Tuning the electronic properties of metal surfaces and graphene by molecular patterning
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Chapter 7

Low-dimensional metal-organic coordination structures on graphene

We report the formation of one- and two-dimensional metal-organic coordination structures (MOCSs) from para-hexaphenyl-dicarbonitrile (NC-Ph₆-CN) molecules and Cu atoms on graphene epitaxially grown on Ir(111). By varying the stoichiometry between the NC-Ph₆-CN molecules and Cu atoms, the dimensionality of the MOCSs can be tuned: for a 3:2 ratio a two-dimensional hexagonal porous network based on three-fold Cu-coordination was observed while for a 1:1 ratio one-dimensional chains based on a two-fold Cu-coordination formed. The formation of the metal-ligand bonding is evidenced by clearly imaging the individual Cu atoms with scanning tunneling microscopy. Scanning tunneling spectroscopy measurements demonstrate that the electronic properties of NC-Ph₆-CN molecules and Cu atoms are modified due to the structural transformation from two-dimensional porous network to one-dimensional molecular chain.
7.1 Introduction

Molecular self-assembly on graphene has drawn constantly increasing attention over the past few years due to its potential for applications ranging from organic electronics over photovoltaics to spintronics [1-3]. Particularly, the chemical inertness and the low density of states near the Fermi level make graphene a perfect choice as a buffer layer to decouple adsorbed molecules as well as atoms from the underlying (metallic) substrate. The low hybridization between the absorbed species and graphene allows for the direct imaging of the molecular orbitals in real space with scanning tunneling microscopy (STM) and even more importantly, it also holds promise to preserve the intrinsic properties of the adsorbed species like magnetic moments or catalytic activity [4,5]. On the other hand, the application of graphene in the field of (high-performance) electronics requires control over the type and concentration of charge carriers as well as the possibility to introduce a bandgap (essential for usage in transistor applications). Theoretical studies showed that the electronic properties can be tuned when an external potential with a certain shape, symmetry and periodicity is applied [6,7]. The periodic potential induced by long-range ordered molecular superstructures has shown the possibility to tune the electronic properties of metal surfaces as well as graphene on a macroscopic scale [8, 9]. Thus, molecular self-assembly on graphene can be viewed as a promising method to tune the electronic properties of graphene on a macroscopic scale. By exploiting the charge transfer, which occurs upon adsorption of specially designed molecules which are either strongly electron-donating or electron-accepting, control over the type and concentration of charge carriers can be obtained [10,11]. Furthermore, through the adsorption of carefully designed organic molecules on graphene an electronic bandgap can be also opened according to theory [12, 13]. The key point in this case is the breaking of the sublattice symmetry
of graphene by transferring charge between the molecules and only one of the two sublattices. This has not been experimentally realized up to now. So far, almost exclusively only commercially available molecules were tested for doping graphene and moreover, the possibility to transfer the knowledge and ideas present for 2D (supra)molecular structures on metallic surfaces has hardly been made use of [14-23]. Interestingly, up to now the approach of adsorbing 2D metal-organic coordination networks (MOCN) on graphene for controllably changing its electronic or magnetic properties has not been pursued – despite the various properties MOCNs have to offer and which are described in abundant reports and reviews for MOCNs on metallic surfaces [24-27]. Moreover, the coordinated metal atoms can also be viewed as an atom dot array decoupled from the underlying metal substrate, which may provide properties unavailable on metal substrates. However, 3D composites made from graphene-related materials and MOCNs [28, 29] have received increasing attention over the last few years while their structural arrangement has not been unraveled to date.

Here, we report a systematic study for the creation of low-dimensional metal-organic coordination structures on graphene epitaxially grown on Ir(111) from para-hexaphenyl-dicarbonitrile (NC-Ph\textsubscript{6}-CN) molecules (Figure 7.1c) and co-deposited Cu atoms. The as-deposited NC-Ph\textsubscript{6}-CN molecules self-assemble on graphene/Ir(111) into a close-packed arrangement consisting of one-dimensional (1D) lines of parallel arranged molecules which appears as a striped pattern. By co-adsorbing Cu atoms and varying the stoichiometry between the NC-Ph\textsubscript{6}-CN molecules and Cu atoms, a basketweave-like pattern, a hexagonal porous network (3:2 ratio) or 1D chains (1:1 ratio) are formed (from low to high amount of Cu atoms). The bright protrusions between the molecules observed in the STM images originate from the presence of the Cu atoms, which indicates the formation of metal-ligand bonding between the
cyano groups of the NC-Ph₆-CN molecules and the co-deposited Cu atoms. The structural transformation of the metal-organic coordination structures (MOCSSs) in dependence of the amount of Cu atoms with respect to organic molecules involves the modification of the electronic properties of both the NC-Ph₆-CN molecules and Cu atoms, as evidenced by scanning tunneling spectroscopy (STS) measurements.

