

# On-Surface Transmetallation of Metal–Organic Frameworks on Au(100)

*Structure, Electronic Properties,  
and Gas-Induced Reactivity*

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## Abstract

Metal–organic frameworks (MOFs) provide a modular strategy for engineering materials with targeted properties by combining metal nodes and organic linkers in a defined geometry. This thesis explores the on-surface assembly of MnTPyP on Au(100) into well-defined, reactive two-dimensional coordination networks. Deposition of Co or Ni, followed by mild annealing, converts the initial monolayer into an ordered, commensurate two-dimensional lattice.

Structural and spectroscopic measurements show that the porphyrin macrocycle remains largely flat on the surface, while the pyridyl groups tilt out of the molecular plane. In addition, the data indicate on-surface transmetallation, i.e., replacement of Mn by Co in the macrocycle. Core level spectroscopy shows that two cobalt species coexist in the final network, consistent with Co(II) in the macrocycle and a Co(I) state at the pyridyl coordination nodes. Across multiple core levels, network formation induces an almost rigid binding energy shift, indicating modified interface energetics rather than only local bonding changes. Momentum microscopy relates this to the valence electronic structure: ligand-derived states retain recognizable molecular fingerprints, while an additional low-binding-energy contribution develops with weak momentum selectivity, consistent with enhanced electronic coupling within the coordinated lattice.

An analogous network is obtained after Ni deposition, with a geometry similar to that of the Co-based system. The Ni  $2p_{3/2}$  spectra likewise reveal two chemically distinct components, assigned to Ni(I) nodes and Ni(II) incorporated into the macrocycle, supporting transmetallation also in the Ni case.

Finally, the chemical functionality of the coordination nodes is probed by exposing both networks to NO<sub>2</sub> and CO. In both systems, gas dosing suppresses the M(I) signature and shifts spectral weight toward higher oxidation states, identifying the +1 node species as the redox-active center, while the macrocycle-bound +2 species remains comparatively inert. Adsorption occurs at room temperature and is reversible upon mild annealing, demonstrating switchable, surface-confined redox chemistry at well-defined coordination nodes.

## Kurzfassung

Metall–organische Netzwerke folgen einem Baukastenprinzip, mit dem sich Materialien mit gezielt einstellbaren Eigenschaften realisieren lassen. Dabei werden Metallzentren und organische Linker in einer wohldefinierten Geometrie kombiniert. Diese Arbeit untersucht die oberflächengestützte Synthese reaktiver zweidimensionaler Koordinationsnetzwerke aus MnTPyP auf Au(100). Durch Deposition von Co bzw. Ni und anschließendes mildes Tempern wird die Ausgangsmonolage in ein geordnetes, kommensurates zweidimensionales Netzwerk überführt.

Strukturelle und spektroskopische Messungen zeigen, dass der Porphyrin-Makrozyklus auf der Oberfläche weitgehend flach bleibt, während die Pyridylgruppen aus der Molekülebene herausgedreht sind. Zugleich zeigen die Daten, eine Transmetallierung, die Ersetzung von Mn mit Co im Makrozyklus. Rumpfniveauspektren belegen darüber hinaus zwei koexistierende Cobalt-Spezies im Netzwerk, wobei Co(II) im Makrozyklus und Co(I) an den Pyridyl-Koordinationsknoten zugeordnet wird. Die Netzwerkbildung führt über mehrere Rumpfniveaus hinweg zu einer nahezu starren Bindungsenergieverschiebung, was auf eine Änderung der Grenzflächen-Energetik und nicht nur auf lokale Bindungseffekte hinweist. Impulsmikroskopie verknüpft dies mit der Valenzbandstruktur: charakteristische molekulare Fingerabdrücke bleiben erhalten, zugleich entsteht ein zusätzlicher niederbindungsenergetischer Beitrag mit schwacher Impulsselektivität, was auf eine stärkere elektronische Kopplung innerhalb des Netzwerks hindeutet.

Ein entsprechendes Netzwerk lässt sich auch nach Ni-Deposition herstellen, mit einer Geometrie, die der des Co-basierten Systems weitgehend entspricht. Die Ni- $2p_{3/2}$ -Spektren zeigen ebenfalls zwei klar unterscheidbare Komponenten, die Ni(I)-Knoten sowie Ni(II) im Makrozyklus zugeordnet werden und damit auch für Ni eine Transmetallierung stützen.

