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Doctoral Thesis

Chemical and Physical Properties of Nanostructures on Surface Investigated by Scanning Probe Microscopy

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Summary

The thesis provides an alternative approach to traditional polymerization technique for synthesising polymers with organic molecules. It focuses on the growth of 1D polymers particularly metal coordinated polymers and polymers with organometallic monomers, on metal surfaces. The properties of these nanostructures on surfaces are studied with the help of Scanning Probe Microscopy (SPM) techniques.

The growth of 1D metal coordinated polymers by co-deposition of transition metals and quinone molecules onto metal surfaces under ultra-high vacuum is explored, and a difference in metal coordination has been observed depending on the choice of metal. The structural and electronic properties of these 1D coordination polymers are characterized by means of STM/nc-AFM with CO-functionalized tips and supported by DFT and other theoretical calculations. The synthesis of H-bonded wires with the same precursor molecule has been discussed to emphasize the difference on metal coordination.

A distinct 1D polymer made up of organometallic ferrocene monomer units on Ag(111) surface has been synthesised and the properties have been characterized with STM/nc-AFM technique. The charge transport in the 1D nanowire has been analysed by carrying out lifting experiments with the STM tip and a transport model has been devised theoretically.

Introduction

The branch of surface science needs high resolving analysis methods to study and control the reactions directly at the surface. The invention of **scanning tunneling microscope (STM) and atomic force microscope (AFM)**, a breakthrough in this discipline serve as efficient tools to image and characterize materials at the atomic and submolecular scale, manipulate single atoms and molecules and investigate their reactivity in the assembled structures on surfaces [1]–[4]. Since then, chemists have been successful in preparing different dimensional (0D, 1D, 2D) molecular nanosystems on surfaces[5], [6].

The backbone of the **1D and 2D nanostructures** is mainly formed through different organic coupling reactions on surfaces such as Ullmann coupling, Glaser coupling, or dehydrogenative coupling etc., contributing to the carbon-carbon covalent bond; through hydrogen bonding and through coordinate bonding resulting in metal-carbon bonds or metal bonds with heteroatoms of the ligand [7]–[10]. In this scenario, low dimensional nanostructures especially one-dimensional (1D) wires on surfaces have been extensively explored and employed due to their future applications in the field of molecular electronics [11]–[15].

Among the various on surface **1D nanostructures**, organometallic nanowires and metal-coordinated polymers are gaining a considerable recognition in the recent years due to their wide range of electrical, magnetic, optical and electrochemical properties. The genre of organometallic species is unique as they integrate the intrinsic properties of the metal with the functionalities of the macromolecules or organic species attached to them and exhibit a

completely different dynamic behaviour or resemble the properties of both the constituents together. [7], [10], [16], [17]

In this thesis, two different 1D polymers have been synthesised on metal surfaces and their structural geometry and electronic properties have been investigated with the help of combined STM/nc-AFM technique under UHV. The common characteristic of both the 1D systems described herein, lies in the presence of metal atoms in the polymer chain but in two different fashions: the first quinone based polymer has metal atoms coordinated with the quinone ligand forming π -d conjugated coordination polymers while the second 1D polymer is in itself made up of metal containing organometallic monomer units i.e. ferrocene. The chemical structures of the 1D nanowires are clearly resolved by obtaining high resolution AFM measurements with CO functionalized tips [18].

Objectives

- Synthesis of 1D long, flexible H-bonded wires formed with **2,5-diamino-1,4-benzoquinonediimines** (2HQDIs) precursor molecules on Au(111) surface.
- Synthesis of 1D long, flexible coordination polymers with transition metals and 2,5-diamino-1,4-benzoquinonediimines (2HQDIs) molecules by dehydrogenative metlation on surface: MQDI (M=Cr, Fe, Co, Ni) wires on Au(111) surface; FeQDI and Cu₂QDI wires on Cu(111) surface.
- Synthesis of 1D long, flexible homo-coupled polyferrocenylenes on Ag(111) surface.
- Characterization of these 1D polymers with the help of low temperature STM/nc-AFM.

