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Self-Assembly

Cyano-Functionalized Triarylamines on Coinage Metal Surfaces: Interplay of Intermolecular and Molecule–Substrate Interactions

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Abstract: The self-assembly of cyano-functionalized triarylamine derivatives on Cu(111), Ag(111) and Au(111) was studied by means of scanning tunnelling microscopy, low-energy electron diffraction, X-ray photoelectron spectroscopy and density functional theory calculations. Different bonding motifs, such as antiparallel dipolar coupling, hydrogen bonding and metal coordination, were observed. Whereas on Ag(111) only one hexagonally close-packed pattern stabilized by hydrogen bonding is observed, on Au(111) two different partially porous phases are present at submonolayer coverage, stabilized by dipolar coupling, hydrogen bonding and

metal coordination. In contrast to the self-assembly on Ag(111) and Au(111), for which large islands are formed, on Cu(111), only small patches of hexagonally close-packed networks stabilized by metal coordination and areas of disordered molecules are found. The significant variety in the molecular self-assembly of the cyano-functionalized triarylamine derivatives on these coinage metal surfaces is explained by differences in molecular mobility and the subtle interplay between intermolecular and molecule–substrate interactions.

Introduction

The self-assembly of organic molecules on metal surfaces has attracted increasing interest over the last two decades in fundamental research as well as for potential applications in organic devices such as organic photovoltaics, organic field-effect transistors or as sensors.^[1] Molecular self-assembly is based on the concepts of supramolecular chemistry, in which non-covalent intermolecular interactions^[2] such as H-bonding,^[3] dipolar coupling,^[4,5] π – π stacking,^[6] and metal coordina-

tion^[7] are employed to create supramolecular architectures.^[8] Highly organized and defect-free structures can be realized because of self-recognition and error correction, which happen by bond breaking and bond formation until an equilibrium structure is formed.

Besides the intermolecular interactions, which can be controlled through specific functional groups, molecular self-assembly on surfaces also depends on the molecule–substrate interactions, which are influenced by the reactivity of the substrate, the crystal structure, the corrugation of the adsorption potential and potential surface reconstructions. Often subtle differences between intermolecular and molecule–substrate interactions can lead to significant differences in the self-assembly and electronic properties of the same molecule on different surfaces.^[9–11] For example, the adsorption of 3,4,9,10-perylene-tetracarboxylic acid dianhydride on Cu(111) and Ag(111) leads to charge transfer from the substrate to the molecule resulting in filling of the LUMO, whereas on Au(111) the LUMO remains empty.^[11] It was also shown that deposition of metal-free tetraphenylporphyrins on Cu(111) leads to mostly isolated molecules due to the strong interaction of the iminic nitrogen atoms with the copper surface, whereas deposition of the same molecules on Ag(111) results in well-ordered islands because of a weaker molecule–substrate interaction.^[12] For fullerenes (C₆₀) on noble metal surfaces the self-assembly and the molecular orientation are determined by a subtle interplay between the intermolecular and molecule–substrate interactions. While the spacing between the C₆₀ molecules is always around 1.0 nm—similar to the (111) bulk lattice spacing of C₆₀—subtle differences in the rotational mobility, orientation and layer growth were observed on gold, silver and copper.^[13]

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These differences can be explained by surface reconstructions, as on Au(111) and Au(110), or by differences in the reactivity of the surfaces.^[13]

The study of molecular self-assembly of organic molecules functionalized with cyano groups is particularly interesting, because the asymmetric charge distribution of the cyano group with the negatively polarized N atom leads to the formation of a local internal dipole. The cyano group can not only participate in H-bonding and dipolar coupling, but it can also efficiently coordinate to a variety of metals.^[14–17] Different molecular patterns such as 0D clusters, 1D chains and 2D islands can be created by changing the number of cyano groups and/or their relative position, as was demonstrated for cyano-functionalized porphyrin and polyphenylene derivatives.^[4,14,18]

Herein, we report on the self-assembly of the cyano-functionalized planarized triarylamine derivative 4,4,8,8,12,12-hexamethyl-4*H*,8*H*,12*H*-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine-2,6,10-tricarbonitrile (**1**, Scheme 1) on coinage metal (111)

Scheme 1. Synthesis of the cyano-functionalized triarylamine derivative **1**. NMP = *N*-methyl-2-pyrrolidone. See Experimental Section for further details.

surfaces. Such planarized triarylamines, so-called heterotriangulenes, are at present of growing interest owing to their potential as stable electron-rich building blocks for optoelectronic organic materials.^[19,20] In our recent study on the self-assembly of **1** on Au(111), we could show that the molecules can undergo H-bonding, dipolar coupling and metal–ligand interaction.^[21] By comparing these results to the self-assembly on Ag(111) and Cu(111), we aim to provide insight into the subtle interplay between molecule–substrate and intermolecular interactions leading to significant differences in the self-assembled patterns. We show that the molecule–substrate interaction, the surface reconstruction [e.g., of Au(111)], the molecular mobility and the intermolecular interactions determine the sizes and the structures of the molecular patterns.

