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Hierarchical Assembly and Reticulation of Two-Dimensional Mnand Ni $-TCNQ_x$ (x = 1, 2, 4) Coordination Structures on a Metal Surface

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Supporting Information

ABSTRACT: We report a scanning tunneling microscopy (STM) investigation of the self-assembly of two-dimensional metal—organic coordination networks comprised of Mn or Ni atoms (M) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) molecules on a Ag(100) surface. The growth is dominated by the coupling of the cyano ligands to the substrate, and this interaction is reduced by lateral coordination of the molecules to metal adatoms. Initially mononuclear M–TCNQ₄ complexes form at room temperature, which hierarchically assemble into reticulated M–TCNQ₂ networks at sufficiently high metal



concentrations. $M-TCNQ_1$ networks with fully coordinated molecules can be obtained at elevated substrate temperatures and sufficient metal concentration. A commensurate α and an incommensurate β phase can be distinguished that are unrelated to the antedecent $M-TCNQ_4$ complexes. The coordination of the cyano groups to metal adatoms alters the balance between lateral interactions and coupling of the molecules to the substrate. This effect is accompanied by distinct changes in the apparent heights of metal centers in the STM data indicating changes in their electronic configuration.

■ INTRODUCTION

Two-dimensional (2D) supramolecular assembly offers an efficient approach to produce complex nanostructures at surfaces with molecular-level accuracy and long-range order.¹⁻⁵ The structures that can be obtained with this method have reached a high level of complexity. Many of the complex assemblies follow hierarchical ordering phenomena starting from relatively simple building blocks.⁶ In general the design of the molecular structures is based on noncovalent interactions with specific bond strengths and geometries allowing for hierarchical organization of the building blocks. Further, metal-organic coordination networks (MOCNs) and complexes consisting of atomic and molecular constituents are of especially high interest due to the distinct charge and spin states of the metal centers and their redox and magnetic properties.⁷⁻⁹ Recent studies have shown great insight into the multiple factors governing the selfassembly of MOCNs, including lateral interactions between adsorbed species, substrate-adsorbate interactions in the vertical direction, and other relevant chemical processes occurring at the molecule-substrate interface.⁵ Substrate interaction is a critical parameter in the self-assembly of coordination architectures. Considering the extreme condition of strong substrate-adsorbate interaction, the adsorbed species adhere to the substrate with no or only little mobility, which inhibits the assembly of ordered adlayers. Oppositely, strong lateral coordination between adsorbates will lead to isostructural supramolecular networks on different substrates since substrates effectively act as platforms supporting the twodimensional network geometry.¹⁰ However, in the majority of systems an intermediate situation is usually encountered in which the competition between lateral and vertical interactions determines the resulting coordination structures. This interplay is of particular importance with regard to hierarchical order since the various levels of organization involve different binding strengths.¹¹

Recently, we showed that the interaction between TCNQ molecules and a Cu(100) surface leads to the lifting up of surface atoms bonded to the cyano groups.¹² Further, the supramolecular assembly of Mn and TCNQ yields a single ordered phase of Mn-TCNQ2 networks on Cu(100).¹³ The observation of only one ordered and coordinatively unsaturated structure is attributed to the strong substrate templating effect that inhibits higher coordination modes of the molecules. Here, we choose a Ag(100) substrate to reduce substrate interaction, which allows the formation of different coordination structures ranging from single complexes to extended and fully coordinated M-TCNQ arrays. We obtained M-TCNQ_x structures where the coordination ratio x can be controlled by adjusting the concentrations of constituents and substrate temperature. Initially mononuclear M-TCNQ₄ complexes form at room temperature by deposition of metal atoms on a TCNQ precursor layer. The increase of metal concentration results in M-TCNQ₂ networks that are hierarchically assembled from the M-TCNQ₄ complexes. The formation of the fully coordinated M-TCNQ1 networks, however, requires elevated substrate temperatures with a network

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structure that is not related to the antedecent $M-TCNQ_4$ complexes. Further, the $M-TCNQ_1$ arrays exhibit distinct topographical features in the STM images. In particular the apparent heights of the metal centers differ from those of the unsaturated networks. This suggests that the electronic configuration of the metal centers changes upon full coordination of the molecules. In addition, while the coordinatively unsaturated networks formed by Mn and Ni are structurally identical, the fully coordinated networks differ strongly, which is associated with the specific properties of the metal adatoms, e.g., atomic size, electron affinity, and electronic configuration.