Instrumentation

The scanning tunneling microscope invented in 1981 by Gerd Binnig and Heinrich Rohrer, is the first scanning probe microscope and since then has been used to study the atomic structure of surfaces. There is a common mechanism inherent to mostly all probe microscopes featuring a feedback system (FS) that controls the distance between the tip and the sample. [19], [20]

The ambient atmosphere can result in adsorption and desorption of atoms and molecules from surface, while UHV is a solution for clean and well-defined surfaces. A stable tunneling process across the vacuum gap is also hindered due to the mechanical and thermal vibrations caused between the tip and the sample. [2] Moreover STM technique relying on the detection of tunnelling current is limited to only conducting samples

These drawbacks of STM led to the development of atomic force microscope (AFM) by Binnig, Quate and Gerber in 1986. During the operation of STM, it was noticed that there are significant atomic forces which act collaterally with the tunneling current and these forces could be used to gain atomic resolution on surfaces, hence AFM came into existence. This force microscope does not depend on the electrical conductivity of the sample hence can be used to image insulators as well. It can be used to image the surface without any surface preparation, thus does not required UHV conditions and can be operated in ambient conditions. [2]

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The major working principle of STM is based on quantum tunneling effect, which can be described as the phenomenon of electrons tunneling through a narrow potential barrier between metal tip and a conducting sample in the presence of an external electric field. The tunneling current is used as a feedback signal in a z-feedback loop. Thus, images are captured at a **constant current mode or topographic mode**. The imaging of atomically smooth surfaces can be more effectively captured at **constant height mode**, where the distance between the tip and sample is kept constant. [2]

The STM operation does not require vacuum but is mostly operated under ultra-high vacuum (UHV) environments as it avoids contamination or oxidation of surfaces. This is necessary for obtaining high resolution imaging of the surface topography as surface

oxidation reduces the conductivity of the surfaces and thus affects the tunneling current and causes problems in imaging. [21]

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The development of qPlus and Kolibri sensors with the force detector tips and in-built deflection sensors has led AFM to exceed the spatial resolution of STM. These quartz based sensors help to perform STM and AFM measurements in parallel with extreme stability and high signal-to- noise ratio. [22], [23]

Results

1. One dimensional Quinoid Based Polymers

Quinones belong to one of the most important classes of π -conjugated molecules with applications covering a broad spectrum ranging from chemistry to materials science, physics to biology, and engineering to medicine. Among them, **2,5-diamino-1,4-benzoquinonediimines** (2HQDIs) are particularly interesting because of the unusual distribution of their overall 12- π electrons system which can be described as two nearly-independent 6- π electrons subunits chemically connected through two C-C single bonds. Importantly, these quinones have attracted considerable interest as ligand in coordination chemistry because their low-lying π^* -orbitals can mix extensively with the valence d-orbitals of a metal center, allowing a full electron delocalization over both metal and ligand. Some chemists have been successful in the formation of coplanar polynuclear NiQDI complexes upto 3 repeat units in solution. The reaction takes place by simultaneous deprotonation of the ligand and metalation resulting in complexes, where the metal center is four fold coordinated to the ligand through two covalent bonds and two coordinate bonds.

The first part of on-surface synthesis focuses on synthesis of 1D H-bonded wires on Au(111) formed by the precursor molecule **2HQDI**. The synthesis procedure and on surface characterization of the H-bonded wires have been discussed with further analysis in Cahlik *et.al.* [24]. The second part of on-surface synthesis and substantial focus of this chapter is to describe the formation of 1D coordination polymers on two different metal surfaces Au(111) and Cu (111), through codeposition of transition metals and **2HQDI** ligand. The MQDI (M=Fe, Co, Ni, Cr) wires show four-fold square planar coordination mode while Cu₂QDI

afford a two-fold linear coordination. The coordination polymers have been characterized using STM and nc-AFM techniques and the properties of these coordination polymers have been studied further [25].

1.1. On surface synthesis of H-bonded wires

Two different types of chains were observed depending on the synthesis process: straight or symmetric chains and canted chains. The STM overview image in **Figure 1** show 3-100 nm long 1D symmetric chains assembled in directions independent of the Au(111) surface herringbone reconstruction, unlike the coordination polymers discussed further. There are characteristic bright spots at the end of these chains (**Figure 1b**) which are absent in the coordination polymers formed with the same ligand. The chains can be manipulated along the surface by contacting them at the end with the tip and moving it laterally. The consecutive lateral manipulations of a 1D straight chain are shown in **Figure 1c**.

