

Self-Assembly of Pd-Cyclometalates and Melem on surfaces: a photo-electron spectroscopy and scanning probe microscopy investigation

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Abstract

The controlled assembly of organometallic complexes at solid surfaces is a key step towards the rational design of nanostructured materials for heterogeneous catalysis. Although the interest in surface-confined molecular systems is increasing, the relationship between molecular structure, deposition technique, and thermally induced morphological changes is still not completely understood. This thesis addresses these open questions for the two specific cases of three palladium cyclometalated (CyPd) complexes deposited on highly oriented pyrolytic graphite (HOPG) investigated by X-Ray photoemission spectroscopy (XPS) and Atomic Force Microscopy (AFM) at UNIGE and of the organic molecule Melem on Au(111) studied by Scanning Tunnelling Microscopy (STM) during a six month stay at the Institute of Applied Physics (IAP) at Vienna University of Technology (TU Wien).

The deposition of CyPd complexes, performed either by drop-casting from a solution of dimethylformamide (DMF) or by sublimation under ultra-high vacuum (UHV) conditions, leads to non-dissociative adsorption as inferred by XPS. The direct comparison of solution-based and vacuum-based deposition routes shows that the same chemical state is obtained. Particular emphasis was placed on the Pd 3d core-level analysis in order to probe the chemical state and stability of the palladium catalytic centre. Structures with different morphologies were evidenced by AFM at the mesoscale, corresponding to dendritic and fibrous networks, as well as dense layered structures which undergo significant changes upon annealing.

Melem molecules sublimated on Au(111) in UHV form Nitrogen-rich carbon-based layers on which metallic atoms can be supported, thus preventing their sintering. Then Fe atoms were deposited on the Melem honeycomb overlayer. This system was investigated by XPS and STM. XPS inspection indicated that Fe atoms end up in a 4-fold coordinated configuration. STM images show that Fe adsorption induces the formation of a more compact Melem structure. Clustering of Fe atoms was negligible up to 2 Fe atoms per Melem overlayer unit cell.

Both investigated systems show that self-assembled C-based nanostructures with metallic centers can be generated by depositing organic/organometallic precursor molecules on surfaces. These nanostructures hosting single isolated metal atoms are stable well above room temperature (RT) and may therefore act as single atom catalysts.

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List of acronyms

1D/2D	1-Dimensional / 2-Dimensional
AFM	Atomic Force Microscopy
BE	Binding Energy
CRM	Critical Raw Materials
CyPd	Cyclometalated Pd complex $C_{22}H_{14}Br_2N_2Pd_2Cl_2$ (dibrominated)
CyPd(1)	Cyclometalated Pd complex $C_{22}H_{16}N_2Pd_2Cl_2$ (non-brominated)
CyPd(2)	Cyclometalated Pd complex $C_{22}H_{16}N_2Pd$ (non-halogenated)
CyPds	Cyclometalated complexes
DFT	Density Functional Theory
DMF	N,N-dimethylformamide
EI	Economic Importance
ESCA	Electron Spectroscopy for Chemical Analysis
HOPG	Highly Oriented Pyrolytic Graphite
HR	High-Resolution
KE	Kinetic Energy
ML	Monolayer
Pd	Palladium
PGMs	Platinum Group Metals
PSPD	Position Sensitive PhotoDetector
PVD	Physical Vapor Deposition
RT	Room Temperature
RT-STM	Room Temperature Scanning Tunneling Microscope
SAC	Single atom catalyst
SR	Supply Risk
STM	Scanning Tunneling Microscopy

T_{Dec}	Decomposition Temperature
TGA	Thermogravimetric Analysis
T_{sub}	Sublimation Temperature
UHV	Ultra High Vacuum
UNIMIB	University of Milano Bicocca
XPS	X-ray Photoemission Spectroscopy

I. Introduction

Over the past few decades, the expansion of industrial activities and technological developments has intensified resource consumption and energy usage and has placed growing pressure on industrial production systems, making sustainability one of the major challenges of modern society.

It has been estimated that approximately 85% of manufactured products rely on catalytic processes at some stage of their production. Therefore, catalysis has a major impact across many industrial sectors, including energy production (petrochemicals), pharmaceuticals manufacturing, novel-materials production (polymers), and environmental remediation [1].

Despite the huge importance of catalysts for industrial and economic activities worldwide [2], many of the most effective catalytic systems rely heavily on metals of high cost (Palladium, Rhodium, Platinum...) and/or of difficult availability. In addition, conventional metal-based catalysts usually consist of micro or nano-sized particles, in which the surface atoms which actively participate in the chemical reaction are only a small fraction of the internal material which is catalytically inactive. This reduces the mass/efficiency ratio of the catalyst and increases the metal loading required to achieve the desired catalytic activity, increasing further economic, resource availability and sustainability concerns. Consequently, it is essential to develop novel catalysts that maximize the efficiency while minimizing the usage of precious metals. This can reduce energy requirements, improve reaction selectivity, minimize by-product formation, and enable more economical synthetic pathways assuring a sustainable alternative. One promising approach is to increase the dispersion of the nanoparticles by reducing their size so that a larger percentage of their atoms is exposed to the reactants. The ultimate limit of this approach corresponds to single isolated atoms deposited on inert templates, known as single atom catalysts (SACs). Given the simplicity of single atoms, only one reaction pathway is possible leading to an absolute selectivity[3][4][5].

The European Union Critical Raw Material (CRM) assessment [6] classifies materials based on supply risk (SR – threshold 1.0) and economic importance (EI – threshold 2.8). Materials exceeding the two thresholds are considered critical. In a recent paper, Bajada et.al [7] discuss the growing concerns associated with the usage of the catalytically active metals, concentrating mainly on the platinum group metals (PGMs). Palladium (Pd), the critical element I investigated, is intensively used in the automotive industry (in catalytic converters), in pharmaceuticals as a catalyst for drug production and in general in chemical processing. Although we are mainly interested in its catalytical properties, Pd finds application also in electronics for its excellent electrical conductivity and high melting point, in dental alloys of which it is a key component, and in hydrogen storage for its ability to absorb it.

In Figure 1 , I report the assessment done for Pd for the years 2011, 2014, 2017, 2020 and 2023 [7]. In 2023, Pd had an EI value of 8.1 and a SR value of 1.5. In that year, the global Pd production reached 210 t, with Russia being the leading supplier (44%), followed by South Africa (34%) [6]. Bajada et.al. forecasted an increase in supply risk close to 10 and an economic importance of 9for 2035, increasing its criticality. This growing need is linked to the increased demand for hybrid cars and to the anticipated growth in chemical industry [8]. The study of Bajada et al. [7] reinforces therefore the necessity to optimize Pd consumption in catalytic processes and suggests that SACs may significantly help in this respect.

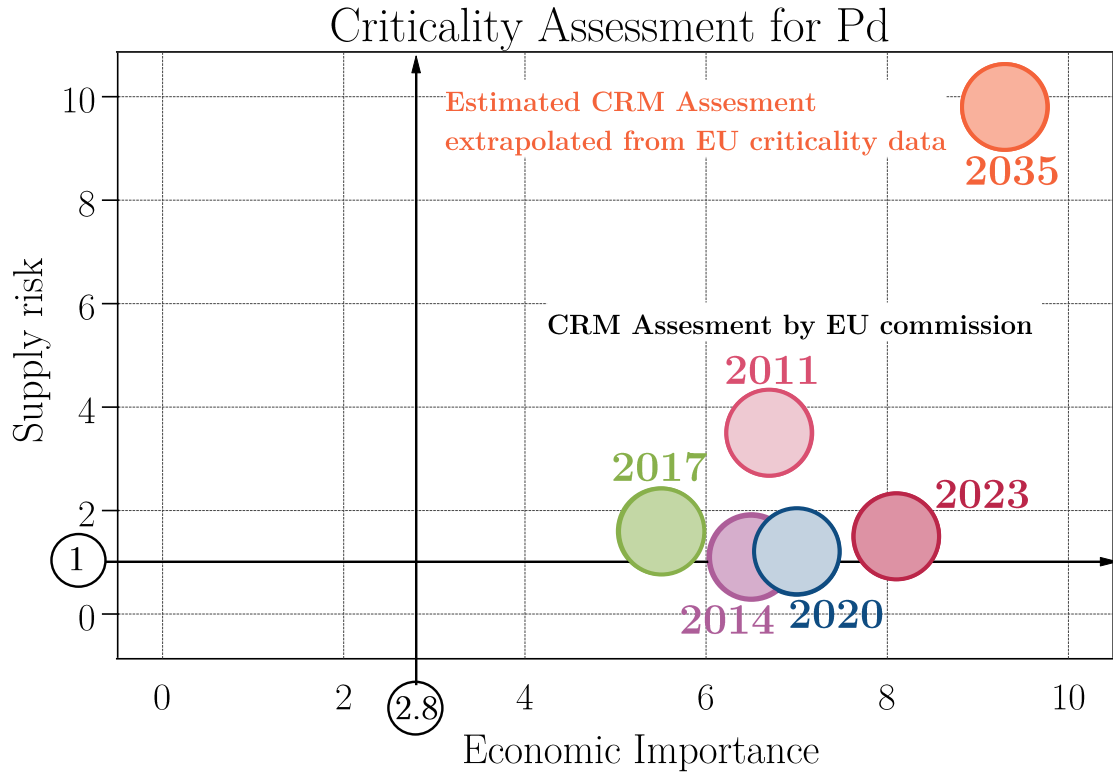


Figure 1: Critical Raw Material Assessment (CRM) for Pd reproduced from [7].

One of the principal challenges associated with SACs is the stabilization of the isolated atoms. Various strategies can be employed in order to avoid their sintering and ensure a stabilized environment. I adopted two approaches are in this thesis work. The first one consists of embedding the metal atoms into the organo-metallic complexes cyclometalates. The second approach consists in depositing them onto a nitrogen-rich organic superlattice self-assembled on a surface.

To this purpose I investigated the interaction and the self-assembly of three different Pd-cyclometalated complexes on highly ordered pyrolytic graphite (HOPG) surfaces and of Fe atoms evaporated on a Melem overlayer on Au(111) in the attempt to create networks with single active sites.

Cyclometalated palladium complexes (CyPd)s represent a particularly suitable platform. They form a pivotal class of organometallic compounds, exhibiting a sufficiently high stability to be employed in catalytic reaction conditions. This stability arises from the presence of E–M–C bonds, where E stays for a donor atom, typically from group 15 or 16, M for the metal center, and C for carbon with either sp^2 or sp^3 hybridization [9][10].

These compounds are characterized by the formation of stable Pd-C bonds, which enhance the robustness of the Pd center, and have drawn considerable interest due to their tunable structural, electronic, and catalytic properties, leaving them highly effective in a broad range of catalytic transformations, including cross-coupling, C-H activation, and oxidative processes [11][12]. The stability, electronic flexibility, and modular ligand design of Pd-cyclometallated complexes make them ideal candidates for homogeneous catalysis and interesting precursors for the preparation of heterogeneous catalysts [13][14]. Beyond molecular design, the organization of such CyPds on surfaces provides an additional level of control over their properties. Surface-supported systems offer a bridge between homogeneous and heterogeneous catalysis, combining the structural definition of molecular systems with the robustness of solid support. In particular, the formation of ordered molecular assemblies enables control over the spatial distribution of the active sites, which may influence catalytic performance through site isolation [15]. A powerful strategy to achieve such organization involves the use of halogen-functionalized molecules capable of undergoing on-surface reactions such as Ullmann coupling, leading to the formation of extended covalent networks. Recent studies have highlighted how surface-mediated Ullmann coupling enables the bottom-up fabrication of well-defined nanostructures and well-ordered 2D networks [16][17].

To the best of my knowledge, only a few studies have so far addressed the surface morphology and the interaction of cyclometalates with the surface using a bottom-up approach. Wilde et al. [18] investigated Pt(II) cyclometalates on Ag(111) by Scanning Tunneling Microscopy (STM) demonstrating that the intermolecular interactions upon 2D confinement are mainly driven by the entanglement of the aliphatic side chains. In a subsequent STM study, Ren et al. [19] reported on tetradentated Pt(II) complexes on (111) noble metal surfaces. They observed the rupture of the C-N bond in the organometallic compound upon annealing and found a strong dependence of the reactivity of the system on the coordination geometry of the compounds and on the nature of the substrate. H. Gersen et al. [20] reported dissociation of Ir(III) phosphorescent emitter molecules on Cu(110). The latter systems were essentially investigated as dyes, while the focus on Pd cyclometallates resides in their catalytic applications.

In order to understand how molecular structure influences surface behavior and catalytic functionality, I adopted a systematic approach in the design of the molecular systems I investigated. A series of closely related Pd-cyclometalated molecules was considered, in

which specific functional groups were progressively changed. This strategy allows for a step-by-step evaluation of how each modification affects both the interaction with the substrate and the ability of the molecules to organize into ordered structures.

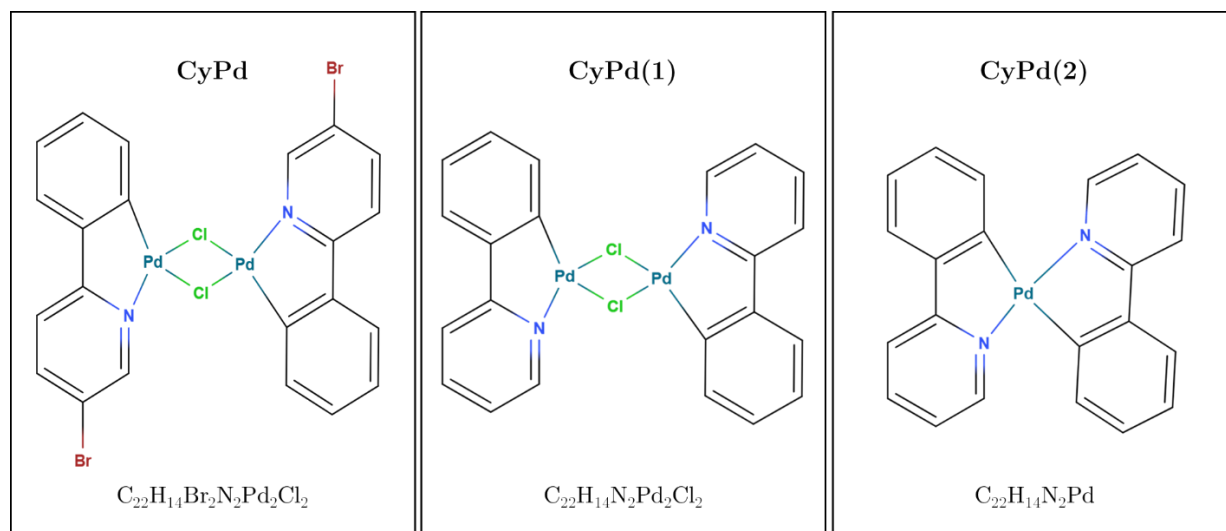


Figure 2: The chemical structure and the chemical formulas of the studied Pd cyclometalated complexes.

The three cyclometalated complexes are reported in Figure 2. They have been deposited on HOPG both by sublimation in vacuum and drop-casted under ambient conditions. They all have a butterfly-shape with two Phenyl-Pyridine wings and a central ring containing the Pd atoms.

I started my experiments with the CyPd/HOPG system, that is the most complex of the three since, besides the double Pd-Cl bridge that affects the local chemical environment of the metal without promoting intermolecular coupling, this molecule also presents two Br substituents in the Phenyl-Pyridine rings. The rationale behind it is that this molecule had already been investigated by sublimation on Ag(110) by the laboratory in which this thesis was conducted [12, 13]. The bromines were supposed to facilitate on-surface coupling processes such as Ullmann coupling, leading to the emergence of an organized network. In the work done by Barcelon et al. [12] and Stojkovska et al. [13] CyPd was deposited at room temperature (RT) and under ultra-high vacuum (UHV) conditions. The different self-assembled geometries were characterized by STM, X-Ray photoemission spectroscopy (XPS) and density functional theory (DFT) calculations.

The choice of the Ag(110) surface was based on the assumption that its relatively high reactivity, would promote on-surface coupling reactions and strongly influence molecular organization via the Ullman coupling reaction. They found, however, that molecular dissociation occurs upon adsorption and that the cross coupling between the fragments leads to the surface assisted synthesis of 6,6'-diphenyl-3,3'-bipyridine admolecules [21], while the Pd atoms move to the silver subsurface. The possibility to employ the CyPd/Ag(110) system as a C-based network doped with catalytically active Pd atoms had therefore to be ruled out.

The investigation of the adsorption of the corresponding non-brominated complex CyPd(1), ($\text{C}_{22}\text{H}_{16}\text{N}_2\text{Pd}_2\text{Cl}_2$) containing only Chlorine, on Ag(110) has been the object of my Master thesis. The structures observed upon deposition by STM indicate dissociative adsorption also for this molecule with the formation of different configurations than for CyPd/Ag(110), with Pd atoms moving to the subsurface. Furthermore, in this case, an Ag surface reconstruction is induced by the halogens.

These results indicate that the interaction between these molecules with the substrate is a key factor governing their organization and reactivity and that the Ag surface is too reactive. To this end, I chose to investigate their adsorption on highly oriented pyrolytic graphite (HOPG), presenting an inert platform that preserves molecular integrity as a model substrate. Comparison of the outcome for the two substrates is essential for disentangling surface-driven processes from intrinsic molecular behavior [3]. I therefore investigated CyPd and CyPd(1) on HOPG.

The last investigated molecule, CyPd(2) ($\text{C}_{22}\text{H}_{16}\text{N}_2\text{Pd}$), lacking halogen substituents, was used as a reference system to establish the intrinsic adsorption behavior of the molecular backbone and the palladium center with Pd linked to 2 N instead of 2 Cl. This makes it possible to distinguish between spontaneous organization and functionality-driven assembly. By comparing these three systems: bromine-functionalized, dibrominated and non-halogenated, it becomes possible to disentangle the respective roles of molecular stability, metal coordination, and intermolecular coupling in driving self-assembly.

Particular emphasis has been placed in the present thesis on the comparison between UHV sublimation and solution-based drop-casting deposition methods of the organic molecules. A critical aspect is thereby learning how to translate the fundamental

knowledge on the nanostructures formed under UHV conditions to scalable and robust systems obtained by drop casting suitable for practical applications.

While UHV deposition provides a highly controlled procedure that preserves molecular purity and enables a precise investigation of surface structures, such conditions remain idealized and require sophisticated instrumentation, strict vacuum environment, and relatively demanding experimental procedures. In contrast, drop-casting is widely recognized as a simple, rapid, and equipment-free solution-based deposition technique, extensively employed for preparing modified surfaces in electrochemistry and catalysis [14]. It is a practical method for forming films directly from liquid solutions at ambient pressure and temperature. Many studies on thin films and device fabrication emphasize that solution-based processing is an important route for producing materials at low cost and at large scale. In organic-inorganic photovoltaics, Organic Light-Emitting Diode (OLED)s, and chalcogenide thin-film research, solution-processed layers, including drop-casted films, are repeatedly cited for their advantages in low cost, high throughput, and scalability, while acknowledging the trade-offs of increased variability in thickness and morphology [15]. For catalyst development, these considerations underscore the importance of investigating deposition strategies that operate outside of vacuum, since materials prepared under ambient conditions are more representative of realistic synthesis environments and industrially relevant production pathways than vacuum-sublimated model systems alone. So far relatively little studies report a direct comparison of surfaces prepared by sublimation and by solution-based deposition by XPS. A direct comparison between different deposition methods has been provided for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films [16]. Moreover, major XPS methodological reviews focus on general sample preparation practices without providing systematic evaluations of drop-casting versus sublimation. Parameters such as solvent–molecule interactions, concentration effects, and evaporation dynamics can potentially modify the chemical composition of the surface-supported system, alter ligand coordination, or influence the stability of the palladium center.

In particular, for Pd-cyclometalated molecules, preserving the coordination environment of the metal after solution deposition is essential, since the catalytic properties strongly depend on the local chemical structure of the Pd active site. For this reason, comparing sublimated and drop-casted systems is crucial for evaluating the stability of the molecular compounds under different deposition conditions. Such a comparison makes it

possible to determine whether the chemical composition observed under controlled UHV conditions is maintained after solution processing, thereby assessing the suitability of these molecular systems for more practical and scalable fabrication approaches. This aspect is especially important in the context of developing sustainable catalytic materials, where solution-processable systems are highly desirable for future applications. The lack of studies reporting direct comparisons of systems prepared by the two deposition methods by XPS reinforces the relevance of the present study for filling the gap in literature.

During my thesis, I visited the Institute of Applied Physics (IAP) of the University of Vienna. There, I had access to a RT-STM facility by which I tried to investigate CyPd/HOPG. The molecules were however too mobile to be imaged at RT.

The other system I investigated is the Fe dosed Melem overlayer on Au(111).

Melem ($\text{C}_6\text{N}_7(\text{NH}_2)_3$) is a planar molecule featuring a heptazine core, characterized by intra and interlayered hydrogen bonds. It is widely recognized as a fundamental building block for the formation of graphitic carbon nitrides. When deposited on Au(111), it forms an ordered honeycomb-like supramolecular network presenting well-defined porous cavities [22]. The work hypothesis was that such nitrogen rich sites might provide a confined coordination environment that could trap and stabilize individual metal atoms. Sintering of the Fe atoms would thus be impeded by the organic template on which such atoms are deposited. The Melem overlayer has therefore been characterized STM as well by XPS both before and after the deposition of the Fe atoms.

II- Experimental Section

II.1 Synthesis and characterization of the molecules

The Pd cyclometalated complexes used in the present thesis were synthesized in form of powders by prof. A. Papagni at Università di Milano Bicocca (UNIMIB) and subsequently used as received for surface deposition studies. All reagents and solvents were purchased from commercial sources (Fluorochem Co.; Tokyo Chemical Industry Co. and Aldrich Chemical Co.) and used as received.

CyPd molecules ($[(5\text{-bromo-2-phenylpyridine})\text{Pd}(\mu\text{-Cl})_2]$) were synthesized from a mixture of PdCl_2 (200 mg, 1.1 mmol), 5-bromo-2-phenylpyridine (292 mg, 1.2 mmol) and CHCl_3 (5 mL) stirred at 100 °C in a sealed tube for 24 h under nitrogen atmosphere, following the protocol reported in ref.[23] and Figure 3. After cooling to RT, the precipitate formed was recovered by filtration and washed several times with CHCl_3 to generate pure CyPd (402 mg, 95%).

Synthesis of CyPd:

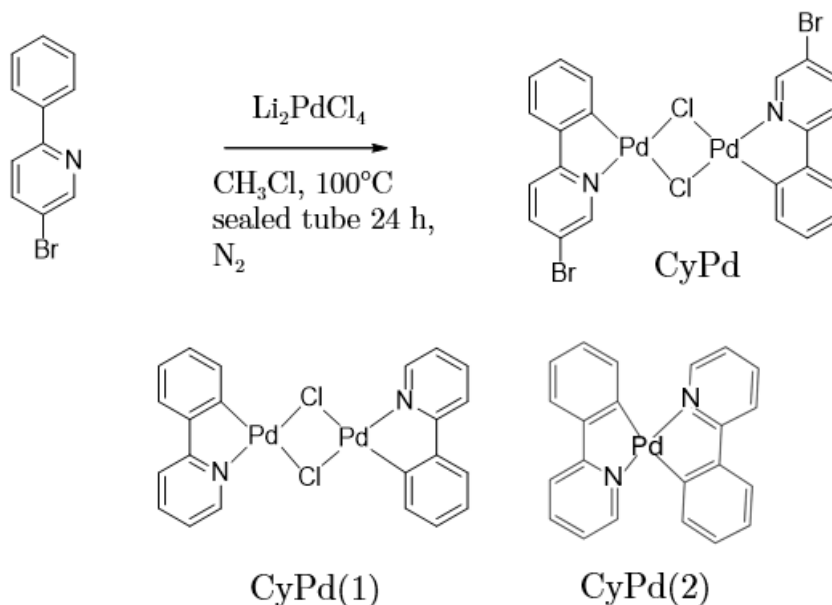


Figure 3: First row: Scheme of the synthesis of $[(5\text{-bromo-2-phenylpyridine})\text{Pd}(\mu\text{-Cl})_2]$ (CyPd). second row: The molecular structure of CyPd (1) and CyPd(2). The synthesis of the other cyclometalated complexes described in the text follows a similar procedure starting from suitable precursors.

For CyPd(1), a mixture of PdCl₂ (200 mg, 1.1 mmol), 2-phenylpyridine (192 mg, 1.2 mmol) and CHCl₃ (5 mL) was stirred at 100 °C in a sealed tube for 24 h under nitrogen atmosphere. After cooling to RT the precipitate formed was recovered by filtration and washed several times with CHCl₃ to afford CyPd(1) in a pure form (282 mg, 86%). The non-halogenated CyPd(2) compound was synthesized according to a similar procedure, described in ref [24].

Immediately after synthesis, the so obtained powders were characterized by thermogravimetric (TGA) analysis by using a Mettler Toledo TGA/DSC1 StarE instrument. Elemental analysis was obtained with an Elementar Vario MICRO cube instrument.

TGA curves of CyPd, CyPd(1), and CyPd(2) are compared in Figure 4. They show an onset of mass reduction, corresponding to decomposition of the molecules, at $T_{\text{dec}} \sim 355^\circ\text{C}$ for CyPd, at $T_{\text{dec}} \sim 340^\circ\text{C}$ for CyPd(1) and at $T_{\text{dec}} \sim 250^\circ\text{C}$ for CyPd(2). The first reduction at $\sim 140^\circ\text{C}$ for CyPd(1) is not significant since it is related to evaporation of solvent residues. The thermal stability increases with the molecular weight of the single complexes, and it establishes a clear limit to the evaporation temperature that can be used in sublimation experiments. Indeed, as it will be detailed in the Results section, the sublimation temperature of the powders was always kept at least 50 °C lower than the corresponding decomposition temperature to rule out possible evaporation of fragments.

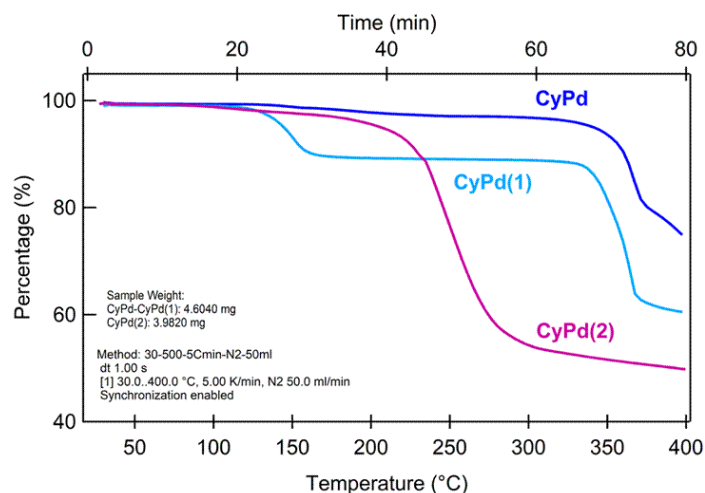


Figure 4 : Thermogravimetric analysis (TGA) curves of CyPd, CyPd(1), and CyPd(2) recorded under N₂ flow at a heating rate of 5 K · min⁻¹. The profiles show distinct thermal stabilities for the three complexes, with CyPd exhibiting the highest decomposition onset temperature, followed by CyPd(1), and CyPd(2) displaying the earliest and most rapid mass loss.

II.2 Experimental Techniques

II.2.1 X-ray Photoemission Spectroscopy

Introduction

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive analytical technique that is used to determine the chemical composition, oxidation state, and electronic structure of the studied material. It measures the kinetic energy of electrons photoemitted from the sample surface when it is irradiated with X-rays.

XPS is a photon-in electron-out technique, and it is surface sensitive because of the short inelastic mean free path (IMFP) of electrons in condensed media. The IMFP is the average distance that electrons can travel in a solid before undergoing collisions with other electrons, phonons or with lattice defects, thus losing energy and being thermalized and absorbed. It follows a universal curve as shown in Figure 5. The highest surface sensitivity of almost 2ML is achieved for electrons with kinetic energy KE=50 eV and it increases up to 10 ML for electrons with KE ~1000 eV. The photon energies used in XPS therefore lie in the soft X-ray range.

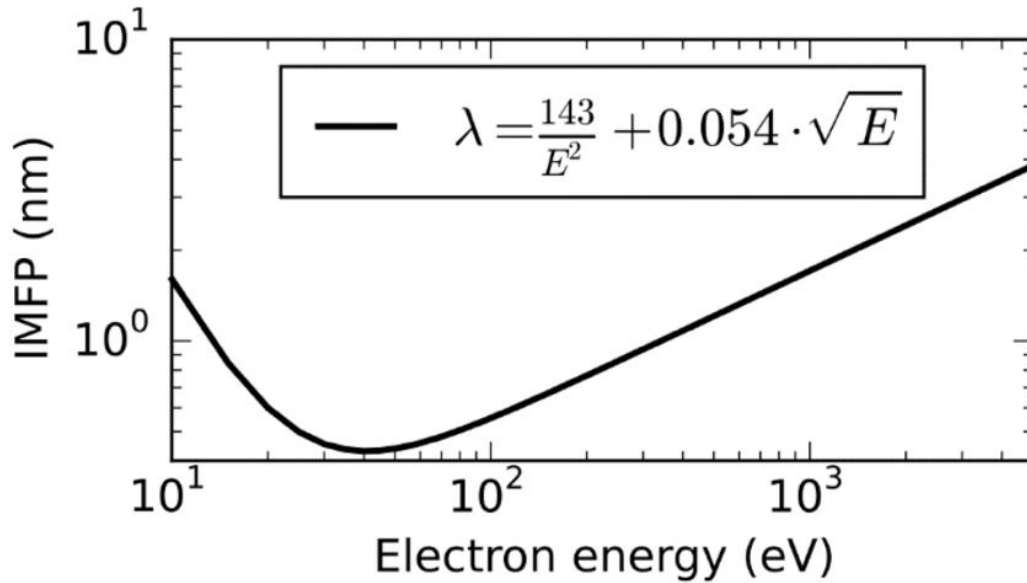


Figure 5: Universal curve for the Inelastic Mean free path of electrons.

XPS is based on the photoelectric effect. When a material is exposed to X-rays, core-level electrons can absorb energy and be ejected from the atom, as shown in Figure 4, (left). The kinetic energy (KE) of these photoelectrons is measured, and their binding energy (BE) is calculated with respect to the Fermi edge using:

$$KE = h\nu - BE - \phi \quad [25] \text{ Eq.1}$$

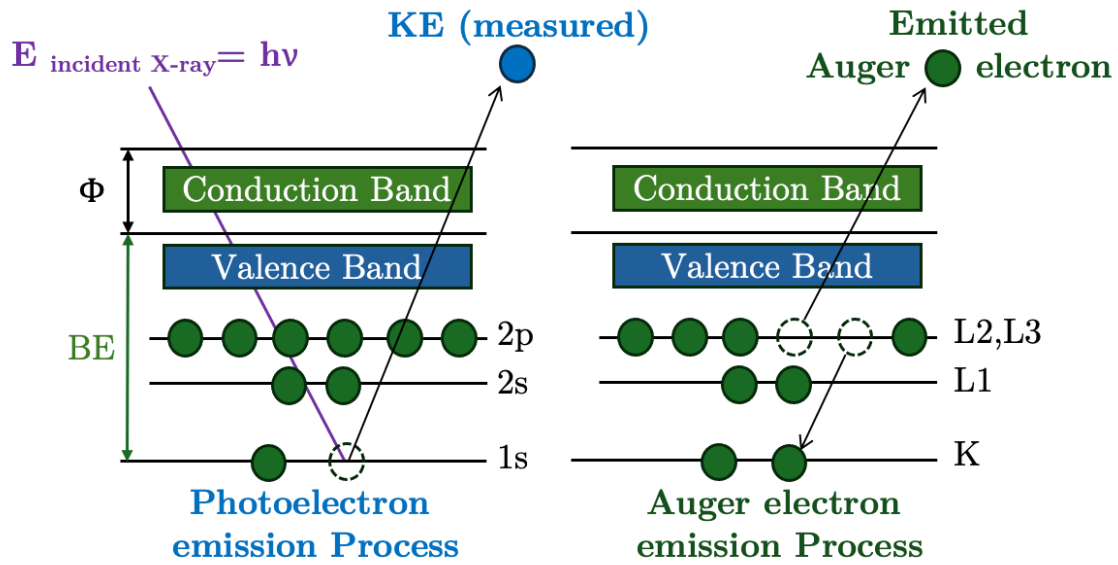


Figure 6 Schematic representation of the photoelectron and Auger electron emission processes in XPS.

Where BE is the binding energy of the electron, ϕ is the work function of the analyser and $h\nu$ is the energy of the incident x-rays.

Knowing both $h\nu$ and ϕ , and by measuring KE, information on the BE of the atoms is obtained.

As mentioned above, core level peaks in XPS result from the emission of core (inner shell) electrons from an atom. Since the latter levels are at well-defined BE values which depend on the atomic structure of each element, the position of each photoelectron peak in the XPS spectrum acts as a distinct fingerprint, enabling the qualitative chemical identification of each element present on the sample surface. The comparison of measured BE with reference databases, such as the NIST XPS database [26] or standard literature values [27], is crucial for identifying the elements present on the surface.. Furthermore,

those core level peaks can undergo small BE shifts (by few eV) caused by the chemical environment and the oxidation state of the emitting atom. For example, a shift towards higher BE values indicates that the atom is bound to a more electronegative atom, leading to a reduced electronic screening of the nucleus and implying that core electrons experience a stronger effective nuclear charge. As a result, more energy is required to extract them from the solid. These shifts, known as chemical shifts, provide information about the chemical state and bonding environment of the atom, distinguishing between different oxidation states, compounds, or surface functional groups. Consequently, XPS serves as both a quantitative elemental tool and a powerful probe of chemical state information, making it indispensable in surface science, materials chemistry, and nanotechnology research.