Results

Scanning tunnelling microscopy

Triarylamine derivatives containing out-of-plane bridging methyl groups on metal surfaces usually exhibit three protrusions in STM images, which give rise to a triangular appearance of the molecules (see Figure S2 in the Supporting Information). This triangular shape arises from the out-of-plane bridging methyl groups, whereas the cyano groups of the molecule are not imaged.^[21,22] This allows the molecular

Figure 1. Close-packed structure of **1** on Ag(111). a) STM image ($25 \times 25 \text{ nm}^2$, $U = -2.0 \text{ V}$, $I = 30 \text{ pA}$). The black circles indicate exemplarily two molecules that are rotated by 180° with respect to the other molecules. b) LEED pattern taken at an incident electron energy of 35 eV. The angle between two chirally different domains is marked in red. c) Tentative model of the molecular arrangement with the unit cell marked in green. The black circle highlights the trimeric H-bonding motif.

orientation in the adsorbate structures to be determined. Submonolayer coverage of **1** on Ag(111) leads to the formation of islands with a diameter of up to several hundreds of nanometres, which often grow over the step edges (see Figures S3 and S4a in the Supporting Information). Figure 1a shows a molecularly resolved STM image of such an island, which shows that the molecules assemble in a well-ordered hexagonally close-packed pattern. Generally, the molecules are oriented in the same direction with one of their three vertexes (i.e., one $\text{C}(\text{CH}_3)_2$ group) pointing to the top. However, some molecules are rotated by 180° , that is, with one vertex pointing down; exemplarily, two are marked by black circles in Figure 1a.

Figure 1c shows the tentative structural model of the molecular arrangement derived from STM as well as from low-energy electron diffraction (LEED) measurements (Figure 1b). The unit cell, marked in green in Figure 1c, has a size of $1.32 \times 1.32 \text{ nm}^2$ and an internal angle of 120° . The cyano group of one molecule points to the phenyl hydrogen atom of a neighbouring molecule forming an H-bonding motif ($\text{C}\equiv\text{N}\cdots\text{H}$), which is well known for other molecules containing cyano-functionalized phenyl rings.^[23] Because three neighbouring molecules are involved in such a $\text{C}\equiv\text{N}\cdots\text{H}$ interaction (see black circle in Figure 1c), we name this a trimeric bonding motif. This $\text{C}\equiv\text{N}\cdots\text{H}$ interaction induces organizational chirality:^[24] the N atom can point to the phenyl hydrogen atom on the left side of the methyl groups of the neighbouring molecule, as shown in Figure 1c, or to the right side (not shown here). Consequently, two chiral domains must exist on the surface. Thus, the two mirror domains that are revealed in the LEED pattern (Figure 1b) are due to the two different chiral domains, which are rotated by 22° with respect to each other (11° with respect to the $\langle 1\bar{1}0 \rangle$ direction of the Ag(111) substrate). Indeed, these chiral domains can also be identified in the STM images (Figure S4 in the Supporting Information). However, no domain boundaries where the two different chiral domains meet were

observed. Thus, we assume that the molecules can easily rotate and translate to adjust to one of the chiral arrangements when two islands with different orientation coalesce, which leads to Ostwald ripening, as previously reported for organic molecules adsorbed on solid surfaces.^[25]

Deposition of one monolayer (ML) of **1** on Au(111) results in a hexagonally close-packed pattern, called phase α in the following. The herringbone reconstruction of the Au(111) surface remains intact underneath the molecules.^[21] The unit cell, marked in green in Figure 2b, has a size of $1.32 \times 1.32 \text{ nm}^2$

Figure 2. Comparison of the different phases for **1** on Au(111). a) STM image of close-packed phase α observed for monolayer coverage ($7 \times 7 \text{ nm}^2$, $U = 2.8 \text{ V}$, $I = 170 \text{ pA}$). c) STM image of porous phase α ($7 \times 7 \text{ nm}^2$, $U = 2.0 \text{ V}$, $I = 70 \text{ pA}$). e) STM image of phase β ($7 \times 7 \text{ nm}^2$, $U = 3.0 \text{ V}$, $I = 140 \text{ pA}$). b), d), f) Tentative structural models of close-packed phase α , porous phase α and phase β , respectively. The unit cells are marked in green, and the coloured ovals and circles indicate different bonding motifs (see text). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission from ref. [21].