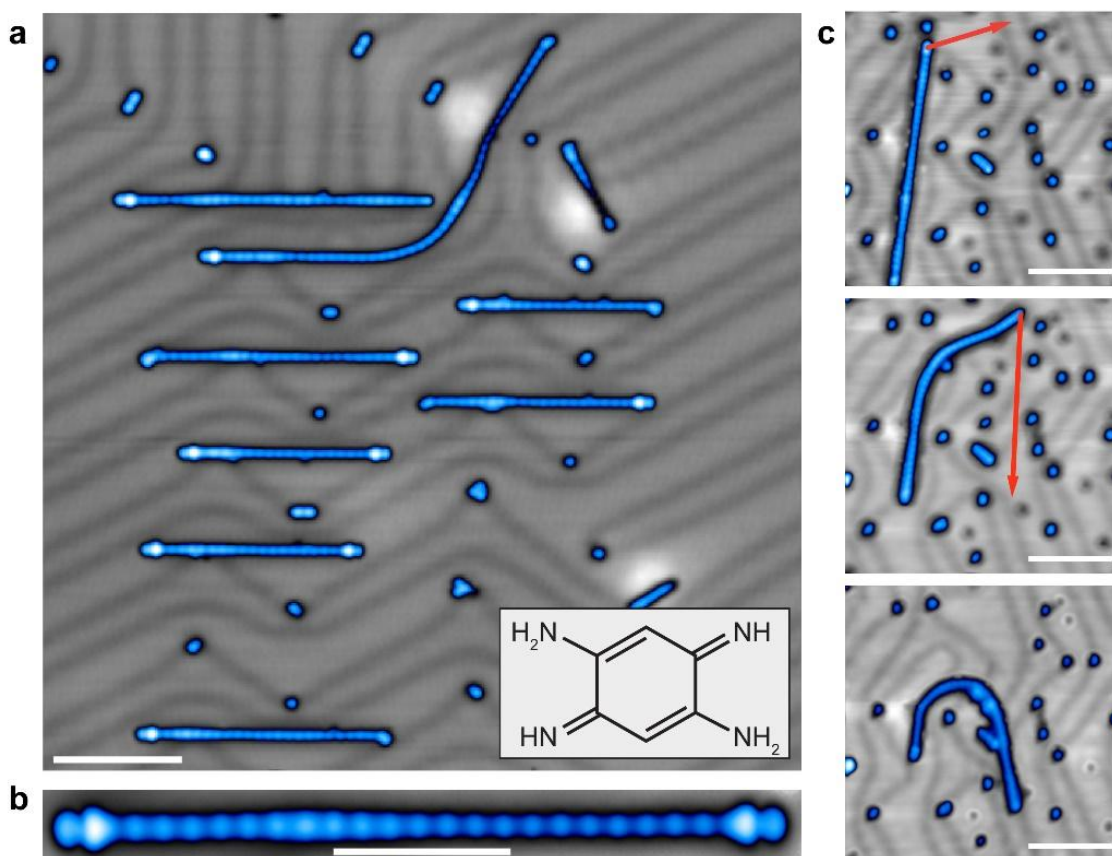


Figure 1: (a) Representative overview STM image of molecular chains and single molecule species. (50 mV, 10 pA, scale bar 10 nm). Inset: 2,5-diamino-1,4-benzoquinonediimine (**2HQDI**) structure. **(b)** Close-up STM image of the symmetric chain with characteristic bright spots at the ends. (30 mV, 5 pA, scale bar 5 nm) **(c)** From top to bottom: sequentially acquired STM images of chain manipulation experiment. Red arrows represent the probe movement after contacting the chain end (all images 100 mV, 10 pA, scale bars 10 nm). Adapted from [24].

The canted molecular chains are completely different from the symmetric chains in growth pattern and structure, **Figure 2a**. They contain more defects and grow significantly along the herringbone reconstruction of the Au(111) surface, also lack the bright spots at the ends. Compared to the symmetric chains, the mechanical stability of the canted chains is really

low thus lateral manipulation is prohibited and the chain splits into segments on moving with the tip (**Figure 2b**).