During the experiment, the work function ϕ of the sample may change due to various reasons, such as the modification of surface species. The evaluation of the BE is therefore usually referred to the Fermi level. The energy scale is then calibrated by fixing the value of the BE of the main photoemission line of the substrate to the value given in the literature.

Other alternative processes may occur due to X-ray irradiation of the sample; such processes generate well recognizable features in the XPS spectra. Among them, the Auger process is schematized in Figure 6 (right): an outer-shell electron fills the inner-shell vacancy created by photoionization, and the excess energy released ejects another outer-shell electron, the Auger electron, whose energy depends only on the atomic energy level difference of the element.

XPS is a quantitative technique, since the intensity of the peaks is proportional to the number of photoemitting atoms. Accordingly, it is possible to determine the relative concentration of species present on the sample surface by comparing the area of the corresponding photoemission lines, weighted by the different photoionization probability and transmission function.

The XPS spectra presented in my thesis were acquired partly at ANCHOR-SUNDYN end-station of the ALOISA beamline at the Elettra synchrotron radiation facility (Trieste, Italy) [28] and partly at UNIGE with a laboratory Electron Spectroscopy for Chemical Analysis (ESCA) apparatus.

In the following, I briefly introduce the characteristics of synchrotron light, and I describe both experimental setups.

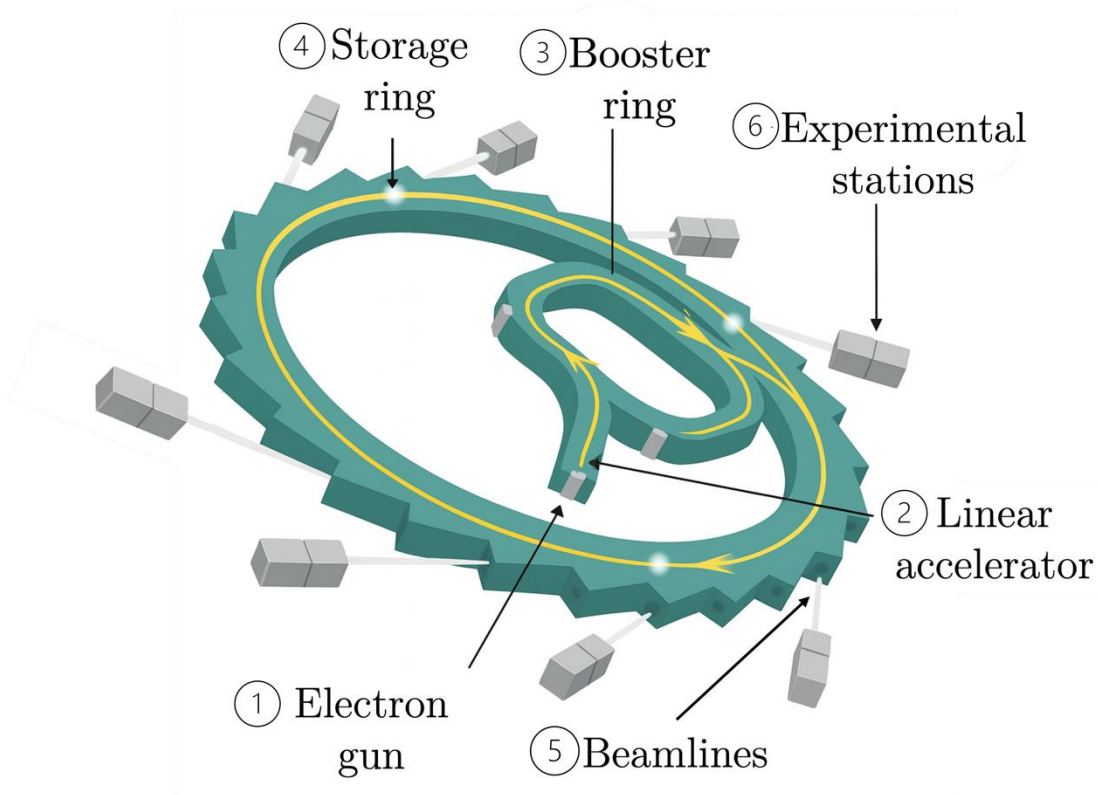


Figure 7: Schematic overview of a synchrotron light source showing the sequence of major components: the electron gun that generates electrons, the linear accelerator that accelerates them, the booster ring that raises them to high energy, the storage ring where they circulate and emit synchrotron radiation, the beamlines that extract and transport the produced photons, and the experimental stations where the monochromated radiation is used for scientific measurements.

Synchrotrons are facilities in which electrons are accelerated at relativistic velocities in a storage ring and radiation (synchrotron light) is generated with extraction devices (undulators and wigglers) and directed into beamlines connected to end-stations (see Figure 7). Electrons are produced by an electron gun (in the center of the figure) and then accelerated to nearly the speed of light by a linear accelerator (LINAC). They are passed eventually through the synchrotron booster ring where their energy reaches 2.0-2.4 GeV before entering the storage ring. Once injected, they circulate for many hours under ultra-high vacuum conditions and are forced to follow a closed path by bending magnets. The insertion devices, placed in the straight segments of the ring, allow to generate synchrotron radiation. The data of the present thesis was recorded at the

ALOISA beamline of Elettra which uses an undulator, so the focus will be on this insertion device.

In the undulator the electrons are deflected from their trajectory by an array of magnets which force them to follow an oscillating path. The electromagnetic radiation produced at each bending interferes coherently. Its wavelength is determined by the macroscopic distance of the magnetic dipoles (of the order of cm), but, given the velocity of the electrons, the generated wavelength is compressed by a double relativistic effect, due to the apparent compression of the undulator length seen by the electron in its inertial frame and to the relativistic Doppler effect caused by observing the radiation in the laboratory frame. The photon energy is thus in the soft X-Rays range. The relativistic effects cause moreover a high collimation of the emitted radiation along the forward direction of the electron trajectory.

ALOISA (Advanced Line for Overlayer, Interface and Surface Analysis) is a multipurpose beamline dedicated to surface studies. The undulator generates photons in the energy range from 130 eV to 1500 eV. The former range is ideal for photoemission studies. The light is selected, collimated and monochromated by a grating-crystal monochromator and further refined by optics (mirrors, slits) to reduce divergence and focus the beam spot. [28]

My measurements have been performed with the ANCHOR-SUNDYN end-station, reported schematically in Figure 8. The setup of this end-station includes a variable temperature (200–900 K) sample holder that is mounted on a 5-axis manipulator (VG), and a load-lock system for fast sample replacement. Both chamber setup and sample holder have been developed in-house. The system operates in UHV conditions, with a typical base pressure of 2×10^{-10} mbar. Sample preparation is performed in situ via physical vapor deposition (PVD) through a 4-crucible evaporator described in section.II.3.2.

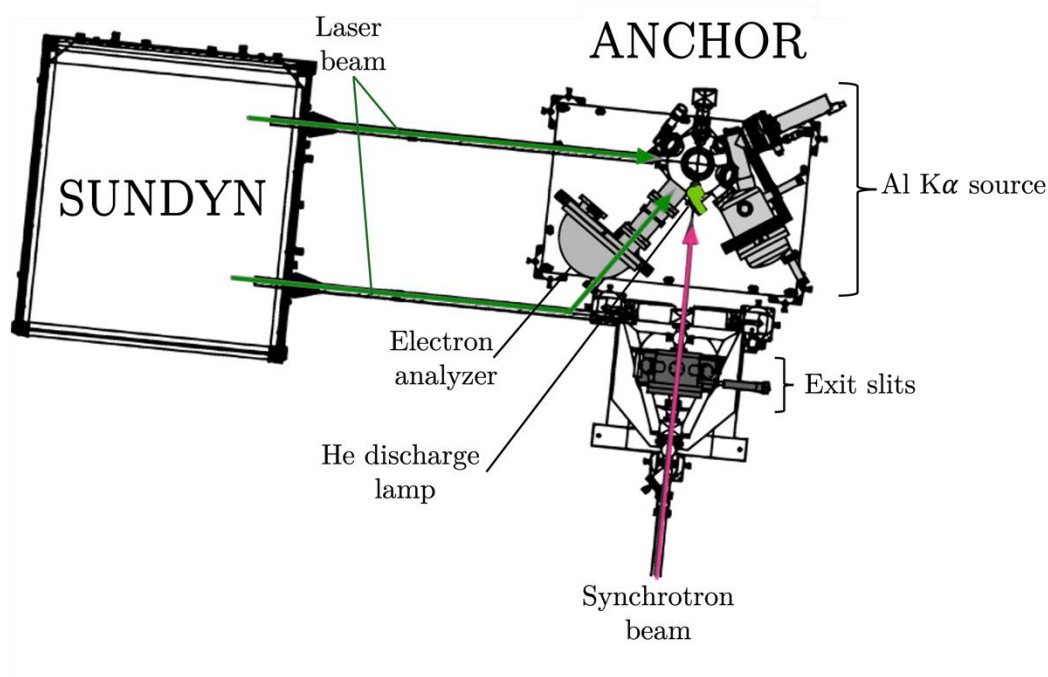


Figure 8 : Schematic of the ALOISA beamline, ANCHOR-SUNDYN end-station at Elettra Synchrotron Trieste. In my experiments, XPS spectra have been recorded at normal emission, using a photon energy $h\nu = 515$ eV for N 1s, Pd 3d, C 1s, Cl 2p and Br 3d. The sample was kept at RT while recording the spectra.

The laboratory XPS apparatus

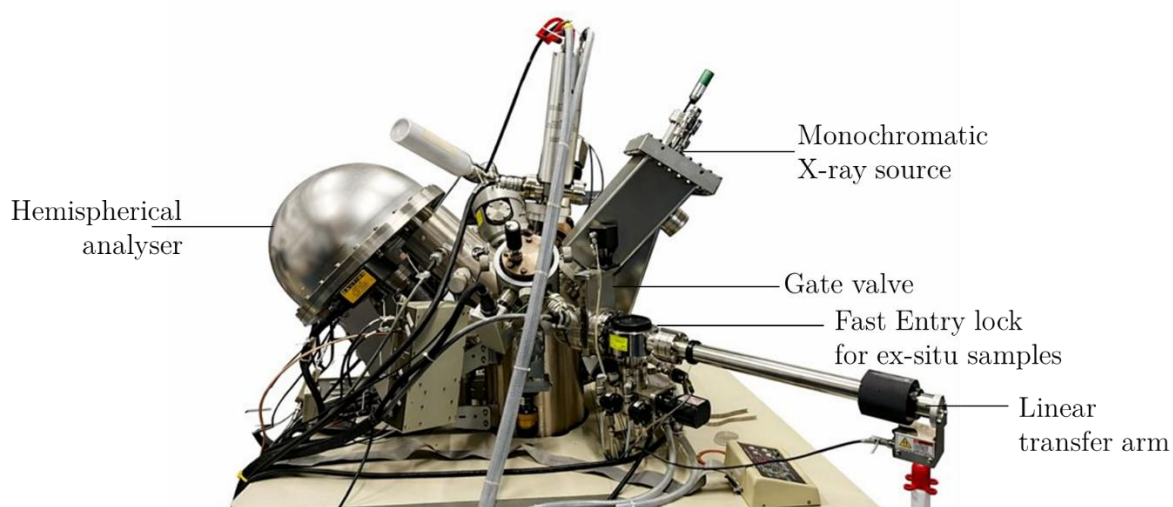


Figure 9: XPS apparatus at DIFI-Lab of UniGE, the different parts of the XPS set-up and of the fast transfer system are marked on the image.

In Genova I had access to a conventional XPS apparatus, dedicated to samples produced ex-situ and hosted in an UHV chamber with base pressure lower than $2 \cdot 10^{-8}$ mbar equipped with a load-lock system for fast sample entry. Spectra were acquired using a hemispherical analyzer model 10-360 and a monochromatic X-ray source model 10-610 (AlK α photons with $h\nu=1486.6$ eV) by Physical Electronics. Photoemitted electrons were collected from a spot of approximately 100 μm diameter at an emission angle of 45° .

XPS measurements and data analysis

The collected data were analysed and plotted using CasaXPS [29] and IGOR Pro (version 6.37, by WaveMetrics Inc.) softwares. For all spectra, the binding energy was calibrated on the C 1s signal of HOPG, set at BE=284.5 eV as from literature data [29]. The spectra of each measurement sequence have been normalized to the background intensity of the clean surface. The core level peaks were fitted with different line shapes after subtracting a Shirley or a linear background, depending on the spectral region. An error of ± 5 % is estimated for the fitted intensities. The fitting procedure is quite complex and differs for each spectral region.

Figure 10 shows the result for the C 1s region of a clean HOPG sample that will be detailed in the following.

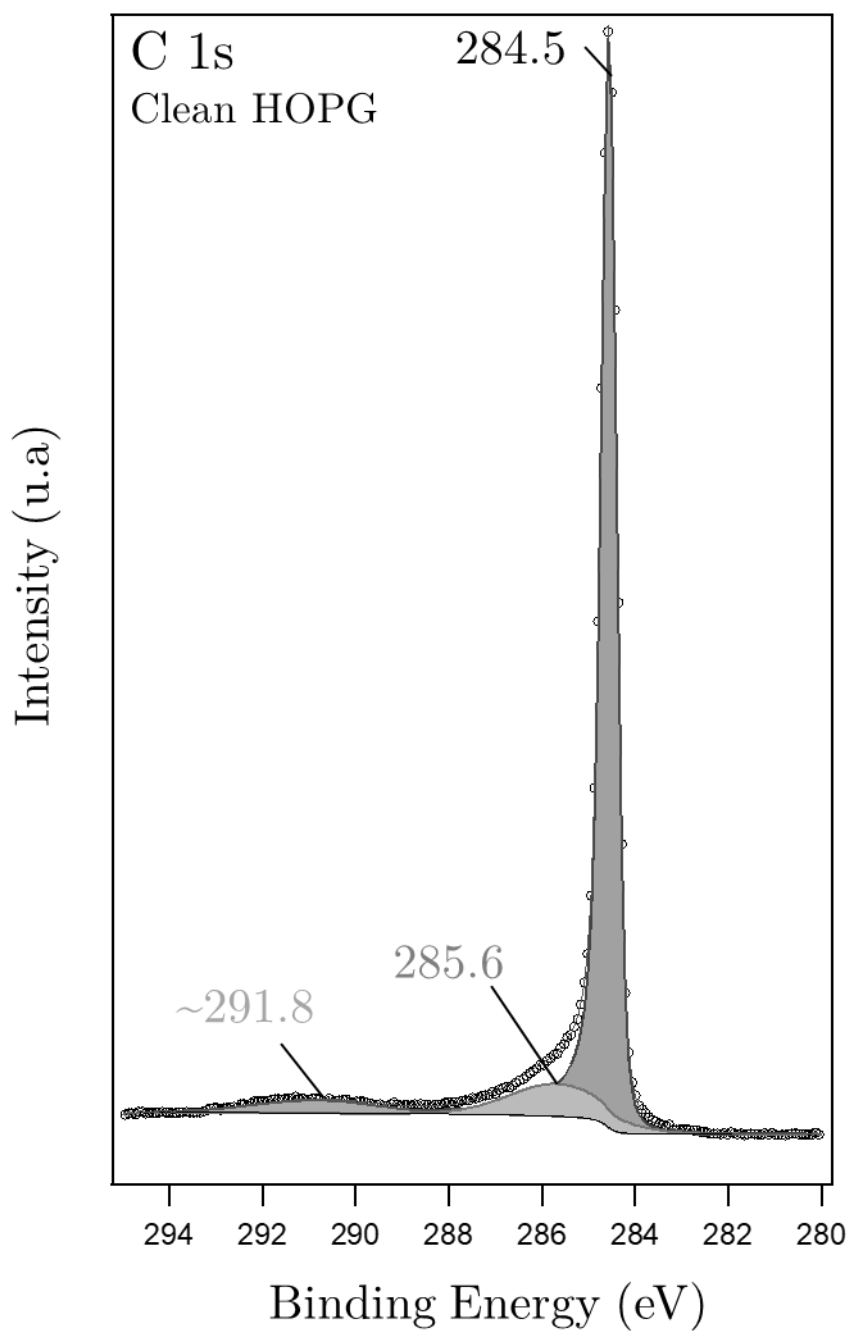


Figure 10: XPS spectra of clean HOPG showing the three components at 284.5, 285.6 and 291.8 eV.

The deconvolution of the C 1s region was challenging because the measured signal contains contributions from both the HOPG substrate and the adsorbed molecules. To discriminate between these components, the C 1s spectrum of a clean HOPG sample was

first fitted and used as a reference. It was reproduced with three components: the sp^2 peak at **284.5 eV**, corresponding to graphitic carbon, a smaller sp^3 feature at approximately **285.6 eV** attributed to defect or edge carbon, and the $\pi\text{--}\pi^*$ shake-up satellite at around **292.0 eV**, characteristic of extended conjugated aromatic systems [26]. The sp^2 component was fitted using a Lorentzian Asymmetric lineshape with tail Damping (Finite Lorentzian **LF**) [30] profile to account for the metallic-like tail of the graphite electronic structure, while the sp^3 and $\pi\text{--}\pi^*$ peaks were fitted using a symmetric Gaussian/Lorentzian product (**GL**) line shape. The FWHM of the sp^2 peak was fixed to **0.39 eV**, and the widths of the sp^3 and $\pi\text{--}\pi^*$ components were constrained until the fitting parameters were optimized. Table 1 presents the fitting parameters that yield consistent and reliable fits across all measured samples.

Table 1: Parameters used for fitting the C 1s spectrum of clean HOPG, including binding energies, line shapes, and FWHM constraints for the sp^2 , sp^3 , and $\pi\text{--}\pi^*$ components. Line shape parameters: $\text{LF}(\alpha, \beta, w, m)$ [30] ; α controls the tailing on the high binding energy (left) side of the peak, β controls the shape of the low binding energy (right) side of the peak, w being the damping/length parameter and m being the parameter that defines the width of the Gaussian function.

Components	Binding Energy (eV)	Line Shape	FWHM
C 1s sp^2 (graphitic)	284.5 (reference)	$\text{LF}(0.76, 1.11, 530, 76, 20)$	0.39 eV
C 1s sp^3 (defects)	$284.5 + 1.15 \approx 285.6$	$\text{GL}(30)$	2.35
C 1s $\pi\text{--}\pi^*$ shake-up	$284.5 + 7.5 \approx 292.0$	$\text{GL}(30)$	3.9

Once the C 1s fit was established on the clean HOPG, the three reference components were propagated to all spectra of the same deposition series. The additional peaks associated with the molecular carbon species were then introduced and fitted with three components, shown in the first section of Table 2. The other sections report the fitting parameters for the other regions of interest.

Table 2: Summary of XPS peak fitting parameters for the molecular component in the C 1s, N 1s, Pd 3d, Cl 2p and Br 3d regions. In the first column I report the chemical assignments, the second column contains the corresponding binding energies (BE), the third column reports the used peak line shape, and the last one contains the full width at half maximum (FWHM) values used for spectral deconvolution. Spin-orbit splitting values are indicated for Pd 3d, Cl 2p, and Br 3d doublets, while asymmetric Lorentzian (LA) and mixed Gaussian-Lorentzian (GL) profiles were applied according to the chemical nature of each species. For LA, the number in parenthesis indicates the percentage of asymmetry. In the case of GL, the number in parenthesis indicates the percentage of Lorentzian contribution to the overall peak shape, for example, GL (30) indicates that the peak is composed of 30% Lorentzian and 70% Gaussian character.

Components	Binding Energy Range (eV)	Line Shape	FWHM
Molecular C	285-287	LA(50)	0.75
Molecular N	399-401	LA(50)	1.3
Pd 3d_{5/2}	335-338	LA(50)	1.5
Pd 3d_{3/2}	BE(Pd 3d _{5/2})+5.2	LA(50)	1.5
Cl 2p_{3/2}	198-201	LA(50)	1
Cl 2p_{1/2}	BE(Cl 2p _{3/2}) + 1.6	LA(50)	1
Br 3d_{5/2}	68-71	GL(30)	1
Br 3d_{3/2}	BE(Br 3d _{5/2}) + 1.0	GL(30)	1

For the N 1s region and deposition at RT, only one component was necessary to fit the data.

In the case of Pd 3d, Cl 2p, and Br 3d regions, the peaks were fitted as spin-orbit doublets, with the appropriate intensity ratios and energy separations imposed to account for spin-orbit coupling following the values present in NIST database [26], as detailed below.

For the Pd 3d region, a Shirley background was first subtracted and the surface Pd chemical states were identified. Each chemical state was fitted with a spin-orbit doublet (Pd 3d_{5/2}, Pd 3d_{3/2}) constrained to a fixed 3:2 area ratio and a spin-orbit splitting of 5.2 eV.

For the Cl 2p region, given the shorter recorded spectral range in the measurements a linear background was subtracted, two chemical states were identified, and each was fitted with a spin-orbit doublet (Cl 2p_{3/2}, Cl 2p_{1/2}) using an area ratio fixed at 2:1 and a spin-orbit splitting of 1.6 eV.

For the Br 3d region, a Shirley background was subtracted, two chemical states were identified, and each was fitted with a doublet constrained to a 3:2 area ratio (Br 3d_{5/2}, Br 3d_{3/2}) and a splitting of 1.0 eV.

An example of spectra fitted as described above are shown in the results and discussion section (Figure 20)

II.2.2 Atomic Force Microscopy

Introduction

Atomic force microscopy (AFM) was invented in 1986 by Binnig, Quate, and Gerber [31]. It is an advanced surface characterization technique used to investigate the properties of different materials at the nanoscale. AFM was developed as follow-up of the STM, that was invented in 1982 by Binnig and Rohrer [32] to study the surfaces of conductive materials. AFM overcomes the need to use a conductive tip and a conductive sample, enabling the study of non-conductive samples with atomic resolution since it operates on detecting interaction forces (atomic forces) between the probe and the surface of the studied sample [31][33].

AFM provides three-dimensional topographic information with a resolution down to fractions of Angstroms under vacuum conditions [31]; therefore, it is considered a fundamental technique for surface science investigations [34]. Its ability to operate in diverse environments (air, liquid, or vacuum) [35][36][37], has broadened its field of application, making it indispensable in different areas of research such as materials science, solid-state physics [38][39], and molecular biology [40].

Analogous to most scanning probe microscopies, AFM operates by approaching a sharp tip to the sample, that raster scans the surface using a feedback loop that adjusts parameters needed to maintain stable tip-sample interaction and generate an accurate image of the surface topography.

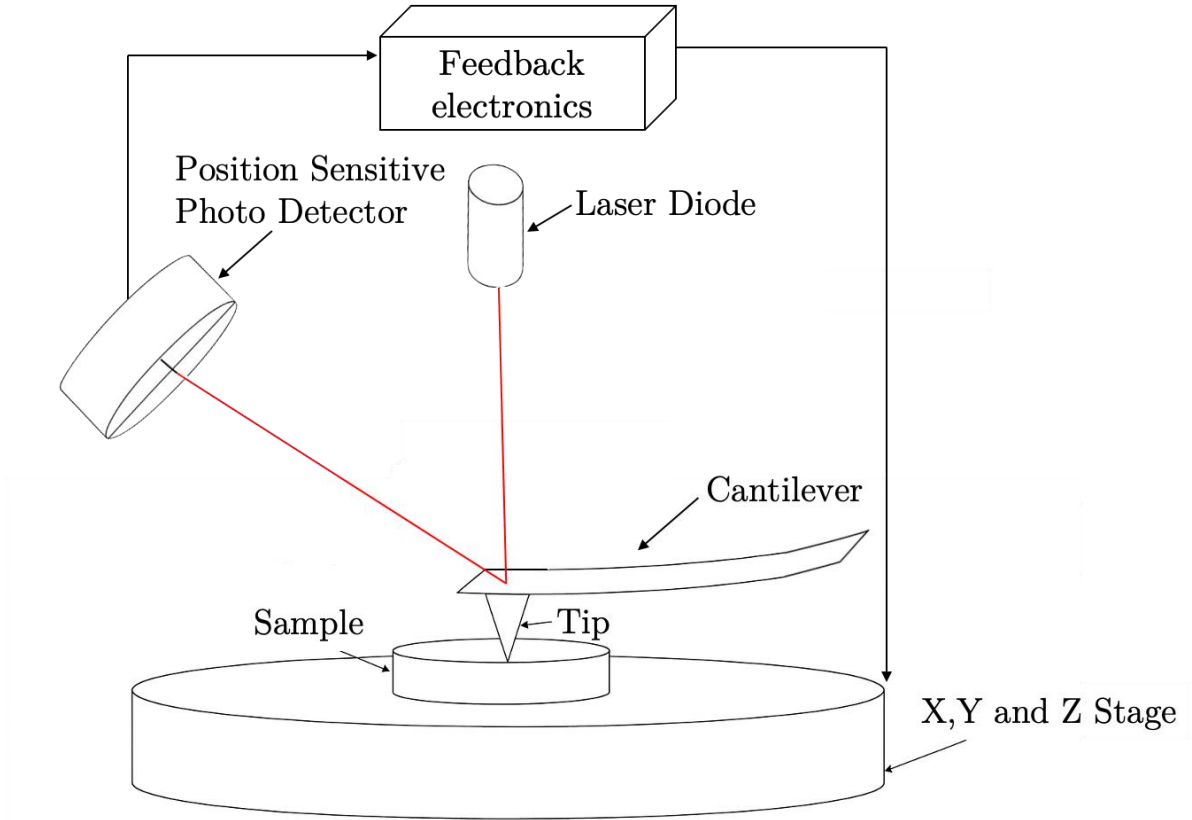


Figure 11: Diagram of conventional AFM scanning head showing the piezo scanner that controls the horizontal (X-Y) and the vertical (Z) movement. A laser beam is reflected on the back of the cantilever (AFM probe) into a photodiode. Tiny displacements are amplified by the optical magnification lever. The diagram shows also the feedback electronics which drives the piezo scanner.

Figure 11 displays the basic configuration for most AFM set ups. This scanning AFM may be used to investigate samples with only a relatively low roughness. The main components of an AFM include the XY and Z scanners, which are typically made of piezoelectric ceramics. These materials enable precise positional control of the tip, as they deform in proportion to the applied voltage, allowing nanometer-scale movement and accurate surface scanning.

Another main component is the AFM probe, consisting of the nanometer-scale tip mounted at the free end of a cantilever, usually made of silicon. The cantilever behaves like a spring and bends in response to tip-sample interactions forces [41]. The latter include van der Waals interactions, and electrostatic, capillary, magnetic and mechanical

contact forces. Different cantilever lengths, materials and shapes, allowing different spring constants and resonant frequencies, may be employed depending on the investigated sample properties. Their choice depends on the type of measurements planned and the employed scanning mode.[42][43] The cantilever can also be coated with specific materials or thin films, depending on the application [44].

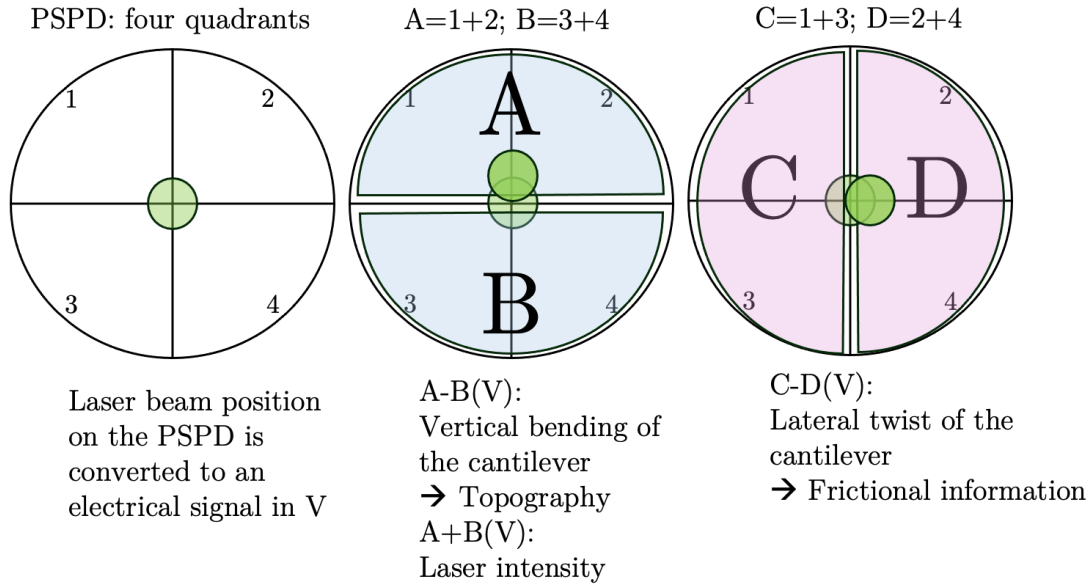


Figure 12: Position Sensitive Photodetector (PSPD) featuring its four quadrants (four cells). The green dot features the laser beam spot focused initially in the middle of the four quadrants. Depending on the cantilevers position and the interaction between the tip and the sample, the beam position may change allowing to obtain the topographical information or other information such as tip distortions induced by frictional forces.

The essential component is the optical detection system used to monitor the deflection of the cantilever (or change in the oscillation frequency/amplitude depending on the scanning mode) [45]. This deflection is caused by the force between the surface and the tip atoms and can be quantified by monitoring the position of the reflected laser beam on the position sensitive photodetector (PSPD) as shown in Figure 12. The detection system consists of a laser beam precisely aimed at the reflective back surface of the cantilever, often adjusted using a lens. The reflected beam is directed into the PSPD, divided into four quadrants. This configuration, illustrated in Figure 11 and Figure 12, allows highly sensitive determination of cantilever motion and thus accurate mapping of

surface features [46]. Initially, the beam position is calibrated by centering the reflected spot on the detector (green dot), determining the reference value for the deflection setpoint, used to establish the zero position. As the probe scans the surface, the cantilever deflects, causing the reflected laser beam to shift its position on the PSPD.

The PSPD is divided into four quadrants (1, 2, 3 and 4). The vertical bending of the cantilever can be determined by measuring the differential signal A-B(V), with region A given by cells 1+2, and region B by cells 3+4. This signal provides the height information (corresponding to the z-piezo position) used to produce a topographic image of the sample. Information on lateral deflection of the cantilever can be deduced by measuring the differential signal C-D(V) between region C (cells 1+3) and region D (cells 2+4). This measurement is used to obtain frictional information; this technique is known as Lateral force microscopy (LFM), that has not been used for my thesis.

The AFM scanner scans the sample line by line, while the PSPD signal is used to create a feedback loop that controls the vertical movement (Z) of the scanner as the probe scans the surface.

In other words, the feedback control is the process that maintains constant imaging conditions by controlling the drive according to the measured signal. The input signal that drives the feedback loop varies with the chosen AFM mode because each mode senses different physical interactions between the tip and the sample, that will be detailed later.

It is considered crucial in AFM measurements to maintain a stable interaction force between the tip and the sample in order to obtain accurate topography, prevent physical damage of the tip and the sample, enable high resolution and ensure quantitative reliability. This system works to keep the error signal-difference between the detector signal and the deflection set point to zero [47].

Here, it is important to highlight the different scanning modes that AFM offers, each designed to probe the tip-sample interaction in a different way. The most commonly used modes are contact, non-contact, and tapping modes. The main difference between those operational modes is in the nature and magnitude of the interaction forces that dominate during scanning. Such forces can be modeled in good approximation by a Lennard-Jones potential as represented in Figure 13[48][49] .

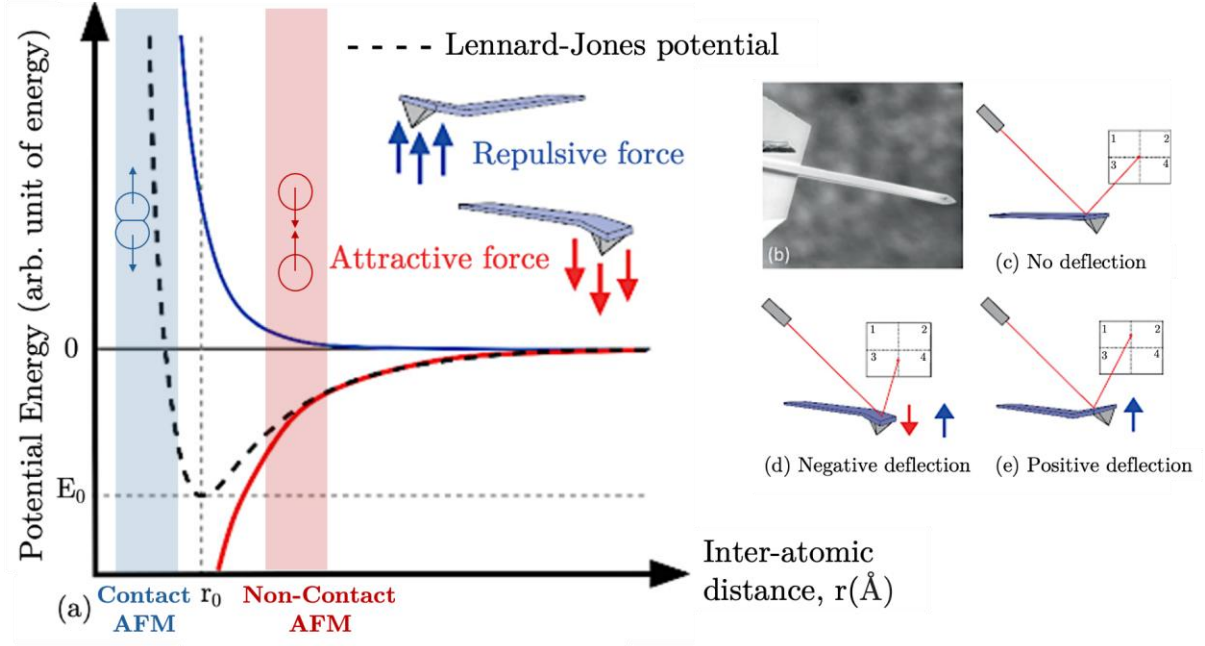


Figure 13: Description of tip-sample interaction using the Lennard-Jones potential and the forces associated with tip deflection. (a) The Lennard-Jones potential, the model potential for tip-sample interaction; attractive forces (red line) and repulsive forces (blue line) are highlighted. $r = r_0$ indicates the minimum value of the potential energy, corresponding to the transition between repulsive (left side) and attractive (right side) total force. (b) SEM image of an AFM tip and cantilever [50]. (c-e) Schematics of the cantilever deflection showing the degree of bending of the cantilever relative to the sample surface. (c) represents the set point where there is no deflection of the cantilever. (d) and (e) correspond to negative and positive deflections, respectively due to attractive and repulsive total force. Reproduced from reference [49].