Abschließend wird die chemische Funktion der Koordinationsknoten durch Exposition gegenüber NO<sub>2</sub> und CO untersucht. In beiden Netzwerken wird das M(I)-Signal durch Gasdosierung unterdrückt und Intensität zu höheren Oxidationsstufen verschoben. Damit wird die +1-Spezies an den Knoten als redox-aktives Zentrum identifiziert, während die +2-Spezies im Makrozyklus vergleichsweise unbeeinflusst bleibt. Die Adsorption erfolgt bei Raumtemperatur und lässt sich durch mildes Tempern rückgängig machen, was schaltbare, oberflächengebundene Redoxchemie an wohldefinierten Koordinationsknoten demonstriert.



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# Introduction

The ability to tailor the electronic structure of materials is a central objective in modern materials science, enabling the targeted design of systems for applications ranging from catalysis to electronics [1–6]. Among the various classes of tunable materials, metal–organic frameworks (MOFs) stand out because of their high modularity, porosity, and functional versatility [7–11]. These hybrid crystalline materials consist of metal nodes interconnected by organic ligands, forming extended networks with well-defined geometries. Owing to the virtually unlimited combination of metal centers and organic linkers, MOFs provide a platform for the rational design of materials with targeted properties [10, 12, 13] and have found applications in gas sensing and storage, photocatalysis, and light harvesting [5, 14, 15]. The importance of MOFs was underscored by the 2025 Nobel Prize in Chemistry, awarded to Susumu Kitagawa, Omar M. Yaghi, and Richard Robson for their pioneering work on reticular chemistry and MOFs [16].

The properties of MOFs can be fine-tuned through strategic control of their constituents. In particular, the oxidation states, coordination environments, and magnetic characteristics of the metal nodes can be adjusted to suit specific functions [17–19]. This is highly relevant for applications such as gas sensing, heterogeneous catalysis, and molecular spintronics [2, 20–22]. For example, frameworks containing magnetic metal centers can serve as ordered arrays of localized spins, a property attractive for next-generation spintronic devices [1, 23]. Key to enabling such advanced functionalities is the realization of highly ordered, low-dimensional networks with large surface areas and accessible coordination sites.

Although most MOFs are known in bulk form, it is also possible to synthesize surface-confined two-dimensional MOFs directly on suitable substrates [22]. In recent years, such surface-supported 2D MOFs have emerged as ideal systems for exploring the interplay between molecular design and material properties at the atomic scale [1, 17, 24, 25]. These frameworks permit direct structural characterization of coordination motifs by scanning probe methods and, at the same time, provide a stable and conductive platform for investigating charge transfer, magnetism, and catalytic activity in a controlled environment. Because of their often high crystalline quality, they can serve as model systems for probing intrinsic electronic [1] and magnetic properties [26, 27] down to the two-dimensional limit.

A particularly powerful strategy for increasing the complexity and functionality of such frameworks is the use of organic ligands with multiple coordination sites, enabling hierarchical metallation [2, 24, 28, 29]. One important class of such ligands is porphyrins, which can host a metal ion in the macrocyclic center while simultaneously carrying functionalized *meso*-substituents capable of coordinating additional metal atoms. This dual-site coordination opens the possibility of constructing heterobimetallic frameworks that may exhibit cooperative behavior or synergistic reactivity [20, 30]. The use of transition metals with open-shell 3d configurations further allows the tuning of magnetic moments embedded in the network [31–33].

In this context, 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) emerges as a particularly versatile linker, as it can coordinate both a central metal ion and peripheral metal atoms through its pyridyl groups. Bimetallic frameworks can be engineered starting from metallated TPyPs (MTPyPs), in which one metal is already incorporated into the macrocycle, while a second metal can coordinate to the four pyridyl substituents of adjacent molecules to form extended networks with a quasi-rectangular unit cell [28, 30, 34]. These MOFs realize single-atom coordination in a well-defined geometry and can exhibit tunable electronic structure [30]. Owing to their distinct coordination environments, the chelated macrocycle metal and the linking metal node can be stabilized in specific, and often different, oxidation states [17, 24, 30]. Depending on the oxidation state, the metal centers may become reactive toward external gases and thereby mediate specific chemical transformations [19, 35]. In addition, heterobimetallic MOFs, in which different transition metals occupy the node and macrocycle sites, are predicted to display enhanced catalytic activity compared with their homobimetallic counterparts [2, 20].