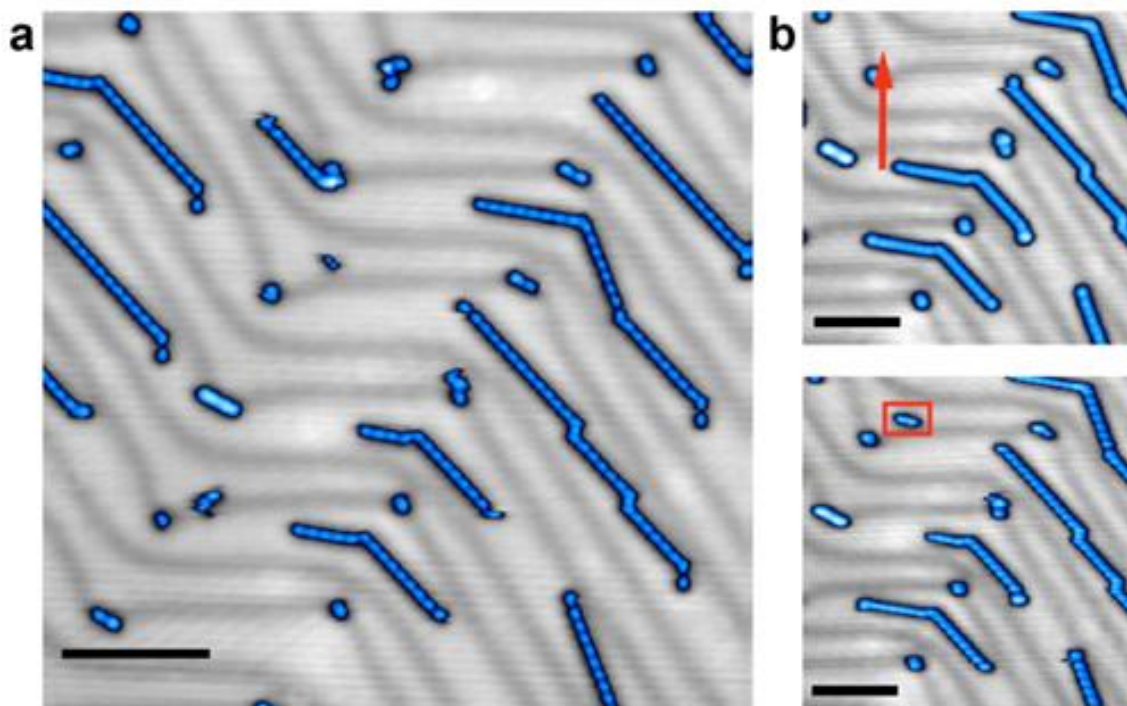


Figure 2: (a) Representative overview STM image of canted molecular chains. (140 mV, 20 pA, scale bar 10 nm) **(b)** STM images (140 mV, 20 pA) taken before and after manipulation experiment. Red arrows represent the probe movement after contacting the chain end (procedure detailed in Methods). Image on the right side (after the manipulation) show apparent splitting of the chain into segments. Scale bars 10 nm. Adapted from [24].

The structure of the two different types of chains as well as the individual species has been investigated with the help of high resolution nc-AFM images with a CO functionalized tip. The synthesis and characterization experiments have been discussed in detail; the nuclear

quantum effects which enhance the cohesion of relatively strong hydrogen bonding has been investigated theoretically (see Cahlik *et.al.* [24]).

1.2. On Surface Synthesis of Coordination Polymers

The on surface synthesis allows synthesis of long metal coordinated wires comprising metal atoms and quinone molecules, as a result of dehydrogenation reaction on the surface. The metals Cr, Fe, Co and Ni are introduced as neutral metal atoms from an electron-beam evaporator while Cu is provided directly by the Cu substrate. The ligand precursor **2HQDI** is deposited simultaneously by sublimation, and is let to react on Cu(111) and Au(111) surfaces with the metal atoms.

The overview STM images of MQDI (M=Cr,Fe,Co,Ni) wires on Au(111) and FeQDI and Cu₂QDI on Cu(111) are shown in Figure 3. The coordination polymers on Au(111) are long and flexible exceeding lengths of 100 nm. They follow the herringbone reconstruction on the Au(111) surface and can be manipulated and bent into different shapes, thus showing a weak interaction with the substrate. In contrast FeQDI and Cu₂QDI wires branch more frequently on Cu(111) surface and also follow specific directions on the substrate. This branching phenomena on Cu(111) is kinetically controlled and can be attributed to the higher diffusion barriers compared to Au(111). The zoom-in STM images of MQDI wires on Au(111) and FeQDI wires on Au(111) show similar periodicity while Cu₂QDI wires on Cu(111) appear significantly wider.