The Lennard-Jones potential, $V(r)$, is a simple model that quantifies the forces between two atoms separated by a distance r :

$$V(r) = E_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right] \quad \text{Eq.(2)}$$

Where E_0 is the depth of the potential well, r is the inter-atomic distance, and r_0 is the interatomic distance at equilibrium. The r^{-12} term mimics the exponential Pauli repulsion (blue curve in Figure 8). The r^{-6} term describes the attractive van der Waals force between atoms (red curve in Figure 8).

Applied to AFM, the total force on the tip results from the mutual interaction of all tip and substrate atoms. When $r > r_0$, the tip-sample interactions are in the attractive regime. For $r < r_0$, the interaction is in the repulsive regime.

In order to select the most appropriate scanning mode, it is crucial to understand the operating principles of each one of them and in which region of the Lennard-Jones potential they operate.

When scanning in contact mode, the tip is in contact with the surface and the topography is acquired by measuring the repulsive interaction between the AFM tip and the sample. In these conditions, $\mathbf{r} < \mathbf{r}_0$, the steep rise in the interatomic potential induces a repulsive force, that will cause the positive deflection of the cantilever (Figure 13e) in proportion to the potential gradient. The Z-feedback loop keeps the force between the tip and the sample constant during scanning by continuously comparing the detector signal with the previously defined setpoint. Any difference between the two causes the system to adjust the scanner position by either approaching or retracting the tip from the sample by modifying the voltage applied to the piezoelectric actuator. This mode provides high-resolution images but implies a risk of sample or tip damage.

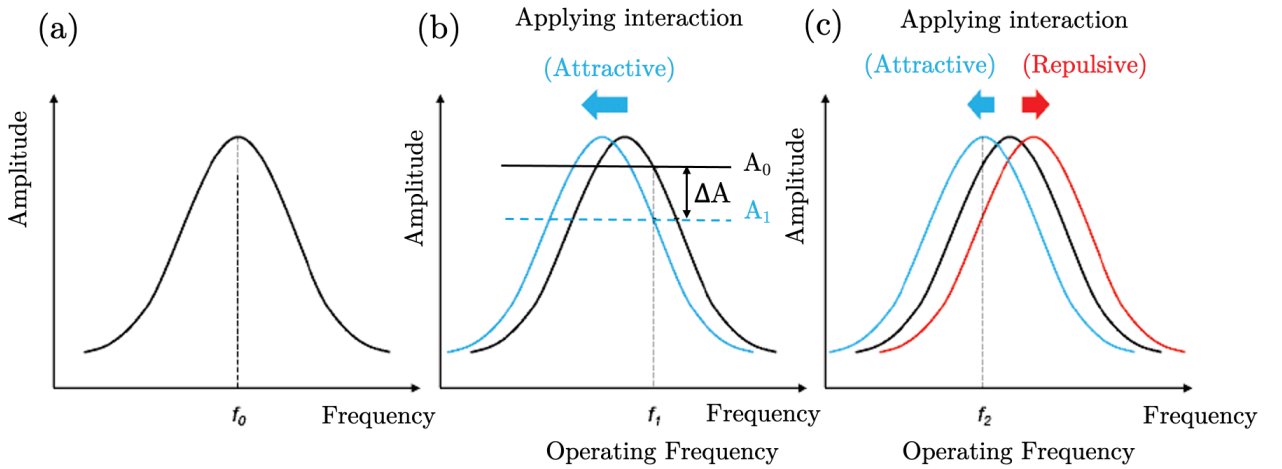


Figure 14: Amplitude–frequency response of an AFM cantilever when (a) no force is applied to it, (b) an attractive force is applied (non-contact mode), and (c) when both attractive and repulsive forces are active (tapping mode). The black curve represents the free oscillation of the cantilever far from the sample (f_0), the blue curve shows the resonance shift caused by attractive tip–sample interactions (f_1) and the red curve shows the shift due to repulsive tip–sample interactions (f_2). A_0 and A_1 are the free and reduced oscillation amplitudes, respectively. ΔA is the change in oscillation amplitude.

When scanning in non-contact mode, $\mathbf{r} > \mathbf{r}_0$, the tip oscillates above the surface without touching it. The topography is obtained by the deflection of the cantilever due to the attractive van der Waals forces between the tip and the sample. In this case, the cantilever oscillates at a frequency slightly higher than its resonance frequency, $f_1 > f_0$.

As the tip moves closer to the sample, the attractive forces induce a downshift in the effective resonance frequency, resulting in a decrease in oscillation amplitude (ΔA) at the fixed driving frequency, as shown in Figure 14b. The Feedback-loop typically controls the amplitude change (or frequency change). The Z-servo compensates for this change to maintain the constant amplitude (or frequency) value, ensuring a stable tip-sample interaction as the tip scans across the XY plane. This scanning mode is less invasive but often provides lower lateral resolution in ambient conditions.

Similar to non-contact mode, tapping mode uses the amplitude of cantilever oscillation to detect changes in the tip-sample interaction forces. However, in this case the cantilever oscillates with larger amplitude compared to the non-contact mode. This scanning mode operates both in attractive and repulsive force regimes, with r oscillating around the r_0 value. It is an intermittent contact mode, where the oscillating tip makes physical contact to the surface and enters the repulsive force regime. This is why the resonance shifts to lower or higher frequencies within one oscillation cycle as the interaction changes from the attractive to the repulsive force regime, respectively. Here, the operating frequency f_2 is typically lower than f_0 to detect the positive and negative change of the oscillation amplitude ΔA in the attractive and repulsive force regime, respectively. ΔA is used as a feedback signal to regulate the Z-scanner motion during imaging changing the tip-sample distance accordingly. By keeping the amplitude and distance constant, the surface topography is deduced from the Z scanner movement.

These modes allow researchers to optimize the imaging conditions to the mechanical properties and sensitivity of their samples [51].

For the experimental work presented in this thesis, a Park Systems NX10 AFM, showed in Figure 15, was employed. This instrument provides high-resolution imaging capabilities and offers versatile operational modes suitable for different sample characterization.

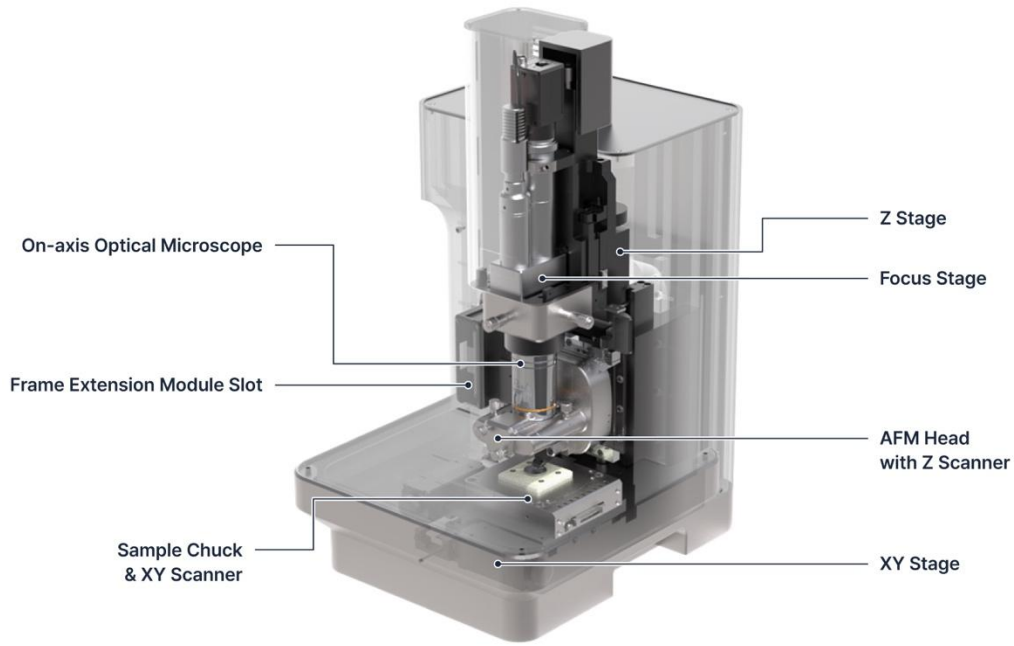


Figure 15: Scheme presenting the Park systems NX10 AFM and its main components.

The NX10 specifications will be detailed below, before doing so it is important to mention that one problem encountered in most AFM systems, mainly the ones with tube-type piezo scanners, is that the X,Y and Z motions are mechanically coupled, which means that movement along X or Y direction will always simultaneously influence the scanner's movement in Z direction, or vice versa. This cross talk and non-linearity caused by the scanner's three axes being non-orthogonal to one another has a more noticeable effect in the case of measuring larger areas or flat samples.

This problem was eliminated completely in NX10, by the physical separation of the Z scanner from the X-Y scanner (Figure 15). The NX system is designed so that the X-Y scanner scans a sample in two -dimensional space, while the Z scanner moves the tip only in the z direction. This design enhances data collection speed with a much higher rate (10~50 Hz) than would be possible with a standard AFM and allows the insertion of larger samples on the sample stage. [51]

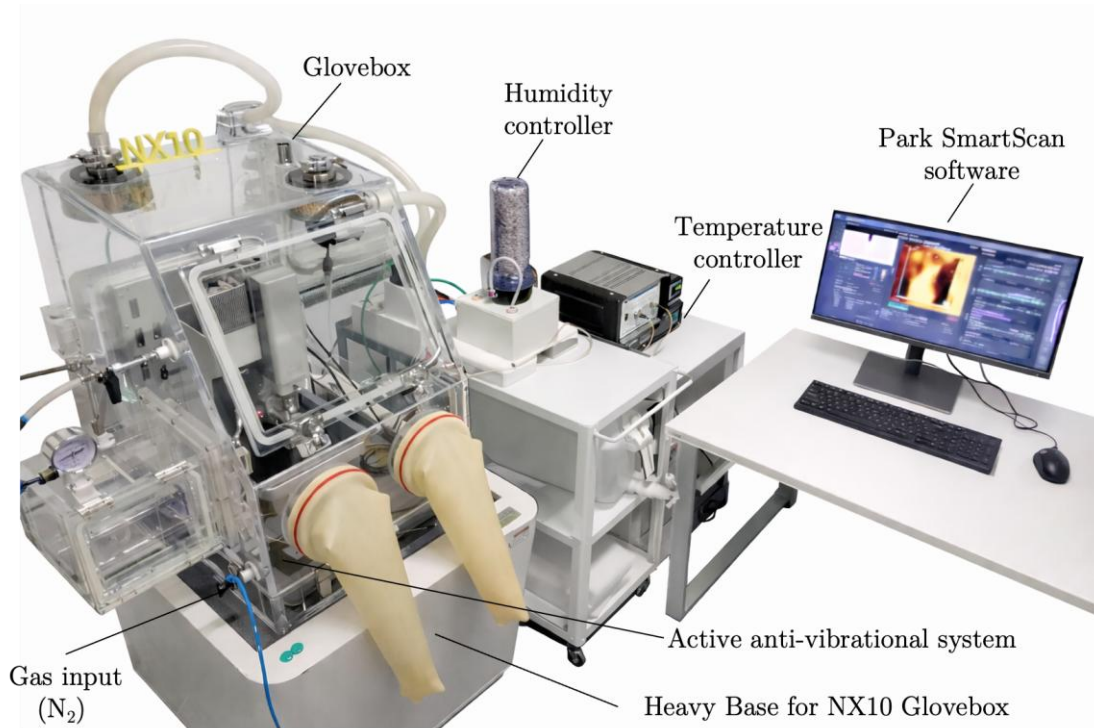


Figure 16: The Park systems NX10 Glovebox.

The NX10 used for this thesis is hosted inside of a Glovebox (Figure 16) that provides controlled atmosphere for samples that are sensitive to oxygen and water vapor. The NX10 Glovebox is also equipped with a humidity control system so that the chamber's atmosphere can be carefully controlled for humidity and oxygen concentration. The characteristics of the Glovebox as taken from the manual are summarized in Table 3.

Table 3: NX10 Glovebox specifications

Glovebox specifications	
Dimension	810 (L) $\times$ 625 (D) $\times$ 710 (H) mm
Weight	50 kg
Working Pressure Range	-12 mbar to +12 mbar from ambient pressure
Working Gas	Air, Argon (Ar), Nitrogen (N ₂)
Humidity Control Range	20% $\sim$ 80% ($\pm 5\%$) (typical)
Description	Control over the humidity levels of the sample environment, from extremely low to very high humidity conditions.

The NX10 is also equipped with a temperature-controlled stage that allows precise temperature control ranging up to 250°C with a 0.1°C sensitivity. The characteristics of the temperature-controlled stage as taken from the manual are summarized in Table 4.

Table 4: Temperature-controlled stage for heating the samples inside the Glovebox

Temperature-controlled stage specifications	
Heating / Cooling Type	Active Heating / Passive Cooling
Heat Shield	NX Standard AFM Head to protect cantilever and AFM head from high temperature
Temperature Range	Ambient to 250 °C
Temperature Resolution	0.1 °C
Sample Size	18 mm $\times$ 18 mm

For this thesis, the non-contact mode is mostly employed to preserve both the tip and the sample. The tip used for the measurement is the supersharp tip (SSS-NCHR from NanoSensors) with a nominal resonance frequency of 330 kHz, force constant of 32 N, a nominal length of 125 μm , and 3.8 μm thickness. [50]

AFM images were analyzed using the open-source software *Gwyddion* [52], applying basic image filtering and plane subtraction procedures to remove background artifacts. The same software was also used to perform two-dimensional autocorrelation analysis for quantitative assessment of surface order and periodicity.

II.3 Sample Preparation

II.3.1 Substrate description- Highly oriented pyrolytic graphite (HOPG)

Highly Oriented Pyrolytic Graphite (HOPG, ZYA) is broadly applied as a substrate for investigating the catalytical behavior of deposited molecules and metal complexes [53][54]. The advantage of this substrate is its chemically inert surface that reduces perturbations induced by the substrate. Molecules deposition is usually performed on freshly cleaved HOPG, consisting of large, ordered graphene terraces, enabling molecules to adsorb on its surface. Its weak van der Waals interaction with the deposited species has been proved to conserve the molecular identity and permit accurate probing of adsorption geometries and self-assemblies [55]. This is what makes HOPG valuable in surface-science investigations as an excellent model substrate for distinguishing the intrinsic catalytic behavior of deposited complexes and for establishing robust correlations between their molecular structure, surface interactions, and catalytic activity.

The HOPG sample is first prepared for molecular deposition by Scotch-tape cleavage, Figure 19, step 1. Then, if the deposition method is sublimation in UHV, it is immediately inserted in vacuum and flashed to 600°C before and after each preparation, to avoid unwanted contamination for the next experiment. In case of drop-casting experiments, a new cleavage is performed before each new preparation.

II.3.2 Sublimation in UHV

The organic molecules were thermally sublimated onto freshly cleaved HOPG under UHV conditions from a quartz evaporator with 4 crucibles available (TCE-BSC by Kentax), shown in Figure 17, that allows to insert the four molecules in vacuum at the same time and to evaporate them independently. The resulting samples were subsequently characterized in UHV by XPS.



Figure 17: 4-cell UHV Evaporator TCE-BS by Kentax. Equipped with a z-travel unit and a corner- and gate- valve, four materials can be loaded and evaporated independently.

II.3.3 Dropcasting from a Dimethylformamide (DMF) solution

The solution containing the precursor molecules was first prepared by dissolution of 3 mg of the molecules powder in the DMF solvent. The mixture was then shaken thoroughly to ensure the total dissolution of the molecules inside the solvent. The final concentration is $\sim 1\ \mu\text{M}$ unless otherwise stated. The initial solution is eventually diluted to reach the desired concentration.

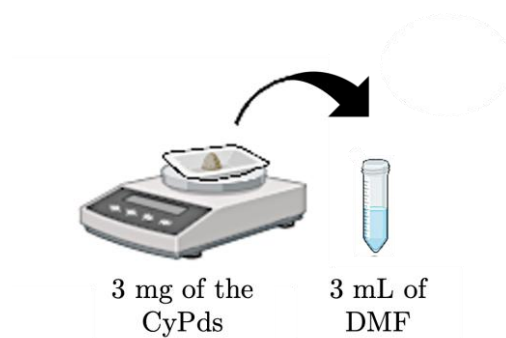


Figure 18: Scheme showing the preparation of the solution containing the precursor molecules.

Once the mixture becomes homogeneous, and after Scotch-tape cleavage of HOPG, a drop of the prepared solution is added onto the HOPG and left to dry overnight (Figure 19).

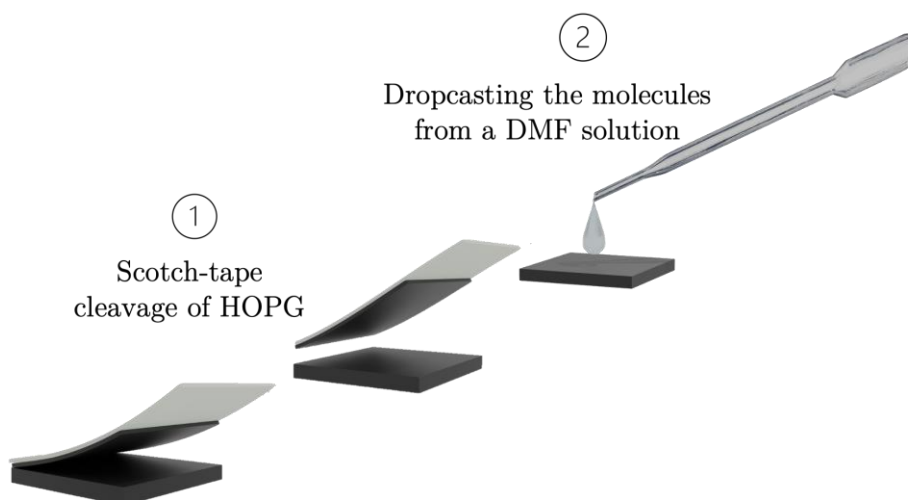


Figure 19: Scheme showing the process of cleaving the HOPG via Scotch-tape and the drop-casting of the solution on the freshly cleaved HOPG.

III- Results and discussion

III.1 Surface Chemical Composition

In this chapter, I will present and discuss the XPS data obtained upon deposition of the three CyPd complexes on HOPG at RT and the subsequent thermal evolution in UHV. The last part of this section is devoted to the comparison of samples obtained by sublimation in UHV and by drop-casting in air, to underline the similarity of the final product from the chemical point of view.

III.1.1 Sublimation in UHV

RT-Deposition

Figure 20 presents the high resolution XPS core level spectra (N 1s, Pd 3d, C1s, Cl 2p and Br 3d) of the three Pd-cyclometalated complexes deposited on HOPG after sublimation in UHV as measured with Synchrotron Radiation. The molecules were sublimated for the same deposition time of 30 minutes but at different temperatures: $T_{\text{sub}}=220\text{ }^{\circ}\text{C}$ for the halogenated CyPd and CyPd(1) molecules and $T_{\text{sub}}=200\text{ }^{\circ}\text{C}$ for the lighter, non-halogenated CyPd(2) species.

The binding energy assignments and corresponding literature values for the three studied molecules are compiled in Table 5 and discussed below.

For all three preparations, the N 1s region shows a single dominant component around 399-400 eV, consistent with its pyridinic nitrogen in the intact molecular backbone.

For CyPd(2), an additional component appears at 400.7 eV, attributed to graphitic like N after annealing, see Fig A.3.

The Pd 3d region shows a well-defined doublet with $\text{BE}(3d_{5/2})=337.9\text{ eV}$, characteristic of Pd (II) in a halide-ligated coordination environment

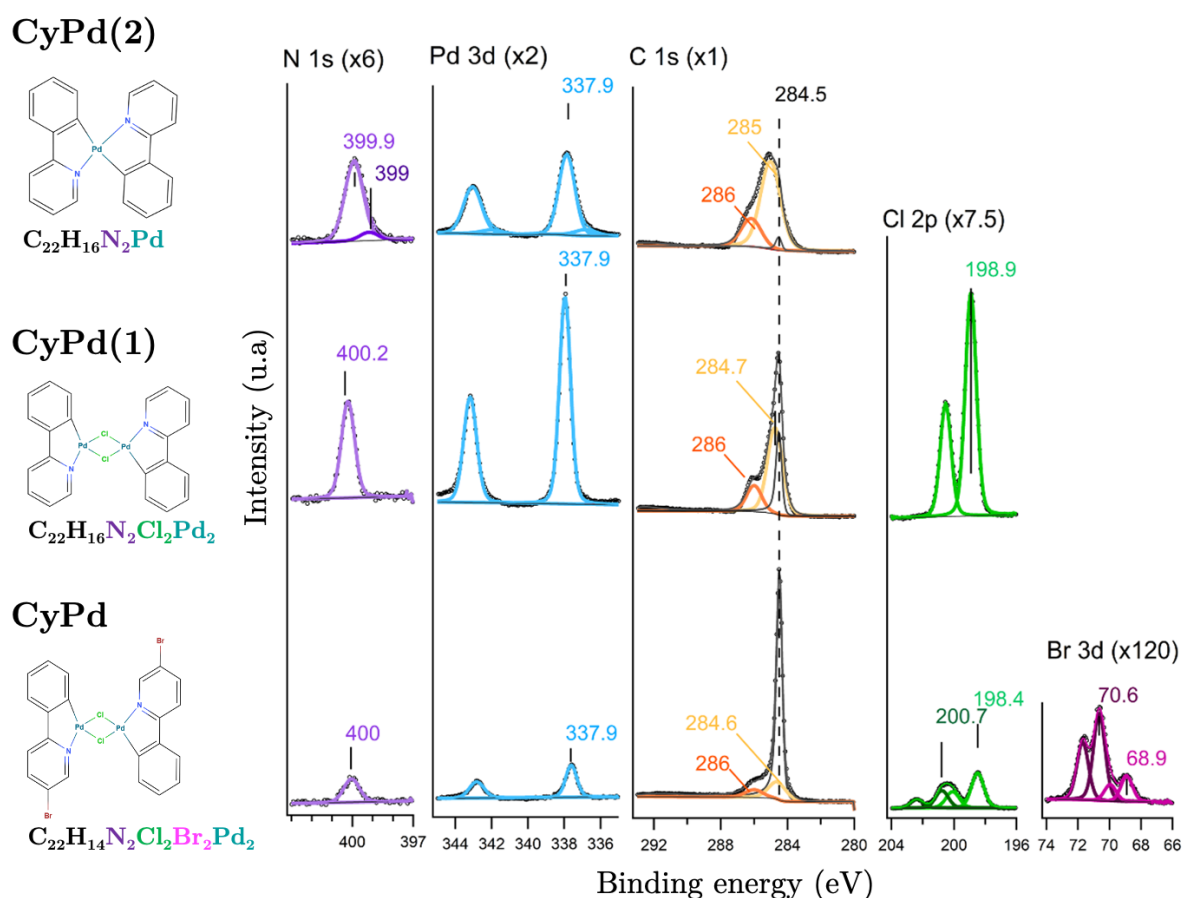


Figure 20: High-resolution XPS spectra of the adlayer obtained after the sublimation in UHV of the three cyclometallated complexes on clean HOPG at room temperature. On the left panels I report the chemical structures, the molecular formula, and the abbreviation name of each complex. On the same line I show the HR-XPS spectra of each complex, recorded at the Elettra Synchrotron Radiation Facility.

The C 1s spectra contain both the contribution of the HOPG substrate, with the main HOPG-C sp^2 peak at 284.5 eV, and those at higher binding energy associated with C–C/C–H and C–N bonds of the molecules. In the halogenated complexes, the Cl 2p and Br 3d regions show main doublets at binding energies BE (Cl $2p_{3/2}$) $\approx$ 198–199 eV and BE (Br $3d_{5/2}$)=70.6 eV, corresponding to spin–orbit doublets for Cl^- and Br^- ligands, that confirm the presence of coordinated chloride and bromide. The extra doublets present at 200.7 eV for Cl 2p and at 68.9 eV for Br 3d, respectively, indicate the occurrence of bond-breaking and hence partial dissociation of the molecule. As I will show in the following (Figure 28), this effect is due to photoinduced damage by the synchrotron light.

The spectra demonstrate that all the elemental constituents of the molecules adsorbed on HOPG have the binding energies expected for an integer molecule. In particular, the Pd centres remain in the +II oxidation state and the halide ligands remain bound to Pd for CyPd and CyPd(1). For CyPd(2), a very small component is present at 336.9 eV that might correspond to detached Pd in the form of isolated single atoms, Pd₁(0). Indeed, as discussed in ref [56], and reported in Figure 21, the BE of isolated Pd₁(0) atoms is significantly up shifted with respect to that of small Pd clusters. The small observed amount at RT of Pd₁(0) can be also due to a limited photon damage. As I will show in the following, its relative weight will increase significantly upon annealing.

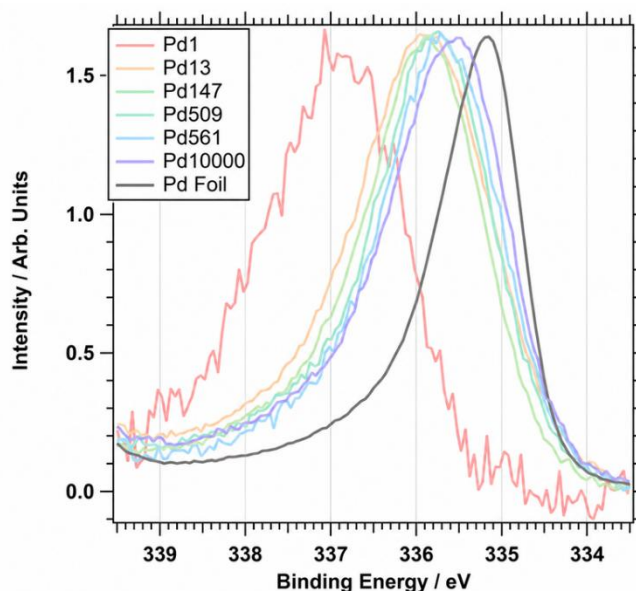


Figure 21: Pd 3d_{5/2} region UHV XPS scans for various sizes of Pd clusters on alumina film, along with Pd foil as a reference. Peak intensities are normalised to 1 in all cases to make shifts clearer. Taken from [56].

Therefore, I can draw the conclusion that all three cyclometalated complexes adsorb intact on HOPG. This first result is at variance with what previously reported for CyPd/Ag(110) [21] and allows the prosecution of my investigation.

I further notice that the attenuation of the HOPG peak in the C1s spectrum is significantly different in the three cases; HOPG remains the dominant peak in the CyPd spectrum. It is of comparable intensity to the molecule related C1s peaks for CyPd(1) and it is almost completely covered in the case of CyPd(2). This indicates that the molecular coverage achieved in the three experiments is different and the largest coverage is obtained for the molecule with the lightest molecular weight.

Table 5: Binding-energy assignments and literature references for the N 1s, Pd 3d, C 1s, Cl 2p, and Br 3d core-level components of the CyPd, CyPd (1), and CyPd(2) complexes. Reported values correspond to the characteristic chemical states identified on the surface. Literature references are provided to support the chemical-state assignments and to allow comparison with previously reported XPS data.

	CyPd	CyPd(1)	CyPd(2)	Assignment	References
N1s	400 eV	400.2 eV	400-400.2eV	N-Pyridine	[57] [58]
			399-399.3 eV	N-Pyridine	
			400.7 eV	N-Graphitic	[59]
Pd3d	337.6 eV	337.8 eV	337.6 - 337.8 eV	Pd-Cl, Pd-N	[60][61]
			335.8-335.6	Pd(0)	[62]
			336.8 - 336.9 eV	Pd ₁ (0)	[56]
C1s	284.5 eV	284.5 eV	284.5 eV	C-HOPG	[63][26]
	285-284.6 eV	284.9 eV	285 eV	C-C, C-H	[64][65]
	286 eV	286 eV	286 eV	C-N	[64]
Cl2p	198.5 eV	198.5 eV	-	Cl-Pd	[66]
	200.7 eV	-	-	Diss-Cl	
Br3d	68.9 eV	-	-	Diss-Br	[67]
	70.7 eV	-	-	Br-C	[68]

Studying the thermal evolution of the deposited molecules is important in order to monitor their stability, changes in the chemical state, and the occurrence of desorption and/or dissociation as a function of temperature.

In this section I will investigate the thermal stability of the adsorbed molecular layers by following the evolution of the XPS spectra of the N 1s, Pd 3d, C 1s, Cl 2p, and Br 3d regions reported in Figure 20 as a function of annealing temperature (Figures 22, 23& 24). After sublimation in vacuum on the substrate at room temperature, the samples were stepwise annealed under UHV up to 400 °C (CyPd and CyPd(1)) and to 600°C (CyPd(2)). After each temperature increment, the sample was cooled down to RT before acquiring the corresponding XPS spectra. This sequence provides direct insight into the chemical transformations occurring within the molecular film, including ligand dissociation, halogen loss, changes in Pd coordination, and eventual desorption of organic fragments.

Figure 22 reports the sequence of XPS spectra recorded after annealing the CyPd/HOPG system, while Figures 23 and 24 report the outcome of the same experiment for CyPd(1)/HOPG and CyPd(2)/HOPG, respectively. It should be noted that, in all cases, the spectra were fitted using the same components described in Figure 20 and listed in Table 5. However, only the raw data are plotted leaving the detailed fitting results to allow a clearer visualization of the spectral variations. The complete fitted datasets are provided in the Appendix.

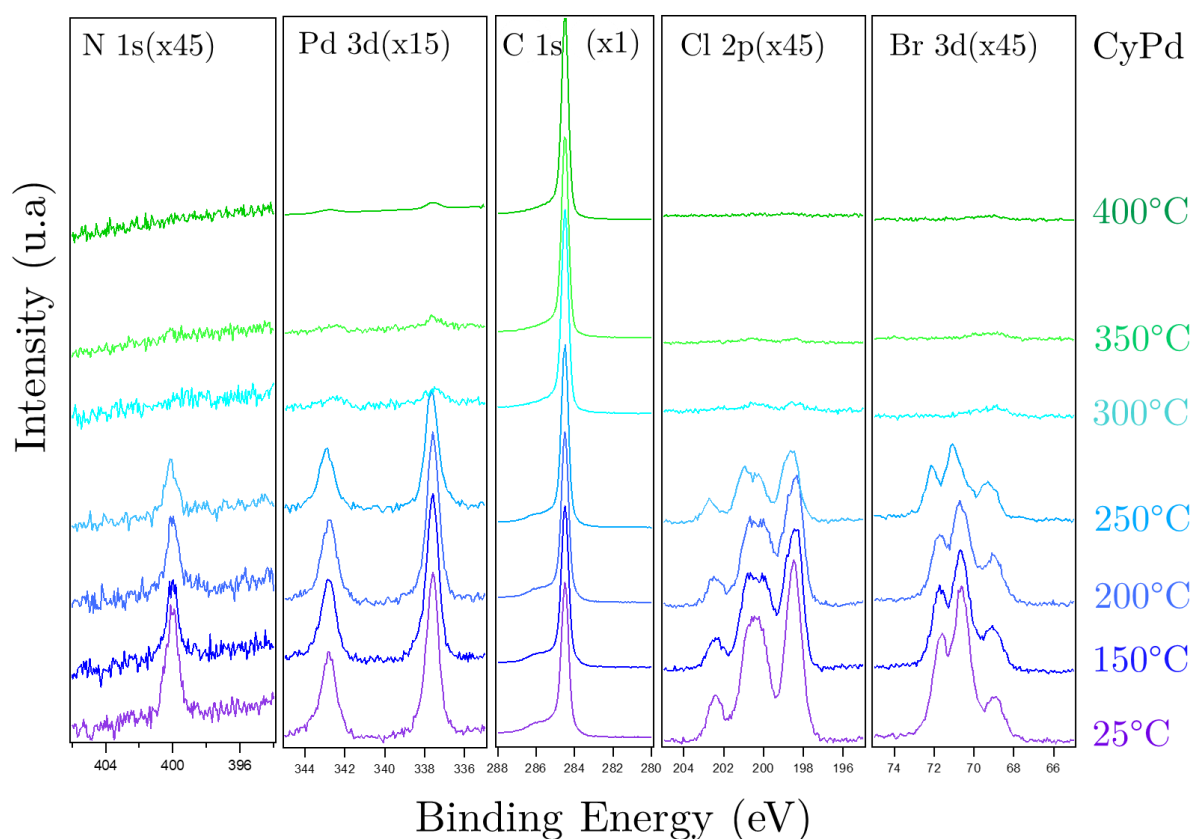


Figure 22: HR-XPS of CyPd showing the thermal evolution starting from RT annealing up to 150, 200, 250, 300, 350 and 400°C. In this graph, only the raw data is plotted, and the spectra were stacked for a better visualization of the thermal evolution. The corresponding spectra showing the different components is reported in Figure A.1 of the appendix.