EXPERIMENTAL SECTION

The experiments were carried out in an UHV chamber with a base pressure of 5×10^{-10} mbar. The Ag(100) surface was cleaned by cycles of Ar⁺ sputtering and subsequent annealing to 750 K. TCNQ (98%, Aldrich) was deposited by organic molecular-beam epitaxy (OMBE) from a resistively heated crucible at a sublimation temperature of 400 K. The coverage of molecules was controlled to be less than 1 monolayer to provide mobility and space for network reticulation upon metal deposition. Ni and Mn were subsequently deposited by an electron-beam heating evaporator on top of the organic precursor layer at a flux of \sim 0.02 ML/5 min. The substrate was held at 300–460 K during metal deposition to investigate the influence of the substrate temperature on the coordination structures. Postdeposition annealing was also used to optimize the structural ordering. The STM images were acquired at room temperature. Typical scanning parameters of 0.1–0.5 nA and $\pm 0.8-1.2$ V are used to avoid interfering with the surface structures. The apparent heights measured in this manuscript do not change within this given bias voltage range. Since tip effects can induce very different STM contrasts all images shown here present the usual contrast we observed for all structures.

RESULTS AND DISCUSSION

TCNQ molecules are mobile on Ag(100) at room temperature as indicated by the fuzziness of the bare substrate in STM images such as Figure 1a. Well-ordered molecular domains are only observed when the coverage is close to one monolayer (ML). Besides step edge decoration, TCNQ forms single big domains extending over entire terraces. Figure 1a shows two mirror-symmetric domains that have a rhombic unit cell. The orientation of the two domains is indicated by blue arrows in Figure 1a. Due to the 4-fold substrate symmetry two other 90° inplane rotated domain orientations are observed. In the high resolution STM image (Figure 1b), individual molecules are imaged as oval protrusions with an apparent size of 6.2 Å \times 8.9 Å. The detailed analysis of the STM data yields the unit cell parameters $|b_1| = 9.2 \pm 0.2$ Å, $|b_2| = 12.0 \pm 0.4$ Å, $\phi = 56.8 \pm 1.9^\circ$, and the domain orientation θ = 18.7 \pm 1.4° (see Figure 1b), which suggests a commensurate (3, 1/1, 4) superstructure with respect to the surface lattice vectors along the close-packed directions. A tentative model is depicted on top of Figure 1b with the unit cell indicated. Similar to the molecular phase on Cu(100), the TCNQ molecules are drawn with their central rings on bridge sites of the substrate optimizing the positions of the nitrogen atoms toward top sites.¹² The molecules adsorb with their long axes approximately 19° from the close-packed substrate direction, leading to nonequivalent binding sites for the cyano groups at cis positions of a molecule. The closest distance between the hydrogen atom of one molecule and the nitrogen of a neighboring molecule



Figure 1. STM images of the TCNQ adlayer on Ag(100). (a) TCNQ molecules self-assemble into an ordered rhombic structure when the coverage is close to 1 ML. Mirror-symmetric domains with the unit cell vectors $b_1 \pm 18.7^{\circ}$ to [011] direction are indicated by blue arrows. The fuzziness of the image indicates the mobility of TCNQ on Ag(100). (b) The rhombic superstructure is represented by b_1 and b_2 unit cell vectors. The unit cell parameters of the model, $|b_1| = 9.1$ Å, $|b_2| = 11.9$ Å, $\phi = 57.5^{\circ}$, and $\theta = 18.4^{\circ}$, agree well with the measured values from STM data.