with an internal angle of 120° . The high-resolution image in Figure 2a shows that the molecules exhibit two different orientations, which are rotated by 180° with respect to each other. Noteworthy, a correlation with the periodicity of the herringbone reconstruction was identified for the two different molecular orientations.^[21] From the tentative structural model in Figure 2b, it becomes apparent that the different molecular orientations lead to two specific interaction motifs: i) An antiparallel

dipolar coupling motif in which the cyano groups of neighbouring molecules are oriented parallel to each other (red oval in Figure 2b) and ii) an H-bonding motif (light blue oval in Figure 2b). The dark blue circle indicates the trimeric motif formed by three molecules undergoing H-bonding. Gas-phase DFT calculations with the optB86b functional showed that the different bonding motifs only vary slightly in binding energy, with the dipolar coupling motif being the most stable.^[21] Similar to what was observed for **1** on Ag(111), two chiral mirror domains rotated by 11° with respect to the $\langle 1\bar{1}0 \rangle$ direction of the Au(111) surface exist; their presence is also due to the fact that the cyano group can point to the left or right of the phenyl hydrogen atom.^[26]

Deposition of less than 1 ML of **1** on Au(111) leads to the co-existence of two different phases, both of which exhibit organizational chirality. Phase α now exhibits many pores, which assemble into a porous network (Figure 2c). Within these porous areas, neighbouring molecules are rotated by 180° , and they exclusively interact through the dipolar coupling motif, which is visible in the tentative structural model shown in Figure 2d. In addition, a second partially porous phase, called phase β , with a unit cell size of $3.77 \times 3.77 \text{ nm}^2$ and an internal angle of 120° was observed (Figure 2e). Whereas for the porous phase α , three neighbouring pores share one molecule, the pores in phase β do not share any molecules. A detailed analysis of phase β shows that the six molecules forming one pore interact through dipolar coupling, whereas bonding between the pores occurs by metal–ligand interaction (Figure 2f; the metal–ligand bond is marked by the dark blue circle). For more details on the self-assembly of **1** on Au(111), see ref. [21].

Figure 3a shows an overview STM image acquired after deposition of submonolayer coverage of **1** on Cu(111). Small islands with a well-ordered molecular arrangement are visible with a maximum island diameter on the order of 50 nm (Supporting Information, Figure S5). Besides, a disordered arrangement is present, in which the molecules form short rows and pores. The molecules adsorbed on both sides of the step edges on Cu(111) show a high degree of disorder, which is in contrast to what was observed on Ag(111) (see Figures S3b and S4a in the Supporting Information) and Au(111),^[21] on which well-ordered patterns observed at the step edges often led to their restructuring.

We start by discussing the disordered areas on Cu(111), which can be seen in more detail in Figure 3b and in Figure S6 in the Supporting Information. The molecules in the disordered areas tend to form a porous structure. However, most of the pores deviate from a hexagonal shape. In Figure 3b, it is evident that the flat edges of the triangle-like molecules are roughly parallel to each other, but there is a lateral offset between neighbouring molecules (see also Figure S6 in the Supporting Information). This specific molecular arrangement indicates that the molecules interact through dipolar coupling. We assume that the main reason for the missing long-range order is the lattice mismatch between the Cu(111) unit cell and the unit cell of a regular hexagonal porous network formed by dipolar coupling. A strong molecule–substrate interaction prevents a more regular ordering of the molecules, because the

Figure 3. Submonolayer coverage of **1** on Cu(111). a) Overview STM image ($60 \times 60 \text{ nm}^2$, $U = 1.0 \text{ V}$, $I = 18 \text{ pA}$). b) Close-up STM image of a disordered area ($25 \times 10 \text{ nm}^2$, $U = -1.0 \text{ V}$, $I = 18 \text{ pA}$). c) Close-up STM image of an ordered island with the unit cell marked in green ($20 \times 20 \text{ nm}^2$, $U = 1.5 \text{ V}$, $I = 13 \text{ pA}$). The blue lines indicate domain boundaries. d) Tentative model of the molecular arrangement of the close-packed structure with the unit cell marked in green; orange spheres indicate Cu atoms.

molecules tend to maintain their preferred adsorption position and orientation with respect to the substrate.