After annealing the CyPd/HOPG layer (Figure 22) to 150°C and 200°C, the N1s intensity begins to decrease. This is also accompanied by a slight reduction in the halogen signals (Cl 2p and Br 3d). The Pd 3d line shape remains dominated by Pd (II)-Cl, showing that Pd retains its initial oxidation state at this stage. The C 1s envelope remains mainly unchanged since it is dominated by the HOPG signal at 284.5 eV. Small reductions of the CyPd related to C 1s lines can, however, be evidenced after careful fitting of the data. A significant transformation occurs when annealing above 250°C since all five spectral regions show a significant reduction in intensity, indicating that the molecules desorb intact off the surface. At 400°C, no detectable intensity is present in the N 1s, Cl 2p, and Br 3d regions, while the small signal of Pd 3d is ascribed to photodissociation. This temperature-dependent XPS analysis demonstrates that CyPd molecules are stable on the graphite surface only below ~200 °C, and fully desorb when heating the sample to 400 °C.

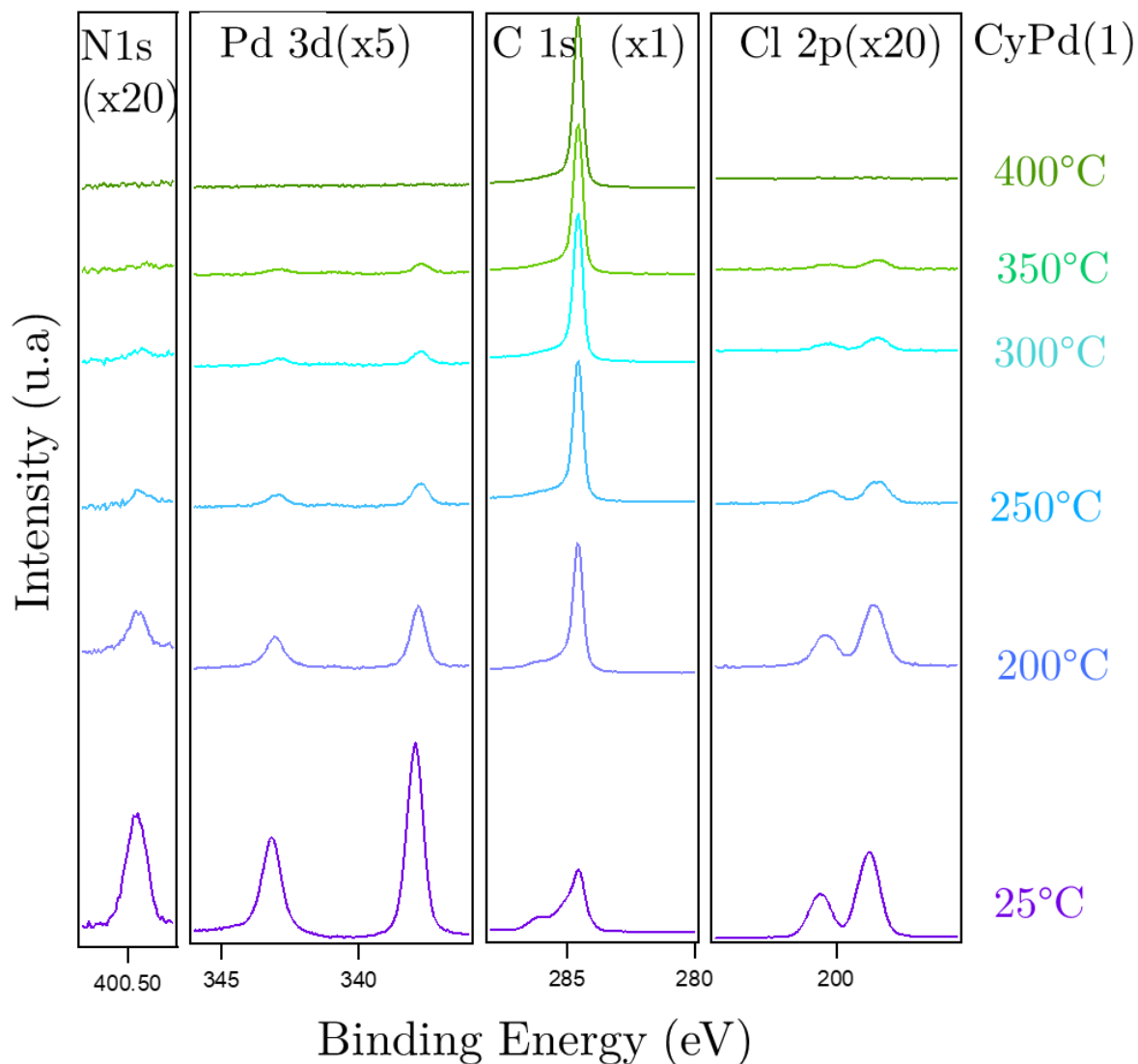


Figure 23: HR-XPS of CyPd (1) showing the thermal evolution starting from RT annealing up to 200, 250, 300, 350 and 400°C. In this graph, only the raw data is plotted, and the spectra were stacked for a better visualization of the thermal evolution. The corresponding spectra showing the different components is shown in Figure A.2 of the appendix.

The corresponding experiment performed for CyPd(1) is reported in Figure 23. The XPS spectra show that, at room temperature, the core level energies of N 1s, Pd 3d, C 1s, and Cl 2p correspond to the intact complex. Upon heating to 200 °C, a significant reduction is observed for the C 1s, N 1s and Pd 3d peaks, while for the Cl 2p signal only a slight reduction takes place. This leads to the hypothesis that upon annealing to 200°C, some CyPd (1) molecules present on the surface partially dissociate. Part of the Cl stays

on the surface or in fragmented molecules while the rest desorbs. Between 250°C and 350°C we observe a slight reduction of the signals also in the other spectral regions, suggesting further desorption. Above 350°C, total desorption has occurred also for the fragments.

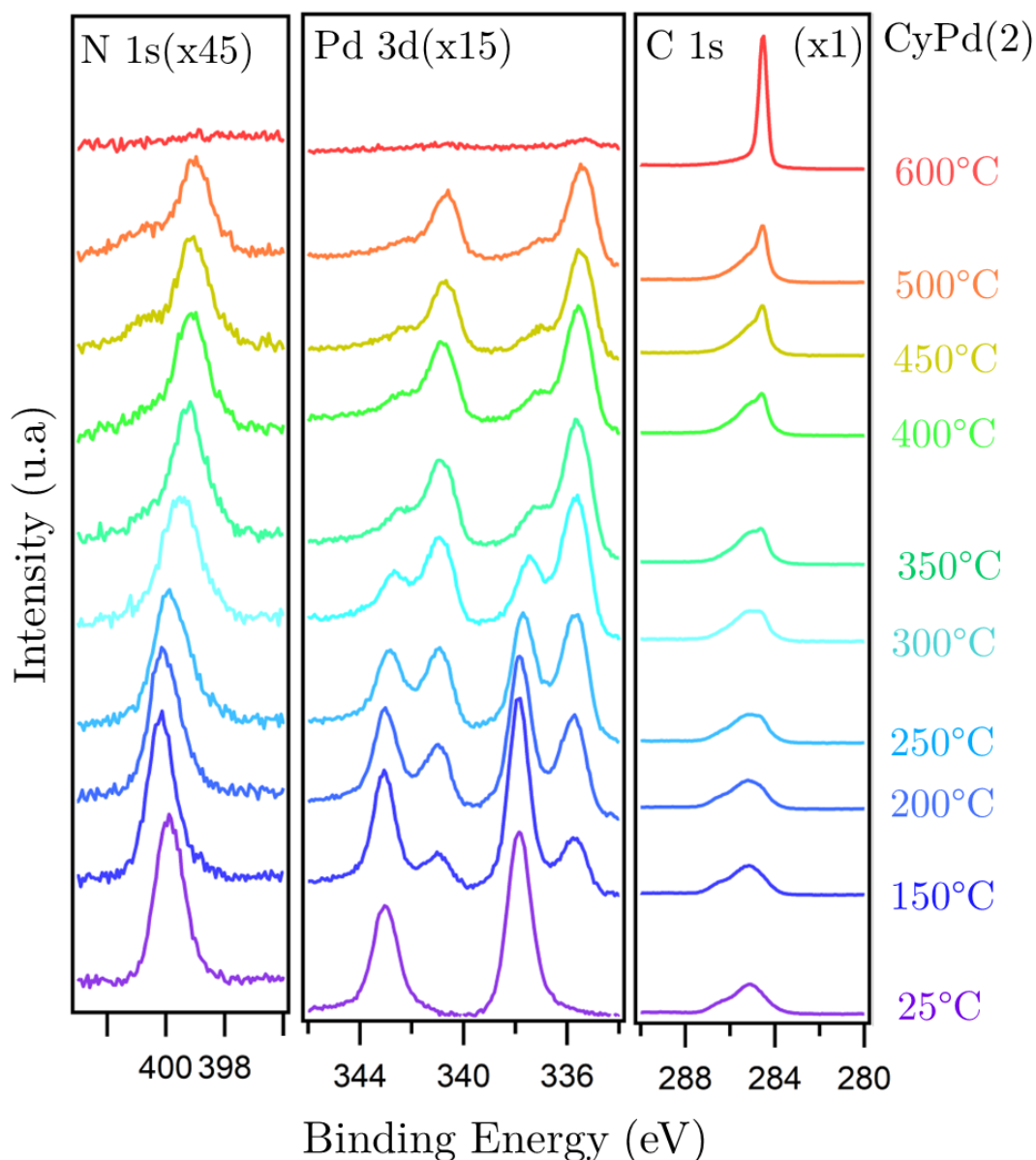


Figure 24: HR-XPS of the raw data showing the thermal evolution of CyPd(2). The spectra are stacked to better visualize the evolution due to annealing the sample. The corresponding spectra showing the components is shown in Figure A.3 in the appendix.

In the case of CyPd (2) (Figure 24), after deposition at RT all the regions show the characteristic peaks of this molecule; the N 1s region exhibits a well-defined peak at ~400 eV, characteristic of pyridinic coordinated nitrogen. The Pd 3d region is dominated by the Pd(II)–N doublet at ~338 eV, confirming the integrity of the molecules, an extra component was needed for a better fit, as described in the section above. In the C 1s region, a weak HOPG peak is observed at 284.5 eV alongside with ligand-derived C–C/C–H and C–N components. The HOPG signal is strongly suppressed indicating an almost fully covered surface and a closed CyPd(2) film.

Annealing reveals a different behavior with respect to the previous compounds since no significant desorption is evident up to 400 °C. Instead, upon annealing, the Pd 3d peak at 338 eV converts into new species with BE around 335.5–336.8 eV, corresponding to Pd (0) (refer to table 3). This conversion starts upon annealing to 150°. At 250°C, the two components are almost of the same intensity and at 400 °C only Pd(0) is present on the surface. The corresponding N 1s spectra show an initial upshift, followed by a downshift to 399 eV, indicating the growth of a low BE component. The line at ~400 eV, dominant at RT, is assigned to N-pyridine bonds of the intact molecule and has an intensity which is compatible with the one of Pd(II). The downshift in BE suggests an increase in electron density at the nitrogen atoms. This is consistent with partial reduction of the Pd center and/or weakening of the Pd–N coordination, which decreases the positive character of N. The additional component in the N 1s spectrum at ~400.7 eV may correspond to graphitic nitrogen (refer to Table 5).

Total intensity vs annealing temperature

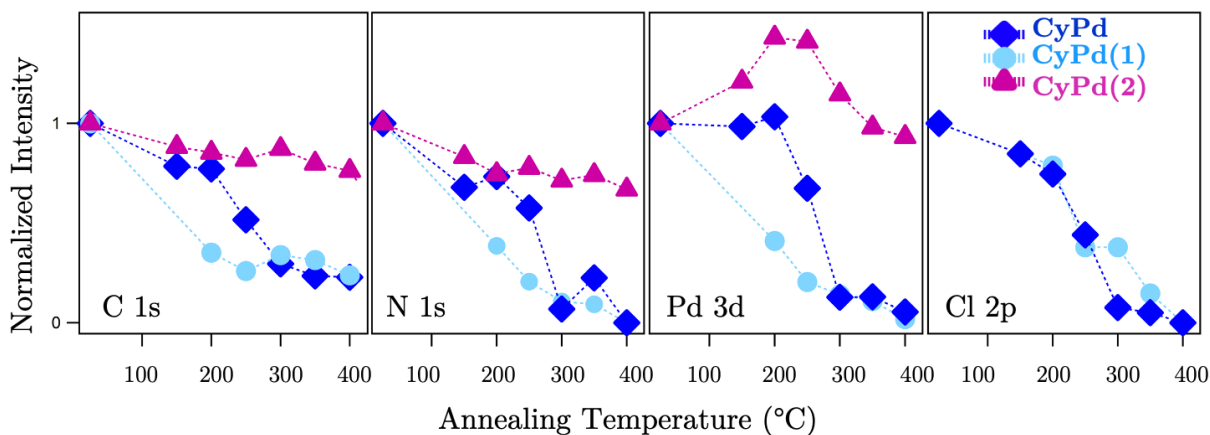


Figure 25: Total intensity of the different molecular elements as from the fitting of the corresponding XPS spectra normalized to the value at RT as function of annealing temperature for the three complexes CyPd, CyPd(1), and CyPd(2). These normalized intensity profiles provide quantitative insight into the relative thermal stability of the molecular layers.

In order to reach a quantitative understanding of the thermal stability of the molecular layers, the total intensity of the different molecular components of the three CyPds is plotted as a function of annealing temperature in Figure 25. The fits of each peak are shown in Figure A1, A2, A3 of the appendix for the three molecules CyPd, CyPd(1) and CyPd(2). Starting with CyPd, there is a ~50% reduction of C 1s, N 1s, Pd 3d and Cl 2p intensities when annealing to 250°C. In case of CyPd(1), when annealing at the same temperature, the reduction is ~80% for C 1s, N 1s and Pd 3d intensities, while the Cl 2p behaves differently reducing by only ~60%. This difference is outside of experimental error and suggests an incomplete dissociation of the molecules leaving Cl on the surface.

CyPd(2) behaves differently than the two halogenated molecules. As the annealing temperature increases, there is a slight reduction for the C 1s and N 1s intensities while the total Pd intensity increases by 40% after annealing to 200°C. This increase may be only apparent if it is related to a different photoelectron diffraction for Pd(II) and Pd(0) or real if the Pd atoms generated by dissociation of the molecules are in contact with the substrate and become less screened due to partial desorption and the thinning of the organic film above them.

The raw data for the Pd region is reported in Figure 26 for a deeper analysis of what is actually happening to the adlayer. This region is particularly relevant since it directly reflects chemical state, coordination environment, and stability of the Pd atoms.

Figure 26 reports the Pd 3d spectral regions of all three molecules; CyPd, CyPd(1) and CyPd(2) at RT, after annealing to 250°C and after annealing to 400°C.

At room temperature, all three complexes show one well-defined Pd (II) doublet at BE~337.8 eV. This BE matches the literature values for Pd (II)-Cl and/or Pd (II)-N, see Table.5, indicating that the molecules are deposited intact on the surface. This holds totally true for the halogenated molecules, while a small extra signal at 336.8 eV was needed to fit the Pd 3d in case of CyPd(2). It indicates, as discussed above, the presence of Pd_i (single Pd atoms due to photon induced damage) [56]. After annealing to 250°C, the spectra of CyPd and CyPd (1) show a significant reduction of the Pd 3d peak intensity without shifts in BE. These molecules undergo therefore desorption without dissociation.

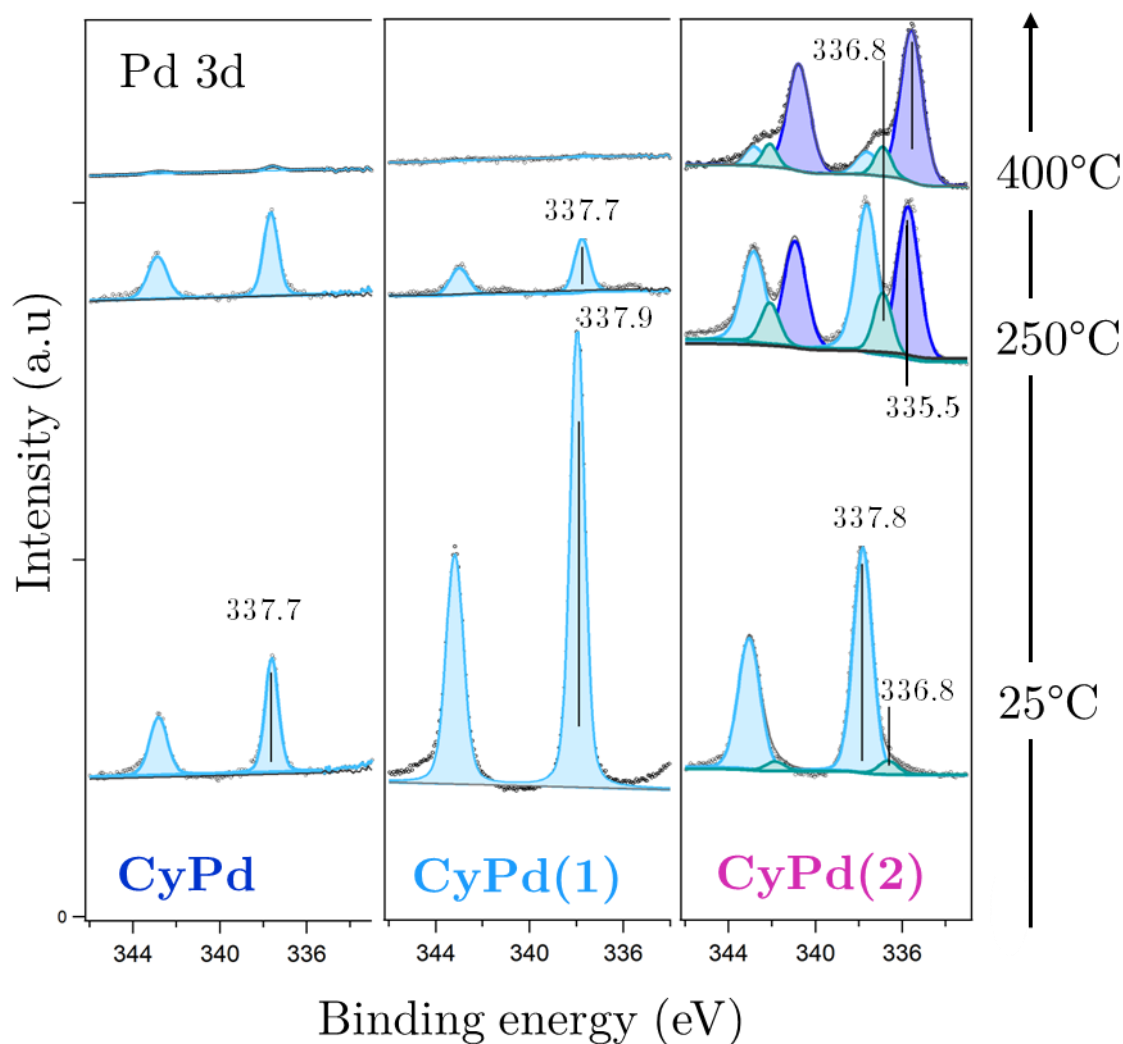


Figure 26: Pd 3d spectra showing direct monitoring of the oxidation state and coordination environment of Pd in CyPd, CyPd(1), and CyPd(2) during annealing from 25 °C to 400 °C. The changes in peak shape, binding energy, and relative intensities provide insight into ligand stability, halogen dissociation, and reduction of Pd(II) to metallic Pd(0).

The de-halogenated molecule, CyPd(2) behaves differently since new Pd components appear at lower BE, corresponding to Pd(0). From literature the peak at 335.5 eV corresponds to Pd atoms aggregated in clusters, while the peak at 336.8 eV corresponds to single neutral Pd atoms, Pd₁ [56]. The formation of Pd(0) indicates breaking of the Pd-N bonds. This reveals that Pd in CyPd (2) undergoes metallic reduction, in contrast to the behavior of CyPd and CyPd (1). The presence of Pd₁(0) and the small, but progressive downshift of the BE of Pd(0) (see Figure 26 and Figure A3) is coherent with what is reported in ref [56] (Figure 21) for clusters of increasing size and suggests that dissociated Pd atoms tend to aggregate when annealing. This hypothesis is comforted

also by the observation that sintering of Pd₁(0) adatoms on alumina starts at 150°C [56] which is also the temperature at which the 335.5 eV component appears in our spectra, FigA.3. The small reduction in intensity observed for the other elements of the molecule and the corresponding increase of the total Pd intensity reported in Figure 25 for CyPd(2) can be explained at this point with a limited desorption of organic fragments leaving Pd atoms at the surface which become more visible due to the thinning of the organic layer above them and/or because of photoelectron diffraction effects.

At high temperature (400°C), CyPd and CyPd(1) show almost no detectable Pd signal, that indicates their total desorption. On the contrary, for CyPd(2) I observe the reduction of the Pd(II) intensity while the Pd(0) signal persists. Therefore, I can conclude that after the breakage of Pd-N bonds, the released Pd atoms aggregate into small metallic clusters/nanoparticles. It is important to mention that at this temperature, some Pd are still inside intact admolecules as witnessed by the persistence of the Pd(II) component.

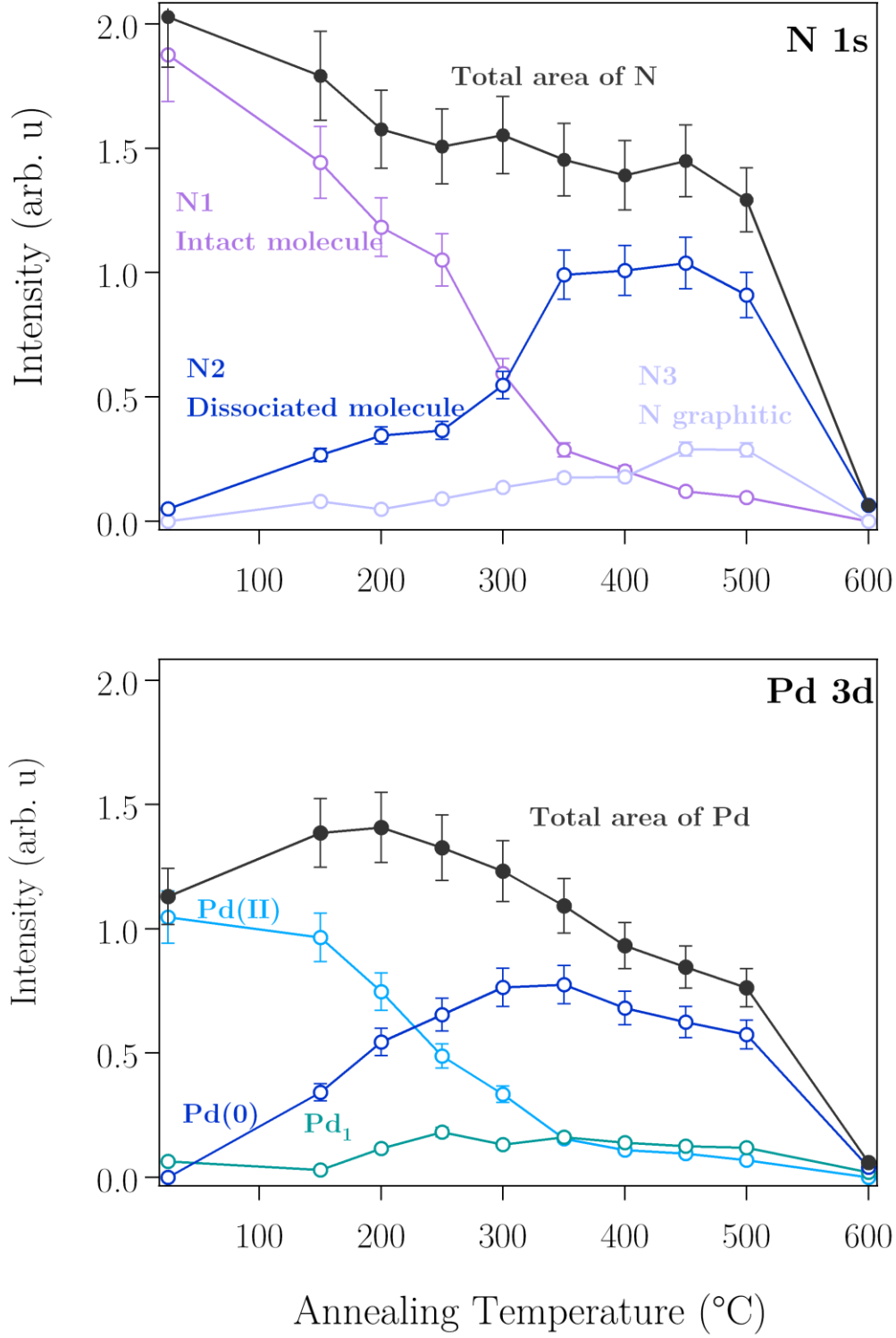


Figure 27: The area of the different components normalized to the corresponding background and to the cross section at 515 eV photon energy as a function of annealing temperature for: a) N 1s and b) Pd 3d.

To better understand the abovementioned phenomenon I plotted the absolute area of the different components for the N 1s and Pd 3d spectral regions of CyPd(2) vs annealing temperature in Figure 27 together with the corresponding total areas normalized to the background and to the cross section of the photoemission lines at $h\nu=515$ eV (0,3981 Mbarn for N 1s and 3,095 Mbarn for Pd 3d [69]). This normalization allows a direct comparison of the stoichiometric ratio between N and Pd which comes out to be 1.9 at RT, a value which is very close to the stoichiometric value of 2 for the intact molecule. This indicates that at room temperature most of the molecules are adsorbed non dissociatively on the surface and undergo dissociation only eventually upon annealing the sample.

Figure 27.a shows the behavior of the three different N components already described in table 5: N pyridine in the intact molecule (N1), N pyridine associated to dissociated molecules (N2) and Graphitic N (N3). The total N area (black line) decreases as the annealing temperature increases. At RT, the total N 1s area is 2.0 arb. u. and is nearly totally due to N1. As the sample is annealed to 150°C, the total N area decreases to 1.8 arb. u. while the one of N1 decreases to 1.44 arb. u.. The difference in intensity is due to the rise of the other two N components: N2 increases to 0.26 arb. u, and N3 to 0.08 arb. u. The decrease of N1 proceeds almost linearly until 300°C above which temperature an abrupt decrease occurs. The behavior of N2 goes in the opposite direction. Upon annealing above 500°C, the N signal vanishes indicating that full desorption has taken place.

The behavior of the Pd signal is reported in Figure 27.b. As mentioned previously Pd(II) corresponds to Pd in intact molecules, while Pd(0) results from molecular dissociation. Upon deposition at RT, the total area of 1.13 arb. u. consists mainly of Pd(II) with a minor Pd_i intensity (0.8 arb. u.). Upon annealing to 150°C, I observe an increase of the total Pd area from 1.13 arb. u to 1.38 arb.u.. This phenomenon results from the decrease in the Pd(II) area (from 1.04 to 0.96 arb. u) that is overcompensated by the increase of Pd(0) intensity in clusters by 0.34 arb. u. while the Pd_i area remains constant. This confirms that initially a thick multilayer was present and that, upon partial dissociation, Pd atoms are left at the surface while the N containing part of the fragments have desorbed. Between 200°C and 400°C, Pd(II) decreases more rapidly while the area of the Pd(0) increases and reaches a plateau above 300°C. A similar behavior has been reported for Pd-containing surface systems, where annealing promotes conversion of Pd(II) into metallic Pd nanoparticles detectable by XPS [70].

Above 500°C, a decrease in both species is observed indicating a complete desorption. This analysis shows that at RT the molecule is adsorbed mostly intact on the surface. Following the behavior of N 1s components, I can estimate that as the sample is annealed to 150°C, ~12% of the molecules present on the surface have desorbed, ~72% are still intact on the surface and ~17% are dissociated forming new species. Upon annealing to 300°C, desorption involves 23% of the molecules while more than 27% of them are converted into N2 species. This confirms the significant dissociation of the compound with organic fragments remaining at the surface. This is coherent with the observation that Pd(0) is the dominant species at this temperature. The hypothesis of the Pd-N bond being broken is thus confirmed.

From the TGA analysis, reported in section II.1 (Figure 4) and from the analysis of the thermal evolution spectra, we can see that CyPd and CyPd(1) layers have different thermal stability than CyPd(2). Annealing the sample induces mostly desorption rather than molecular dissociation. This means that, for these complexes, the energy of the desorption barrier is lower than the dissociation energy. On the contrary, CyPd(2) undergoes decomposition at approximately 100 °C lower temperature than the other two investigated CyPds. Upon annealing, bond cleavage therefore occurs prior to desorption, which means that dissociation becomes the dominant pathway. Once bonds break, the resulting radical fragments may interact with surface defects or with other radicals, generating species that are more stable on the surface.

III.1.2 Dropcasting from a DMF solution

XPS comparison of sublimated vs drop-casted molecules

In this section, I report on a direct comparison of the surface chemical state when the cyclometalates are deposited on HOPG by sublimation in UHV and by drop-casting under ambient conditions.

Figure 28 compares XPS spectra recorded for the CyPd/HOPG system produced by two different deposition techniques and analyzed either using synchrotron radiation or conventional monochromatic X-ray source.

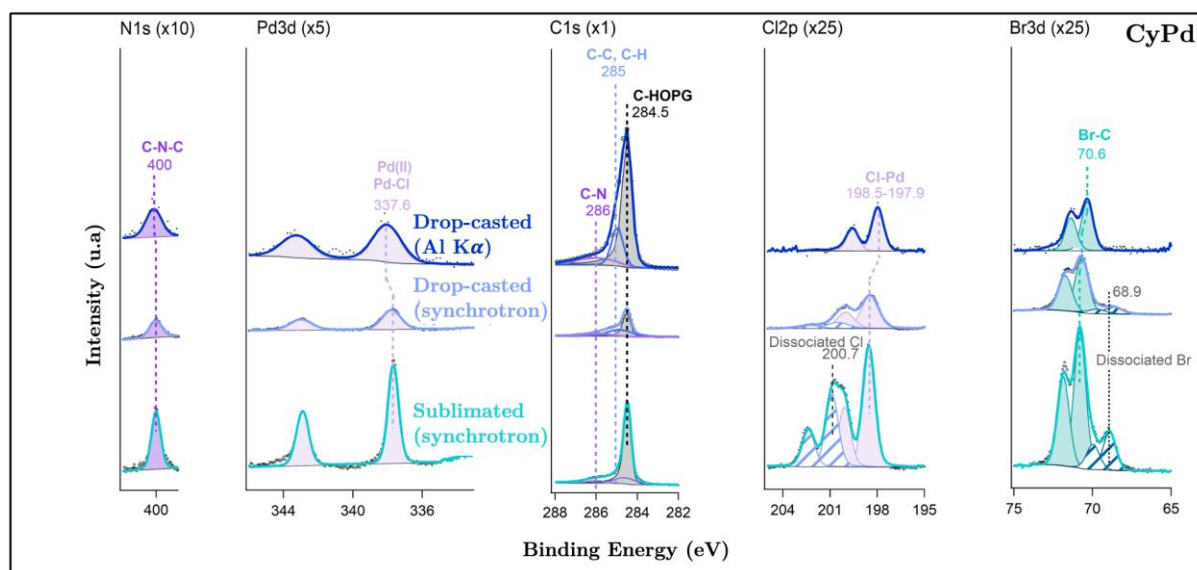


Figure 28: High-resolution XPS spectra of CyPd molecules deposited onto HOPG. Bottom (sublimation in UHV-cyan) and Middle (drop-casting-light blue) line spectra are measured with synchrotron radiation. Top line spectra correspond to the drop-casting preparation analysed with the laboratory X-ray Al $K\alpha$ source (dark blue). The spectra show core-level regions for N 1s, Pd 3d, C 1s, Cl 2p, and Br 3d. The peak assignment for each region is indicated on the Figure and summarized in Table 3.

The spectra recorded with synchrotron light (cyan blue (bottom) and light blue (middle)) are qualitatively very similar. Despite the different coverage achieved by sublimation and drop-casting, all components are found at the same binding energy (previously discussed in section III.1.1). No extra components, attributed to residues of the solvent (DMF),

are detected in the DC- sample XPS spectra. This is indicative that the chemical state of CyPd molecules is not affected by the deposition methods.

