Supramolecular Networks

Ordering and Stabilization of Metal–Organic Coordination Chains by Hierarchical Assembly through Hydrogen Bonding at a Surface**

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Self-organization of organic molecules into supramolecular networks is an efficient strategy for nanometer-scale patterning of surfaces.[1–6] Specific supramolecular architectures can be designed by choosing molecular building blocks with distinct size, geometry, and bonding interaction, as has been demonstrated extensively in solution-based coordination chemistry[7–10] and, in recent years, on surfaces.[11–15] The technological potential of controlled structural and chemical patterning of surfaces has driven an interest in the rational design of highly ordered and regular networks at solid surfaces, which require selective and directional bonding interactions, such as hydrogen bonding[16–18] or metal–organic coordination.[11,13,19,20] Reversible (noncovalent) bonding motifs allow for efficient error-correction during the growth process and long-range structural order in the resulting supramolecular architecture.[11]

One-dimensional (1D) copper–pyridyl coordination chains at surfaces were demonstrated recently using low-coordination (twofold) copper–pyridyl bonding, and resulted in metastable chains on a Cu(100) surface at room temperature with random spacing between neighboring copper–pyridyl rows and irregular chain lengths.[21] Although some supramolecular 1D systems have a regular arrangement because of substrate mediation,[22] these copper–pyridyl

chains, as well as other 1D supramolecular systems, do not exhibit regular interchain distances or chain lengths, and have limited stability at room temperature.[21,23–25] The ability to produce well-ordered, self-assembled nanostructures, that have a 1D character, at surfaces is highly desirable. Herein, we report a strategy for long-range ordering and stabilization of 1D coordination systems at surfaces by cooperative assembly with an additional molecular species by a secondary (hierarchical) interaction.

Linear polyaromatic bipyridine molecules **P1** and **P2** (Scheme 1), are known to self-assemble into 1D supramolec-
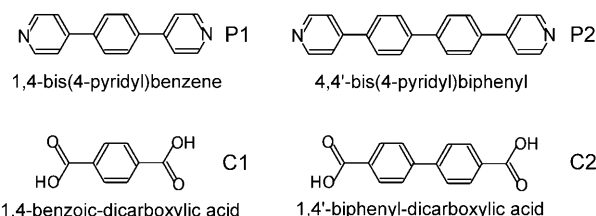
Scheme 1. Polyaromatic bipyridine molecules, **P1** and **P2**, and bis(carboxylic acids), **C1** and **C2**.

ular chains on a Cu(100) surface.[21] The pyridyl groups coordinate to Cu adatoms, of which a sufficient population forms on the Cu(100) surface at room temperature by 2D evaporation from the substrate atomic step edges.[26,27] Steric limitations imposed by the substrate result in 1D chains with twofold metal–ligand coordination. However, these chains exhibit thermal instability at room temperature and are distributed randomly on the surface, that is, with irregular interchain distances and random chain length. Only at high surface coverage is there a regular interchain spacing, apparently owing to a substrate-mediated repulsive interaction.[21] It is desirable to gain better control, that is, rational design, of supramolecular systems for bottom-up patterning of surfaces, especially for such 1D systems; the objective is to improve both the room-temperature stability of the chains, as well as the regularity of chain length and interchain spacing. One way of improving the ordering of 1D supramolecular chains on a surface is to first pattern the surface chemically with 1D anisotropy.[28,29] Another possible route, which does not require a specific surface-modification step, is to design the molecular system with a hierarchical bonding motif,[30] employing multiple ligand species and bonding motifs to enable access to a greater level of structural and functional complexity.[31]

Herein, we demonstrate improved stability and ordering of these 1D coordination chains, by cooperative assembly

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with a second molecular species through hydrogen bonding. As a consequence of the multicomponent approach, two orthogonal geometric parameters, along the pyridyl chain and between adjacent chains, can be tuned independently. The second species used to order the copper–pyridyl chains is a linear bis(carboxylic acid), **C1** or **C2** (Scheme 1). The molecules are sequentially vapor-deposited on a Cu(100) surface at room temperature, annealed at 410 K, and then investigated by scanning tunneling microscopy (STM) at room temperature. Carboxylic acids **C1** and **C2**, alone on the Cu(100) surface, both form thermally stable 2D hydrogen-bonded networks,[17,32] but coordination interactions with Cu adatoms of the substrate do not occur. The carboxylate groups of these molecules deprotonate during the adsorption or subsequent annealing,[17,33] leaving a net negative charge on the functional groups and enabling the electrostatic (hydrogen-bond-type) interactions to stabilize the homoligand phases[13] and other bonding, as described below.

