999994 0.9333200000000019 0.0521799999999999
0.9333200000000019 0.5333299999999994 0.0521799999999999
0.7333199999999991 0.9333200000000019 0.0521799999999999
0.9333200000000019 0.7333199999999991 0.0521799999999999

0.7333199999999991	0.7333199999999991	0.0521799999999999
0.1333300000000008	0.9333200000000019	0.0521799999999999
0.5333299999999994	0.5333299999999994	0.0521799999999999
0.3333299999999996	0.9333200000000019	0.0521799999999999
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