Vice versa, comparison of the spectra of DC-samples analysed with the different X-ray sources (light blue (middle) and dark blue (top spectra) reveal small differences related to the lower resolution and to the different photoionization cross section of the laboratory source with respect to synchrotron light. More importantly, we observe that partial dissociation of the halogen atoms, witnessed by the minority doublets at 200.7 eV and 68.9 eV in the Cl 2p and Br 3d regions, occurs only when the system is illuminated with synchrotron light, that is much more intense than the conventional X-ray source. The doublets present in the halogen's region correspond to dissociated halogens (see Table 5). They are present at room temperature and are due to photo-induced damage and not to annealing [71].

Considering this, it is possible to directly compare the spectra of CyPd(1)/HOPG (Figure 29) and CyPd(2)/HOPG (Figure 30), obtained at ALOISA by sublimation in UHV and in Genova by drop casting. Despite the different coverage obtained following the two different deposition procedures, all components are found almost at the same binding energies. Drop-casted samples show an additional component at ~ 289 eV, at a value suitable for C=O, COOH and carbonate bonds due to contaminants derived from exposure of the sample to the atmosphere during and after preparation. Indeed, I remark that all samples prepared and measured ex-situ present a contamination of adventitious carbon due to interaction with the atmosphere. Such contamination usually corresponds to a major component at ~ 285 eV [72], that in the present case cannot be resolved, and by species containing C and O, generating an XPS intensity around 288-289 eV.

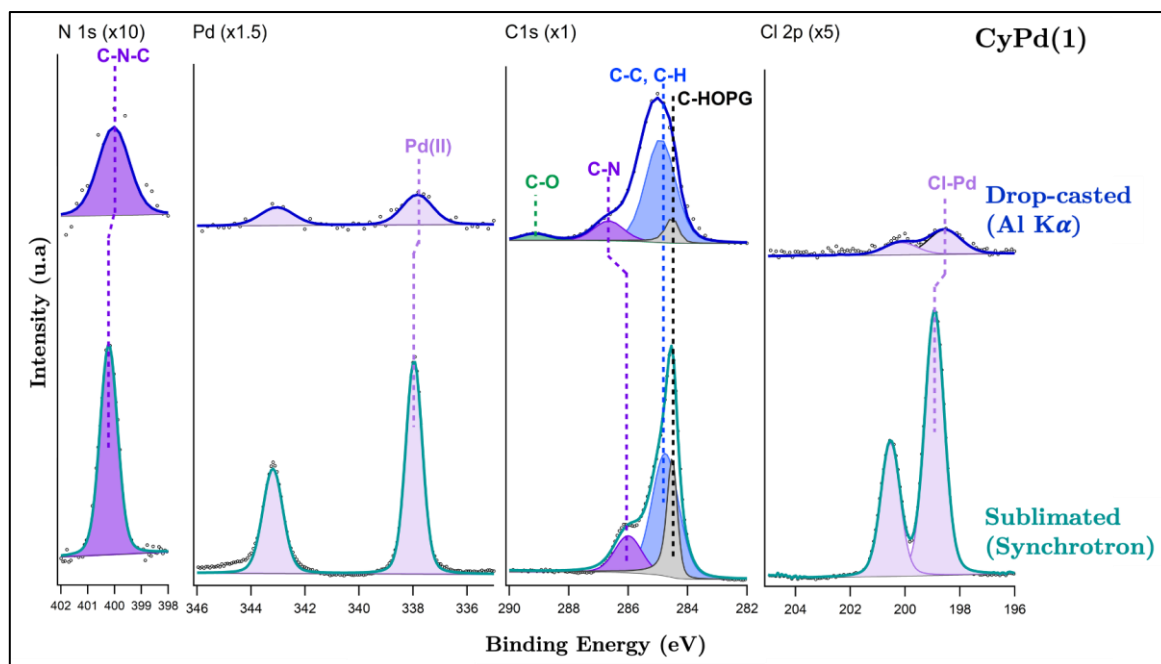


Figure 29: High-resolution XPS spectra of CyPd (1) molecules deposited onto HOPG: Bottom line spectra: measured by synchrotron radiation sublimated in ultra-high vacuum (UHV, cyan). Top line spectra: analyzed with a laboratory X-ray Al $K\alpha$ source, drop-casted (dark blue). The spectra show the core-level regions for N 1s, Pd 3d, C 1s, Cl 2p, and Br 3d.

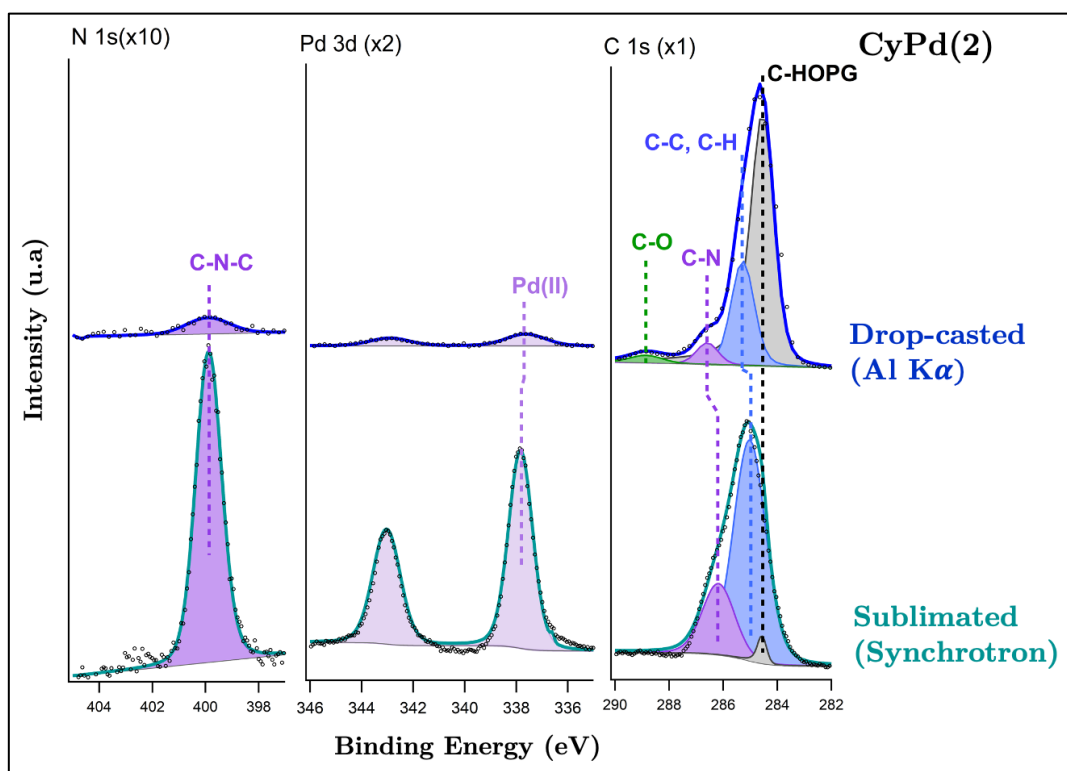


Figure 30: High-resolution XPS spectra of CyPd (2) molecules deposited onto HOPG: Bottom line spectra: measured by synchrotron radiation sublimated in ultra-high vacuum (UHV, cyan). Top line spectra: analyzed with a laboratory X-ray Al $K\alpha$ source, drop-casted (dark blue). The spectra show core-level regions for N 1s, Pd 3d, C 1s, Cl 2p, and Br 3d.

Since the chemical composition of the system remains unaffected by the deposition method, the thermal stability of molecules deposited by drop-casting or by vacuum sublimation is expected to be equivalent.

All the above results lead to the conclusion that:

Pd cyclometalates adsorb non dissociatively at RT on HOPG. This conclusion is at variance with what previously reported for CyPd/Ag(110) [21] [58] where dissociation occurs and aligns with the inherently low chemical reactivity of HOPG surfaces.

The chemical composition of the system does not depend on the deposition method. Therefore, the thermal stability of molecules deposited by drop-casting or by vacuum sublimation is equivalent.

These results are important in view of possible applications of the CyPd network for catalytic purposes, since deposition by wet methods is simpler, cheaper and less time consuming than preparation in UHV.

III.2 Morphological analysis at the Mesoscale by AFM

III.2.1 Self-assembly of Pd-cyclometalates drop-casted on HOPG.

The self-assembly of the three molecules has been studied by AFM to gain information on the morphology of the overlayer at the mesoscale.

As mentioned in the experimental section, before each preparation the HOPG sample was scotch-tape cleaved to generate a flat and clean surface. A typical image of a clean HOPG sample before the deposition of the molecules is reported in Figure 31. The image shows large flat terraces interspaced by monoatomic or biatomic steps. It represents therefore a good substrate for the growth of the metalorganic overlayers.

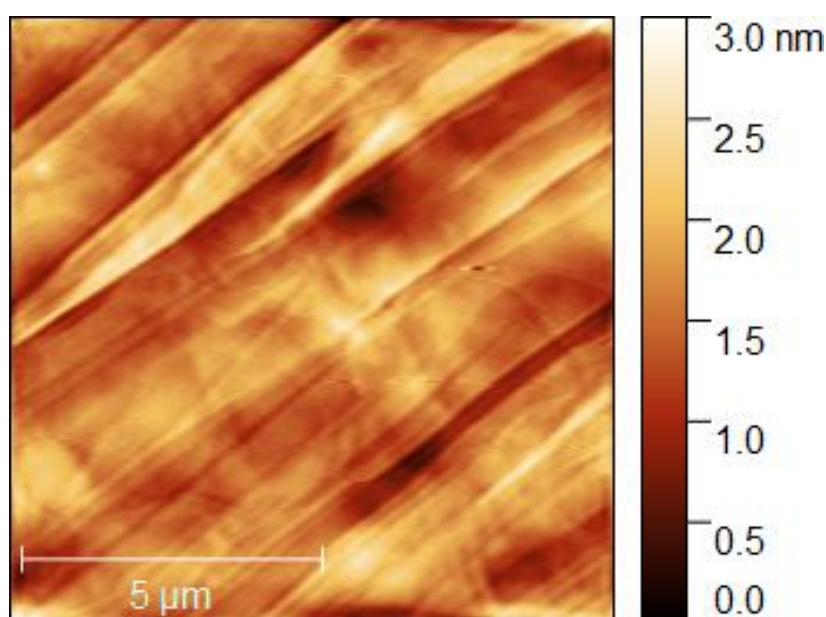


Figure 31: AFM image of freshly cleaved HOPG ($10 \times 10 \mu\text{m}^2$).

The samples were prepared by drop-casting from a DMF solution ($\sim 1.5 \mu\text{M}$) on the substrate at RT. They were left overnight in air to allow for the evaporation of the solvent. The very next day, they were introduced into the AFM glove box and analysed in a low humidity atmosphere ($\sim 10\%$, obtained by fluxing N_2 gas). The overviews of the samples covered with the different overlayers are shown in Figure 28.

AFM inspection reveals the formation of self-assembled structures at the mesoscale. They are different for the three compounds. For CyPd (panel a) I observe fractal islands. For CyPd (1) two types of structures are present (see panels b and c); they consist of a ramification of filaments of different size and of a more uniform and granular layer, respectively. CyPd (2) forms granular features that cover almost all the surface. In the following I will detail these structures and describe their thermal evolution upon annealing up to $T=250\text{ }^{\circ}\text{C}$, that is the maximum temperature allowed by the AFM heater.

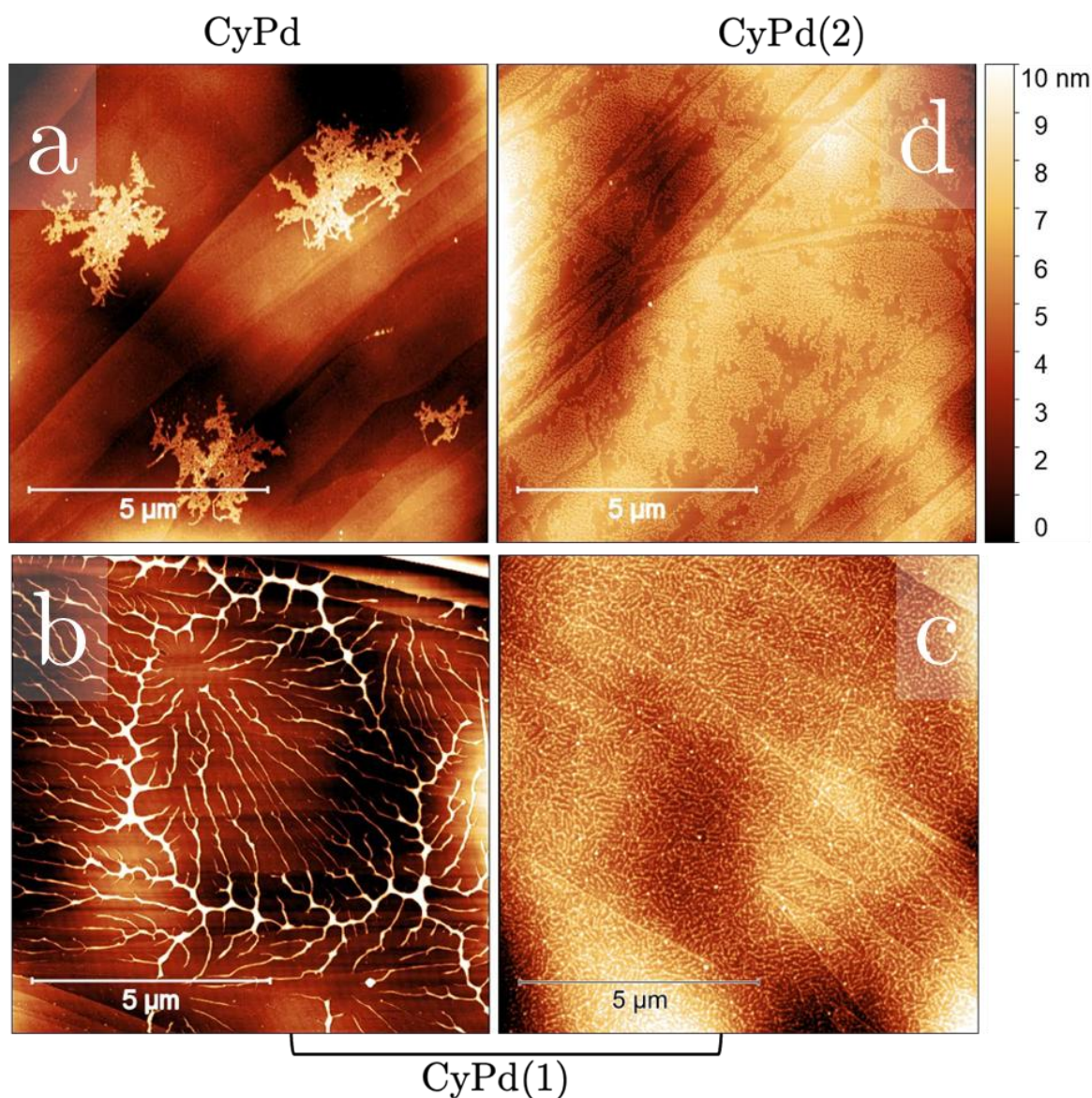


Figure 32: Overview AFM images ($10 \times 10\text{ }\mu\text{m}^2$) of self-assemblies observed after drop-casting the molecules on freshly cleaved HOPG: a) CyPd; b) and c) CyPd (1); d) CyPd (2).

III.2.2 CyPd/HOPG

As evident from the overview in Figure 32a, when drop-casted on HOPG at RT, CyPd forms fractal structures of lateral size ranging approximately between 1 and 5 μm . Figure 33 reports the enlarged image of the bottom-left island of Figure 32a, together with some details of its internal structure.

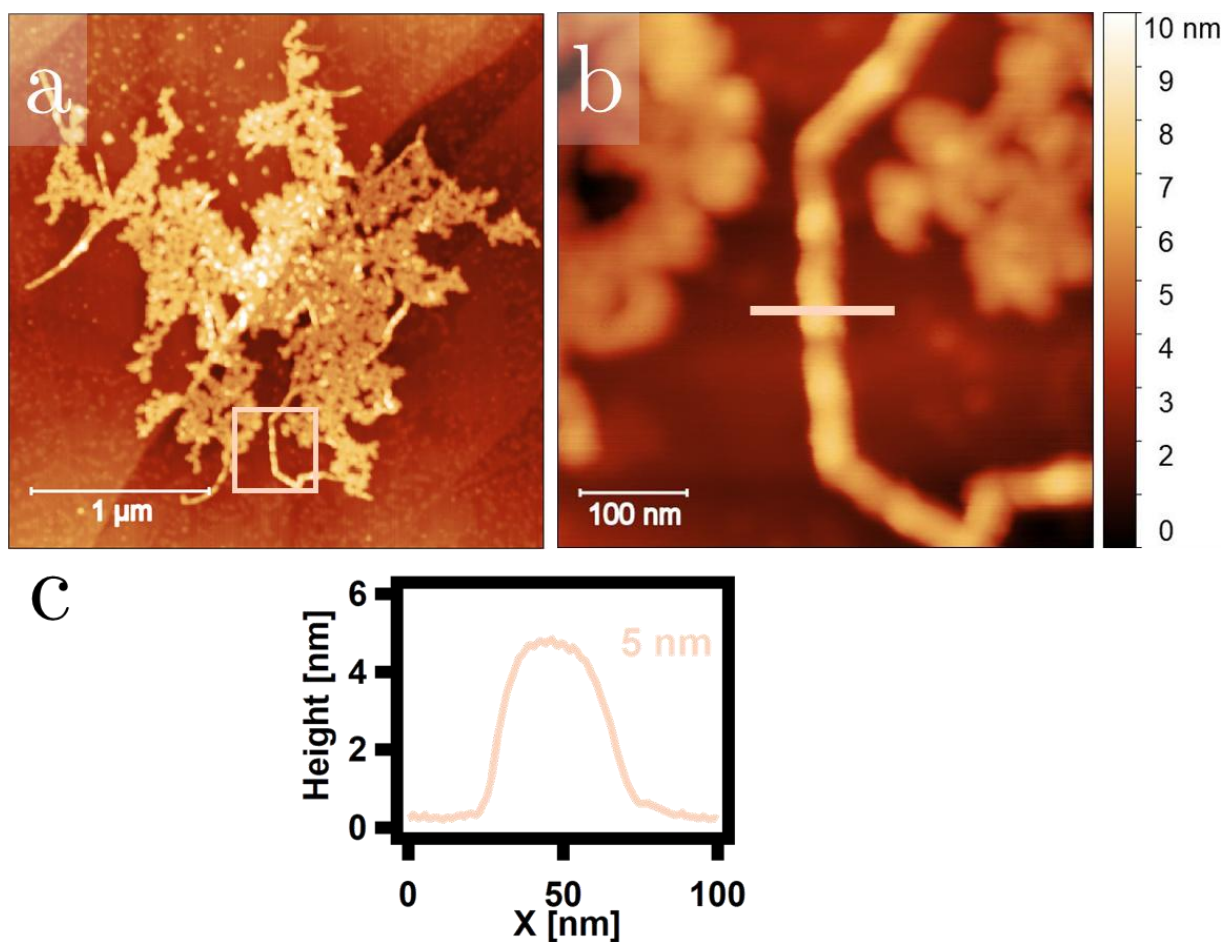


Figure 33: DC-CyPd/HOPG at RT. (a) AFM image of the bottom-left island present in the overview of Figure 32a (image size: $3 \times 3 \mu\text{m}^2$) (b) Enlargement ($0.5 \times 0.5 \mu\text{m}^2$) of the area marked by the square, showing the presence of an isolated filament at the periphery of the island. (c) Height profile of the filament in panel b (cut along the marked path).

It is evident (panel a) that the fractal islands are formed by smaller features of globular shape merging with each other and creating areas at higher and smaller density. Isolated filaments of some 30 nm width and 5 nm height are visible at the periphery of the islands.

The topmost surface of these filaments (panel b) is not perfectly flat, suggesting that they consist of globular units. After annealing to 150°C for 10 minutes, the CyPd islands of Figure 33a rearrange as shown in the overview reported in Figure 34a.

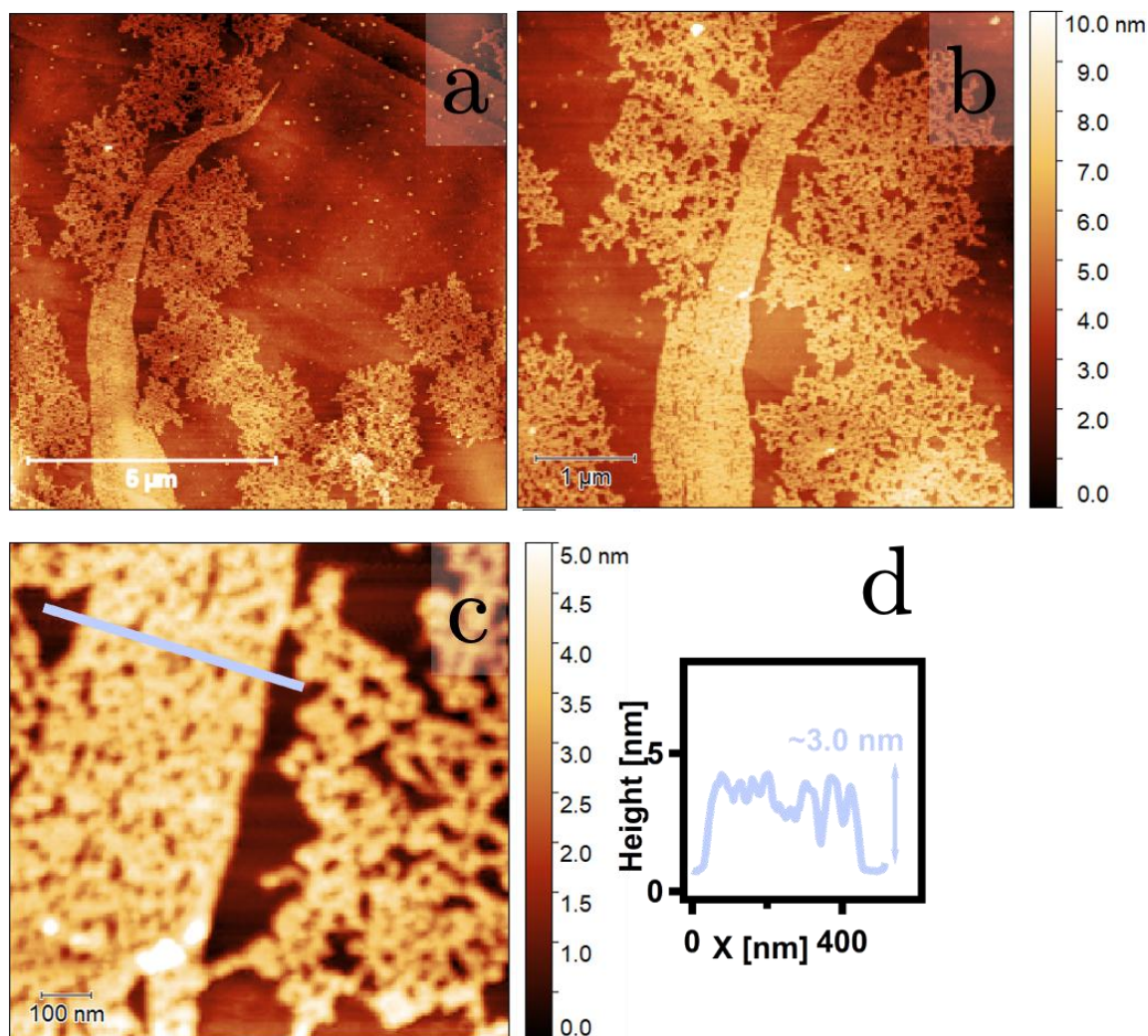
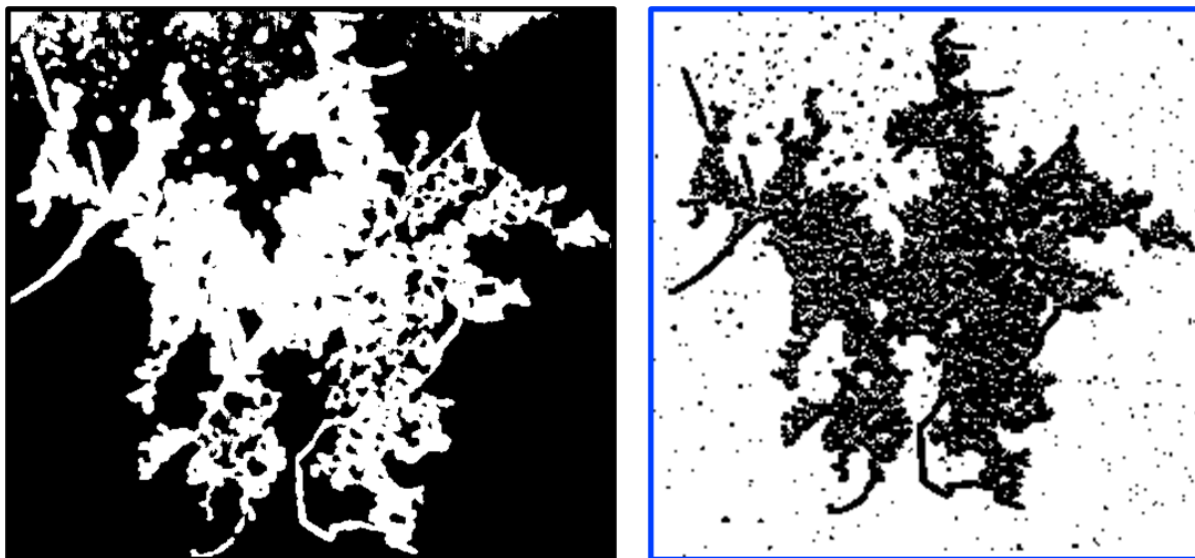


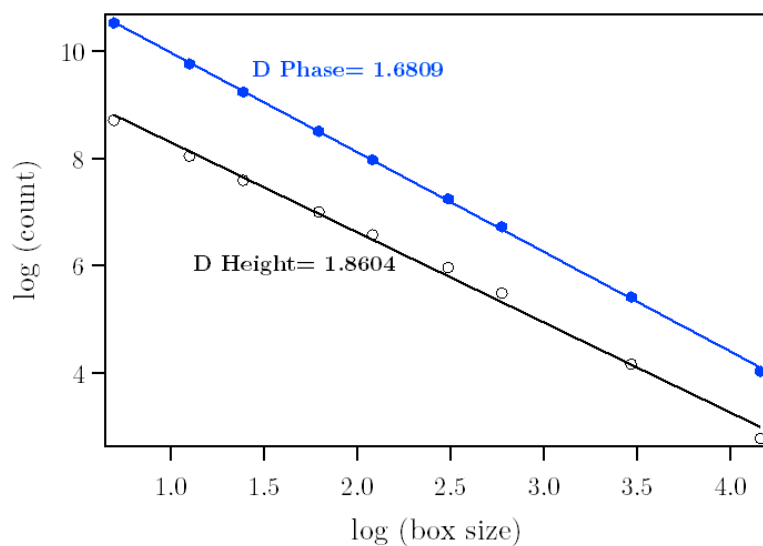
Figure 34: DC-CyPd/HOPG annealed to 150°C: (a) 10 x 10 μm²; (b) 5x5 μm² image of the features shown in (a); (c) 0.5x0.5 μm² image of the features shown in (b); (d) line scan cut along the path marked in panel c) and showing the height of the self-assembled structure.

The islands tend to coalesce, and the surface is now covered by regions of two different densities, as evidenced by the enlarged images reported in panels b) and c). A more compact central stripe and looser side islands are present, the latter being reminiscent of the initial fractal shape observed after the growth at RT. The fraction of surface covered by CyPd is now larger while the average height is lower (~3 nm, see line scan in panel d), suggesting that the total CyPd coverage is almost preserved. This conclusion is coherent with the XPS information reported above, that indicates a limited desorption upon annealing at this T.



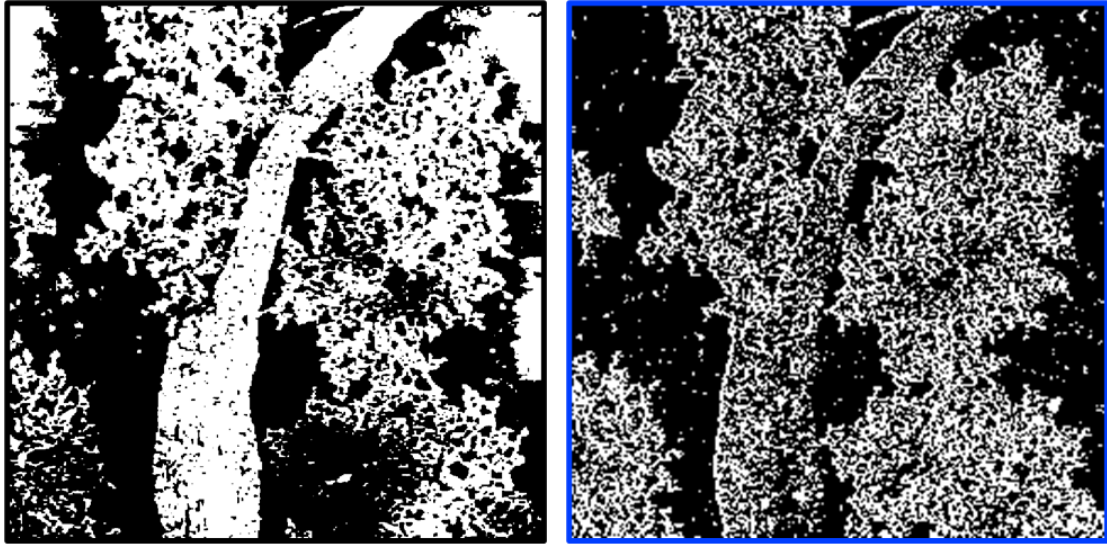
a) Z height image in binary

b) Phase image in binary

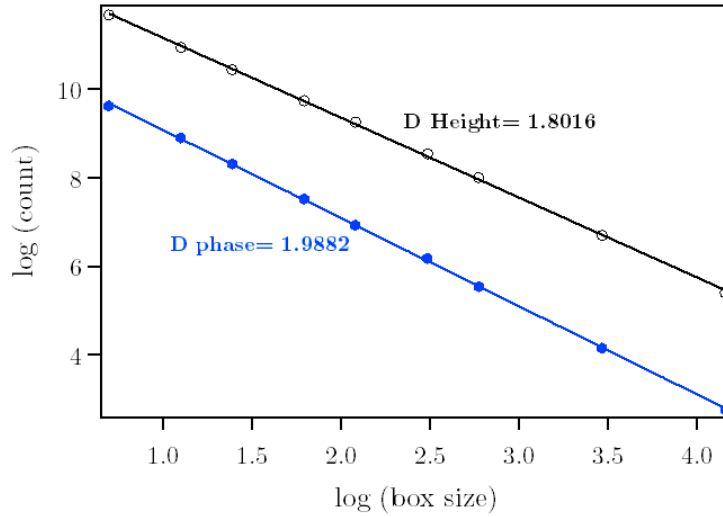


c) Fractal box count

Figure 35: AFM image of Figure 33 converted to binary format to study the fractal dimensions; a) Z height image b) Phase image, Images size: $3 \times 3 \mu\text{m}^2$ c) Fractal box count done using ImageJ software.



a) Z height image in binary b) Phase image in binary



c) Fractal box count

Figure 36: AFM image of the island after annealing to 150°C in Figure 34 converted to binary format to study the fractal dimensions; a) Z height image b) Phase image. Image size: 5x5 μm^2 , c) Fractal box count done using ImageJ software.

Figure 35 shows the binary images of the fractal islands discussed above, as well as the fractal box count from which we can deduce the fractal dimensions of the islands. The fractal box count method is an empirical technique used to determine the fractal dimension (D) of complex, irregular shapes or images by measuring how their detail changes with scale. It involves overlaying grids of decreasing box sizes over an image and counting the number of boxes that intersect the object. The fractal dimension is the slope of the log-log plot shown in Figure 35 (c). Analysis was performed on 9 islands at RT, and the average fractal dimension obtained was (1.82 ± 0.01) for Z height images, and (1.71 ± 0.03) for phase images. Those values are compatible within the error. They indicate a dense and complex branching of those structures.

A similar analysis was performed on the island of Figure 34 (AFM image), measured after annealing the layer to 150°C , Figure 36. It shows that the fractal dimension is 1.80 for the height image and 1.99 for phase image.

This increase in the phase image suggests that annealing slightly compacts the structure, a larger statistics would be necessary for further speculation.

III.2.3 CyPd (1)/HOPG

After depositing CyPd(1), two types of self-assemblies are observed, as shown in Figure 32b and 32c. They correspond to different DC-preparations measured under nominally identical conditions. As it is well known from literature [73][74][75], the morphology of molecular self-assemblies of drop-casted samples is affected by several factors, including temperature, nature of the solvent, solvent evaporation rate and surface properties. So, even if controllable deposition parameters (temperature, concentration of the solution, drying time etc...) were nominally the same, it is possible that some other variables, e.g. the percentage of humidity under the hood during drop-casting and solvent evaporation, were overlooked. Considering that CyPd(1)/HOPG was the first system I investigated by drop-casting, it deserves surely further investigation to clarify these points but, unfortunately, it was not possible to perform additional preparations in the time available for my thesis. The first self-assembly (Structure I) looks like a branched dendritic network distributed across the whole HOPG surface (see Figure 32b and enlargements in Figure 37). The self-assembly has a hierarchical structure, with larger filaments up to 8 nm high and a few tens of nm wide (navy blue trace in the line scans of panel c) from which narrower ramifications branch out (4.5 nm height and 20-30 nm wide, light purple trace). Much thinner filaments are also observed in-between the ramifications of the main structure. As evident from the corresponding line scan (cyan blue), these features are ~ 0.4 nm high and ~ 10 nm wide (possibly less, since deconvolution of the tip is not considered at this stage). Therefore, they are likely to consist of a single layer of molecules arranged in a narrow ribbon. Finally, I observe that the angle formed by those ramifications is approximately 120° (or 60°) depending on the orientation. The radial and tree-like pattern suggest anisotropic growth, likely guided by molecular diffusion fronts and substrate crystallographic directions.

