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Assembling Isostructural Metal–Organic Coordination Architectures on Cu(100), Ag(100) and Ag(111) Substrates

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Supramolecular architectures at surfaces offer an efficient and effective method for patterning of nanometer-scale structures with molecular-level accuracy and long-range order.^[1–4] Non-covalent metal–organic nanoarchitectures are a topic of growing interest due to the structural and chemical variety of systems that can be generated in 2D networks^[1,5–8] or 1D chains,^[9,10] stabilized by bonding that is analogous to 3D solution-based coordination systems.^[11] A strategy developed recently for surface patterning is to deposit organic ligands and metal centers which self-assemble into highly-ordered lattice networks stabilized by metal–organic coordination interactions.^[1,2,12] A general question for these systems is how much of the structural order is actually due to the coordination interaction within the organic layer and how much can simply be attributed to templating by the single-crystal metal substrate. A recent example showed a two-fold Cu–pyridyl coordination system where the substrate interaction was sufficient to destabilize the in-plane coordination bonding in the case of a poor match between the substrate lattice and ligand length. We explore this competition by comparing the growth of a metal–organic coordination network using similar Cu–N bonding, but with a higher coordination number, in three substrate environ-

ments. We demonstrate herein that by selecting a sufficiently strong metal–organic coordination motif, a robust two-dimensional nanoarchitecture can be assembled with a nearly identical structure on Cu(100), Ag(100), and Ag(111) substrates, which differ significantly in surface symmetry and lattice constant.

The competition between intra-network forces (e.g. molecule–molecule and molecule–metal interactions) and network–substrate interactions (e.g. molecule–substrate and metal–substrate interactions) is a critical issue in the formation of these two-dimensional networks.^[13] Depending on the relative strength of these interactions, effective self-assembly of coordination architectures can either be severely hindered or structurally guided. In the limit of the strong adsorbate–substrate interaction, the resulting nanostructure is completely determined by templating of the substrate and can change dramatically when the same molecular components assemble on a different substrate or when molecules with the same interaction sites, but of different sizes assemble on an identical substrate. In a recent study, bipyridyl molecules,^[9] differing in length by only one phenyl ring, exhibited completely different growth dynamics under identical surface and growth conditions. The differences in growth were attributed to commensurability of the 1D coordination structure to the substrate. In that case, the coordination interaction was too weak to compensate for a less-than-ideal commensurability situation and so the thermal excitations at room temperature were able to destabilize the coordination architecture.

In the opposite limit of strong inter-adsorbate interaction compared to adsorbate–substrate interaction, the resulting structure is determined by interactions between adsorbates.^[14] However, the substrate interaction may still lead to specific growth directions on the surface and some distortion of the network structure. For example, Stepanow et al.^[15] studied three dicarboxylic acid molecules coordinated with Fe at a Cu(100) surface. They found similar 2D coordination structures for each molecule, which differed in length from 7 to 16 Å. Templating effects from the substrate were determined to play a significant role in the final 2D supramolecular structures of those systems. Surface studies of a series of NC–(phenyl)_x–CN molecules ($x=3–5$)^[7,16] found three-fold coordination of the ligand cyano groups at Co centers, which resulted in honeycomb structures at the Ag(111) surface at low temperatures. These examples have addressed issues related to the commensurability of surface structures with substrate lattices by studying coordination systems of similar structure based on molecules of different size on an identical substrate.

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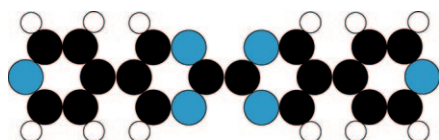
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Herein, we illustrate a metal–ligand coordination system which produces the same supramolecular structure on three different substrates: Cu(100), Ag(100) and Ag(111). We demonstrate that in a 2D architecture composed of the novel ligand 5,5'-bis(4-pyridyl)(2,2'-bipyrimidine) [PBP, Scheme 1] coordinated to Cu adatoms in a three-fold geometry, commensurability differences with the substrate can be compensated through a slight distortion of coordination configuration, producing similar network structures on substrates with different surface sym-



Scheme 1. 5,5'-bis(4-pyridyl)(2,2'-bipyrimidine) [PBP]. Color legend: N (blue), C (black), and H (white).

metries and lattice constants. Compared to the case of the 1D chains stabilized by two-fold Cu–N coordination, this three-fold coordination bonding is robust and nearly identical on the three substrates examined. The ligand PBP was synthesized by reacting 5,5'-dibromo-2,2'-bipyrimidine and 4-pyridineboronic acid under Suzuki cross-coupling conditions.