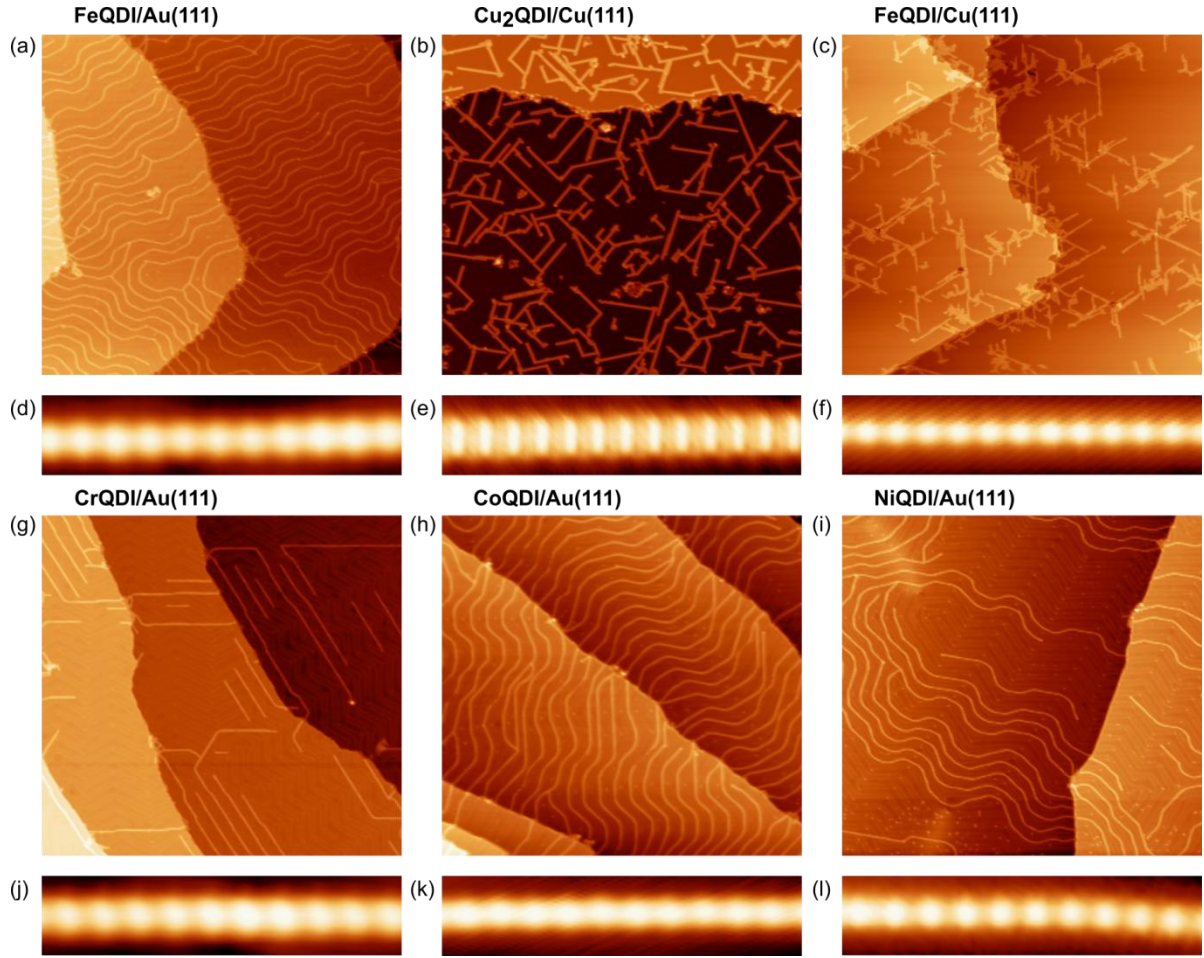


Figure 3: STM images of {Cr, Fe, Co, Ni}QDI wires on Au(111) and of Cu₂QDI and FeQDI wires on Cu(111). The overview images are 200 × 200 nm² and the zoom-in images are 8 × 2 nm². Imaging parameters (bias voltage, tunnel current set point): (a) (500 mV, 10 pA); (b) (1.2 V, 10 pA); (c) (500 mV, 20 pA); (d) (-200 mV, 23 pA); (e) (300 mV, 30 pA); (f) (-200 mV, 50 pA); (g) (100 mV, 30 pA); (h) (350 mV, 10 pA); (i) (100 mV, 42 pA); (j) (30 mV, 10 pA); (k) (-400 mV, 32 pA); (l) (100 mV, 42 pA). Adapted from [25]

The periodicity difference in the coordination polymers has been examined and is in agreement with nc-AFM observation (Figure 4). The images show that FeQDI wires on Au(111) as well as on Cu(111) show the same periodicity of $\sim 7.7 \pm 0.1$ Å while Cu₂QDI wires on Cu(111) show a periodicity of 6.8 ± 0.1 Å. The nc-AFM images clearly shows that MQDI wires on Au(111) and FeQDI wires on Au(111) are isostructural showing a four-fold square

planar coordination geometry. On the other hand, Cu₂QDI wires on Cu(111) surface show two-fold linear coordination geometry with the two nitrogen atoms of the ligand arranged side-by-side. The coordination mechanisms of the 1D wires have been understood better with the help of theoretical calculations.

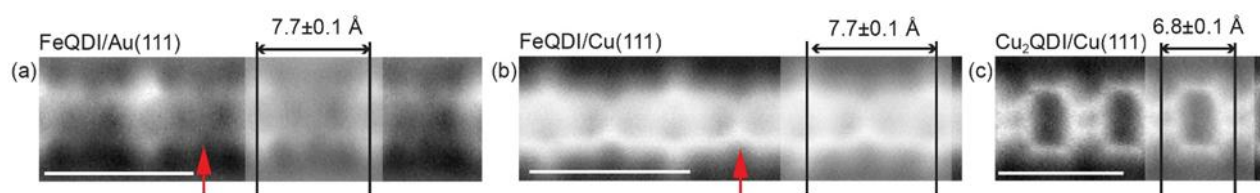


Figure 4: High resolution constant height nc-AFM images with CO modified tip of **(a) FeQDI** wires on Au(111) **(b) FeQDI** wires on Cu(111) and **(c) Cu₂QDI** wires on Cu(111). Both (a) and (b) exhibit the same characteristic "x-like" contrast feature (marked by red arrows) between adjacent molecular units and same lattice periodicity, clearly distinct from the contrast and the periodicity between the neighboring molecules in **Cu₂QDI** wires. [Scale bars: 1 nm; Aosc = 50 pm]. Adapted from [25]