7.2 Results and discussion

After the growth of graphene on Ir(111), the graphene quality was checked by STM and LEED measurements. The atomically resolved STM image (Figure 7.1a) shows the Moiré pattern originating from the lattice mismatch between graphene and Ir(111). In the low-energy electron diffraction (LEED) pattern (Figure 7.1b), the Moiré pattern can be discerned by the satellite spots around the (1,1) spots of Ir(111) [31, 32]. Both experiments indicate the successful synthesis of graphene. Figure 7.1c shows the molecular structure of NC-Ph₆-CN: six phenyl rings are joined by single C-C bonds with a terminal cyano group at each end of the molecule. MOCNs from the family of this molecule (NC-Phₙ-CN with n=3,4,5,6) have been extensively studied on mainly Ag(111) and Cu(111) surfaces [33-37]. Figure 7.1d shows the close-packed arrangement of NC-Ph₆-CN when deposited on graphene/Ir(111) held at room temperature. Individual NC-Ph₆-CN molecules can be easily recognized by their rod-like shape. Similar to the arrangement of NC-Ph₆-CN on Ag(111) for close to monolayer coverage [38], the molecules arrange in a striped pattern on graphene/Ir(111). Within one stripe, the molecules are parallel to one another, while every fourth molecule a shift along the long axis of the molecule with this distance of one phenyl ring occurs. The detailed discussion of this molecular striped pattern will be presented elsewhere [39].
Figure 7.1. (a) STM image (9.7 nm × 9.7 nm, U = −0.5 V, I = 120 pA, T = 77 K) of graphene grown on Ir(111) showing atomic resolution as well as the Moiré pattern. (b) LEED pattern of graphene epitaxially grown on Ir(111) taken at an energy of 138 eV. The presence of the graphene Moiré pattern can be identified by the satellite spots around the first-order Ir spots. (c) Chemical structure of the NC-Ph₆-CN molecule. Carbon atoms are gray, nitrogen atoms blue, and hydrogen atoms white. (d) STM image (25.4 nm × 19.3 nm, U = −0.5 V, I = 20 pA, T = 77 K) of the as deposited NC-Ph₆-CN molecules on graphene/Ir(111). The molecules arrange parallel to one another in a striped pattern.
Upon deposition of a very small amount of Cu atoms onto the close-packed arrangement of NC-Ph$_6$-CN on graphene/Ir(111), the striped pattern was transformed into a basketweave-like pattern. Though the parallel arrangement of the molecules is still observed (marked by black lines in Figure 7.2a), some packages of parallel molecules are rotated by 60° with respect to the other molecules and moreover, some molecules are also arranged in a head-on configuration (marked by red lines in Figure 7.2a). In the head-on configuration, the cyano groups of the involved molecules point directly towards each other. The electrostatic repulsion between the partially negatively charged nitrogen atoms of the cyano groups would make this arrangement energetically unfavorable unless metal-ligand bonding takes place between the cyano groups and the deposited Cu atoms. To investigate this in more detail, a close-up STM image was taken (Figure 7.2b). The round bright protrusions can be assigned to the central Cu atoms of the metal-ligand bonds which take place between three NC-Ph$_6$-CN molecules and one Cu atom. For MOCNs on metal surfaces, the metal centers are rarely imaged by STM [40-42]. The protrusions resolved between three adjacent molecules provide a direct evidence of the three-fold metal coordination bonding formed between the Cu atom and the cyano groups of neighboring molecules. The proposed molecular model is shown in Figure 7.2c. Due to the three fold metal coordination bonding between the molecules and the Cu atoms, a near rhombic shape structure is formed. In the cavity of the rhombus, the NC-Ph$_6$-CN molecules are stacked in a side to side configuration. The unit cell of the basketweave-like pattern is marked in orange in Figure 7.2a, the size of the unit cell is measured to be a = 5.6 nm, b = 4.5nm and α = 77°.
Figure 7.2. (a), (d) and (g) STM images of the self-assembled molecular structures from NC-Ph$_6$-CN molecules and co-deposited Cu atoms at different molecule to atom ratios. Structural evolution of the MOCSs with decreasing molecule to atom ratio: the basketweave-like pattern (a), hexagonal porous network (b) and molecular chains (g). (b),(e) and (h) Close-up STM images with intramolecular resolution of the basketweave-like pattern (b), hexagonal porous network (e) and molecular chains (h). In all three STM images, the Cu atoms are clearly resolved as round protrusions between neighboring NC-Ph$_6$-CN molecules, which reveals the formation of metal-ligand bonds. (c),(f) and (i) Molecular models of the basketweave-like pattern (c), hexagonal porous network (f) and molecular chain (i). The Cu atoms are depicted by red spheres. Scanning parameters: (a) 17.4 nm × 13.5
nm, $U = -0.5 \, \text{V}$, $I = 20 \, \text{pA}$, $T = 77 \, \text{K}$; (b) $8 \, \text{nm} \times 8 \, \text{nm}$, $U = -0.5 \, \text{V}$, $I = 20 \, \text{pA}$, $T = 77 \, \text{K}$; (d) $34.8 \, \text{nm} \times 27.2 \, \text{nm}$, $U = -1 \, \text{V}$, $I = 20 \, \text{pA}$, $T = 77 \, \text{K}$; (e) $8 \, \text{nm} \times 8 \, \text{nm}$, $U = -0.5 \, \text{V}$, $I = 120 \, \text{pA}$, $T = 77 \, \text{K}$; (g) $8.3 \, \text{nm} \times 18.8 \, \text{nm}$, $U = -2 \, \text{V}$, $I = 10 \, \text{pA}$, $T = 77 \, \text{K}$; (h) $1.1 \, \text{nm} \times 5.7 \, \text{nm}$, $U = 1 \, \text{V}$, $I = 10 \, \text{pA}$, $T = 4.5 \, \text{K}$.