Upon adsorption at room temperature on Ag(111) or Ag(100), the PBP molecule self-organizes into a dense row structure (Figures 1a and c, respectively), even for submonolayer coverages. The rows pack closely together on the substrate and seem to be stabilized by an intermolecular electrostatic or hydrogen bonding-like interaction of the type C–H...N,^[14,17] as illustrated in the suggested model drawn in Figure 1b. On the Ag(111) substrate, high-resolution STM images clearly resolve the individual molecules in this dense structure. The separation between the parallel rows of alternating molecule orientation is 13.4 Å (---- in Figure 1b) and the spacing of the molecules along the row in the direction of the row is 8.0 Å. The molecule axis is rotated 50° from the chain

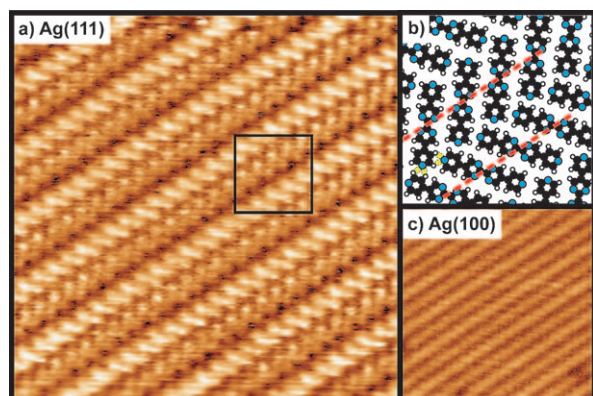


Figure 1. PBP on a) Ag(111) and c) Ag(100) forming close-packed rows. A model of the molecular packing on Ag(111) is shown in b) with (----) to guide the eye along the molecular rows and yellow highlighting in lower left to indicate potential hydrogen-bonding. STM images are a) 18.0 nm × 18.0 nm and c) 17.4 nm × 17.4 nm.

direction. Alternating rows are related by a reflection and a 180° phase translation along the row direction, which allows for hydrogen bonding at the pyridyl head group of each molecule to the side of the pyridyl ring of a molecule in a neighboring row. The orientation of the ribbons is observed in 60° separations, indicating alignment along the low-symmetry directions of the 2D C₃-symmetric Ag(111) surface. A very similar structure is observed on the Ag(100) substrate (with domain rotations of 90° on that C₄-symmetric substrate), with the alternating 1D molecule ribbons separated by 14.0 Å (Figure 1c).

Addition of Cu atoms to the PBP molecules at either of the silver surfaces allows the formation of an open network lattice as shown in Figures 2a and b for Ag(100) and Ag(111), respectively. The sample was held at room temperature while Cu atoms were evaporated onto the surface which already had a sub-monolayer PBP coverage, then the sample was annealed at 400 K for several minutes. The 2D metal-organic coordina-

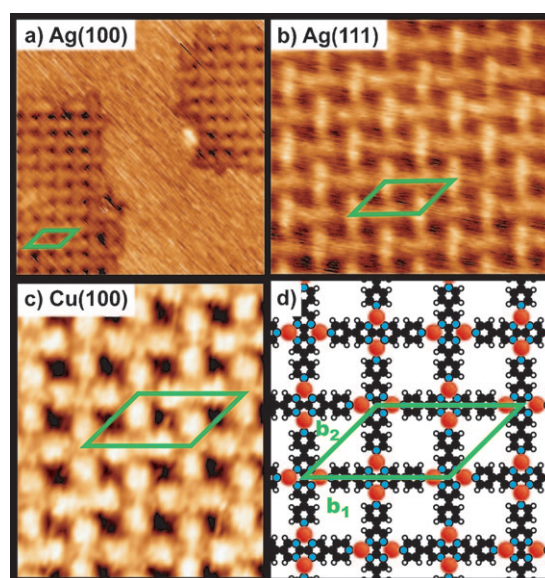


Figure 2. STM images of PBP–Cu two-dimensional coordination networks formed at the a) Ag(100), b) Ag(111), and c) Cu(100) surfaces. A molecular model of the coordination structure is shown in (d). The structural unit cell is highlighted by a green parallelogram in each panel and is defined in Table 1. The STM images are a) 15.0 nm × 16.0 nm, b) 10.8 nm × 10.1 nm, and c) 5.2 nm × 6.3 nm in size.