In the case of Cu₂QDI wires, 12 membered macrocycles involving the 12 π electrons of the ligand has been identified which are electronically independent and prevents a full electron delocalization over the wire. The macrocycles are not formed in MQDI wires on Au(111) and FeQDI wires on Cu(111) which clearly states the difference in the coordination mechanism of Cu₂QDI wires. The aromatic character of the macrocycle in Cu₂QDI wire has been predicted with the help of ACID plot, NICS plot and also HOMA calculations. These aromaticity predictions have also been made for FeQDI wires on Au(111) for comparison. These predictions clearly show that the macrocycles constituting the Cu₂QDI wire are antiaromatic in nature thus forming a new class of macrocyclic compounds on surface.

2. Synthesis of Polyferrocenylenes on Ag(111) surface

The remarkable discovery of **ferrocene** in the 1950's attracted a wide range of scientists and chemists due to its extraordinary chemistry and electronic properties thus gave birth to a prominent class of compounds called *metallocenes* in organometallic chemistry. Ferrocene containing polymers, especially **polyferrocenylenes** are an attractive target owing to their phenomenal properties due to the short distance between the directly bonded ferrocene units through the covalent bonding between the adjacent cyclopentadienyl (Cp) rings.

There have been several attempts and developments in the synthesis of polyferrocenylenes after Korshak and Nesmeyanov et.al. described them for the first time in the early 1960's. A large number of polymerization reactions using different monomers were proposed but most of the polymers synthesized were low weight, insoluble and impure. Herein, one dimensional (1D) polyferrocenylene nanowires on Ag (111) surface with lengths up to 50 nm, representing the longest homo-coupled polyferrocenylene has been synthesized by thermally induced on surface Ullmann coupling (deiodination) of 1-1' diidobiferrocene (**Fc₂-I₂**) molecules under ultra-high vacuum.

The precursor molecules **Fc₂-I₂** were deposited by the process of sublimation using E-beam evaporator onto clean Ag(111) surface. The self-assembly of molecular adsorption was characterized by STM imaging (**Figure 5a**). The individual molecules in the islands were resolved as double protrusions under constant height scanning mode (**Figure 5a inset**), each protrusion resembling a ferrocene unit of the molecule. The polymer islands with two different stacking have been observed in the STM topography images under constant height (**Figure 5b inset**)

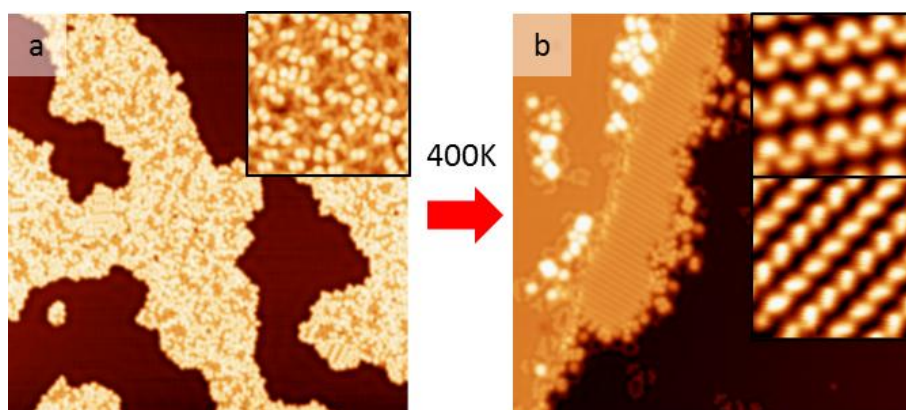


Figure 5: Polymerization of Diiodobiferrocene on Ag(111): (a, b) STM overview of the diiodobiferrocene islands on Ag(111) before and post on-surface polymerization, respectively. Scanning parameters: (a) $V = -500$ mV, $I = 20$ pA, size: 100×100 nm², inset: $V = -100$ mV, $I = 20$ pA, size: 8×8 nm²; (b) $V = -100$ mV, $I = 20$ pA, size: 40×40 nm², insets: constant height current images, $V = 1$ mV, size: 3×3 nm². Adapted from [26]

The high resolution AFM images on the 2D polymer islands (**Figure 6a, b**) with CO functionalized tip show distinct contrasts for the two different stacking. The molecular periodicities of the two islands, both along the row and between the rows have been measured. In this regard, a meander and a zig-zag models of two PFc conformers have been proposed and justified with DFT calculations and AFM simulations (**Figure 6d, e**) on Ag(111) surface.