The remaining of the side to side arrangement of the molecules indicates the possible lack of Cu atoms in forming metal-ligand interactions. Therefore, sample with stoichiometry (Cu/molecule) of 1:1.5 was prepared to study the molecular self-assembly at higher stoichiometry. As shown in Figure 7.2d, the hexagonal porous network becomes the dominant phase at the stoichiometry (Cu/molecule) of 1:1.5. Zoom-in image with intramolecular resolution was taken to gain insight into the bonding of the hexagonal porous network. As shown in Figure 7.2e, the six phenyl rings of the NC-Ph$_6$-CN molecule and the Cu atom are clearly resolved, which unambiguously demonstrates that the hexagonal porous network formed on graphene/Ir(111) was stabilized by the three-fold metal coordination bonding between the deposited Cu atoms and the cyano group of the molecules. The unit cell of the hexagonal porous network is marked in orange in Figure 7.2d, the size of the unit cell is measured to be $a = b = 5.7 \, \text{nm}$ and $\alpha = 60^\circ$. Figure 7.2f demonstrates the molecular model for the hexagonal porous network structure, which shows a good agreement with the STM image. Compared to the extensive research work carried out on metal surfaces, the metal coordination bonding is poorly investigated on graphene surface. To the best of our knowledge, this is the first experimental observation of molecular porous network stabilized by metal coordination bonding on graphene. The well-ordered metal coordinated porous network is highly appealing since it bears great potential in two aspects. For graphene, the periodic potential induced by the porous network may modify the electronic properties of
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graphene and may ultimately allow for tailoring the band gap of graphene. For the adsorbed atoms and molecules, the presence of graphene decouple them from the underlying metal substrates, which may preserve the magnetic moments, catalytic activity and other intrinsic properties.

Samples with the stoichiometry (Cu/molecule of ∼1:1) was also prepared to investigate the self-assemblies at even higher stoichiometry. As shown in Figure 7.2g, the dominant phase of the molecular self-assembly becomes the one dimensional molecular chain. Zoom-in image of the molecular chain is acquired at 4.5 K, since the molecular chain is more stable at lower temperature and STM image with better resolution can be obtained. In the zoom-in image (Figure 7.2h), a bright protrusion is resolved between two adjacent molecules in the molecular chain, which manifests the formation of the metal coordination bonding in the molecular chain. By depositing more Cu atoms, the structure of the molecular self-assembly transforms from two-dimensional porous network to one-dimensional molecular chain. The corresponding intermolecular interaction also change from three-fold metal coordination bonding to two-fold metal coordination bonding. The transformation of the molecular arrangement demonstrate the flexibility and versatility of the coordination bonding between the Cu atoms and the carbonitrile functional groups, which is in line with previous research results [36, 43]. Another point worth noticing is the observation of Cu atoms in the STM image. It’s been reported that the metal atom centers of the coordinated self-assemblies on metal surfaces can be imaged by STM under special tip conditions [40-42]. But in the current study, the Cu atoms have been observed on different samples with different tip conditions with different scanning parameters. Therefore, we propose that that the observation of the Cu atoms in the current study does not stem from a special tip condition but
from the low electronic hybridization between the Cu atoms and the underlying graphene.