tion produces an open two-dimensional network structure (see Figure 2a). The molecules form a brick-wall-like pattern with each molecule having a Cu atom at each of the side coordination locations located near the molecule center (see Figure 2d). Two additional Cu atoms coordinate at the pyridyl end groups of the molecule. This leads to a 2D coordination structure where each Cu atom is coordinated by three N atoms from two different molecules and each molecule is coordinated to four Cu atoms—two in a bidentate bonding at the molecule equator and two at the molecule ends. Two-dimensional Cu–pyridyl coordination at surfaces has been reported previously in similar trigonal-planar geometries,^[6] and in other geometries and coordination numbers.^[3,8,9] The unit cell is

drawn as a green parallelogram in Figure 2, with one lattice vector aligned with the axis of one of the two PBP molecules in each unit cell.

In the absence of Cu atoms on the Ag substrates, the molecules pack into dense islands through hydrogen bonding, which are stable at room temperature (as seen in Figure 1). Upon addition of Cu atoms on the Ag substrates, the open network structure (Figures 2a and b) forms immediately. It is clear that the presence of Cu is necessary for this transition to occur. These experiments provide evidence for Cu-N coordination in this structure. This also demonstrates that the interaction is selective, in that it requires Cu for formation and does not accept Ag adatoms [from, e.g., the step edges on Ag(100)] as effective coordination centers.

Evaporation of the molecule onto the Cu(100) substrate allows for the same open lattice network structure to form (Figure 2c). In this case, evaporation of Cu to the surface is not necessary, as sufficient Cu adatoms are available by 2D evaporation from the substrate step edges to engage with the PBP molecules in 2D supramolecular coordination.^[9] Coordination islands of limited size (~5–8 nm) are already formed at room temperature. Annealing to higher temperature gives progressively larger domains: after annealing at 400 K, the domains are approximately 15 nm in size, and after annealing at 475 K (Figure 2c), the network domain size is comparable to the size of the atomic terraces on the Cu(100) surface (more than 100 nm wide).

In Table 1 we list the lattice spacing for the three substrates as well as the related unit cell vectors for the PBP–Cu network overlayer. The structures have been inferred from STM determination of the island rotation and measurement of the periodic spacing in the networks. In the case of the Ag(100) and Ag(111), the observed spacing is very close (within statistical deviation) to a commensurate surface growth, which is the structure described in Table 1 and Figure 3. Commensurate growth is consistent with the large domain formation and absence of strain boundaries in the networks. On the Ag(100) surface, the molecule axis is oriented in the [010] direction. We

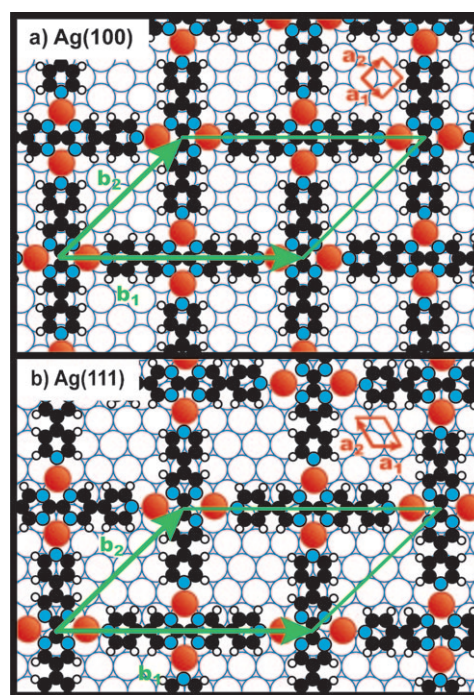


Figure 3. Schematic model of PBP–Cu coordination network structures on a) Ag(100) and b) Ag(111), inferred from STM measurements. Network orientation and periodic spacings determined from STM data are in close agreement to these models, which allow for structures commensurate with the substrate. Basis vectors of the unit cell of the substrate (red) and network (green) are related by the matrices given in Table 1.

also note that there is a close match between the hollow site separation (4.09 Å) along this direction and the distance between the centers of the aromatic pyridine or bipyridyl rings of the molecule (4.16–4.20 Å). The network is perfectly square with no distortion. Only one network domain orientation is observed, consistent with the symmetry of the substrate.