amounts to about 3.0 Å as indicated by red dotted lines in the model. This length is too long to be a hydrogen bond and thus we assume that hydrogen bonding does not account for the packing of the molecules. Since the molecular azimuthal orientation renders the cyano groups pointing to the top sites of the substrate, a substrate-mediated mechanism analoguous to that proposed for the Cu(100) substrate presumably dominates the molecular packing.¹² However, no stable domains were observed at submonolayer coverages, in contrast to the rectangular TCNQ domains assembled on Cu(100).¹² We ascribe this behavior to the weaker substrate–TCNQ coupling on the Ag(100) surface.

Ni or Mn atoms are subsequently deposited onto the TCNQ precursor layer to obtain charge-transfer complexes. The cyano groups of the TCNQ molecules react readily with the metal atoms at room temperature, leading to the formation of mononuclear M-TCNQ₄ complexes as shown in Figure 2. The coordination structures formed by the two metals are geometrically identical. Figure 2a represents an overview STM image of Ni-TCNQ4 structures and Figure 2b shows the details of a Mn-TCNQ₄ domain. Two chiral forms of M-TCNQ₄ complexes, R (clockwise-folded) and S (anticlockwise-folded), are identified and highlighted by yellow and black squares in Figure 2, respectively. Such chiral monomers arise from surface confinement and, thus, one represents the mirror image of the other with respect to the substrate [011] direction. M-TCNQ₄ monomers are mobile and only observed at step edges or in well-ordered M-TCNQ₄ domains formed at sufficiently high concentrations as shown in Figure 2a. The domain size increases with coverage or postdeposition annealing treatment and can reach about 100 nm in width.

The M–TCNQ₄ domain presents a racemic mixture of the R and S monomers as indicated by the alternate yellow and black squares in Figure 2, panels a and b. Two domain orientations are identified and indicated by the $\mathbf{b_1}$ unit cell vectors oriented approximately $\pm 19.0^\circ$ with respect to the substrate [011] direction (Figure 2a). Both domains consist of the same R and S monomers but differ in their packing. As a consequence one domain is not superimposable onto the other by in-plane rotation or translation but they are mirror-symmetric with respect to the substrate [011] direction. The unit cell of the M–TCNQ₄ superstructure is indicated by the $\mathbf{b_1}$ and $\mathbf{b_2}$ vectors in Figure 2. The lattice size, equivalent to the second shortest metal–metal



Figure 2. (a) STM image of Ni–TCNQ₄ domains on Ag(100). Mirrorsymmetric R and S Ni–TCNQ₄ monomers are observed. The monomers self-assemble into ordered hydrogen bond-assisted networks at sufficiently high coverage. Such Ni–TCNQ₄ domains are racemic, i.e., composed of alternately packed R and S monomers as highlighted by yellow and black squares, respectively. Due to the substrate symmetry two mirror domains are observed. (b) High resolution STM image of Mn–TCNQ₄ phase with R and S monomers and the unit cell marked. The structure is identical to Ni–TCNQ₄. (c) Structural model based on distances and orientations measured in STM images. Metal coordination and potential intercomplex hydrogen bonds, highlighted by orange dotted lines, amount to 1.9 and 2.4 Å, respectively.