Close inspection of the ordered islands (Figure 3c) shows that neighbouring molecules have the same orientation. However, some domain boundaries where the molecules are rotated by 180° with respect to their neighbouring molecules are also present (see light blue lines indicating two domain boundaries in Figure 3c). These domain boundaries are mostly stabilized by antiparallel dipolar coupling. Noteworthy, the close-packed islands on Cu(111) are mostly oriented parallel to the close-packed $\langle 1\bar{1}0 \rangle$ direction of the Cu(111) surface. This observation is also confirmed by the LEED pattern, in which no

rotational domains were observed for **1** on Cu(111) (Figure S7 in the Supporting Information).

On comparing the close-packed patterns on Cu(111) with those observed on Ag(111) and Au(111), some subtle differences can be recognized. First, the unit cell on Cu(111) ($1.4 \times 1.4 \text{ nm}^2$) is slightly larger than that on Ag(111) or Au(111) ($1.32 \times 1.32 \text{ nm}^2$). The unit cell dimensions are 5.5 times the nearest-neighbour distance of the Cu(111) substrate (0.255 nm). Thus, we assume that the close-packed network on Cu(111) forms a coincidence lattice,^[27] which can be described by an (11×11) superstructure containing four molecules. Second, the edges of the molecular triangles are slightly rotated away from the unit-cell directions on Ag(111) and Au(111), but they are parallel to the unit-cell directions on Cu(111) (see the tentative structure models in Figure 1c, Figure 2b, Figure 3d and Figure S8 in the Supporting Information). A careful inspection of Figure 3c reveals that the cyano groups in the close-packed network on Cu(111) point towards each other (Figure 3d). As this orientation is energetically unfavorable due to the repulsion between the partially negatively charged N atoms, we assume that the molecular network is stabilized by metal–ligand interaction with native copper atoms. Such coordination bonds between cyano groups and native copper atoms were reported, for example, for cyano-functionalized porphyrin or helicene molecules on Cu(111),^[14,15] Although the coordinated metal atom is generally not visible by STM, enhanced contrast is visible at the position of the coordinated metal atom under specific tunnelling conditions, which is generally assumed to be a signature for metal coordination (Figure S8a in the Supporting Information).^[21,28,29]

X-ray photoelectron spectroscopy (XPS) measurements

To further confirm the assumption of a metal–ligand bonded network on Cu(111) in contrast to a H-bonded/dipolar-coupled network for the phase α on Au(111), we performed XPS measurements of the N 1s region for multilayer and submonolayer coverage of **1** on both Au(111) and Cu(111) (see Figure 4 and Table 1). In the spectra of multilayers on Au(111) and Cu(111), two peaks can be distinguished (Figure 4, top spectra).^[30] The peak at 399.4 eV can be assigned to the nitrogen atom of the cyano group, and its binding energy is comparable to those reported for other cyano-substituted molecules.^[31,32] The peak slightly above 401 eV can be assigned to the central N atom of the triphenylamine unit (Scheme 1). The area ratio of the two N 1s peaks (central N/cyano N) is 1:2.8 on Au(111) and 1:3 on Cu(111), which is close to the theoretical value of 1:3. After deposition of 0.85 ML on Au(111), the same two peaks are observed. However, the peaks show slight shifts towards lower binding energies, which we assign to final-state effects and possible changes in the work function. For this sample, mostly phase α was observed by STM, whereby the molecules undergo dipolar coupling and H-bonding, but no metal coordination. In contrast, for 0.85 ML on Cu(111) a clear shoulder at lower binding energies is observed. This spectrum can only be fitted with three components. The peak around 400.5 eV can again be assigned to the central N atom, and is only shifted

Figure 4. N 1s XP spectra taken on Au(111) (a) and on Cu(111) (b) for multi-layer coverage of **1** [top, 4 ML on Au(111) and 6 ML on Cu(111)] and 0.85 ML of **1** (bottom). The dotted lines indicate the measured data, and the thin black lines represent the fits. The spectrum for multilayer coverage on Cu(111) was multiplied by a factor of 0.2 for better visibility.