In the case of Ag(111) we still observe a nearly square lattice in spite of the C₃ symmetry of the substrate (Figure 2b, Figure 3b). Measurement of many STM micrographs indicates that actually this is a slightly rectangular lattice with pore side lengths of 12.4 ± 0.2 Å and 12.7 ± 0.1 Å as measured by STM (average values of measurements over large network domains from many STM images). The coordination structure has been stretched slightly and the spacing value matches very well to integral multiples of the substrate atomic rows in the [0 1 $\bar{1}$] direction and to a $2 \times$ high-commensurate structure in the [$\bar{2}$ 1 1] direction. The coordination structure is therefore strained, but still robust enough to maintain the same general coordination scheme and to produce a coordination architecture with long-range order at the substrate. Three different orientations of the network are observed in the STM results, consistent with the symmetry of the substrate.

The network structure on the Cu(100) surface is nearly perfectly square. There is a small ($\sim 4^\circ$) shear distortion from a perfectly square lattice in order to accommodate agreement to the substrate structure and dimensions. Eight rotational domains of the structure are observed by STM which are separat-

Table 1. Substrate lattice constant for the three single-crystal metal substrates used herein and the basis vectors for the PBP–Cu coordination network on each substrate. Unit cell basis vectors, \mathbf{b}_1 and \mathbf{b}_2 , are sketched in Figure 3 and were chosen so that \mathbf{b}_1 is parallel to the axis of one of the two PBP molecules per unit cell. The orientations of \mathbf{b}_1 with respect to the substrate are listed in the last column.

Substrate	Nearest neighbor distance $ \bar{a} $	Supramolecular network basis vectors	Molecule axis direction (\mathbf{b}_1)
Ag(100)	2.89 Å	$\begin{pmatrix} \bar{\mathbf{b}}_1 \\ \bar{\mathbf{b}}_2 \end{pmatrix} = \begin{pmatrix} 6 & 6 \\ 6 & 0 \end{pmatrix} \begin{pmatrix} \bar{\mathbf{a}}_1 \\ \bar{\mathbf{a}}_2 \end{pmatrix}$	[0 1 0] or [0 0 1]
Ag(111)	2.89 Å	$\begin{pmatrix} \bar{\mathbf{b}}_1 \\ \bar{\mathbf{b}}_2 \end{pmatrix} = \begin{pmatrix} 9 & 0 \\ 7 & 5 \end{pmatrix} \begin{pmatrix} \bar{\mathbf{a}}_1 \\ \bar{\mathbf{a}}_2 \end{pmatrix}$	[0 1 $\bar{1}$], [1 0 $\bar{1}$], or [1 $\bar{1}$ 0]
Cu(100)	2.55 Å	$\mathbf{b}_1 = 23.0$ Å, $\mathbf{b}_2 = 16.2$ Å, $\mathbf{b}_1 \nrightarrow \mathbf{b}_2 = 41^\circ$	$\pm \sim 10^\circ$, $\pm \sim 30^\circ$ from [0 1 0] or [0 0 1]

ed by $\pm 10^\circ$ or $\pm 30^\circ$ from the low symmetry [010] and [001] directions. The many domain orientations and lattice distortion indicate that there is not a simple match of the network structure along the low symmetry directions of the surface.

A nearly identical metal-organic coordination structure is produced on the three substrates with different lattice constant and surface symmetry. This indicates clearly that in this 2D coordination system, stabilized by a three-fold trigonal planar coordination scheme, the coordination interactions are sufficiently strong to compete with substrate interactions. In addition, the three-fold coordination also shows flexibility, that is, it can tolerate a slightly distortion in bond length and angle to cope with the substrate commensurability.