distance, is measured to be approximately 28.1 Å from the STM data. Based on these structural parameters, a tentative model is proposed in Figure 2c. The superstructure is described by the commensurate matrix (9, 3/-3, 9), which gives a periodicity of $9.5a_0 = 27.5$ Å ($a_0 = 2.89$ Å, the nearest neighbor distance of the Ag(100) substrate) and domain orientations of $\pm 18.4^{\circ}$ with respect to substrate [011] direction, both in good agreement with STM data. In the model we assume that metal centers reside on energetically favorable hollow sites of the substrate. Four molecules arrange around one metal center with their central ring adsorbed close to bridge sites. The metal-cyano bond is estimated to be 1.9 Å from the model, which is in good agreement with similar metal-cyano bonds in bulk compounds.¹⁴⁻¹⁷ The orientation of the molecules remains nearly identical to those in the molecular phase (see Figure 1). This indicates that the substrate-molecule interaction prevails upon metal coordination; that is, three cyano groups remain directly bonded to the surface. Further, the R complexes are composed of molecules with the long axes $+19^{\circ}$ from the [011] direction while S complexes are composed of -19° oriented molecules. The reason why the two equivalent molecular orientations leads to opposite chiral binding motifs is the breaking of molecular symmetry upon adsorption, where only the cyano group pairs at trans positions have identical adsorption sites but not those at cis positions (see Figure 1c). Therefore, there are no clockwisefolded (R) monomers formed by -19° oriented TCNQ molecules and vice versa. The racemic packing of R and S monomers is likely



Figure 3. (a and b) STM images and (c) structural model of Ni–TCNQ₂ networks on Ag(100). The STM images of Mn–TCNQ₂ networks are nearly identical. The M–TCNQ₂ networks are homochiral and composed of either R or S monomers. Therefore the R domains are mirror symmetric to the S domains with the b_1 unit cell vectors oriented $\pm 38.7^{\circ}$ with respect to the substrate [011] direction measured from the model. The alternate apparent heights of metal centers are attributed to differences in their adsorption sites and local binding configurations.

mediated by intercomplex hydrogen bonds as depicted by orange dotted lines in Figure 2c. The bond length is estimated to be 2.4 Å, which can be reasonably attributed to weak hydrogen bonds. Each $M-TCNQ_4$ binds to four adjacent complexes by four hydrogen bonds in total. Due to the weak strength of hydrogen bonds, individual $M-TCNQ_4$ monomers can reversibly attach to the networks, as revealed by the continuously changing domain edges and the presence of mobile single $M-TCNQ_4$ complexes.

A phase transformation occurs upon increasing the metal concentration and yields a reticulated two-dimensional coordination structure with a chemical composition of M-TCNQ₂. Again, the structures formed by the two metal species are indistinguishable. Figure 3 presents STM images measured on Ni-TCNQ₂ networks. High-resolution STM images show that the M-TCNQ₂ networks comprise the antecedent M-TCNQ₄ monomers as primary building blocks as highlighted by the colored squares. The M-TCNQ4 monomers are interconnected by additional metal atoms located at their corners. Interestingly, adjacent M-TCNQ₄ complexes are of the same chirality. Therefore, the formation of M-TCNQ₂ networks is a chiroselective process which can be viewed as the rearrangement of the M-TCNQ₄ complexes from the hydrogen bond-assisted racemic domains to incorporate further metal atoms as coordination nodes. Consequently, the resultant R and S M-TCNQ₂ domains are homochiral and mirror-symmetric to each other. The stable domain boundaries indicate that the M-TCNQ₄ complexes are stronger bound within the M–TCNQ₂ networks. Quantitatively, each TCNQ molecule monodentately coordinates to two metal atoms at trans positions, which accounts for the structural stability.