Table 1. N 1s binding energies and the ratio of the peak areas for multi-layer and submonolayer coverage of 1 on Au(111) and Cu(111).				
System	NC ₃	E_b [eV]	Ratio	
		C≡N...H	C≡N...Cu	
4 ML/Au(111)	401.3	399.5		1:2.8
0.85 ML/Au(111)	400.6	398.8		1:3.4
6 ML/Cu(111)	401.1	399.4		1:3.0
0.85 ML/Cu(111)	400.5	399.2	397.5	1:1.7:1.4

slightly with respect to the spectrum of the multilayer, similar to what was observed for **1** on Au(111). The peak around 399 eV has a similar binding energy to that at lower binding energy for 0.85 ML of **1** on Au(111) and thus can be related to the N atom of the cyano group undergoing H-bonding or dipolar coupling. The peak at 397.5 eV can be related to a C≡N...Cu metal–ligand interaction. The ratio of the area of the peak at highest binding energy (triphenylamine unit) to that of the two peaks assigned to the cyano N atom is 1:3.1, which is very close to the stoichiometric value. A shift to lower binding energy for metal-coordinated cyano N atoms was reported for tetracyanoquinodimethane (TCNQ) on Cu(100) and for its coordination to Mn. The N 1s binding energy for the metal-coordinated TCNQ is higher (398.7 eV) than that reported here, but the trend is the same.^[31,33] Thus, the XPS data add further evidence for the metal–ligand interaction of **1** with native Cu atoms on Cu(111). Note that, for the sample measured, both the close-packed and the disordered phase were observed by STM. Thus, the peak at 399.2 eV can be assigned to the molecules in the disordered areas, which are mostly stabilized by dipolar coupling.

Computational results

To gain further insight into the molecule–substrate interactions, which seem to play a prominent role in the self-assembly of **1** on coinage-metal surfaces, we performed DFT calculations

including van der Waals interactions with the optB88-vdW functional. The choice of the optB88-vdW functional was based on recent detailed studies of molecular adsorption on several metal surfaces.^[34] The adsorption energies were calculated for three different adsorption configurations for each of the three surfaces investigated. The configurations were chosen in such a way that the inner rings of the molecules coincide with a substrate atom, a bridge or a hollow site. The calculated adsorption energies vary between 2.62 and 2.73 eV for Ag, 2.82 and 3.06 eV for Cu and 2.92 and 3.50 eV for Au. In Table 2 and Figure 5, the most stable adsorption configuration for each surface is reported.

Table 2. Binding energy, arching (Figure S1 in the Supporting Information), shortest distance between the metal atom (M) and the N atom (N) of the cyano group d_{M-N} , overlap of the van der Waals radii $d_{vdW} = d_{M-N} - d_{vdW,M} - d_{vdW,N}$ ^[35] and displacement of the metal atoms (buckling) for Ag(111), Au(111) and Cu(111).

Surface	E_{bind} [eV]	Arching [°]	d_{M-N} [Å]	d_{vdW} [Å]	Buckling [Å]
Ag(111)	2.73	156	2.54	−0.73	0.02
Au(111)	3.50	157	2.58	−0.63	0.04
Cu(111)	3.06	148	2.08	−0.87	0.20

The results of the DFT calculations for a single molecule adsorbed on Au(111), Ag(111) or Cu(111) show strong arching of the molecule, that is, bending of the cyano groups towards the surface, while the methyl groups are rotated away from the surface (see Figure 5 and Table 2). The angle between the two methyl groups is 108°, similar to that obtained from X-ray structure analysis for similar triarylamines.^[20] Additionally, on Cu(111) an out-of-surface displacement of the Cu atom underneath the N atom of the cyano group of approximately 0.2 Å is observed, but neither the Ag nor the Au surface undergoes any noticeable restructuring. The stronger N–Cu interaction is also manifested in stronger overlap of the van der Waals radii of the N and Cu atoms^[35] compared to **1** on Ag(111) or Au(111) (Table 2). Surprisingly, the stronger interaction of the molecule with the Cu surface leads only to a slightly larger binding energy compared to Ag(111), and it is even smaller than for Au(111).^[36] The reason for the lower binding energy on Cu(111) could be that the strong arching and buckling is energy-consuming and consequently the total energy of the most stable configuration is lower than that for Au(111). Note that for calculating the total binding energy, the energy of the flat molecule in the gas phase and of the undistorted surface were used. Furthermore, the unreconstructed gold surface was used in the calculations, which might lead to slightly higher adsorption energy as the stress that is induced in the gold surface due to the missing reconstruction might be partly reduced by the adsorption of the molecule.

Discussion

In the following, we address the remarkable differences in the self-assembled patterns observed for **1** on the three (111)-ori-

Figure 5. Most-stable adsorption configurations of **1** on Ag(111) (a, d), Au(111) (b, e) and Cu(111) (c, f). The side views (d, e, f) show the strong arching of **1**. Colour code: light grey: Ag, yellow: Au, orange: Cu, blue: N, dark grey: C, light pink: H.

ented coinage metal surfaces. Surface-confined molecular self-assembly depends mostly on 1) the mobility of the molecules on the surface, 2) the competition between intermolecular and molecule–substrate interactions and 3) the thermal energy brought into the system.^[3a,9a] Since the molecules were deposited with the samples kept at room temperature and all of the STM measurements shown in the main part of the paper were performed at 77 K, the thermal energy gained by the molecules is similar for the different cases and thus will not be considered further.