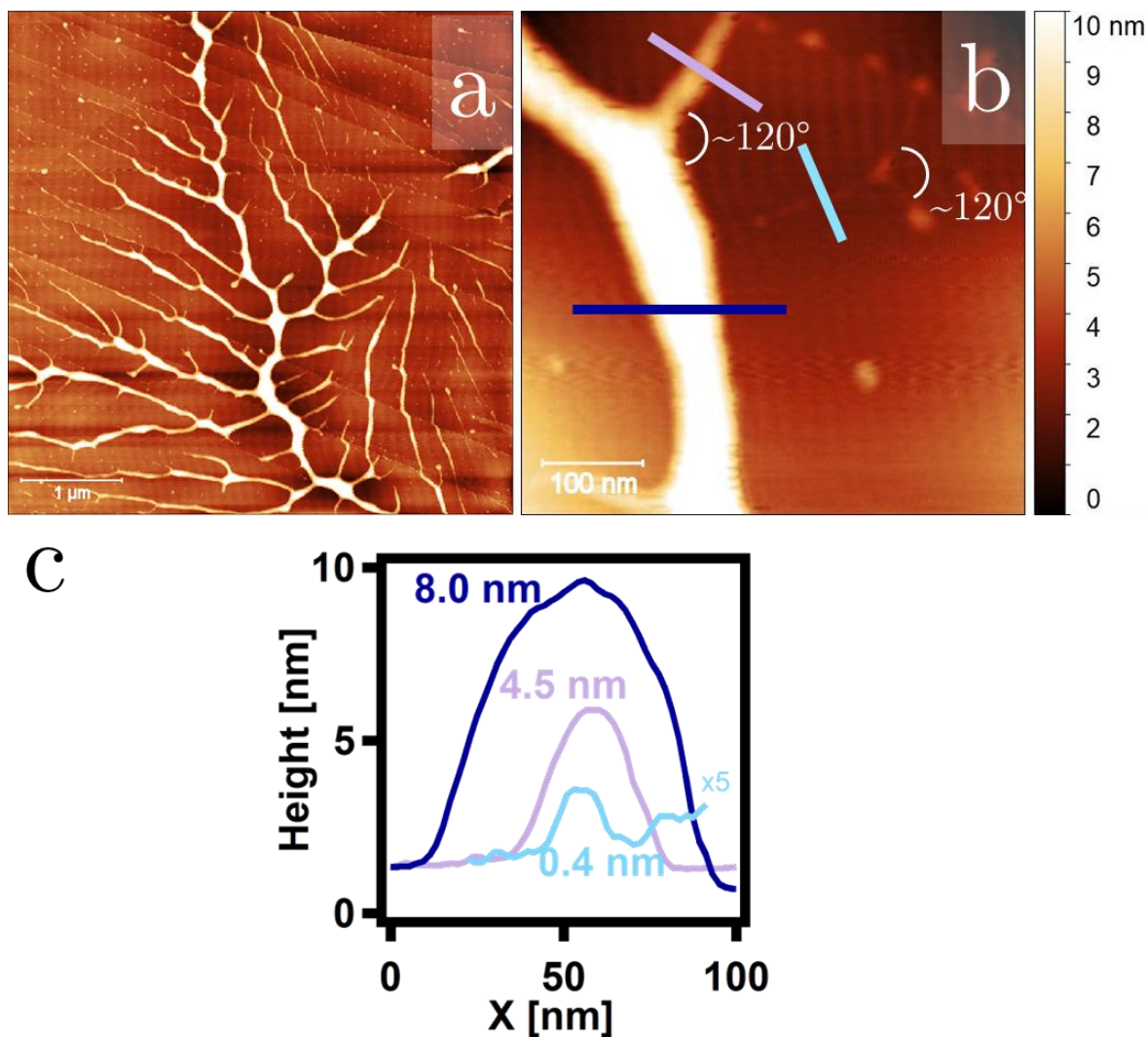


Figure 37: AFM images showing structure I of DC-CyPd (1)/HOPG at RT. (a) 5x5 μm² AFM image of the structures shown in Figure 32. (b) 0.5x0.5 μm² image of a ramification showing branches of different size. The angle between adjacent filaments is marked as well as the path corresponding to the line scans reported in panel c).

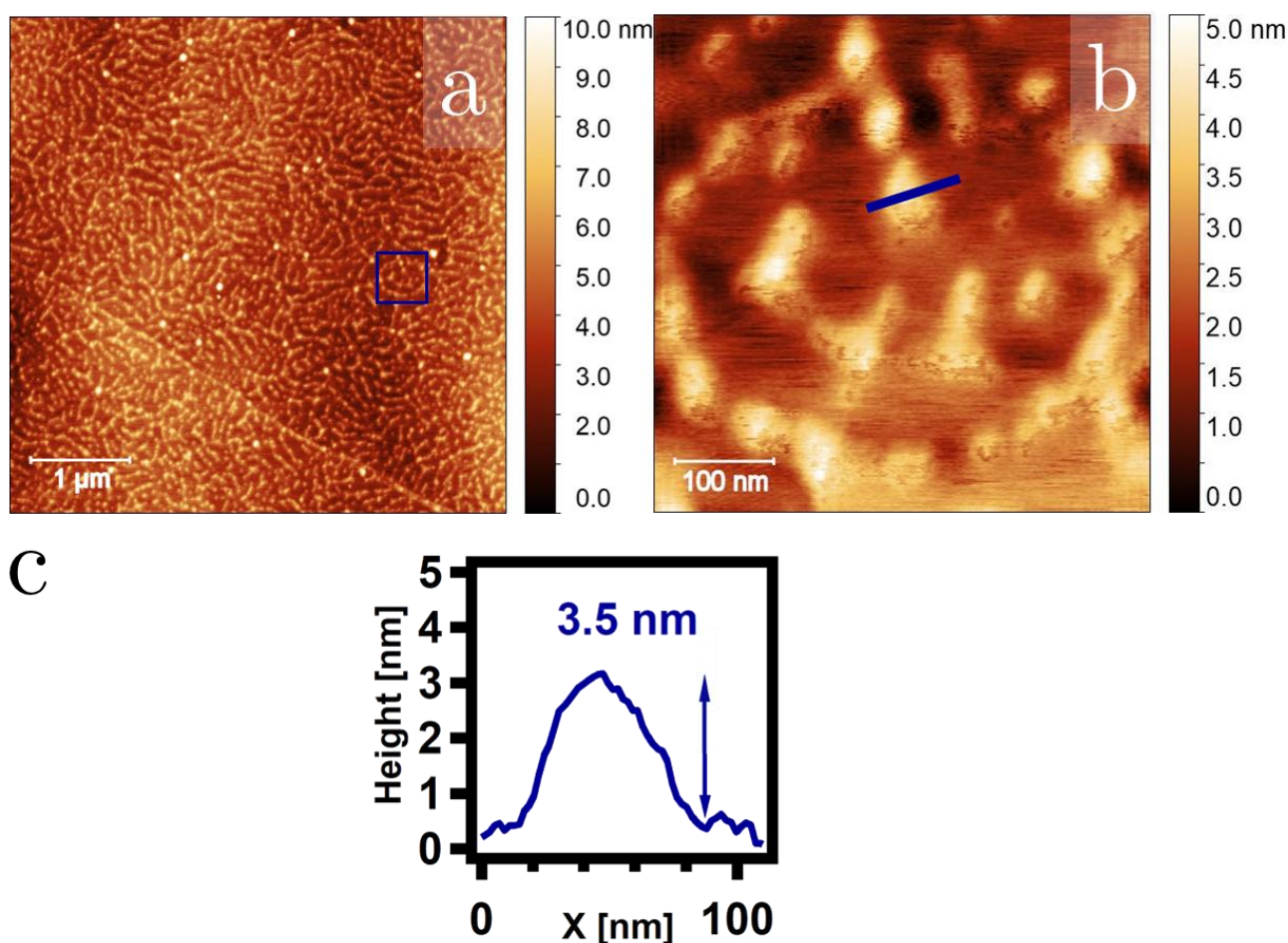


Figure 38: AFM images showing structure II of DC-CyPd (1)/HOPG at RT. (a) $5 \times 5 \mu\text{m}^2$ AFM image over part of the surface shown in Figure 32(c). (b) $0.5 \times 0.5 \mu\text{m}^2$ image of the area marked by the dashed square in panel a. The blue line corresponds to the height profile reported in panel c).

The second self-assembly (Structure II) consists of dot-like features of 3.5 nm height and some tens of nm width arranged in short rows (looking like sticks) (see Figure 32c and the enlargement in Figure 38). This morphology suggests the formation of few-layer molecular assemblies, rather than large aggregates. The individual domains appear interconnected and nearly uniform in width ranging from 30-50 nm, suggesting the formation of two-dimensional molecular networks stabilized by non-covalent interactions such as π - π stacking or hydrogen bonding [76]. This kind of structure typically arises during solvent evaporation in the drop-casting process, leading to anisotropic self-assembly and domain formation.

The thermal evolution of this second structure was investigated after step-annealing the sample to 100°C, 150°C, 200°C and 250 °C for 10 minutes using the heating stage of the

AFM and operating under controlled atmosphere, i.e. in N₂ flux to maintain a low humidity percentage (~10%). After each heating step, the sample was left to cool down to RT under controlled atmosphere and AFM analysis was performed eventually. The outcome is reported in Figures 39 and 40. The overviews in Figure 39 were acquired in different spots close to the center of the sample. However, the morphology of the CyPd(1) layer is quite uniform, as demonstrated by the similarity of the images at RT shown in Fig. 32c and Fig. 38a, so that I can safely assume that the sequence in Figure 39 is representative of the thermal evolution of the overall sample. The details of the different assemblies are magnified in Figure 40. Panel a) evidences the cobweb of filaments covering the surface at RT and the presence of a few higher clusters among them. The latter can be up to 9.5 nm high, as shown by the line scan on the right side of the figure. Upon annealing to 100°C (Figures 39b and 40b), the molecules are organized in islands of relatively uniform height (approx. 1.5 nm) and irregular shape, some of which are crossed by higher features in form of roundish clusters or filaments (see Figure 40b). After heating to 150 °C (Figure 39c and 34c), the surface layout changes dramatically: now the adsorbates coalesce in extended islands of ~2 nm height and quite uniform density, that cover part of the surface leaving large areas of clean HOPG. In addition, globular aggregates of 5-6 nm height are spread both on CyPd(1) islands and on bare HOPG. At step edges these aggregates tend to be smaller and aligned with the step. At 200 °C, the total CyPd(1) coverage reduces, according to XPS analysis. Coherently, the large, flat islands disappear, small molecular clusters decorate the steps, and the remaining molecules aggregate in corrugated filaments approx. 20 nm wide and with much lower average height (0.8 nm) than those observed at lower T. Finally, at 250°C (see Figure 39e and 34e), HOPG terraces appear to be covered by a thin film of ~0.3 nm thickness, i.e. reasonably corresponding to one single monolayer of molecules. Only a few higher aggregates are present at steps and in the middle of the terraces.

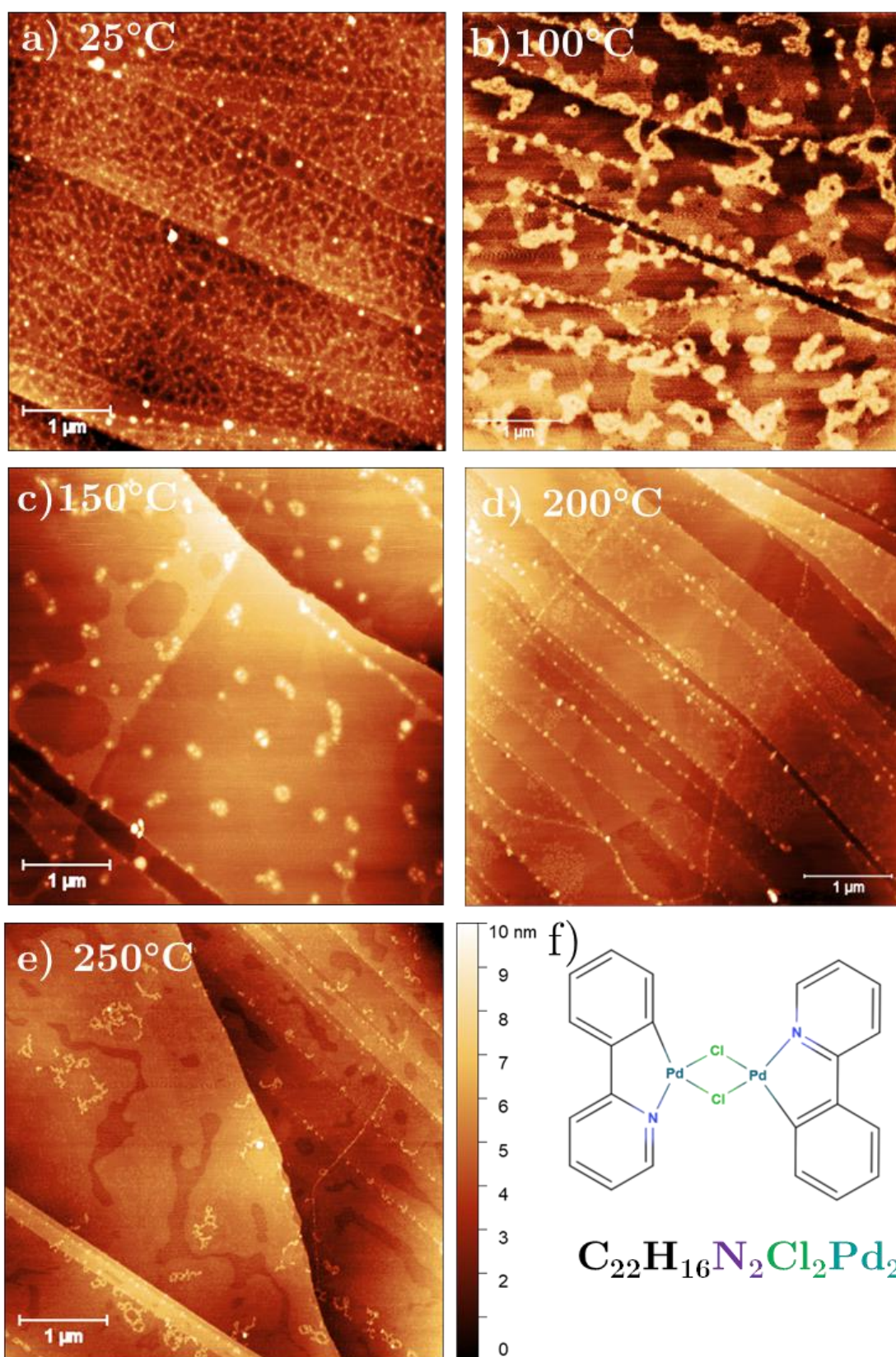


Figure 39: AFM images recorded on the CyPd (1)/HOPG system after annealing structure II to 100, 150, 200 and 250 °C for 10 minutes. Image size: 5x5 μm^2 . Bottom left: molecular structure of CyPd (1).

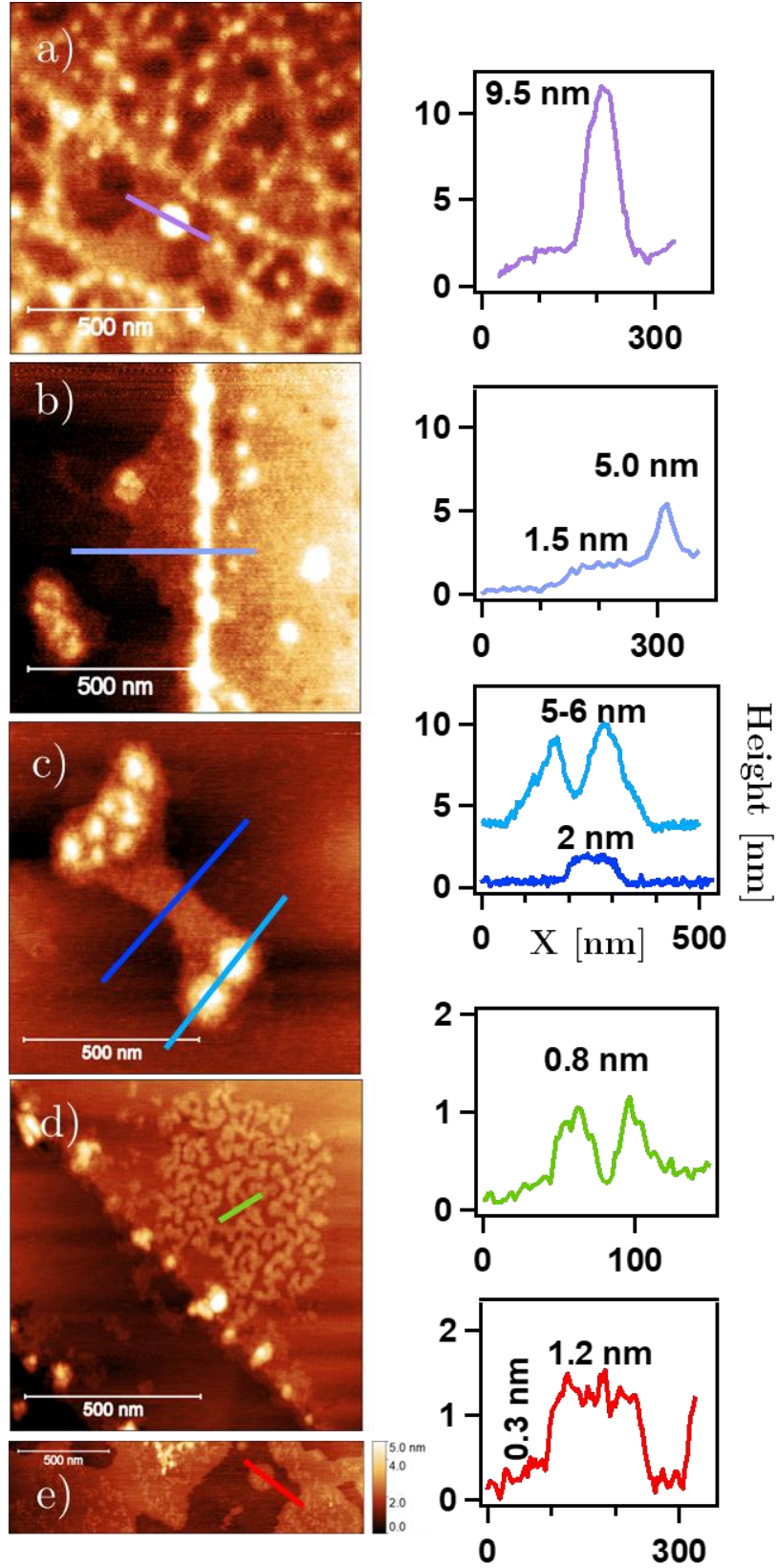


Figure 40: AFM images ((a) to (d): $1 \times 1 \mu\text{m}^2$, (e) $3 \times 0.5 \mu\text{m}^2$) showing the details of the features shown in Figure 39 for structure II. a) RT, b) 100°C, c) 150°C, d) 200°C and e) 250 °C. On the right of each AFM image, I report the line scan corresponding to the cut shown on the image.

In a few cases, it was possible to record the images at the same spot before and after annealing to understand how the given structures evolve. A first example is reported in Figure 41, showing the thermal evolution from 100°C to 150°C. At 100°C, the overlayer is more extended than after heating to 150°C and also the density of higher clusters is larger. This is coherent with the 30% coverage drop estimated by XPS.

Since the distance between the two clusters in the blue oval remains the same, I can use them as topographical markers. I notice changes in surface morphology, feature density, and domain structure. Some features rearrange, and new ones form. Due to some desorption/ displacement of the admolecules when annealing to 150 °C, the triangle on the right bottom part of the Figure (white circle) gets larger but also its central hole becomes wider. At the same time, most of the stripes on the terraces disappear, remaining concentrated on the step edges of HOPG. The features shown inside the black box in Figure 41a rearrange completely forming a dumbbell like island, whose detailed image is shown in Figure 40c. Overall, the higher temperature promotes particle coalescence and surface smoothing, consistent with increased molecular mobility leading to domain growth and reduced nanoscale heterogeneity. Another contributing factor could be Ostwald ripening during thermal treatment, where smaller features dissolve and redeposit onto larger ones, increasing average feature size while reducing overall feature density.

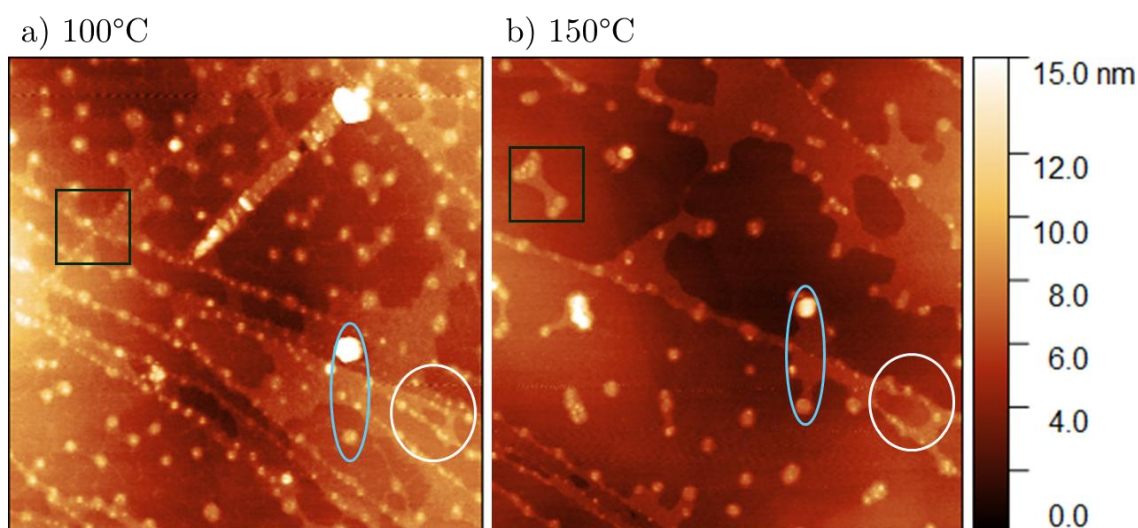


Figure 41: AFM images ($5 \times 5 \mu\text{m}^2$) of DC-CyPd(1)/HOPG at RT, arranged in structure II and heated to a) 100°C and b) 150°C. These images were taken at the same spot. Features directly compared in the text are marked by ovals/squares for a better visualization.

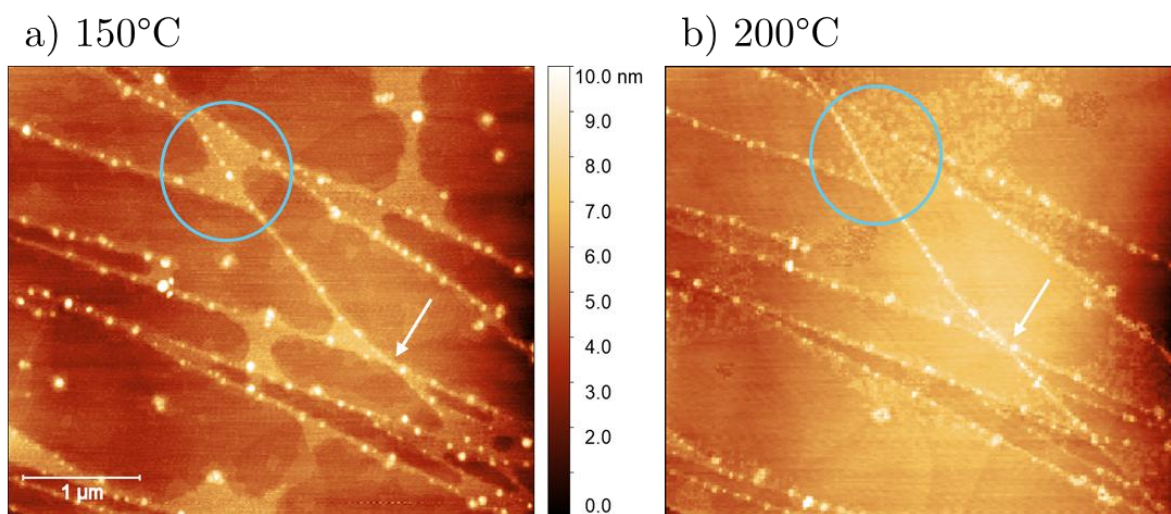


Figure 42: AFM images ($5 \times 5 \mu\text{m}^2$) of DC-CyPd(1)/HOPG at RT, heated to a) 150°C and b) 200°C . These images were taken at the same spot on the sample. The same features are marked in blue and white to better visualize the thermal evolution.

At another spot on the surface, I investigated the evolution caused by annealing from 150°C to 200°C (Figure 42). Reference points are marked with a blue circle and a white arrow. It is apparent that the island just below the circle disappeared and that the compact islands (e.g. inside the circle) spread over a wider area. From Figures 42, 40c and 40d, I deduce that the thickness of the islands decreased from 2.0 nm at 150°C to 0.8 nm at 200°C . After annealing the cluster density at the step edges increased.

In a second phase of the experiment, I also drop-casted CyPd (1) from a DMF solution ($\sim 1.5 \mu\text{M}$) on HOPG at 50°C . The AFM images showing the morphology of the so-obtained sample are shown in Figure 43. This experiment was carried out to evaluate the reorganization of the film at 50°C and to assess the role of solvent evaporation and molecular mobility.

After deposition, the sample was kept at 50°C for 15 minutes under the hood to evaporate the solvent. Then it was cooled to RT and transferred into the AFM glovebox. There, it was analysed in a low humidity atmosphere ($\sim 10\%$ while fluxing N_2 gas). I observe that in this case the self-assembled layer differs significantly from the one of the RT preparation. Unlike the RT sample, the surface exhibits a continuous “net”-like feature, uniformly distributed across the entire surface (Figure 43b) and of average height of ~ 0.95 nm (see line scan in Figure 43 c).

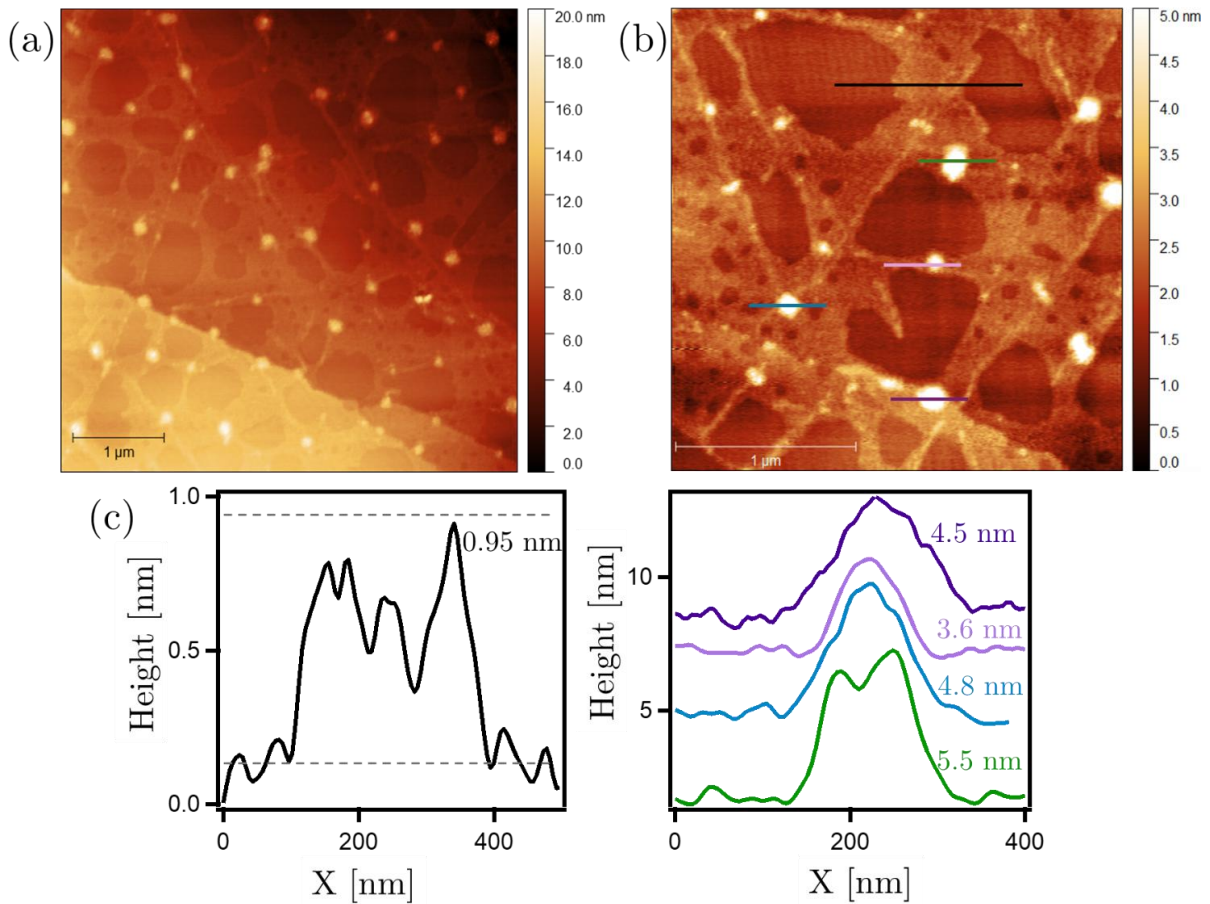


Figure 43: AFM images of DC-CyPd (1)/HOPG deposited on heated HOPG at 50°C. (a) Overview image (image size: 10x10 μm^2) (b) Detailed image (2x2 μm^2) of features similar to those shown in panel (a). (c) Height profile of the features shown in panel b (cut along the marked paths).

In addition to this interconnected network, discrete nanoclusters are also observed; they are approximately 100 nm in diameter and with heights ranging from ~ 3.6 nm to ~ 5.5 nm. This self-assembly is clearly different from the one obtained after RT deposition and might only slightly remind the layers observed at 100-150 °C. The higher deposition temperature may influence the adsorption process in two aspects: on one side, it reduces the evaporation time of the solvent, thus accelerating the rate at which CyPd (1) units are deposited on the surface. On the other side, it increases the mobility of the adsorbate, favoring the formation of more extended structures. The coexistence of the thin network structure and of larger nanoclusters arises from the combination of these partially contrasting effects.

At RT, DMF (high boiling point, slow evaporation) dries gradually, giving sustained contact-line pinning and capillary flow, which often produces smoother films or ring-like accumulation. At 50 °C, DMF evaporates much faster, creating strong temperature gradients along the droplet surface; this triggers Marangoni flow, earlier depinning, and rapid solute immobilization, so the drop-cast film looks markedly different.

III.2.4 CyPd (2)/HOPG

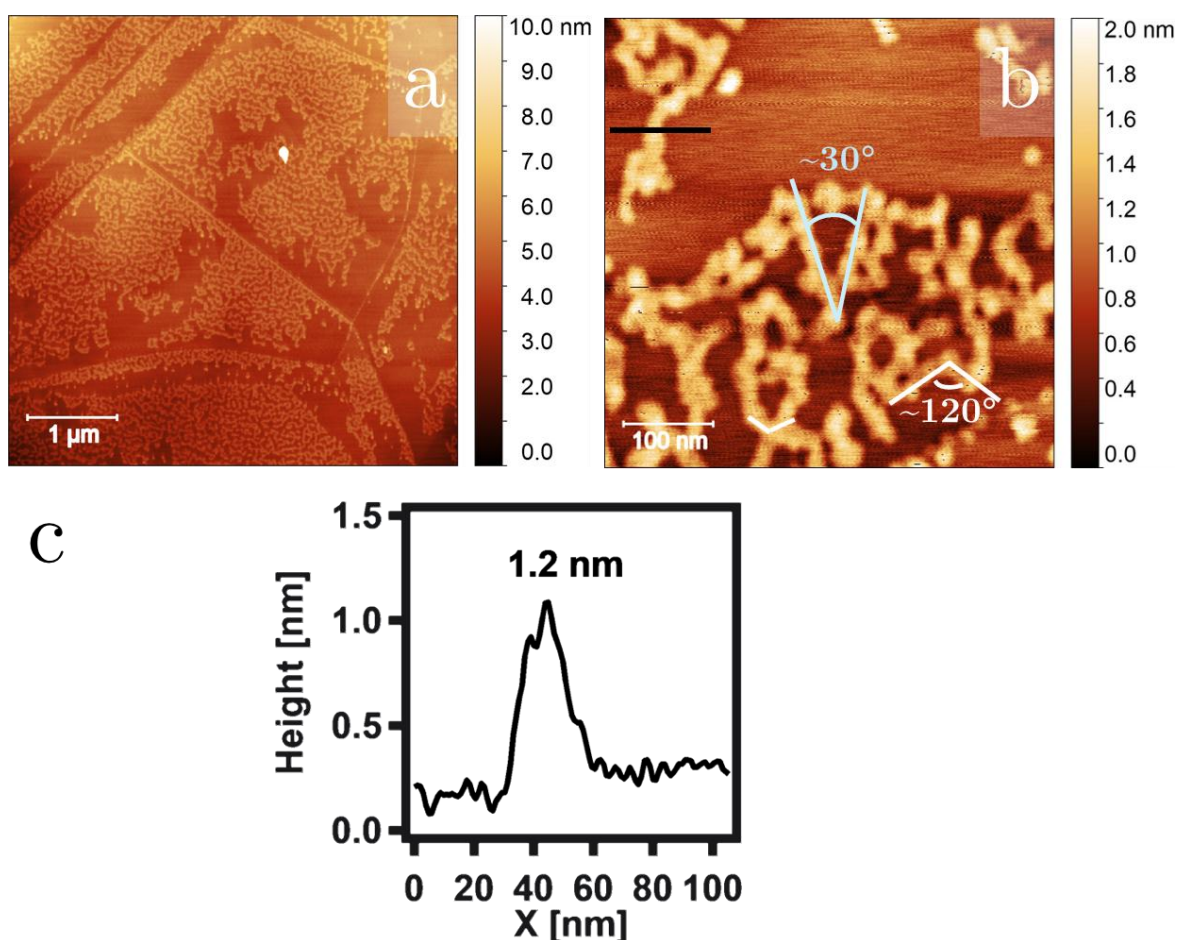


Figure 44: AFM images of DC-CyPd(2)/ HOPG at RT. (a) 5x5 μm² AFM image of the features shown in Figure 29. (b) 0.5x0.5 μm² zoom-in on the features shown in panel a). (c) Line scan across one of the characteristic corrugated filaments (marked in b).