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The STM image presented in Figure 3b shows that the nearest-neighboring metal centers are not identical but exhibit alternate apparent heights. Our tentative model (shown in Figure 3c) provides an explanation to this phenomenon. Based on the STM analysis, individual M-TCNQ4 complexes are arranged according to the superstructure matrix (5, 4/-4, 5)with their metal centers positioned over hollow sites (M^{hollow}) and with the same azimuthal orientation as in the M-TCNQ4 domains. The additional metal centers connecting the M-TCNQ₄ complexes thus reside on top sites of the substrate (M^{top}) . This configuration is consistent with STM images that display two types of metal centers; that is, the brighter M^{hollow} and darker M^{top}. A careful analysis of the STM images shows that TCNQ molecules are slightly closer to the brighter centers, which is consistent with our model. A close inspection of the tentative model reveals that the $M^{\rm top}-\text{cyano}$ and $M^{\rm hollow}-\text{cyano}$ bonds are not equivalent in either bond angles or lengths, which is highlighted by the inequivalent red dotted squares formed by the four nitrogen atoms around the two types of metal centers (Figure 3c). These differences in the binding configuration, as well as adsorption sites, explain the alternate apparent heights of the metal centers in STM images. Furthermore, in both Mn- and Ni-TCNQ2 networks, metal vacancies are observed as indicated by white dotted circles in Figure 3b. All metal vacancies are observed at the Mtop sites, which can be well explained by our model since top sites are less favorable and $N-M^{top}$ bonds are expected to be weaker because of nonoptimal bond angle and length. We also observed interstitial metal atoms as indicated by white arrows in Figure 3b. The metal atoms trapped in the pores cannot coordinate to more than one or two molecules simultaneously (cf. Figure 3c) and are thus mobile and

hop between the pores of the $M-TCNQ_2$ networks. The apparent height of the M^{hollow} centers has not changed compared to the $M-TCNQ_4$ monomers, i.e., $Ni^{hollow} = 0.7$ Å and $Mn^{hollow} = 1.2$ Å relative to the molecule. The apparent heights measured by STM are associated with the local electronic configuration of the metal centers embedded in the M-TCNQ_x structures. Therefore, we anticipate that the electronic properties of the M-TCNQ₄ constituents do not undergo significant modifications upon further metal coordination. On the other hand, the difference between the apparent heights of $M^{\rm hollow}$ and M^{top} within M-TCNQ₂ networks amounts to about 0.4 Å for both Mn- and Ni-TCNQ₂ networks. This distinction in heights cannot unambiguously be attributed to the difference in adsorption site or variation in the coordination bonds and is likely due to both effects. Such a height modulation of the metal centers was not observed in the nearly identical Mn-TCNQ₂ networks assembled on Cu(100), where the domains grow uniformly.¹³ The M-TCNQ₂ composition is identical to the most common magnetic metal-cyanide crystals, but the coordination structure of the surface-supported M-TCNQ2 networks differs strongly from the bulk compounds. Instead of forming TCNQ dimers or incorporating additional ligands to limit the coordination ratio, ^{14,15,18,19} here TCNQ molecules form two coordination bonds to 4-fold metal centers, leaving two of the cyano groups bonded to the substrate.¹³

The last stage of structural transformation results in $M-TCNQ_1$ networks at high metal concentrations in which all cyano groups monodentately coordinate to 4-fold metal centers. In contrast to the geometrically identical domains formed by Mn and Ni with coordinatively unsaturated TCNQ, the fully coordinated Mn- and Ni-TCNQ₁ networks differ significantly in both



Figure 4. STM images and geometrical models of $(a-c) \alpha$ and $(d-f) \beta$ Ni-TCNQ₁ phases. The lattice of the α phase is square whereas the β phase is rhombic, as indicated by the unit cells depicted on the STM images. Structural models are proposed based on the dimensions and orientations from STM data. From the models, the α phase is commensurate to the substrate while the β phase is not. The incommensurability is related to the reduced substrate coupling and results in distinct STM topographical features.

structural order and topographical features. In the case of Ni, two types of Ni-TCNQ₁ structures are observed, i.e., the square α phase and the rhombic β phase shown in the left and right panels of Figure 4, respectively. The formation of Ni-TCNQ1 networks requires an elevated substrate temperature during metal deposition or postdeposition annealing treatments as well as a sufficiently high metal concentration. At a preparation temperature of 400 K only small domains of α and β networks are obtained besides the dominating Ni-TCNQ2 networks with excess Ni adatoms residing in the cavities. After postdeposition annealing treatments above 400 K, the Ni-TCNQ₂ phase converts into α and β Ni-TCNQ₁ networks. Below 440 K, the α domains are larger and more often observed than the β phase. Above 440 K, the β phase grows quickly both in domain size and relative coverage. A complete transformation into Ni-TCNQ₁ is obtained at 460 K with the coverage ratio of $\alpha:\beta = 1:1.6$. The maximum domain widths of α and β networks are 40 and 120 nm, respectively. Further increase of the annealing temperature results in the decomposition of TCNQ molecules.