**Figure 7.3.** (a) Orange curve: STS on the Cu atom in the molecular chain, position marked by the orange square in the inset. Blue curve: STS on the Cu atom in the porous network, position marked by the blue square in the inset. Red curve: STS on the molecule in the porous network, position marked by the red sphere in the inset. Black curve: STS on the molecule in the porous network, position marked by the black sphere in the inset. (b) STM image taken on the porous network for resolving the molecular orbitals in real space. Scanning parameters: (a) 8 nm × 8 nm, U= 2.4 V, I= 350 pA, T=4.5 K.

The experimental observation shows that the molecular network stabilized by three fold Cu coordinated bonding can transform into molecular chain stabilized by two fold Cu coordinated bonding by tuning the molecule to atom ratio. These two structures represent a unique model system to investigate the modification of the electronic properties of the ligand molecule and the metal atom when the bonding motif is changed. The red curve in Figure 7.3a exhibits the STS acquired on the molecule consisting the porous network (position marked by red sphere in the inset), two strong
peaks are observed at the energy of -4.0 eV and +2.4 eV with a broad gap region between the peaks. Since the dI/dV signal is proportional to the local density of states, tunneling through the molecular orbitals can lead to the peaks in the dI/dV spectra which corresponds to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [44]. Therefore, the peaks at the -4.0 eV and +2.4 eV correspond to the HOMO and LUMO of the NC-Ph\textsubscript{6}-CN molecule in the porous network respectively, giving a band gap of 6.4 eV. For the molecules in the molecular chain, the HOMO and LUMO is found at -4.2 eV and +2.1 eV respectively, giving a band gap of 6.3 eV (see the black curve in Figure 7.3a). The modulation of molecular states induced by the bonding between the molecule and the metal atoms have been reported in different systems [45-49]. Behind the change in the molecular arrangement observed in the current study, the underlying driving force is the transformation of the bonding motif from three-fold metal coordination to two-fold metal coordination. Therefore, the different features observed in the STS spectra may stem from the different hybridizations between the molecules and the coordinated Cu atoms. The clearly resolved Cu atom in the STM image allows for performing STS measurements directly on the Cu atoms to investigate the influence of the structural transformation on the electronic properties of the Cu atoms. For the Cu atoms in the porous network, a strong peak is observed at +2.3 eV for the unoccupied states of the Cu atom (blue curve in Figure 7.3a). While the peak is shifted to +1.8 eV for the Cu atom in the molecular chain (orange curve in Figure 7.3a). The modulation of the electronic properties of the coordinated Cu atoms is in agreement of the shift of the molecular orbital of the NC-Ph\textsubscript{6}-CN molecules, which demonstrates that the change in the bonding configuration has a drastic influence of the electronic properties of the constituents. To further investigate the electronic structures of the molecules,
STM image is taken at +2.4 eV to resolve the spatial distributions of the LUMO of the molecules consisting the porous network. As shown in Figure 7.3b, the phenyl rings of NC-Ph₆-CN molecules are clearly resolved in the STM image, and the Cu atoms appear as bright protrusions in between neighboring molecules.

7.3 Summary and Conclusion
In conclusion, we have performed an experimental study on the metal coordinated self-assembles formed by NC-Ph₆-CN molecules and deposited Cu atoms on graphene surface. By tuning the stoichiometry between the deposited Cu atoms and the molecules, different kinds of molecular self-assemblies can be formed including basketweave-like pattern, hexagonal porous network and one dimensional molecular chains. The electronic properties of the molecules and coordinated Cu atoms are modified due to the change of the bonding motif associated with the structural transformation. The ordered metal coordinated self-assemblies hold the promise in tuning the electronic properties of graphene by molecular patterning.

7.4 Experimental methods
The experiments were carried out in a two chamber ultrahigh vacuum system (base pressure of 4 × 10⁻¹¹ mbar) housing a commercial low temperature STM (Scienta Omicron GmbH). The Ir(111) substrate was cleaned by repeated cycles of Argon ion sputtering followed by annealing to 1300 K. Graphene was grown via chemical vapor deposition by exposing the Ir(111) substrate held at 1200 K to a partial pressure of 4 × 10⁻⁷ mbar ethylene gas for 3 mins. The NC-Ph₆-CN molecules were heated to 550 K inside a commercial molecule evaporator (OmniVac) and deposited onto the graphene/Ir(111) substrate held at room temperature. The Cu atoms were
deposited with an electron beam evaporator (Oxford Applied Research Ltd). STM measurements were performed at both 77 K and 4.5 K with a mechanically cut Pt/Ir wire in constant current mode. All bias voltages are given with respect to a grounded tip. The STM images are analyzed with the WSxM software [30]. STS measurements were performed at 4.5 K by using a lock-in amplifier (modulation amplitude of 10 mV (rms) and frequency of 677 Hz).
References


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