The self-assembled structure formed after drop-casting CyPd (2) on HOPG at RT is reported in Figure 44. As evident from the large overview in Figure 32d) and from the

zoomed images of Figure 44, the morphology is different than after adsorption of the other two molecules since now almost all the surface is covered with granular like features. The steps are fully covered, and the terraces present islands of irregular shape always starting from the top of the step edges. Therefore, we can reasonably deduce that the self-assembly nucleates at the steps and extends then on the flat HOPG terraces. A more detailed inspection of the CyPd (2) adlayer (see Figure 44b) shows that the self-assembly consists of a dense network of short and corrugated granular-like filaments among which areas of bare HOPG can be detected. The filaments can form closed structures of nearly polygonal shape or bend/intersect with each other, forming angles of approximately 120° (white lines on Figure 44.b). Such behaviour suggests an influence of the HOPG high symmetry directions. In some cases, an angle of $\sim 30^\circ$ is observed between adjacent features (baby blue in Figure 44.b), which may correspond to the angle between the armchair and zigzag directions of the substrate. The height of the granular filaments is of approximately 1.2 nm (see line scan in Figure 44.c), i.e. lower than the average height measured for CyPd (1) assemblies. Despite that, the cobweb of filaments covering the surface looks denser than for CyPd (1). Upon step-annealing to 100°C , 150°C and 250°C , respectively, the layer of Figure 44 reorganizes in novel configurations, as shown in Figure 45 and 40. Figure 45(a-c) and Figure 46.a report a different spot of the DC-CyPd (2) layer as deposited at RT with respect to the one of Figure 44. The morphology of the surface and the apparent height of the filaments are in agreement with what is observed previously and confirm therefore the uniformity of the preparation. Upon annealing to 100°C (Figure 45 d-f), the surface rearranges into well-defined islands of 4 nm height and ~ 60 nm width. This evolution is directly compared in Figure 46, that images the same area before and after annealing. At 100°C ; the morphology shows discrete and more ordered nanoclusters separated from each another. The elongated network-like features present at RT transform into individual, oval/rod-shaped structures. The breakdown of the interconnected network into isolated nanoclusters following annealing is indicative of thermally activated surface diffusion, leading to domain coarsening and partial dewetting of the molecular film.

After annealing to 150°C (Figure 45g-i), a further significant reorganization of the self-assembled layer occurs. The surface is no longer covered with small, separated islands, but with a densely packed network in which granular-like filaments are interconnected to larger 3D-clusters of approximately 2.2-4.0 nm height. The similarity of these filaments with the ones observed at RT must be only apparent and I suppose that the net-like

morphology observed at this temperature is related to the partial dissociation of CyPd(2) and to the presence of organic fragments rearranging on the surface. The network covers a smaller fraction of the surface with respect to layer observed at RT, but the presence of higher features accounts for the limited reduction of the intensity observed in the XPS spectra of the corresponding experiment. Furthermore, the bare areas of HOPG are crossed by several straight and uniform filaments of 0.5 nm height and a few nm width (signaled in the white square, and in the line scan), hence compatible with the formation of 1D assemblies consisting of a single monolayer of molecules.

Finally, after annealing to 250°C (Figure 45j-l), the surface is again almost entirely covered by a molecular layer with internal structure similar to the ones observed at RT and 150 °C but with average height of 0.8 nm. The layer is thus likely to assume a more 2D structure, that justifies its increased extension. I recall that the XPS analysis of CyPd (2) indicates that the molecule tends to dissociate at this temperature. The fragments remain at the surface as Phe-Pyr units and metallic Pd (in the form of Pd (0)).

At 250°C, almost 50% of the molecules should be dissociated but it is not possible to distinguish them on the basis of AFM data.

At this temperature (Figure 45j)-l) I also observed the occasional presence of a few very large 2.5 nm high filaments, one of which is present in Figure 45j-l. They correspond to a different agglomeration of molecules, but their origin and structure are not clear at the moment.

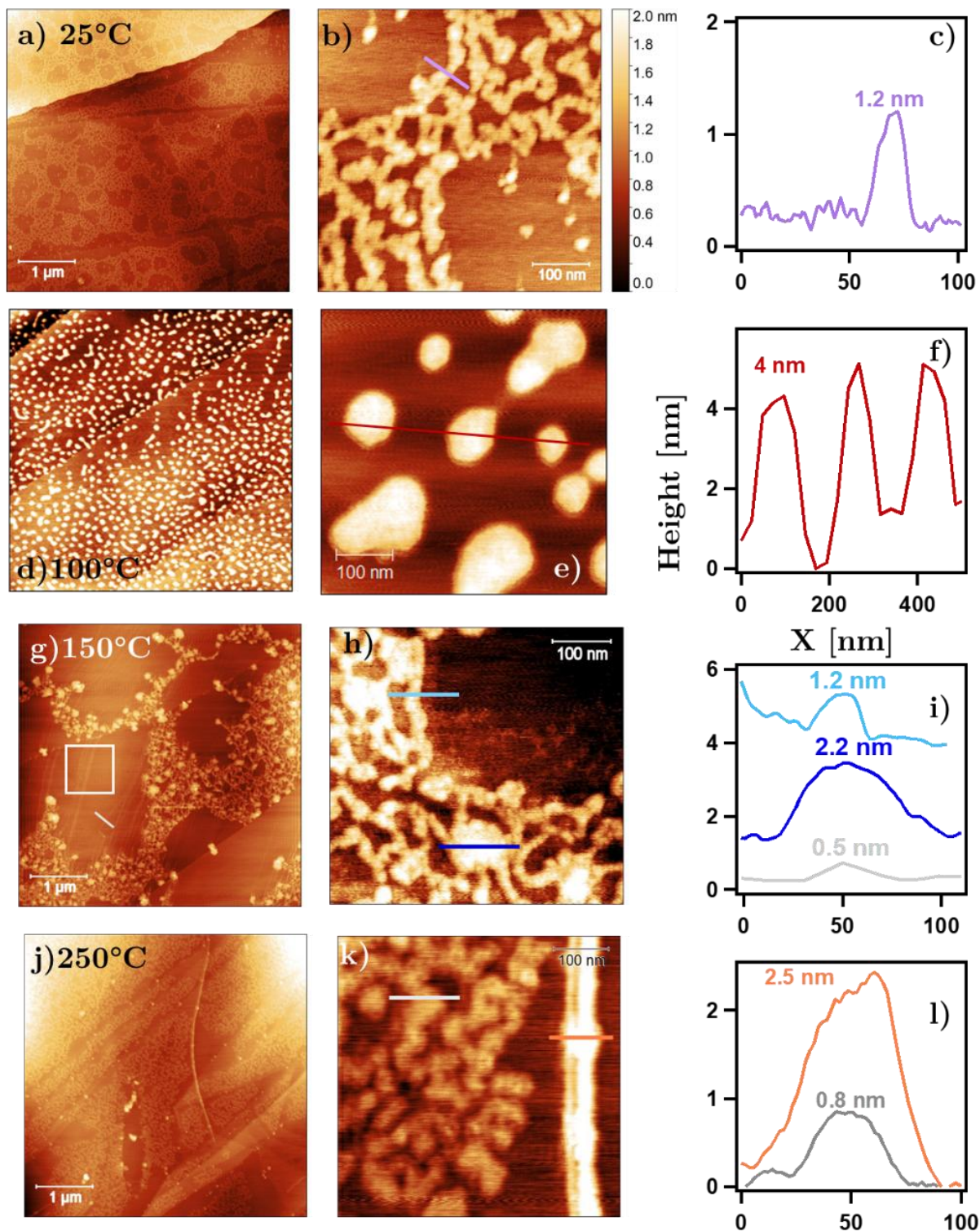


Figure 45: AFM images of DC-CyPd (2)/HOPG. First column on the left shows an area of 5x5 μm² immediately after growth (a) RT, and following annealing to (d) 100°C, (g) 150°C, and (j) 250°C. The second column (b, e, h and k) corresponds to 0.5x0.5 μm² enlargements at each temperature. The height profiles corresponding to the reported line scans are shown in the last column (c, f, i and j). All images were recorded after cooling to RT.

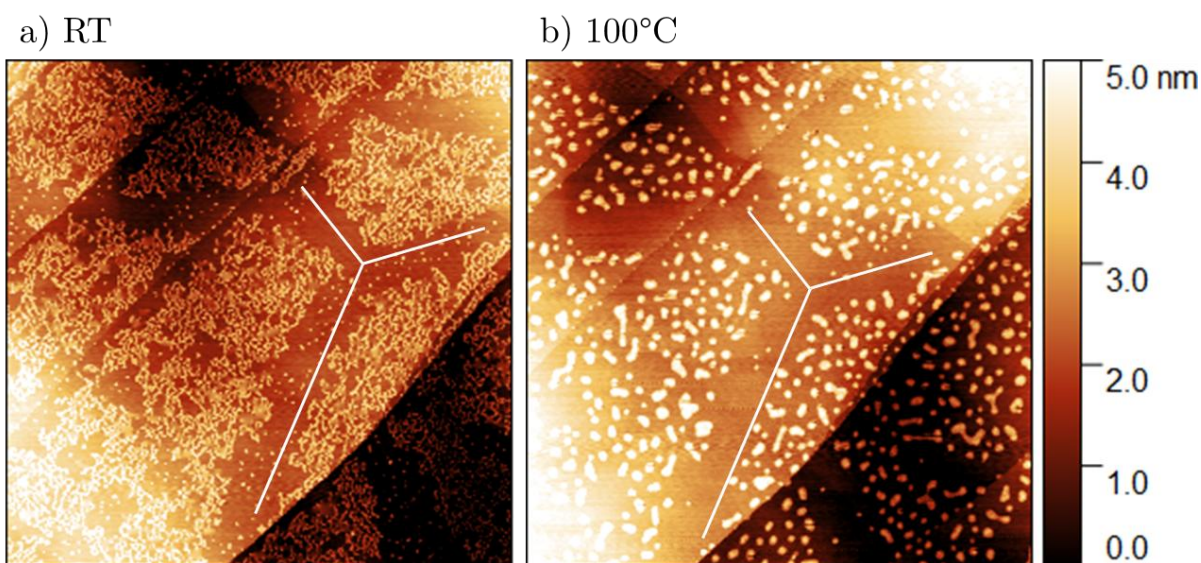


Figure 46: AFM images of DC-CyPd (2)/HOPG at RT a) $5 \times 5 \mu\text{m}^2$ b) 100°C . These images were taken at the same spot, marked in white (Y) to better visualize the thermal evolution.

The three Pd cyclometalated complexes were also deposited on HOPG by sublimation in UHV during my internship in TU Wien. I tried measuring their morphology by RT-STM. Unfortunately, the mobility of the ad molecules at RT was too high and did not allow to obtain suitable images. In the framework of producing nanostructures with metallic active sites using a bottom-up approach, another molecule, Melem was deposited on Au(111) and Fe was then dosed into the overlayer created by this latter molecule. In the next section, I detail the experiment and the results obtained.

IV- Melem on Au(111): a potential SAC stabilizer

IV.1 Introduction

Single-atom catalysis (SAC) has emerged as an effective strategy to maximize catalytic efficiency and selectivity while minimizing the use of scarce and precious metals by supporting the catalytically active metal atoms (M) on a suitable, inexpensive surface [4][77][78]. In comparison to nanoparticle-based catalyst systems, SAC systems maximize the active sites since all atoms are exposed. They allow, moreover, for a much more limited number of pathways for chemical reactions due to the simplicity of their structure thus enhancing selectivity towards a particular product. One of the major challenges in achieving stable SAC structures involves tackling the high surface energy of an individual metal atom, which makes it thermodynamically favourable to form aggregates or nanoparticles, particularly under reaction conditions [79][3]. Thus, to overcome this limit, the support should have strong anchoring interactions, holding atoms securely while preserving their active property.

Nitrogen-rich carbon-based supports have been generally suggested as potential supports for SACs owing to their potential in stabilizing metal atoms by coordination with nitrogen from these supports in well-defined active M-N-C motifs[80][81]. Among nitrogen-rich carbon-based supports, carbon nitride structures have a high nitrogen content in nitrogen and are stable in catalytic environments while offering tunability in their coordination ability.

In addition, experimental and theoretical studies have also indicated the ability of such M-N-C layers to immobilize transition metals in an effective manner, simultaneously modifying the metal's electronic structure in a catalytically favourable way.

Surface science studies using well-defined substrates have further demonstrated that molecular precursors such as melamine can be employed to form ordered carbon nitride layers on metal surfaces, allowing precise control over metal coordination at the atomic scale. It has been demonstrated in recent research by Gammelgaard et al. [82] that melamine-derived carbon nitride monolayers supported on Au(111) can stabilize Co atoms in an M-N-C configuration providing a model system for SAC suitable for controlled ultra-high vacuum investigations. Elaborating on this principle, in the present

work, Melem, a heptazine-based, nitrogen rich molecular building block, and a core component in the synthesis of graphitic carbon nitride, has been employed to create an ordered molecular network on Au(111).

When deposited on Au(111) Melem forms a porous overlayer on the underlying herringbone reconstructed substrate[22]. Compared to melamine, the Melem overlayer contains a higher density of pyridinic nitrogen sites and exhibits greater structural rigidity, making it a promising candidate for stabilizing isolated metal atoms[22][83][84].

By depositing Melem on Au(111) and subsequently dosing transition metals, this study investigates the interaction of Fe atoms deposited on the Melem based template.

This approach provides a well-defined surface model to examine the formation of M–N–C coordination environments, metal clustering behavior, and the limits of single-atom stabilization relevant to SAC design.

IV.2 Experimental technique (RT-STM)

For the experimental investigation I used Scanning tunnelling microscopy (STM), a surface investigation technique used to probe structure and morphology of conductive and semiconducting materials with atomic resolution. The method relies on bringing a sharp metal tip in near contact with the sample surface, enabling electrons to tunnel through the vacuum separating tip and surface when a voltage difference is applied. The current flow is thereby exponentially sensitive to the tip-surface distance changing by one order of magnitude per nanometer. This extreme sensitivity enables to study the surface morphology with atomic resolution when scanning the surface at constant current.

IV.2.1 Experimental Setup

All experiments were carried out using a room-temperature scanning tunnelling microscope (RT-STM, Omicron) housed within an UHV chamber operating at a base pressure around 1×10^{-10} mbar. The system is equipped with standard facilities for surface preparation, molecular deposition, and surface characterization, including XPS (Specs) for chemical analysis, Figure 47.

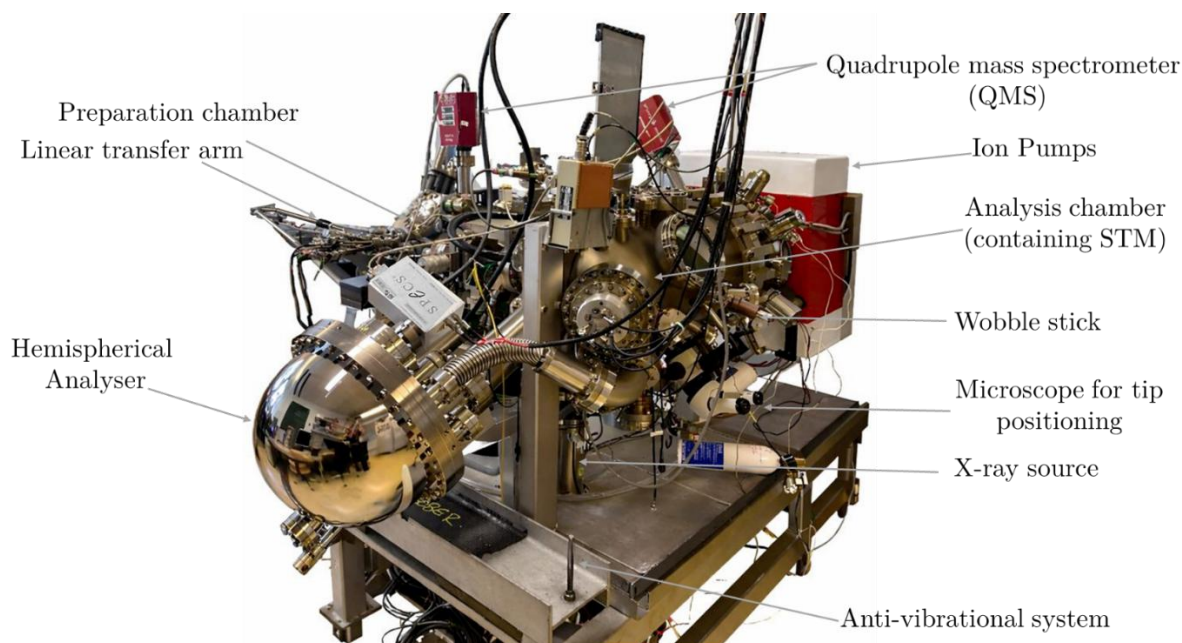


Figure 47: Omicron RT-STM at TU-WIEN iap. The main surface analysis tools are indicated.

Substrate Preparation

The Au(111) single-crystal substrate was cleaned through repeated cycles of argon ion sputtering and thermal annealing to obtain an atomically flat and contamination-free surface. Each cleaning cycle consisted of Ar^+ ion sputtering (Ar pressure in the chamber 1×10^{-6} mbar, 1 kV, for 15 min) followed by annealing at approximately 600°C for 15 min under UHV conditions. The quality of the cleaned surface was verified by STM imaging, which revealed the characteristic herringbone reconstruction pattern.

Molecular Deposition

Melem molecules, provided by Gianvito Vilé's group (Politecnico di Milano, Milan, Italy), were deposited into the Au(111) surface by sublimation from an evaporator (EV300-Omnivac), Figure 48. Prior to the deposition, the crucible containing the molecules was thoroughly outgassed at 250°C for 12 hours under vacuum to remove any volatile contaminants. During deposition, the Au(111) substrate was maintained at 200°C allowing surface diffusion and the formation of a uniform monolayer. The deposition rate was adjusted to achieve monolayer coverage using a quartz microbalance.

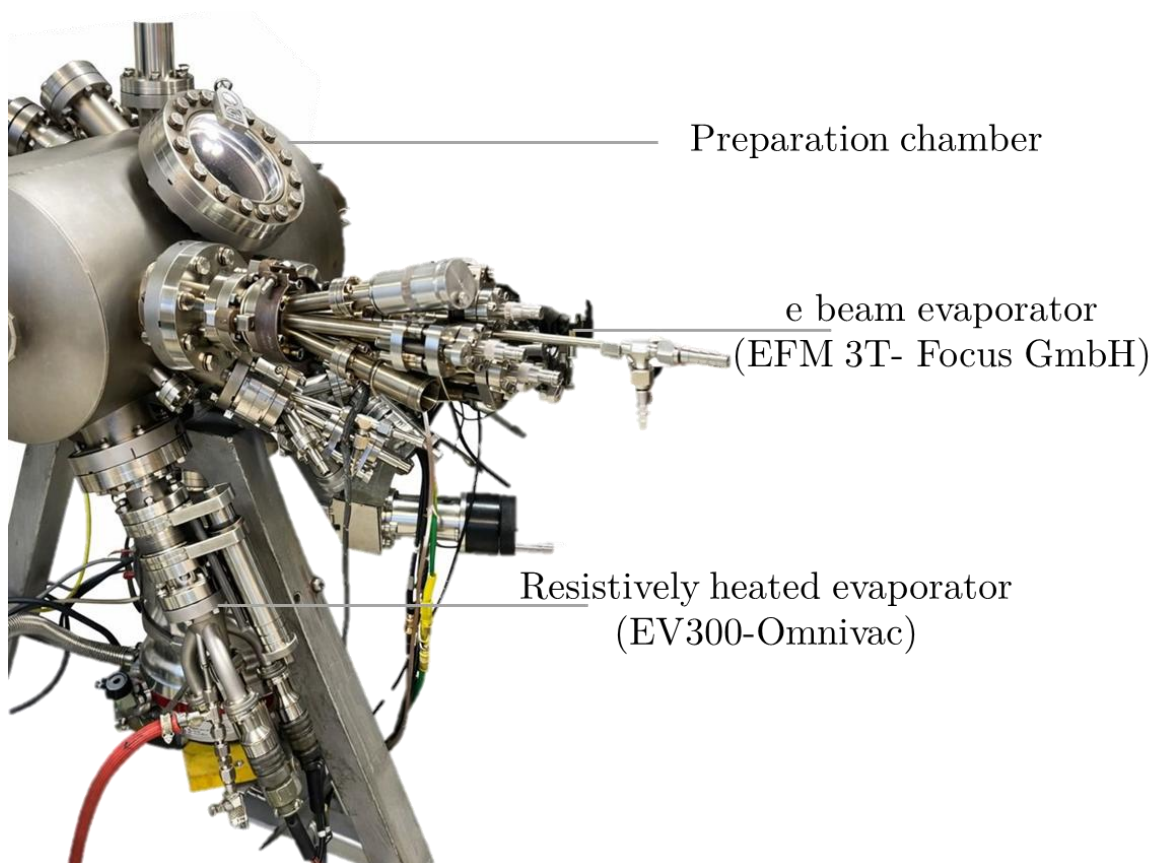


Figure 48: Image of the preparation chamber showing both evaporators used to deposit the organic molecules (Melem) (EV300) and the metal atoms (Fe) (EFM 3T).

Creation of M-N-C networks

After the deposition of 1 ML of Melem on Au(111), the surface was exposed to Fe atoms by an e-beam evaporator (EFM 3T- Focus GmbH) in a controlled dosage process. These metal atoms (M) interact with the nitrogen sites (N) of the Melem overlayer, leading to their coordination within the molecular network, forming single-atoms or arranging into nanosized clusters. Upon mild annealing, these species reorganize resulting in stable metal-organic nanostructures. In this thesis, the main focus was on investigating the morphological and chemical composition of those systems on Au(111). Although the catalytical properties of those metal-organic networks were not investigated, the Melem overlayers are likely to be suitable as molecular templates and chemical hosts that can capture and stabilize reactive metal atoms, providing a model for designing single-atom catalysts and surface-coordinated nanomaterials with control at the atomic level.

Following deposition, the sample was directly transferred into the STM in UHV (10^{-10} mbar) at RT. STM inspection has been performed in constant-current mode using an electrochemically etched tungsten tip. The applied bias voltages (V_s) are referenced to the sample. The imaging parameters were optimized for each measurement, typically employing tunneling currents in the range of 0.2–0.5 nA and negative bias voltages which gave the best contrast and the least interaction.

Surface composition and cleanliness were independently verified using XPS under UHV and at RT, confirming the chemical purity of both the Au(111) substrate and the deposited Melem film.

IV.3 Preliminary Results

IV.3.1 Characterization of the self-assembly of Melem/Au(111)

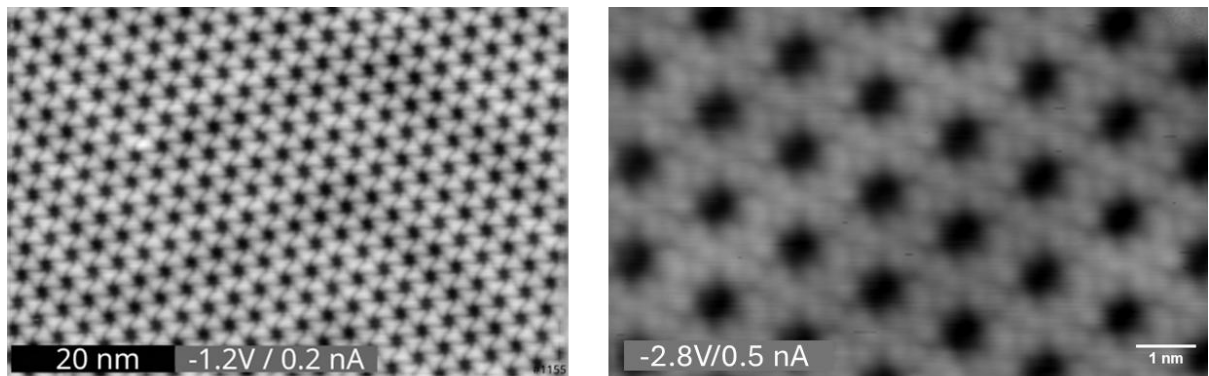


Figure 49: STM image of Melem self-assembly structures on Au(111) surface, left ($70 \times 45 \text{ nm}^2$, $V = -1.2 \text{ V}$, $I = 0.2 \text{ nA}$), right: ($10 \times 7 \text{ nm}^2$, $V = -2.8 \text{ V}$, $I = 0.5 \text{ nA}$)

After deposition of Melem onto Au(111) at 200°C , the sample was introduced into the STM as soon as it had cooled down to RT. Inspection at negative bias, allowed for a good contrast which reflects the occupied electronic states of the system. The bright features shown in

Figure 49 correspond to regions of enhanced local density of states associated with the π -conjugated molecular framework, whereas the dark spots are assigned to the pore centers, where the electronic density is significantly reduced. At positive bias, on the contrary, an important interaction of the tip with the admolecules impeded to produce suitable images of the overlayer.

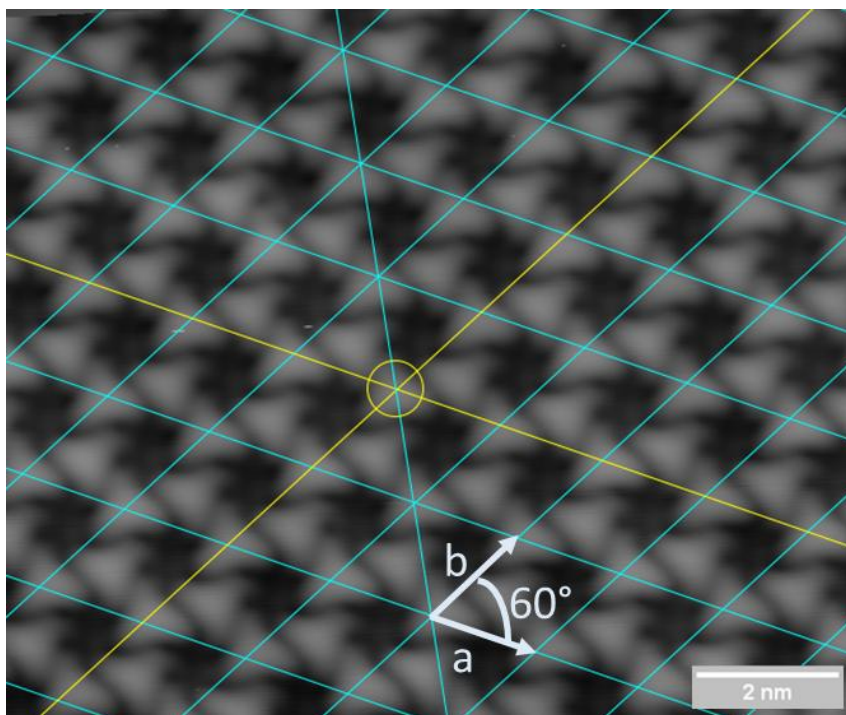


Figure 50: STM image of 1 ML of Melem on Au(111) showing the periodicity and the unit cell of the honeycomb reconstruction with $a=b=1.37$ nm, $\alpha=60^\circ$ (5×4.5 nm², $V=-1.2$ V, $I=0.2$ nA).

Figure 49 and Figure 50 show STM images of the Melem monolayer on Au(111). The molecules self-assemble in a honeycomb network that exhibits a long-range order.

The overlayer lattice highlights the periodic porous structure formed through directional hydrogen bonding between the nitrogen-rich Melem admolecules. The unit cell is defined by the two equivalent lattice vectors, a and b (1.37 nm), rotated by an angle of 60° , consistent with a hexagonal symmetry that matches the one of the underlying Au(111) surface. The bright protrusions in the STM images correspond to single Melem admolecules, while the darker regions correspond to substrate areas visualized through in the empty pores of the honeycomb lattice as will be discussed below.

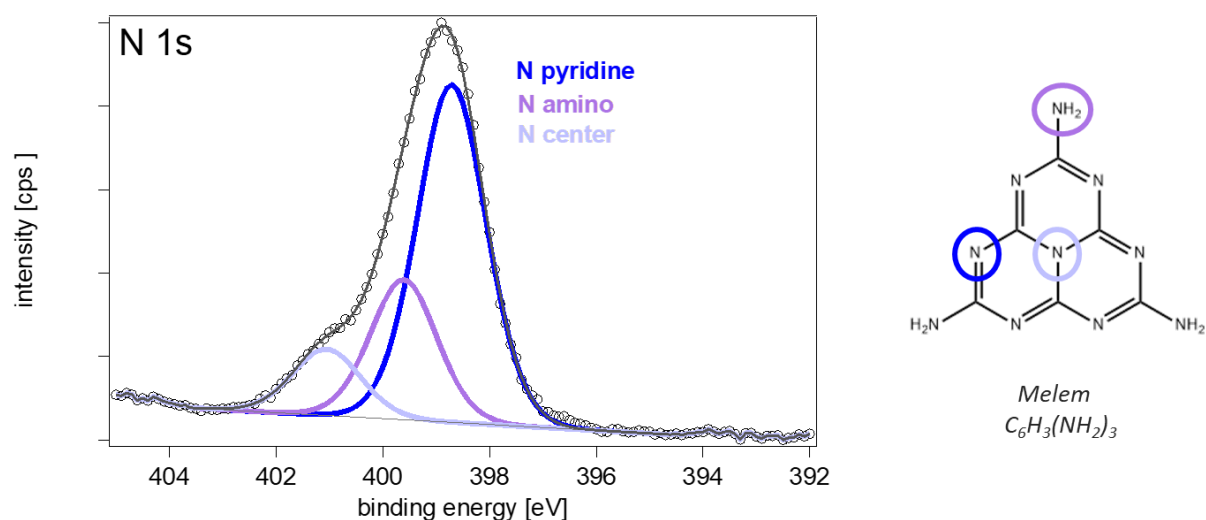


Figure 51: left: XPS spectra (Al K α at 300K, 70° grazing emission) of the N 1s spectral region for Melem deposited on Au(111) with peak deconvolution. The raw data (grey) is fitted with three components corresponding to pyridinic nitrogen (blue), amino nitrogen (purple), and the central heptazine nitrogen (lila). Right panel: the molecular structure of melem with the different nitrogen species highlighted.

In Figure 51, I show the XPS N 1s spectrum of Melem. Peak deconvolution allows to resolve the nitrogen components due the different chemical environments inside the molecule, i.e. pyridinic nitrogen (398.1eV), amino nitrogen (399.1eV), and the central heptazine nitrogen (400.6eV)[84]. The dominant peak corresponds to pyridinic nitrogen, i.e. to the sp²-hybridized atoms in the triazine rings constituting the core framework of the Melem molecule. The amino nitrogen accounts for the terminal -NH₂ groups. The central nitrogen atom of the heptazine unit contributes with a small component at higher binding energy. The molecular structure displayed next to the spectrum provides the spatial locations of these nitrogen species. They provide, therefore, a direct linkage between the observed spectral features and the chemical bonding environment. Altogether, the deconvolution confirms the chemical integrity of Melem and gives a hint on how its multiple nitrogen functionalities contribute to its surface chemistry and its self-assembly behaviour.