In the α phase the TCNQ molecules orient perpendicular to their neighboring molecules, which is clearly shown in the enlarged STM image in Figure 4b. Due to the square structure of the α phase, two mirror-symmetric domains are observed (cf. Figure 4, panels a and b). The domain orientation is defined by the **b**₁ vector along the second-shortest Ni-Ni direction. The structure is similar to the Ni-TCNQ₂ network with all pores filled by metal atoms. However, there are three distinguishing features demonstrating that the α Ni–TCNQ₁ network does not comprise Ni-TCNQ4 monomers as building blocks. First, the metal centers at trans positions of a molecule have the same apparent height. Second, the α network is more densely packed than the Ni-TCNQ₂ phase. The length of the **b**₁ vector is 11.8 \pm 0.5 Å (cf. Figure 4b) measured from the STM data. In fact, the packing density of the molecules is highest in this phase even compared to the pure molecular phase. Third, the b_1 orientation is measured to be $13.8 \pm 1.2^{\circ}$ from the substrate [011] direction. Thus, the formation of the α phase requires the dissolution of the Ni-TCNQ₂ network and is not simply a rearrangement of Ni-TCNQ₄ monomers and Ni atoms. This explains the high preparation or postannealing temperatures required for the structure transformation into α Ni-TCNQ₁ networks. Based on the above parameters, a geometrical model is proposed in Figure 4c. The square unit cell is described by the commensurate superstructure (4, -1/-1, -4). Both the orientation, $\pm 14.0^{\circ}$ from substrate [011], and the length, 11.9 Å, of the b_1 vector are in good agreement with the STM measurements. Furthermore, the Ni atoms reside alternately on hollow and top sites in the model, which explains the alternate heights of Ni centers along the orientation of the diagonal of the unit cell. TCNQ molecules are fully coordinated with their central rings adsorbed on bridge sites and pack perpendicularly to each other. The angle enclosed between the [011] direction and the long axis of the molecules is about $\pm 30^{\circ}$ differing from the orientation in the unsaturated networks. The inequivalent bonding of cyano groups at cis positions are indicated by the red dotted squares in Figure 4c. The lengths of the coordination bonds are estimated to be 2.0-2.2 Å, which fall in the range of typical metal-cyano distances, while the bond angles are 147.9-149.5° measured from the model. The apparent heights of the two types of Ni centers in the α Ni-TCNQ₁ network relative to molecules are +0.2 and -0.2 Å, which are substantially different from those in Ni $-TCNQ_2$. This shows that the α phase is not only structurally independent of Ni-TCNQ4 monomers, but also electronically different from either Ni-TCNQ4 or Ni-TCNQ2. The electronic variation is expected to arise from the full coordination of the TCNQ molecules. We propose that the fully coordinated TCNQ molecules are virtually lifted away from the surface since the substrate bonding via the cyano groups is weakened by the lateral coordination.9,13