It is clear from the STM images that the molecular islands on Cu(111) are considerably smaller than those on Au(111) and Ag(111). This can be explained by taking into account the mobility of the molecules. We assume that the molecules are much less mobile on Cu(111) than on Au(111) and Ag(111), and thus only small islands, less than 50 nm in size, are present for submonolayer coverage on Cu(111). Furthermore, on Cu(111) often domain boundaries in the ordered patches were found, whereas no domain boundaries were observed for the different chiral domains on Au(111) and Ag(111). This is surprising, because different islands probably coalesce during their growth. Thus, the absence of domain boundaries on Au(111) and Ag(111) can be related to higher molecular mobility. Even within the islands, the molecules can easily rotate and translate to adjust to one of the chiralities, whereas on Cu(111) rotation of the molecules seems to be hindered. Similar differences in the mobility and thus in the size and shape of molecular patterns on Cu, Ag and Au have been reported earlier.^[3a,9a,12] For example, the adsorption of submonolayer coverages of metal-free tetraphenylporphyrin molecules at room temperature leads to close-packed patterns on Ag(111), whereas isolated molecules are found on Cu(111) due to the strong interaction

of the iminic N atoms with the copper surface.^[12] Thus, we assume that the reduced mobility and the preference of specific adsorption positions for **1** on Cu(111) due to the strong molecule–substrate interaction compared to Ag(111) and Au(111) is the most important factor determining the size of the islands.

The second factor, the interplay between intermolecular and molecule–substrate interactions, is more difficult to access, especially because different intermolecular interactions are present on the different surfaces. Recently, we reported that **1** can undergo I) H-bonding, II) dipolar coupling and III) metal coordination.^[21] First we compare the bonding motifs I and II for Au(111) and Ag(111). Gas-phase calculations showed that the dipolar coupling motif is slightly more stable than the trimeric motif, and a single H-bond is the least stable.^[21] Besides the similarities of the hexagonally close-packed networks of **1** on Ag(111) and Au(111), for example, the same unit-cell parameters and orientation, some subtle differences in the intermolecular interactions are observed, which we believe to originate from the different molecule–substrate interactions. Although the lattice constants of Au(111) and Ag(111) are similar (4.07 Å for unreconstructed Au and 4.09 Å for Ag), on Ag(111) the molecules interact exclusively through H-bonding, whereas on Au(111) both H-bonding and dipolar coupling interactions are found in phase α . Generally, molecules tend to pack in the densest arrangement possible to reduce the surface free energy. To achieve this goal, different options are possible for the molecules studied. Either all molecules are oriented in the same direction and the hexagonal close-packed network is stabilized exclusively by H-bonding, as observed for Ag(111) in Figure 1 a and c, or the molecules adopt two different orientations (rotated by 180° with respect to each other) and consequently interact through dipolar coupling and H-bonding. The

latter option is the case for the close-packed arrangement on Au(111), as shown in Figure 2a and b. We can only speculate about the reasons why the networks on Ag(111) and Au(111) are formed by different intermolecular interactions. We found that the herringbone reconstruction of the Au(111) surface, which is preserved underneath the molecules, plays a subtle role in the molecular orientation with respect to the surrounding molecules. Specifically, we observed a correlation of the orientation of the molecules with a periodicity similar to that of the herringbone reconstruction.^[21] Thus, we assume that the herringbone reconstruction and more specifically the alternating hcp and fcc sites influence the orientation of neighbouring molecules. This could explain the differences in the bonding motifs on Au(111) and Ag(111) for the hexagonally close-packed patterns, which at first glance are identical. A second significant difference in the structures observed on Au(111) and Ag(111) are the porous superstructures, which were found for less than 1 ML coverage on Au(111), whereas the pattern on Ag(111) did not exhibit any pores, even at low coverages. We assume that the presence of a hexagonally porous structure on Au(111) is also favored by the underlying herringbone reconstruction. Note that the pores are exclusively formed by dipolar coupling interactions, which are also present in the close-packed structure on Au(111), whereas on Ag(111) the molecules interact exclusively through H-bonding.