IV.3.2 Characterization of Fe/Melem/Au(111)

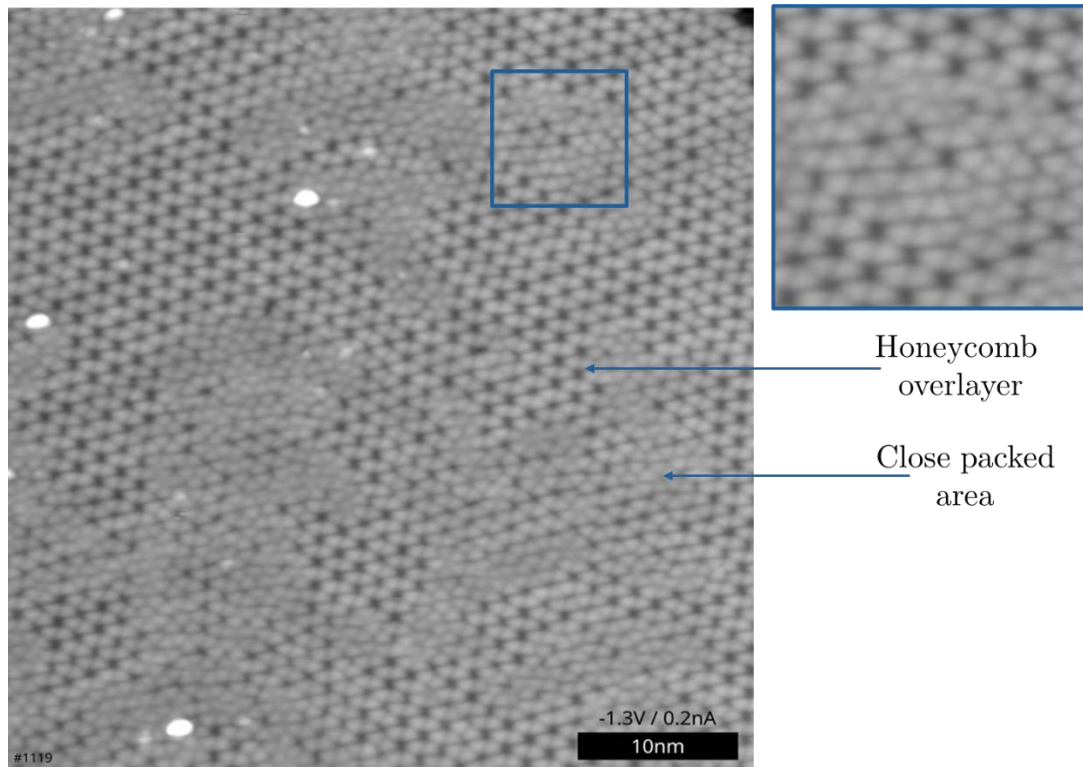


Figure 52: STM image recorded for 2 Fe atoms/overlayer unit cell deposited on top of 1 ML Melem/Au(111). The different structures are marked: Honeycomb overlayer observed after deposition of Melem on top of Au(111), Close packed area observed after deposition of Fe in Melem ($V=1.3V$, $I=0.2$ nA). On the top right corner, I provide a zoom of 10×10 nm² showing both structures. Image size 45×45 nm².

Upon dosing the Melem-covered Au(111) with Fe atoms, I observe the formation of close-packed surface regions, whose coverage increases with Fe coverage. As shown in Figure 52, at a coverage of 2 Fe atoms per supercell the compact areas correspond to 22% of the surface. The coverage is reduced to 10% for 1 Fe atom per supercell (not shown). In the STM image 4 elliptical Fe clusters of 1.6 nm $\times$ 1.0 nm are present. Subsequent experiments show that upon increasing the Fe dose to 3 Fe atoms/overlayer unit cell, an important clustering of the Fe atoms takes place (not shown) [3]. These clusters persist upon subsequent annealing to 300 °C.

Figure 53 shows the XPS spectra corresponding to the bare Melem overlayer and after Fe deposition. I observe a shift in the N 1s peak maximum from 398 eV to 399 eV.

This indicates a depletion of pyridinic N caused by the interaction of N and Fe atoms. The higher BE corresponds indeed with the value reported for Fe on graphitic-like carbon nitrides [85]. I conclude therefore that the Fe atoms occupy the fourfold site between the N atoms of the Melem admolecules. Additional measurements are, however, required to fully resolve the contributions of the different nitrogen species and to conclusively determine the Fe–N bonding configuration.

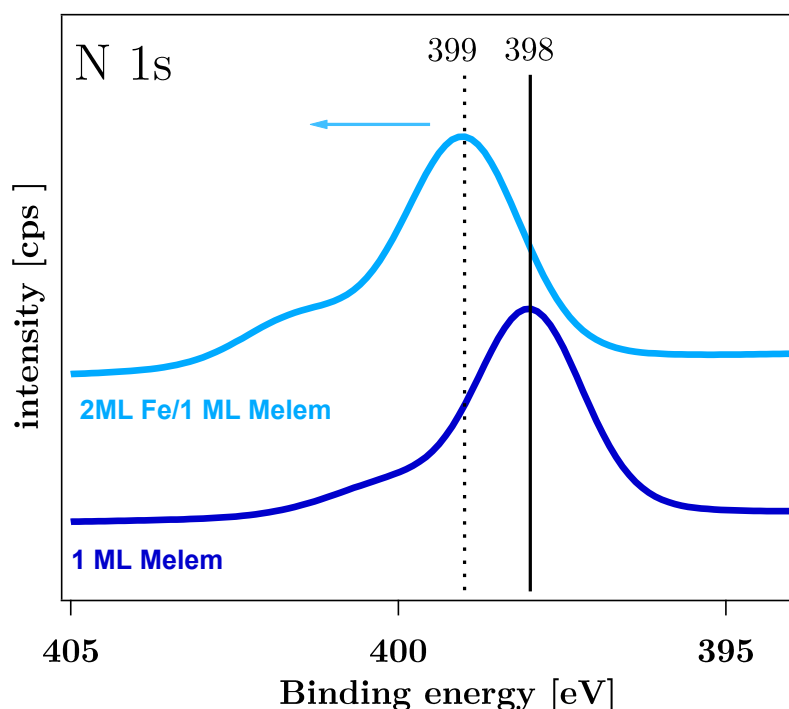


Figure 53: XPS spectra of the N 1s region for two different preparations measured in nominally identical conditions by an AlK α x-ray source. Bottom line spectrum (dark blue) corresponds to 1 ML of Melem deposited on Au(111). Top line spectrum (light blue) corresponds to 2 Fe atoms/overlayer unit cell /1 ML of Melem. Notice the main peak shift from 398 eV to 399 eV.

Previous research has demonstrated that nitrogen-rich molecular adlayers on Au(111) can serve as a template for the incorporation of metals, but the specific coordination sites formed are heavily dependent on whether the molecular layer is intact or has undergone some reaction. To the best of my knowledge, while the self-assembly of Melem on Au(111) has been investigated [22], experimental studies combining metal atom deposition with intact Melem supramolecular networks on surfaces remain scarce [82]. In contrast, metal stabilization has primarily been explored in melamine-derived carbon

nitride-like layers formed upon thermal treatment. This highlights the relevance of investigating metal adsorption on intact Melem networks.

In the study by Gammelgaard et al. [82], melamine was used as a precursor for the formation of the final carbon nitride-like template on Au(111). They first deposited Melamine, then they dosed this surface with Co atoms, the whole system was then heated which drove an on-surface reaction/condensation leading to a carbon nitride-like monolayer on Au(111), rather than an intact Melamine layer. Co atoms became incorporated into nitrogen-terminated pockets in that reacted layer.

In the present thesis, Melem was used instead of Melamine and Fe instead of Co. In order to polymerize the whole surface and deposit isolated Fe atoms, I tried firstly to dose the Melem overlayer with Fe atoms at RT. The Fe atoms are expected to occupy nitrogen-rich sites or pore regions defined by the supramolecular network, forming M–N_x-type interactions analogous to those observed in carbon nitride systems. A study by Allasia et al., [86] tackled the importance of understanding the real structure of Ni atoms on N-rich Melem supports. They claim that in many SAC studies, people assume a “uniform active site”, but in reality, the surface is structurally heterogeneous, and multiple types of binding sites are formed. They suggest a novel and general structural model for CN_x-based SACs, that fits with their calculations reported in Fig. 48, but they claimed that morphological analysis is missing. In our experimental study, I conclude that the closed packed structures shown in Figure 52, are similar to the structural model suggested by Allasia et al.

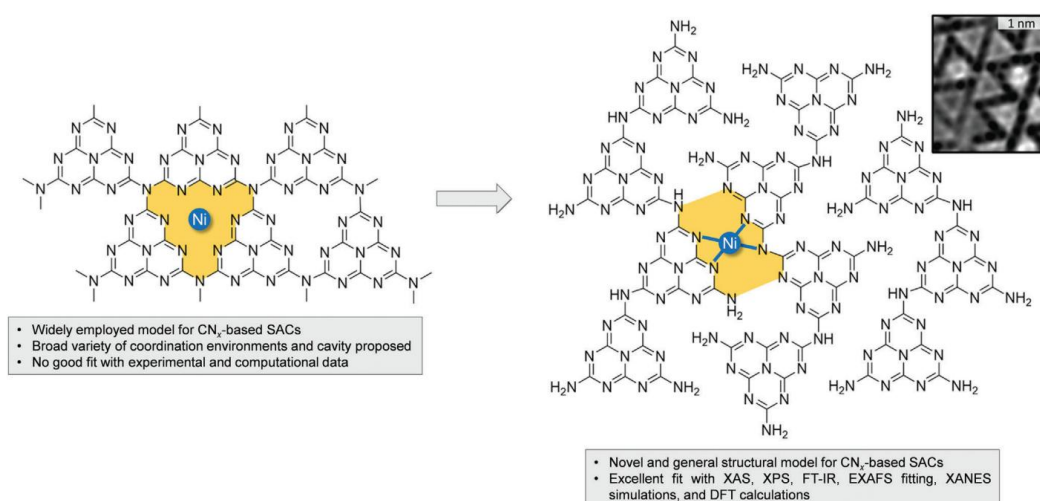


Figure 54: Comparison of structural models for carbon nitride-based single-atom catalysts, highlighting metal coordination within Melem-derived units and extended polymeric CN_x frameworks. The evolution toward filament-like structures capable of stabilizing metal atoms is illustrated. Reproduced from [86].

V- Conclusions and perspectives

My thesis work focused on the production and characterisation of C-based nanostructures containing metallic centres able to stabilize single metallic atoms, starting from organic/organometallic precursors. For this purpose, two systems were investigated. At the IMEM-DIFI laboratory, I performed a surface characterization following the deposition of three Pd-cyclometalates of decreasing complexity on HOPG: CyPd, CyPd(1) and CyPd(2). Two different deposition techniques were employed: sublimation in UHV and drop casting under ambient conditions. XPS analysis performed during a beamtime at the ALOISA beamline of the Elettra Synchrotron radiation source and in the lab at UNIGE with a conventional X-Ray source proved that, following both deposition procedures, the molecules adsorb intact on the HOPG surface. The molecular integrity is thus preserved independently of the deposition method. No evidence for DMF solvent residues were found by XPS inspection when the film was prepared by drop casting. This confirms that this procedure may represent a promising alternative strategy for the preparation of such molecular systems, especially in the context of simpler and more scalable approaches. The thermal stability of the different adlayers was studied by step annealing the sample. A 50% desorption of the brominated and chlorinated CyPd film occurs upon annealing to 250°C with no evidence for dissociation. In the case of the debrominated CyPd(1) adlayers, annealing to 200°C leads again to a 50% reduction of the C, N and Pd intensities but the Cl signal persists indicating that partial dissociation has taken place. For the halogen free CyPd(2) molecule, annealing leads to important dissociation resulting in the release of single Pd atoms which eventually aggregate into nanoparticles. Upon annealing to 200 °C I observe a 40 % increase of the Pd total intensity which may be associated either to the different photoelectron diffraction of Pd(II) and Pd(0), or to Pd atoms accumulating at the HOPG surface. The latter would become more visible due to the desorption of the outermost layers of the CyPd(2) film. XPS inspection evidences the formation of Pd₁(0) single atoms. This observation, accompanied by a shift of the N1s peak from 400 eV to 399 eV indicates Pd-N bond cleavage, and the release of single Pd atoms at the surface. Upon further annealing up to 250°C, Pd(0) clusters form, with Pd(II) always present in intact molecules. A recent study has shown that the coexistence of metallic Pd with the oxidized Pd(II) species can generate synergic effects and improve catalytic performance [87]. Further reactivity

studies should be performed to test the catalytic activity of the above investigated systems.

The drop-casted preparations have been analysed with AFM at atmospheric pressure and under controlled humidity conditions ($< 10\%$). I find that the three cyclometalates self-assemble in different ways. The brominated molecules (CyPd) form fractal structures that extend all over the surface when annealed to 150°C . The non-brominated molecules (CyPd(1)), form two types of structures. The first consists of filaments of different length that rearrange into a branched dendritic network and is distributed all over the surface and follow the HOPG high symmetry directions. The other structure consists of dot-like features. Upon annealing, the ad molecules rearrange and a smoother morphology is observed. When this molecule was drop-casted on hot HOPG ($T=50^{\circ}\text{C}$), I observed a reorganization of the film. This phenomenon is connected with the rapidity of solvent evaporation and with enhanced molecular mobility. A significantly different morphology is obtained with respect to the films obtained after deposition at RT. This surface exhibits continuous net-like features distributed in a continuous way over the whole surface. For the last molecule, CyPd(2), the mesoscale morphology of the adlayers is definitively different than the one obtained for the other CyPds. In this case, the whole surface was covered with granular like features that follow the high HOPG symmetry directions. Upon annealing, the height of the granular structures decreases from 1.2 nm to 0.8 nm. This shows that, upon annealing, a smoother film morphology is obtained suggesting a thermally activated molecular mobility and a reorganization into more stable configurations. Similar observations hold also for the other Pd cyclometalates. The main differences in the self-assemblies can be attributed to numerous factors: a) the presence/absence of halogens, b) the temperature of the sample and c) the evaporation rate of the solvent.

The other approach I explored during my stay in Vienna at TU Wien corresponds to the stabilization of single metallic atoms by dosing them onto N-rich networks. To this purpose, I explored Melem films on Au(111), both bare and after the deposition of Fe atoms onto the overlayer. Melem forms a well-ordered honeycomb self-assembly, that can stabilize metal atoms. After dosing Fe, closed packed areas are observed. XPS inspection of the N1s region before and after Fe deposition, evidences a shift from 399 eV to 398 eV, which is indicative of the Fe in the 4-fold coordination sites. These results are in line with a recent theoretical studies of Allasia et al. [86].

Coming to the future perspectives of these studies, I notice that, despite the insights gained in this work, several additional aspects of Pd cyclometalates on HOPG remain to be clarified. In particular, morphological STM inspection at the sub-nanoscale is still missing and would be necessary to complement the results obtained by HR-XPS. Unfortunately, when I tried to perform such study during my stay in Vienna, STM inspection was jeopardized by the high mobility of the admolecules in at RT. Such measurements need therefore to be repeated at lower temperature with the LT-STM facility of UNIGE which was still under maintenance during my thesis period. Complementary characterization techniques, such as vibrational spectroscopies (infrared absorption or high-resolution electron energy loss spectroscopies) or ultraviolet photoemission spectroscopy (UPS) would be, moreover, valuable to fully resolve the electronic structures of the adsorbed species. In parallel, DFT calculations would be needed to confirm the adsorption geometries and reaction pathways inferred from the experimental data. Finally, studying the reactivity of these systems by exposing them to reactive gases under controlled conditions would allow to link structural properties with catalytical functionality.

For Melem-based templates, it would be interesting to study the self-assembly on other transition metal substrates or the doping with other catalytically relevant atoms. Comparing different metal atoms would lead to a better understanding the coordination behavior and reactivity, leading to an improved comprehension of how these systems can be tailored for applications in catalysis.

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Appendix

As mentioned in section III, in this appendix I report the same series of HR-XPS spectra already shown in (Figures 22, 23& 24). of the main text together with the fitting components.

HR-XPS Spectra: Thermal evolution of CyPd

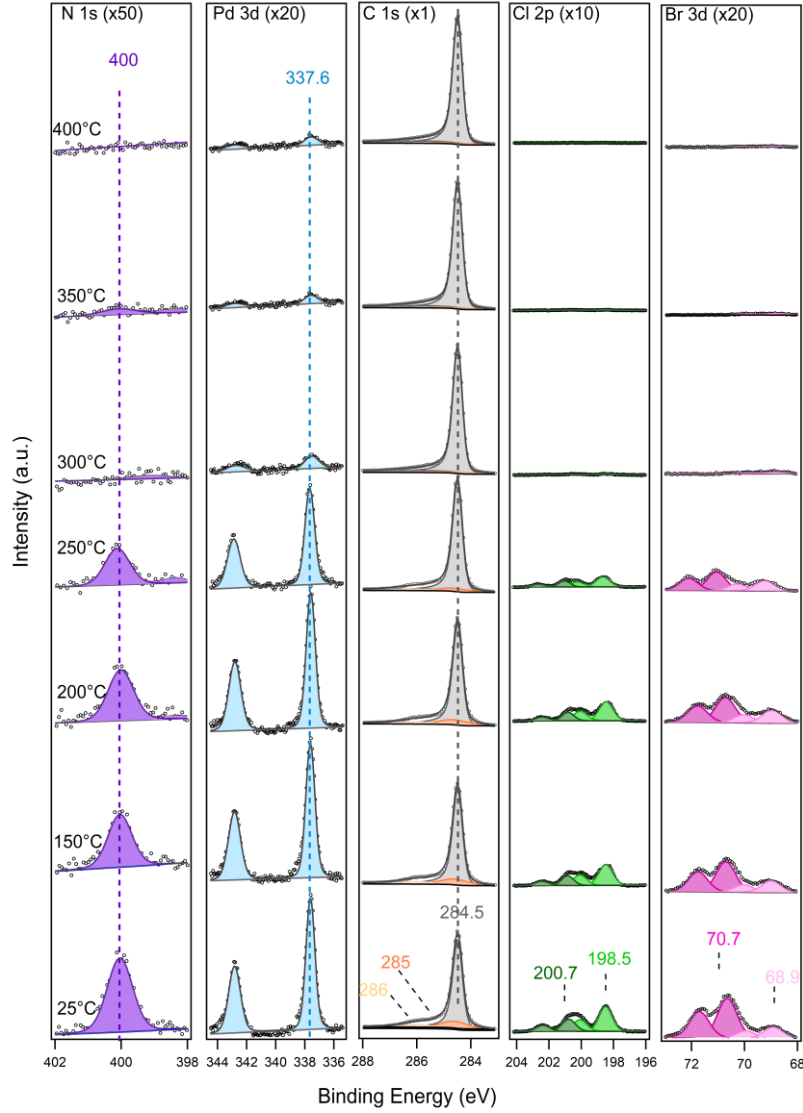


Figure A.1: HR-XPS spectra showing the thermal evolution of CyPd after UHV sublimation on HOPG at RT (first row) and after step-annealing to 150°C, 200°C, 250°C, 300°C, 350°C and 400°C. From left to right the panels refer to the N1s, Pd3d, C1s, Cl2p and Br3d spectral regions. All the fitting components have already been discussed and assigned in section X, and in Table 5. Here I notice that all these lines do not shift in energy with increasing temperature but only shrink in intensity. This indicates that the chemical state of the admolecules does not change upon annealing and that the molecules desorb intact.

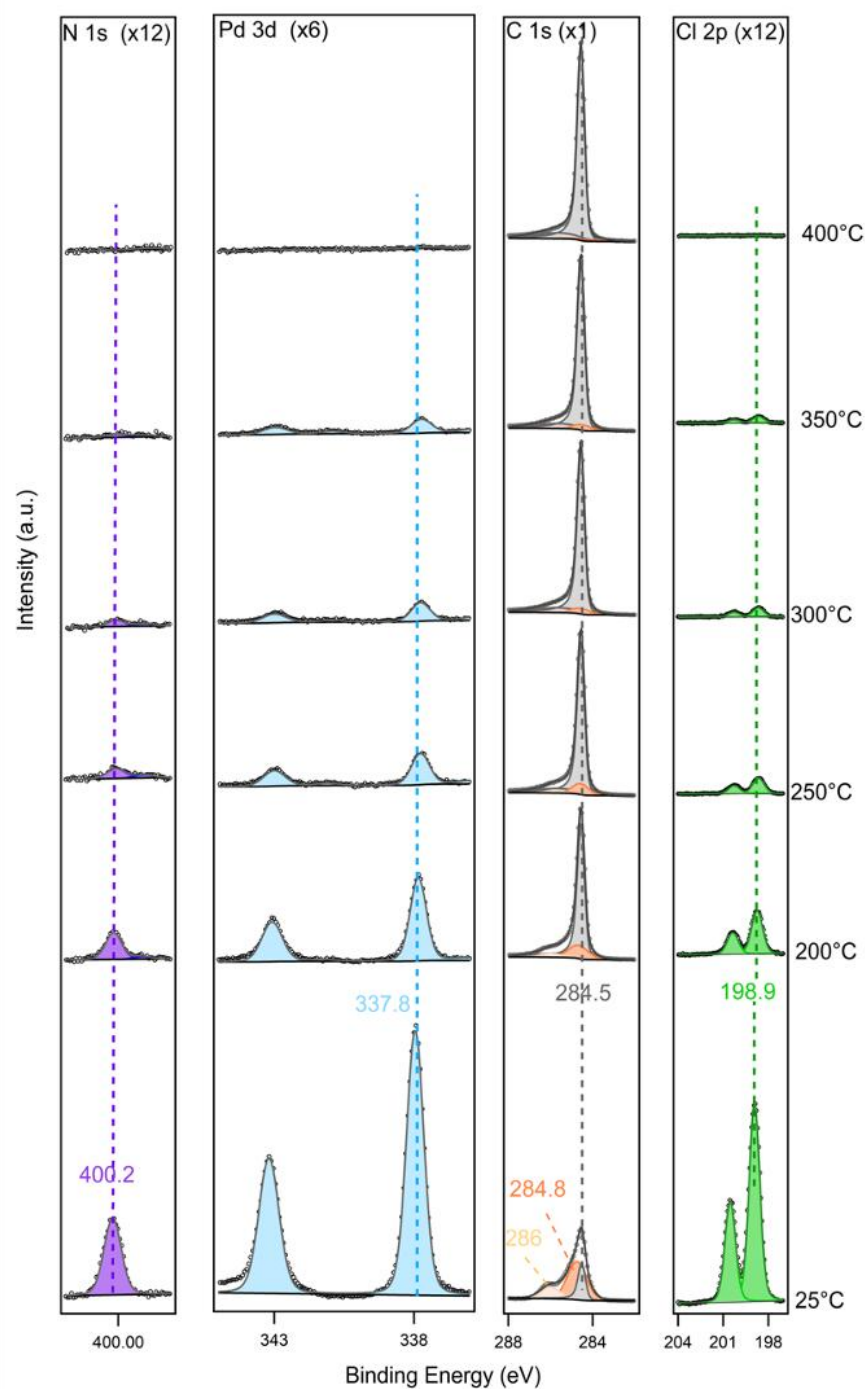


Figure A.2: HR-XPS spectra of the thermal evolution of CyPd (1), upon sublimation on HOPG kept at RT followed by annealing to 200°C, 250°C, 300°C, 350°C and 400°C. From left to right the panels refer to the N1s, Pd3d, C1s and Cl2p spectral regions. The fitting components have been discussed in section III. The peaks assignments are presented in Table 5. It is noticeable that upon annealing, no shifts are observed. Instead, the total intensities decrease as the temperature increases. For C1s, after deposition at RT, the graphite component (284.5 eV) is hidden due to the high molecular coverage. Upon annealing to higher temperatures, molecular desorption occurs and it becomes the major peak. The Cl2p spectrum could be reproduced with only one doublet at all temperatures confirming the absence of photon induced damage.

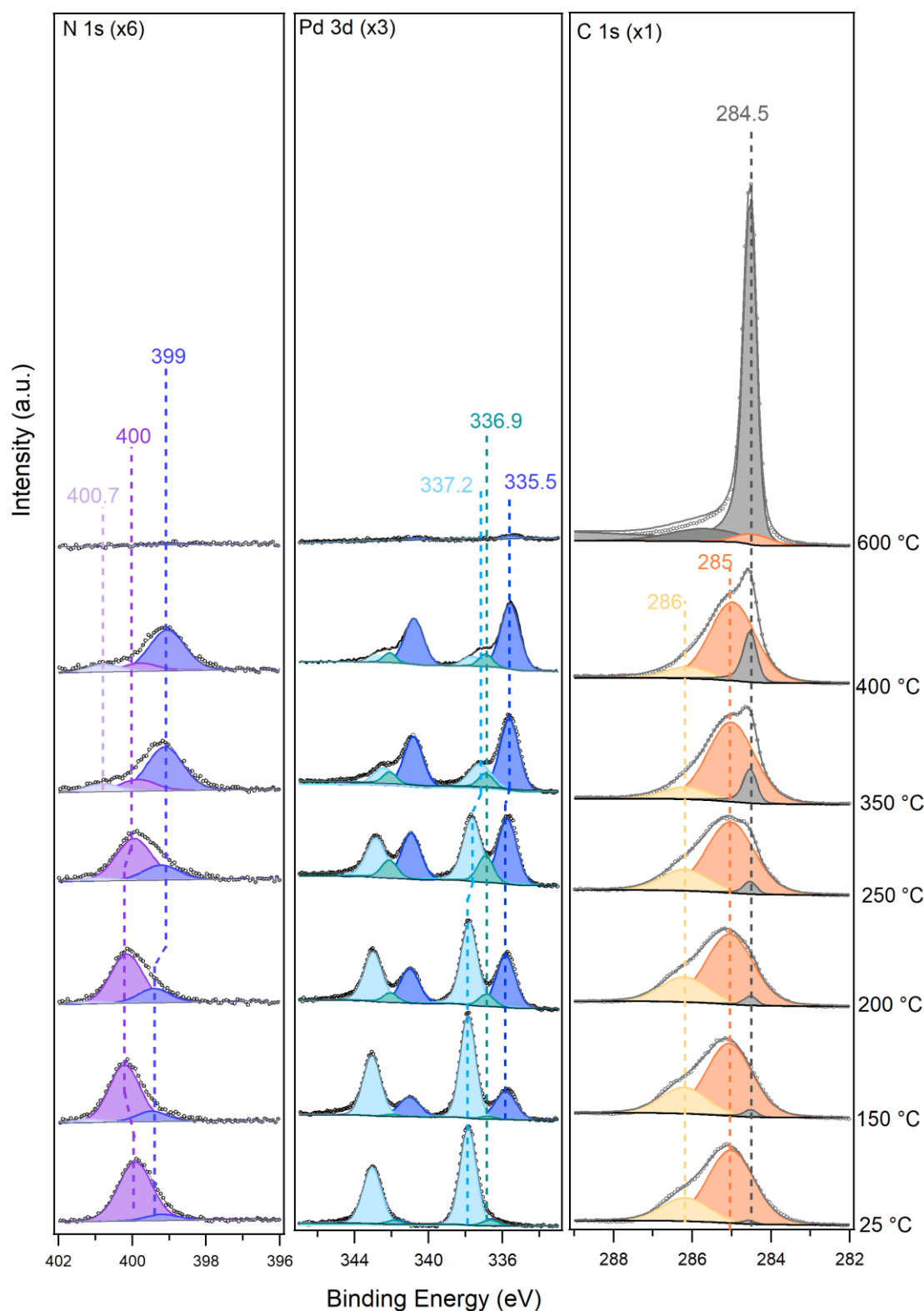
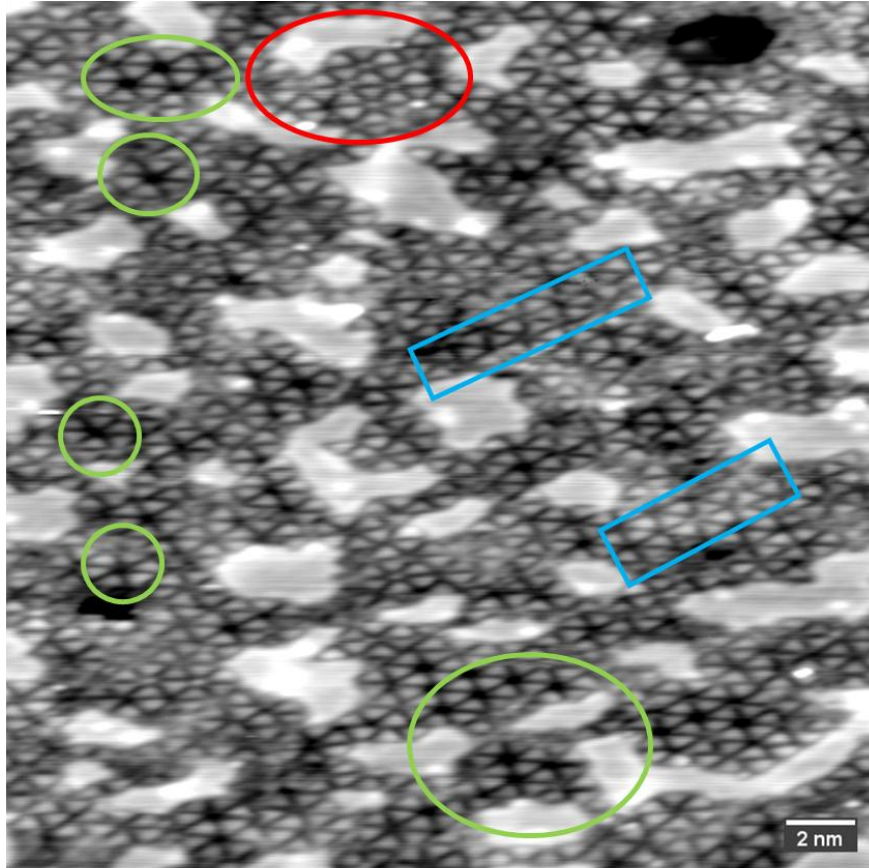


Figure A.3: HR-XPS spectra of the thermal evolution of CyPd (2) upon sublimation on HOPG kept at RT followed by annealing to 150°C, 200°C, 250°C, 350°C, 400°C and 600°C. From left to right the panels refer to the N1s, Pd3d and C1s spectral regions. It is evident that upon annealing new components arise in the N1s and Pd3d spectral regions. All the fitting components are discussed in section III and summarized in Table 5.

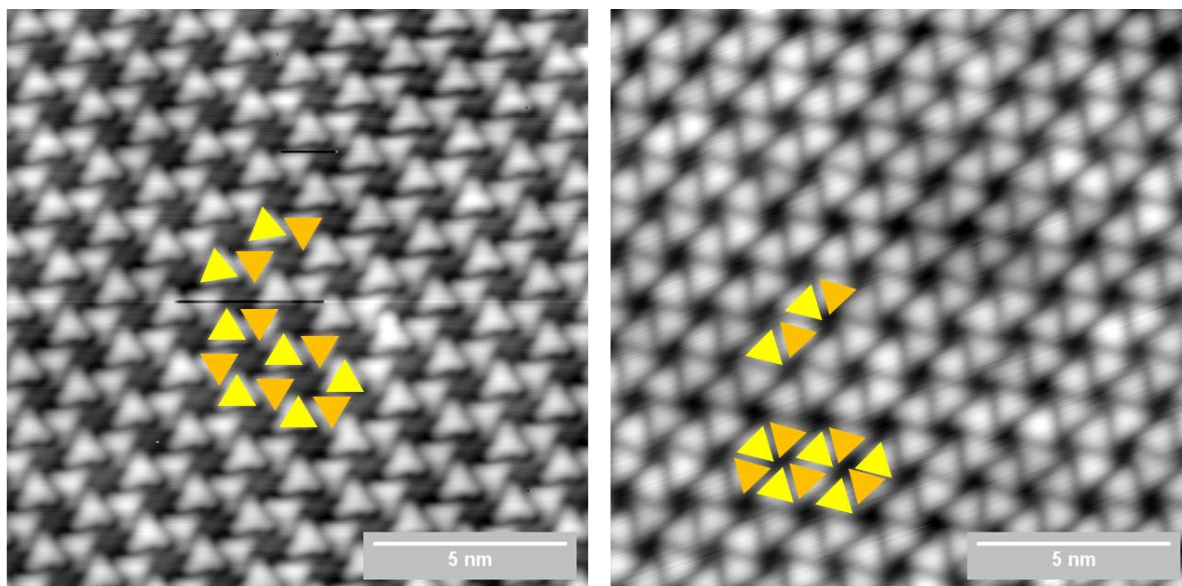
STM Images: Trial experiments of Fe/Melem/Au(111)



25x25 nm², -3.0 V/0.5 nA, Annealed to 200°C

Figure A.4: STM image (25x25 nm²) of a trial experiment after 10 mins of Fe deposition on 1 ML of Melem and annealed to 200°C.

As a first trial to calibrate the deposition of Fe atoms on Melem, I deposited Fe for 10 mins with the following parameters (I_{Fil} 2.03 A, I_{emis} 8.8 mA, I_{Flux} 14.7 nA). The sample was then annealed to 200°C. In this STM image, I observe 3 types of structures: Melem in the honeycomb configuration (Green circled areas), Honeycomb configuration with “a dot” in the middle (Red circled area), closed packed configuration (Blue rectangles). While I have no models for the Red and the Blue configurations, this experiment allowed to calibrate the dose needed to deposit single isolated Fe atoms.



a) 1 ML Melem
on heated Au ($\sim 100^\circ\text{C}$)

$15 \times 15 \text{ nm}^2$, $-0.2 \text{ V}/0.5 \text{ nA}$

b) Melem and Fe codeposited
on heated Au ($\sim 100^\circ\text{C}$)

$15 \times 15 \text{ nm}^2$, $-1.0 \text{ V}/0.2 \text{ nA}$

Figure A.5: STM images ($15 \times 15 \text{ nm}^2$) (a): 1 ML Melem/Au(111) showing the honeycomb overlayer and (b) Codeposition of 1 Fe atom/ 1 Melem atom on heated Au(111) to 100°C .

Another experiment that was conducted was the codeposition of both the precursor (Melem) and the metal atom (Fe) at the same time hoping that the whole surface will be polymerized. It was a hard experiment to conduct and due to the lack of time no repetition or optimization of the codeposition procedure was possible. It is hard to tell if Figure A.5 (b) corresponds to the closed pack surface or is an effect due to thermal drift while recording the STM image.

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