The high resolution AFM image of free polyferrocenyle chain on Ag(111) surface is shown in **Figure 6c**. The ferrocene units exhibit different apparent heights depending on the configurations on the silver surface: perpendicular when cyclopentadienyl rings are oriented perpendicular to the substrate and inclined when the cyclopentadienyl units are inclined at an angle of $\sim 45^\circ$ from the surface.

With the help of scanning tunneling spectroscopy (STS), the electronic structure of the 2D islands as well as free-standing 1D molecular wire has been identified (**Figure 6g**). The meander polymer island has comparatively a lower band gap than the zig-zag polymer island. The electronic structure of single polyferrocenylene chain has also been analysed, wherein the dI/dV spectrum of the perpendicular configuration is similar to the zig-zag polymer island while the inclined configuration shows no band gap corresponding to a metallic behaviour.

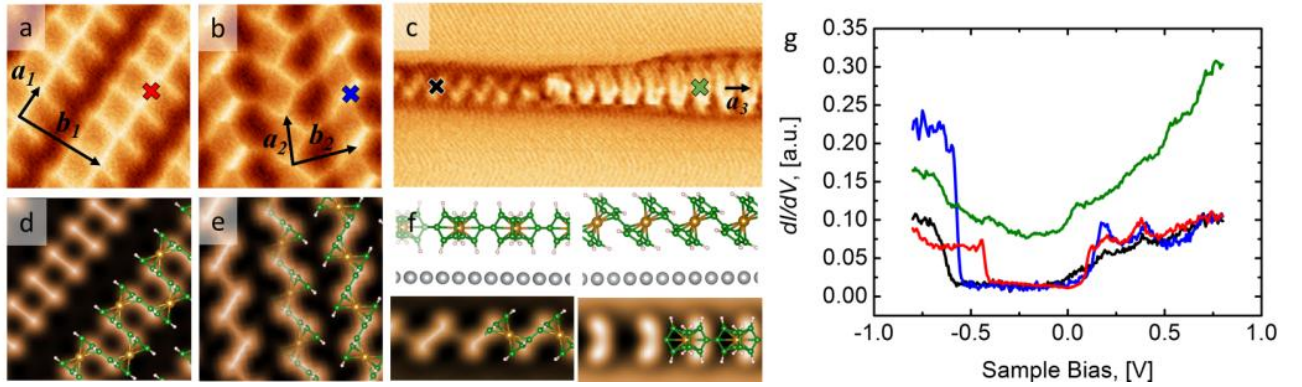


Figure 6: Arrangement and Electronic Structure of Polyferrocenylene in Self-Assembled Islands and Individual Chains: (a-c) High resolution constant height frequency shift images for the two polyferrocenylene 2 islands with different molecular arrangement and the isolated polymer chain. Molecular periodicity highlighted by a and b vectors. (d-f) Simulated AFM images for the polyferrocenylene islands with different molecular arrangement and the isolated polymer chain. (d, e) Proposed top view ball-stick models are superimposed over the simulated images. (f) Proposed side- and top-view ball-stick models are shown. (g) dI/dV measured on the two islands and the free chain of polyferrocenylene. Red, blue, green, and black graphs correspond to measurements on meander island, zig-zag island, inclined configuration and perpendicular configuration of the free chain, respectively. The positions of spectroscopy are marked in (a-c) by crosses of the same color. Scanning parameters: $V = 10$ mV, $A_{osc} = 50$ pm, (a, b) size: 2×2 nm², (c) size: 8×4 nm². Model: Fe, C, H, Ag atoms correspond to the yellow, green, white, and silver colors, respectively.

In addition, **lifting experiments** by STM tip has been performed to study charge transport and mechanical response along single molecular nanowires. The I/V spectra has been recorded as a function of tip-sample distance, which depicts opening of an apparent band gap as the chain is lifted slowly from the surface.

Conclusions

The dissertation confers **two different types of 1D polymers** or nanowires on metal surfaces, which differ on the coupling reactions and nature of covalent bonding between the individual monomer units. The structure and properties of the 1D polymers have been investigated and characterized using **low temperature scanning tunneling microscope/atomic force microscope (LT-STM/AFM)** under ultra-high vacuum conditions. The experimental evidence has been supported by non-contact AFM (nc-AFM) image simulations, clearly resolving the chemical structures of the 1D nanowires as obtained by high resolution AFM measurements with CO functionalized tips. A combination of experimental and theoretical study provided a complete analysis of different structural, chemical and electronic properties of the 1D polymers on the surface.