In our previous study of 1D chain formation from bipyridyl-Cu coordination,^[9] the coordination interaction was quite weak. Chains formed from 1,4-bis(4-pyridyl)benzene (11.3 Å in length) were *meta*-stable at room temperature (coexistence with lattice gas phase) and the longer 4,4'-bis(4-pyridyl)biphenyl (15.5 Å) did not form stable chains, except at low temperatures. The weak coordination interaction there compared to the present case can be considered in terms of the modified coordination interaction. By inclusion of the bipyrimidine segment in the central part of the molecule here, we increase the Cu:N coordination number in the 2D network from two to three to stabilize a coordination structure independent of the substrate. The strong but flexible coordination interactions allow small modifications of the network structure to adapt to the substrate rather than instability of the network or a transition to a different structure or ordering.

We have shown the assembly of a metal-organic coordination system with sufficient intra-network interaction to overcome differences in substrate structure and symmetry. By using three-fold N–Cu coordination interactions, an isostructural open square network structure is stabilized at three different substrates. The fine details of the structure adapt appropriately to maintain the same coordination geometry and general network structure on Cu(100), Ag(100) and Ag(111). Such nanopatterning of surfaces by supramolecular self-assembly allows excellent structural control and can be of use for growth templates and designed surface functions. This study demonstrates that strong intra-network coordination with a high degree of robustness and stability can form isostructural supramolecular networks at different surfaces.

Experimental Section

All experiments were conducted in ultra-high vacuum chambers with base pressures in the low 10^{-10} mbar range. Sample preparation and scanning tunneling microscopy (STM) measurements were made *in situ*. The Cu(100), Ag(100), and Ag(111) substrates were cleaned by cycles of Ar⁺ sputtering and annealing to 800 K (Cu substrate) or 850 K (Ag substrates). The organic molecule 5,5'-bis(4-pyridyl)(2,2'-bipyrimidine) [PBP, Scheme 1] was evaporated from a Knudsen-type crucible at 465 K onto the metal substrate, which was held at room temperature. In some experiments on the Ag substrates, Cu was subsequently evaporated from a high purity Cu rod by heating with electron-beam bombardment. After deposition, the samples were annealed at 400 K, unless noted other-

wise, for several minutes. STM measurements were made *in situ* at room temperature, except most of the STM imaging on Ag(111) was done using a low temperature (5 K) STM. The pure PBP growth structure on Ag(111) was also verified in room temperature STM experiments.

Synthesis of 5,5'-bis(4-pyridyl)(2,2'-bipyrimidine) [PBP]: A solution of 1,4-dioxane (100 mL) and 2 M Na₂CO₃ (10 mL) was taken in a clean 250 mL flask and N₂ gas was bubbled through the solution for 10 min. To this solution 5,5'-dibromo-2,2'-bipyrimidine^[18] (0.318 g, 1 mmol), 4-pyridineboronic acid (0.350 g, 2.85 mmol), and Pd(PPh₃)₄ (0.165 g, 0.143 mmol), were added and heated to reflux at 125 °C for 24 h. The solvent was evaporated and the crude solid was extracted with water/CHCl₃ mixture in a separating funnel. The chloroform-soluble unreacted 4,4'-dibromobipyrimidine was separated and the insoluble precipitate found in the interface between the water and CHCl₃ layer was filtered and washed with diethyl-ether to give analytically pure compound of PBP (yield 0.250 g, 80%) without any chromatographic purification. Further purification was carried out by sublimation at ~350 °C under 0.3 mbar pressure to isolate white powder. ¹H NMR (300 MHz, [D₆]DMSO, 25 °C): δ = 9.5 (s, 4H, bipyrimidine), 8.8 (d, 4H, ³J_{H,H} = 4.71 Hz, pyridine), 8.03 (d, 4H, ³J_{H,H} = 4.49 Hz, pyridine) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3026 (s), 1594 (s), 1521 (ms), 1423 (vs), 1376 (s), 1320 (ms), 1130 (s), 1050 (broad), 822 (s), 777 (s), 769 (s), 668, 647, 639, 569, 471 cm⁻¹ (broad). The molecular structure of PBP was determined by single-crystal X-ray analysis (see the Supporting Information). CCDC 287407 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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