The second fully coordinated Ni–TCNQ₁ structure, denominated as the β phase, is presented in the right panels of Figure 4. Within a single domain of the β phase the TCNQ molecules orient parallel to each other. Figure 4, panels d and e, shows mirror-symmetric domains with the domain orientations marked parallel to the molecular long axes. The 90°-rotational domains are also observed and attributed to the substrate symmetry. The rhombic unit cell is depicted in the high resolution STM image of Figure 4e. The unit cell parameters are measured to be $|\mathbf{b}_1| = 11.3 \pm 0.2$ Å, $|\mathbf{b}_2| = 7.2 \pm 0.3$ Å, $\phi = 85.6 \pm 1.5^\circ$, and $\theta = 58.5 \pm 2.5^\circ$ (see Figure 4e). These dimensions and angles indicate that the β Ni–TCNQ₁ network is incommensurate to

the Ag(100) substrate. The geometrical model (Figure 4f) is based on the measured distances and orientations. Due to both the rhombic lattice and incommensurability, the four metal-cyano bonds are not equivalent in the coordination geometry and also have some variations in angle and length. Therefore, each Ni center has a distorted 4-fold coordination as highlighted by the red dotted diamond in Figure 4f. This strongly distorted geometry could be virtually only a 2-fold coordination along the short diagonal of the unit cell. The analysis of the STM data shows that the boundaries of the β networks terminate along both diagonals of the unit cell, meaning that the bonding strength along the longer diagonal is similar to that along the shorter. However, we observed a continuous modulation of the apparent height of Ni centers along the shorter diagonal. The inset of Figure 4d displays a line profile along the short diagonal of the unit cell running across both Ni atoms and TCNQ molecules. The dashed black line indicates the uniform apparent height of TCNQ. The Ni positions are indicated by markers at a distance of 1.3 nm. It can be clearly seen that the Ni centers exhibit a wavelike pattern in the apparent height from 0 to 0.5 Å relative to the molecules. (See Figure S1 in the Supporting Information for an STM image with enhanced contrast that cleary shows the apparent height modulation of the Ni atoms.) This phenomenon could originate from the network incommensurability with the Ni centers being sensitive to their atomic environment.²⁰ Neighboring profiles along the shorter diagonal of the unit cell do not exhibit a clear periodicity, however, they are also not completely unrelated. The wave-like pattern of adjacent profiles appears to be shifted by about half of the wavelength shown in the inset of Figure 4d, i.e., ~ 8 nm or 7–8 unit cells (see also Figure S1).

The metal-cyano bond length of the β phase is measured to be 1.9–2.3 Å from the model, which is similar to that of the α phase. On the other hand, the bond angle in the β phase given by the model is 160.4–170.8°, which is very close to the optimal linear configuration. Note, that the variations in bond length and angle are due to the two nonequivalent metal-cyano bonds in the rhombic unit cell. The optimal bond angles are expected to lead to a strong intranetwork interaction which explains the formation of huge β domains above 440 K despite the incommensurability. The β network is favorable at elevated temperatures, which indicates that thermal energy is required to achieve an incommensurate structure in which the adsorbates do not reside entirely on preferential adsorption sites, however with dominating lateral interactions.

The Ni-TCNQ1 networks are structurally independent from the unsaturated structures and concomitantly the metal centers embedded in the networks exhibit distinguishing apparent heights that originate in part to differences in the hybridization with the substrate. This is further exemplified by using Mn as coordination centers. Mn forms similar α and β type networks, which, however, exhibit pronounced differences to Ni-TCNQ₁. At a substrate temperature of 460 K, α Mn-TCNQ₁ domains of a maximum width of 15 nm are obtained (see Figure 5). Besides the formation of only small α domains there are many Mn vacancies and large voids. Defects cannot be reduced even by annealing up to 470 K until the molecules decompose at higher temperatures. The inset of Figure 5 shows a close view of the structure. The orientation of the molecules varies from a perfect alternating perpendicular arrangement. In addition the Mn centers are imaged nonuniformly with some topographical depressions indicating missing Mn atoms. Small patches of β Mn-TCNQ1 networks are also observed but present only a minor coverage as indicated in Figure 5. Since identical structures are



Figure 5. STM images of $Mn-TCNQ_1$ networks. The structures resemble $Ni-TCNQ_1$ networks, however, with considerably less structural order. The inset shows the nonuniformity of Mn centers which can be attributed to the structural disorder of the $Mn-TCNQ_1$ networks. The Mn centers are imaged as depressions with respect to the TCNQ molecules.