Besides H-bonding and dipolar coupling, metal-coordination interactions were found on Cu(111) and Au(111). Although there are examples of metal coordination of cyano-containing molecules with native adatoms on Cu(111)^[14,33] and Au(111)^[37] surfaces, to the best of our knowledge metal-coordinated networks on Ag(111) surfaces with native adatoms have not yet been reported. However, recently it was shown that copper phthalocyanine molecules can coordinate to native Ag atoms on an Ag(100) surface.^[38] Furthermore, the coordination of cyano-functionalized molecules to silver atoms in solution in 3D metal-organic frameworks has been reported earlier.^[39] Sirtl et al. showed that the bond dissociation energy of two benzonitrile molecules binding to a silver atom on a silver surface is considerably lower than that calculated for a similar bond involving a copper atom on a copper surface.^[17] Thus, we assume that the lack of metal coordination on Ag(111) is due to a lower bond energy of the CN...Ag bond on the silver surface in comparison to a CN...Cu bond on a copper surface. This is in line with our DFT calculations, which show much stronger bending of the molecule and a larger overlap of the van der Waals radii for the Cu surface compared to the Ag surface (Table 2).

The reduced island size for **1** on Cu(111), the buckling of the first metal layer and the distortion of the molecules indicate that the molecule-substrate interaction for Cu(111) is the strongest, while it is the weakest for Ag(111). This contradicts the binding energies calculated by DFT (see Table 2), for which the following sequence is observed: Ag < Cu < Au. This example shows that one must be careful when comparing solely binding energies obtained from DFT calculations. First, a strong interaction, which leads to distortion of the molecule and of the surface, can result in too small a total binding

energy, as is the case for **1** on Cu(111), because the energy that is consumed by surface restructuring and buckling of the molecules is not taken into account in the DFT calculations. Second, the calculations for a Au(111) surface must always be carried out with care, because neglect of the herringbone reconstruction leads to additional stress in the gold surface be decreased by adsorption of molecules, resulting in too high a binding energy. Last but not least, our calculations were done for isolated molecules, that is, not considering intermolecular interactions. It is possible that the arching of the molecules is reduced if they undergo dipolar coupling or H-bonding. However, the arching of a single molecule, the displacement of the underlying Cu metal atom and the overlap of the van der Waals radii provide additional insight into the molecule-substrate interactions and help in the interpretation of our experimental observations.

Conclusion

We studied the self-assembly of cyano-functionalized, planarized triarylamine derivative **1** for submonolayer to monolayer coverage on coinage metal surfaces. Three different intermolecular interactions—dipolar coupling, H-bonding and metal coordination—were found. On Ag(111), independent of the coverage, a hexagonally close-packed phase in which the molecules interact exclusively through H-bonding exists. In contrast, on Au(111) two well-ordered phases stabilized by all three possible bonding motifs were observed for submonolayer coverage. On Cu(111), only small patches of ordered molecules stabilized by metal coordination exist together with areas of disordered molecules, which interact mostly by dipolar coupling.

We suggest that the molecular mobility and molecule-substrate interaction are mainly responsible for the structure formation, while the intermolecular interaction (with the three different available bonding motifs) helps to adapt to the specific molecule-substrate interactions. The strong interaction of the cyano group with the copper surface leads to a displacement of the copper atom underneath the N atom and strong arching of the molecule. We propose that the differences in the intermolecular interactions observed on Au(111) compared to Ag(111) for the close-packed structures are related to the herringbone reconstruction, which leads to subtle differences in the molecule-substrate interactions on Au(111) compared to Ag(111).

Experimental and theoretical details

Experimental details

Materials and general methods: Reagents were purchased at reagent grade from Acros and Sigma-Aldrich and used without further purification. Analytical TLC was performed on aluminium plates coated with 0.20 mm silica gel containing a fluorescence indicator obtained from Macherey-Nagel; visualization was performed with a UV lamp (254 or 366 nm). Column chromatography was performed on silica gel (230–400 mesh). The synthesis of 2,6,10-tribromo-4,4,8,8,12,12-hexamethyl-4*H*,8*H*,12*H*-benzo[1,9]qui-

nolizino[3,4,5,6,7-*defg*]acridine (**2**) was performed according to the literature procedure.^[20] Melting points were determined in open capillaries with a Büchi M-560 melting-point apparatus. ¹H and ¹³C NMR spectra were recorded with Bruker Avance 300 and 400 spectrometers and referenced to the residual solvent signal as internal reference (¹H: CD₂Cl₂ 5.32 ppm; ¹³C: CD₂Cl₂ 53.8 ppm). Chemical shifts are reported in parts per million (ppm) relative to the signal of TMS. IR spectra were recorded with a 660-IR (Varian, ATR mode) spectrometer. UV/Vis measurements were performed with a Cary 5000 UV/Vis/NIR (Varian) spectrophotometer in a quartz cuvette (1 cm) at room temperature. High-resolution mass spectra were obtained with a MicrOTOF II (Bruker, HR-ESI-MS) mass spectrometer at the Institute of Organic Chemistry, University Erlangen-Nürnberg.