Deposition of both **C1** and **P1** onto the surface results in a highly ordered supramolecular structure, as shown in Figure 1. The left side of Figure 1a shows the pyridyl species **P1** in 1D coordination chains along the [011] substrate direction. They are interconnected by a hydrogen-bonding-type interaction (dashed lines in Figure 1b) with the carboxylate molecules **C1**, resulting in a thermally robust architecture. Morphological changes in the supramolecular structures, that is, changes in domain edges indicating attachment/detachment of molecules, are not observed by STM sequences on the time-scale of one hour, in spite of the low Cu coordination number of two. That stability is in sharp contrast

to the copper–pyridyl chains alone (i.e., without **C1**), which varied significantly on a time-scale of minutes at room temperature, owing to the reversibility of coordination and the coexistence of the 1D-coordination chain phase with a 2D lattice gas of molecules on Cu(100).[21] A tentative molecular model of the cooperative assembly phase is displayed in Figure 1b and described in more detail in the Supporting Information.

Although the cooperative assembly with the carboxylate molecule **C1** (Figure 1) stabilizes the pyridyl rows, it does not disrupt its internal structure. That is, the structure of the copper–pyridyl coordination chains in the **P1/C1** mixture is identical to that without ligand **C1**—the orientation on the substrate as well as the segment periodicity $x = [(15.2 \pm 0.2)$ Å] (measured by STM) along the chains are identical with the spacing and orientation for the pure Cu-coordinated bipyridyl chain phase.[21] The bipyridyl chains are bridged by two **C1** molecules per **P1** ligand, which determine the regular interchain distance $y = [(15.2 \pm 0.2)$ Å] (measured by STM). Both the segment spacing along the rows and the distance between neighboring chains are six-times the surface lattice constant $d = 2.55$ Å of Cu(100) (see Figure 1b). On the right side of Figure 1a, a homotopic network of **C1** (next to the **P1/C1** mixture) forms, owing to an excess of **C1** in this experiment. In both the homotopic network and the bridged chain assembly, **C1** molecules pack along the [011] direction of the substrate with an intermolecular distance of $3d$. Both species of molecule keep the same periodicity and orientation relative to the substrate as in their homotopic supramolecular networks. Thus, the **P1/C1** architecture represents a cocrystallization of the coordination-stabilized phase of **P1** and the hydrogen-bonding phase of **C1**, which is apparently commensurate with the substrate. In contrast to the recent report of cocrystallization in purely hydrogen-bonded molecular assemblies at surfaces,[34] the system reported herein relies on hierarchical organization which utilizes coordination bonding along the 1D chains and hydrogen bonds between the chains.

The high degree of ordering over large areas is shown in the STM topograph of a typical **P1/C1** assembly (Figure 2).
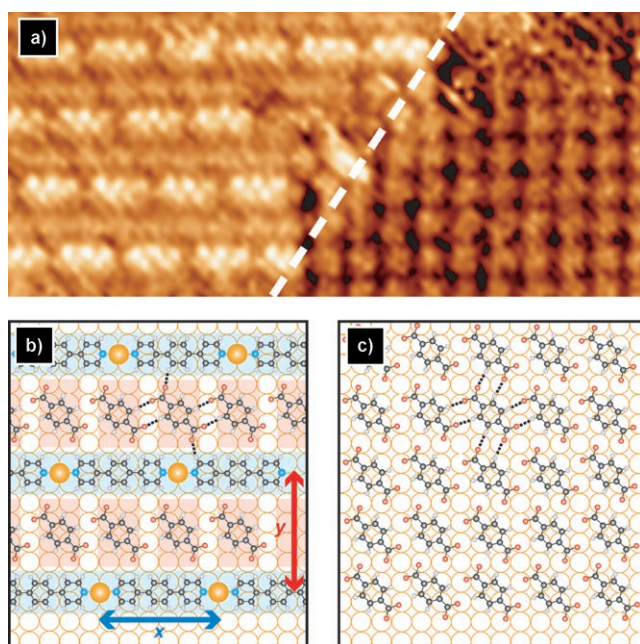
Figure 1. a) High-resolution STM topograph (140 Å × 63 Å) of the self-organized **P1/C1** cocrystallization phase (left side) with the homotopic **C1** network adjacent (right side). b) Molecular structural model of the copper-coordinated bipyridine rows bridged by bis(carboxylate) molecules through hydrogen bonding (dashed lines). c) Schematic model of the hydrogen bonded **C1** network. See text for details. Cu yellow, N blue, O red.[13]

Figure 2. STM overview (650 Å × 400 Å) displaying extended and highly ordered domains of thermally stable **P1/C1** mixed phase. Two rotational domains (90° separation based on substrate symmetry) are seen here separated by a single atomic step in the Cu(100) substrate.

Based on this image and many other STM images, we find the **P1/C1** system to have typical domain sizes in the range 50-80 nm, usually limited by the size of the substrate terraces. Highly regular rows of 1D-coordinated bipyridines can be assembled using the multicomponent approach, with a well-defined spacing in extended domains and thermal stability at room temperature. The cooperative assembly builds up on two distinct levels of interaction leading to structural hierarchy in the system. The 1D character of the assembly is defined by the copper–pyridyl coordination motif while the thermal stability and ordering of the rows is determined by the carboxylate hydrogen-bonding motif.