synthesized at unsaturated coordination numbers irrespective of the metal species, the reason dictating the structural variations of the Mn- and Ni-TCNQ1 networks is likely related to the full coordination configuration. The fully coordinated TCNQ molecules become conformationally rigid from bending or stretching and thus the coordination network has little freedom to relax itself to fit the substrate periodicity. A long-range ordering requires the precise match between the network and the substrate periodicity or dominating interadsorbate interactions. In other words, small variations in the metal atomic size and the related metal-cyano bonding might be sufficient to induce the significantly different ordering behavior of the Mn- and Ni-TCNQ1 structures. This limitation due to the surface confinement are absent in bulk compounds and hence isostructures can easily evolve for the different metal species.¹⁸ In addition to geometrical considerations, the inherent electronic dissimilarity of Mn and Ni is expressed in specific differences in the metal-TCNQ interaction, such as charge transfer and local coordination geometries. The electronic configuration of metal atoms and molecules can be further altered by the interaction with the substrate. This is signified by the metal-TCNQ selfassembly on Cu(100) where Mn-TCNQ₂ forms well-ordered domains whereas Ni-TCNQ does not show any ordering.²¹ A combination of these factors has to be considered to explain the differences in the growth on the different surfaces and for different coordination structures on the same substrate.

Analogous bonding motifs and geometrical structures of both α and β networks have been synthesized in bulk metal—cyanides.^{17,22–24} The networks found on the surface represent sheets of the continuous bulk structures with the coordination limited to two dimensions. The bulk analogues exhibit electrical conductivity and/or magnetic ordering. Although it remains to be shown, we anticipate that the fully coordinated networks might show, at least in part, the electronic properties of their parent bulk compounds since all cyano groups are engaged in coordination bonds with a reduced interaction with the substrate. We note that no further ordered structure was observed upon increasing the metal concentration.

The dependence of the network stoichiometry on the relative molecule and metal concentration ratios has been also observed for other metal—organic networks at surfaces.^{25–27} The increased metal concentration leads to the full saturation of the coordination bonds of the molecule with a transition from mononuclear to dinuclear Fe-carboxylate coordination centers.^{25,26} Moreover, also the structures with higher metal concentration require a higher preparation temperature, however no hierarchical organization depending on the adsorbate concentration was observed. In addition all networks were found to be commensurate to the surface lattice with no particular coordination related electronic effect present at the metal centers.

In conclusion, we have shown two levels of phase transformations, i.e., the hierarchical assembly from M-TCNQ4 monomers to M-TCNQ₂ networks driven by metal concentration and the thermally activated transformation into fully coordinated M-TCNQ1 networks. All structures consist of regular arrangements of 4-fold coordinated Mn or Ni centers with interdistances ranging from 7.2 to 19.4 Å mediated by TCNQ molecules. Changing the coordination number of TCNQ molecules effectively alters the interplay between inter-adsorbate and substrate-adsorbate coupling. In the unsaturated networks the substrate determines the general adsorption geometry of the molecules. The M-TCNQ4 complexes are stable building blocks that can be arranged via hydrogen bonds or further metal coordination. At full coordination of the molecules the lateral interactions start to dominate the growth which is revealed in the formation of incommensurate networks. This structural transformation is associated with electronic changes of the metal centers that are revealed by the variations in the apparent heights measured with STM. Considering the magnetic properties of $M-TCNQ_x$ bulk compounds, we anticipate potential magnetic coupling in the two-dimensional M-TCNQ_x structures. Finally, employing other transition metal species and more inert substrates would provide further information to systematically understand the growth phenomena and concomitant properties.

ASSOCIATED CONTENT

Supporting Information. Figure S1 showing the height modulation of the Ni centers in the β Ni-TCNQ₁ network at enhanced contrast. This material is available free of charge via the Internet at http://pubs.acs.org.

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