The advanced possibilities of synthesising such polymers on surface help to overcome the challenges faced in solution polymerization. The limits of solubility and purity do not allow producing polymers of large molecular weight thus only short oligomers have been synthesised ever. It is also not possible to separate individual polymers in solution and study their physical and chemical properties, thus making the on surface characterization techniques an asset for studying such systems. Even though there is a huge progress in the field of UHV on surface chemistry, there are a lot of hurdles in bringing the pure academic research into application. It is possible to get individual polymers on surface but cannot be transferred outside the UHV system for further characterizations such as mass analysis.

The ultimate goal here is to demonstrate the new possibilities of synthesizing long flexible metal coordination polymers and organometallic polymers and characterize their material properties, which has not been possible in solution.

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Overview of own publications

- **Vijai M. Santhini**, Christian Wackerlin, Aleš Cahlík, Martin Ondraček, Simon Pascal, Adam Matěj, Oleksandr Stetsovych, Pingo Mutombo, Petr Lazar, Olivier Siri and Pavel Jelínek ; 1D Coordination π -d Conjugated Polymers with Distinct Structures Defined by the Choice of the Transition Metal: Towards a New Class of Antiaromatic Macrocycles. *Angew.Chem. Int. Ed.* **2021**, 60, 439–445.

Recently π -d conjugated coordination polymers have received a lot of attention owing to their unique material properties, although synthesis of long and defect-free polymers remains challenging. A novel on-surface synthesis of coordination polymers with quinoidal ligands has been introduced under ultra-high vacuum conditions, which allows formation of flexible coordination polymers with lengths up to hundreds of nanometers. Also, this approach allows the incorporation of different transition-metal atoms with four- or two-fold coordination. Remarkably, the two-fold coordination mode revealed the formation of wires constituted by (electronically) independent 12-membered antiaromatic macrocycles linked together through two C-C single bonds.

- **Vijai M. Santhini**, Oleksandr Stetsovych, Martin Ondraček, Jesus I. Mendieta Moreno, Pingo Mutombo, Bruno de la Torre, Martin Švec, Jiri Klivar, Irena G. Stára, Hector Vazquez, Ivo Stáry, and Pavel Jelínek; On-Surface Synthesis of Polyferrocenylene and its Single-Chain Conformational and Electrical Transport Properties. *Adv. Funct. Mater.* **2021**, 31, 2006391.

Metallopolymers contain multiple redox-active centers allowing extra control of their intriguing properties, unlike intrinsically conductive organic polymers. In this context, ferrocene polymers are particularly attractive but the research of the iconic poly(1,1'-ferrocenylene), a main-chain ferrocene polymer with the most densely bound redox-

active iron centers, has been practically stopped because it is an insoluble and rather inhomogeneous material. The synthesis of polyferrocenylene on the Ag(111) surface is reported, based on the Ullmann coupling of 1',1'''-diiodo-1,1''-biferrocene. Conformationally flexible single-chain nanowires up to 50 nm in length, thus overcoming the limits of conventional solution polymerization, are characterized by scanning probe microscopy techniques achieving atomic resolution. Electrical conductivity measures are performed on the single chain in the longitudinal directions revealing apparent metal-to-semiconductor transition (depending on the number of ferrocene units lifted from the surface). A simple transport model is also established to rationalize this observation.

- Aleš Cahlík, Jack Hellerstedt, Jesús I. Mendieta-Moreno, Martin Švec, **Vijai M. Santhini**, Simon Pascal, Diego Soler-Polo, Sigurdur I. Erlingsson, Karel Výborný, Pingo Mutombo, Ondrej Marsalek, Olivier Siri, and Pavel Jelínek; Significance Of Nuclear Quantum Effects In Hydrogen Bonded Molecular Chains. *ACS Nano* **2021**, DOI: 10.1021/acsnano.1c02572.

In hydrogen-bonded systems, nuclear quantum effects such as zero-point motion and tunneling can significantly affect their material properties through underlying physical and chemical processes. The influence of nuclear quantum effects on the hydrogen bond strength remains doubtful in the context of both structural and electronic implications thus there is a lot of room to explore such effects. In this regard, hydrogen-bonded one-dimensional quinonediimine molecular networks have been studied which may adopt two structural configurations depending on the synthesis parameters and two isomeric electronic configurations via proton transfer. It has been demonstrated that concerted proton transfer promotes a delocalization of π -electrons along the molecular chain, which

enhances the cohesive energy between molecular units, increasing the mechanical stability of the chain and giving rise to distinctive electronic in-gap states localized at the ends. These findings demonstrate the identification of a class of isomeric hydrogen-bonded molecular systems where nuclear quantum effects play a dominant role in establishing their chemical and physical properties.