4,4,8,8,12,12-Hexamethyl-4H,8H,12H-benzo[1,9]quinolizino[3,4,5,6,7-*defg*]acridine-2,6,10-tricarbonitrile (1**):** A mixture of **2** (70 mg, 0.12 mmol) and CuCN (177 mg, 1.98 mmol) in dry *N*-methyl-2-pyrrolidone (5.0 mL) was heated at 180 °C for 72 h. After cooling to RT, the mixture was diluted with H₂O (50 mL), adjusted to pH 2 with aqueous HCl (1 M) and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic layers were washed with H₂O (3 × 20 mL), dried (MgSO₄) and filtered, and the solvents were removed in vacuo. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to afford **1** (41 mg, 77%) as a white solid. *R*_f = 0.46 (SiO₂, CH₂Cl₂); m.p. 232 °C (decomp); ¹H NMR (300 MHz, CD₂Cl₂): δ = 1.63 (s, 18H), 7.72 ppm (s, 6H); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 33.13, 36.20, 108.66, 119.48, 128.52, 131.61, 134.56 ppm; IR (neat): $\tilde{\nu}$ = 2966 (w), 2923 (w), 2200 (m), 1597 (w), 1428 (s), 1288 (s), 1174 (m), 1092 (m), 1019 (m), 872 (m), 799 cm⁻¹ (s); UV/vis (CH₂Cl₂): λ_{max} (ϵ) = 257 (72700), 313 (59600), 349 (sh, 87500), 356 nm (90900 M⁻¹ cm⁻¹); HR-ESI-MS: *m/z* calcd for C₃₀H₂₄N₄Na⁺ [*M*+Na]⁺: 463.1899; found: 463.1904.

Sample preparation and measurements: All experiments were performed under ultrahigh vacuum (UHV). The metal single crystals purchased from MaTeck were cleaned by repeated cycles of argon-ion bombardment (1–1.5 keV) and subsequent annealing to 400 °C for Ag(111) and Au(111) and 450 °C for Cu(111). The molecules were sublimed in situ onto the single crystals held at room temperature. The evaporation rate, which was between 0.3 ML min⁻¹ and 0.7 ML min⁻¹, was monitored by means of a quartz crystal microbalance. The STM experiments were performed in a two-chamber UHV system equipped with a sample preparation chamber, containing an MCP LEED (Omicron NanoTechnology) and a second chamber housing a commercially available STM (Omicron NanoTechnology). All STM images were acquired at 77 K, unless otherwise stated, with a mechanically cut Pt/Ir wire in constant-current mode. The tunnelling bias is given with respect to a grounded tip. WSxM was used to analyse the STM images.^[40] The XPS experiments were performed in a separate UHV system equipped with a preparation chamber and an analysis chamber containing an Al_{Kα}/Mg_{Kα} twin-anode X-ray gun and a hemispherical energy analyzer (Thermo Fisher). The analysis chamber also houses LEED optics (SPECS) and a commercially available STM (Omicron NanoTechnology), which was used at room temperature to calibrate the coverage before the XPS experiments were performed. Al_{Kα} X-rays with a photon energy of 1461.6 eV were used for the XPS measurements. The Cu 2p_{3/2} and Au 4f_{7/2} peaks at 932.6 and 84.0 eV, respectively, were used for binding energy calibration.^[41]

Theoretical details

All calculations were carried out within the DFT framework, as embedded in the Vienna ab initio Simulation Package (VASP).^[42] The

calculations were performed by using the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE)^[43] as well as by including the non-local interactions through the self-consistent van der Waals DFT (optB88-vdW)^[45] functional as implemented in the VASP package.^[44] The interaction between the valence electrons and ionic cores was described by the projector augmented wave (PAW) method.^[45] A kinetic-energy cutoff of 400 eV was used for the wave functions. The adsorption on Ag(111), Au(111) and Cu(111) surfaces was simulated by placing the molecule on one side of a (6 × 6) slab containing three layers with 19 Å of vacuum separating the two surfaces. A *k*-point mesh of 3 × 3 × 1 was used for these calculations. During the structural optimization, the atoms of the molecule and the first-layer substrate atoms were allowed to relax. The bottom two layers of the substrate were kept fixed. The relaxation was done with a 0.01 eV Å⁻¹ force criterion. The adsorption energies of three different adsorption configurations were evaluated, and only the most stable configuration is reported in the text.

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