Owing to the selective nature of the bonding interactions, the geometric parameters x and y (Figure 1 b) can be tailored independently by variation of the backbone size of the appropriate molecular species. This concept is tested experimentally by replacing the bipyridine or the carboxylic acid with a molecule incorporating the same functional group, but a different backbone length (**P2** and **C2**, in both cases an additional phenyl ring is inserted, see Scheme 1). Figure 3 a
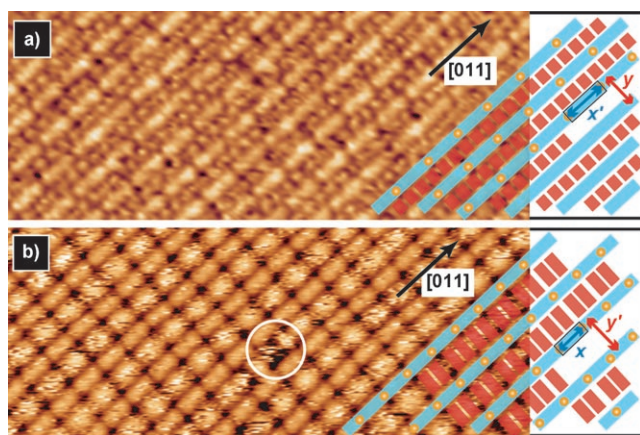

Figure 3. STM topographs (250 Å × 100 Å) of the hierarchical assembly of a) **P2/C1** and b) **P1/C2** (with missing **C2** defect circled). These mixtures demonstrate the possibility of tuning the geometric parameters x and y (see Figure 1 b) independently by modular replacement of the molecular building blocks.

shows the STM topograph of the assembly of a mixture of **P2/C1** and Figure 3 b the assembly of **P1/C2**. In both cases, the self-organization of the molecules results in highly ordered structures, which are thermally stable at room temperature and form large, uniform domains (see the Supporting Information). Extended Cu–**P2** coordination chains do not form at room temperature,[21] so the room-temperature stability gained here by the addition of the **C1** ligand is especially significant. As for the **P1/C1** mixture, the pyridyl ligands form 1D copper-coordinated chains along the [011] direction of the substrate, which are interconnected by the carboxylate species. Compared to the **P1/C1** mixture described above, the **P2/C1** mixture exhibits a longer segment spacing along the copper–pyridyl coordination rows ($x' = 19.6$ Å), which matches the segment spacing for the Cu–**P2** chains reported previously.[21] Although this chain segment spacing is not commensurate to the substrate lattice the

stability of the system is maintained by the interactions with the **C1** ligand. In the **P1/C2** case the longer carboxylic acid results in a larger separation between neighboring bipyridine chains ($y' = 20.4$ Å). The distance y' matches exactly the spacing in the pure **C2** network phase for bridging carboxylate molecules[32] and suggests commensurability with the substrate ($8d = 20.4$ Å).

In summary, we have demonstrated the concept of stabilizing and ordering 1D coordination structures at room temperature (without disturbing chain structure and orientation), by cooperative assembly with a hydrogen-bonding species at a surface. Selective interactions led to structural hierarchy, where the 1D copper–pyridyl coordination structure is defined by a Cu coordination number of two, while the ordering and stabilization is performed by hydrogen-bonding interactions with the second molecular species. The selective interactions also allow for straightforward control of the supramolecular system by choice of the building blocks. Geometric parameters of chain segment length and interchain spacing can be tuned independently. This concept gives an additional handle for rational design of complex supramolecular architectures, which could potentially be transferred to various other low-dimensional coordination structures with selective interactions on Cu(100) and other surfaces.

Experimental Section

All sample preparations and measurements were performed in situ under ultra high vacuum (UHV) conditions (ca. 2×10^{-10} mbar). The Cu(100) surface was cleaned by cycles of sputtering with Ar$^+$ ions and annealing to 800 K. Each of the bipyridines, **P1** and **P2** (synthesized according to literature methods),[35,36] and bis(carboxylic acids), **C1** and **C2** (purchased from Fluka Chemie GmbH and Sigma–Aldrich Chemie GmbH, respectively), are sequentially evaporated from a Knudsen cell onto the substrate held at room temperature during deposition. Subsequently, the substrate was annealed between 410 K and 450 K for 10 min. Under these conditions, the carboxylic functional groups deprotonate completely to carboxylate moieties.[17,37] The supramolecular networks were analyzed by a home-built scanning tunneling microscope in the constant current mode with currents of approximately 0.1 nA and a sample bias between 0.1 and 1 V.

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