At the same time, low dimensionality introduces additional challenges. Interfacial effects arising from the interaction between the molecular building blocks and the supporting substrate become crucial, since both the reactivity and the symmetry of the substrate can strongly influence the structural and electronic properties of the resulting frameworks. This can increase network flexibility and allow the organic linkers to adopt multiple conformations [25, 36]. Graphene, for example, is highly attractive for catalytic applications because of its chemical robustness and tolerance toward oxidizing conditions. However, in the growth of porphyrin-based bimetallic MOFs, its hexagonal symmetry often gives rise to several rotational domains, which hinder long-range order [30, 34]. A practical strategy to suppress such rotational degeneracy is to use support substrates whose symmetry matches that of the MOF overlayer. Since the frameworks considered here are fourfold symmetric, cubic single-crystal surfaces cut along the (100) plane provide suitable templates. At the same time, the substrate should interact only weakly with the framework in order to preserve the intrinsic properties of the adlayer. Gold, as a noble metal, is therefore a natural choice [37, 38]. In this context, Au(100) provides a fourfold-symmetric and comparatively weakly reactive support.

This thesis focuses on the investigation of Co- and Ni-MnTPyP/Au(100) metal-organic frameworks, which are surface-supported bimetallic systems composed of cobalt or nickel nodes coordinated to manganese porphyrin ligands on a gold substrate. By combining low-energy electron diffraction (LEED), X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and momentum microscopy (MM), this work aims to elucidate the structural, electronic, and chemical properties of these hybrid frameworks. By clarifying how coordination behavior and substrate interactions determine the resulting two-dimensional networks, this thesis contributes to the broader goal of designing multifunctional MOFs for electronic, magnetic, and catalytic applications. More specifically, the thesis is organized as follows:

- **Chapter 1** introduces the fundamental concepts relevant for two-dimensional metal-organic frameworks. It outlines the properties of the individual building blocks, discusses self-assembled molecular layers as precursors to extended networks, and introduces the general concepts underlying surface-supported MOFs.

- **Chapter 2** describes the specific components of the model systems investigated in this work, namely Au(100), MnTPyP, and the transition metal nodes. The focus is on their geometric and electronic properties, as well as on the role of the Au(100) substrate in guiding self-assembly and coordination.
- **Chapter 3** provides an overview of the experimental techniques used in this thesis. It begins with low-energy electron diffraction (LEED) as a probe of surface geometry and then discusses photoemission spectroscopy in the X-ray and ultraviolet regimes (XPS, UPS), including angle-resolved photoelectron spectroscopy (ARPES). This is extended to momentum microscopy (MM), which captures the full momentum-resolved band structure, and to photoemission orbital tomography (POT), in which experimental momentum maps are compared with theoretical momentum distributions. Finally, X-ray absorption spectroscopy (XAS) is introduced as a complementary technique that provides element-specific geometric and electronic information.
- **Chapter 4** presents the preparation and experimental results for the MnTPyP/Au(100) self-assembled monolayer and the Co–MnTPyP/Au(100) framework. The discussion is organized by first addressing the geometric structure and then the electronic structure. Wherever possible, complementary methods and reference compounds are used to support the interpretation.
- **Chapter 5** presents the corresponding experimental results for the nickel-based framework. As in Chapter 4, the geometric arrangement is discussed first, using LEED and scanning tunneling microscopy (STM), followed by the investigation of the electronic structure by XPS.
- **Chapter 6** addresses the changes in the electronic structure of the MOFs upon gas exposure. The two frameworks are exposed to NO<sub>2</sub> and CO, and the resulting changes are investigated by XPS.
- **Chapter 7** summarizes the main findings of the thesis and places them in a broader context. It concludes with an outlook on possible future directions and applications of surface-supported metal–organic frameworks.





# 1

## Fundamental concepts

This chapter provides an overview of the fundamental electronic and geometric properties of the building blocks that form the investigated metal–organic frameworks (MOFs). It begins with the relevant organic molecules and discusses their electronic structure and molecular conformation. This picture is then extended to metallated tetrapyrroles such as metallated porphyrins (MPs). Afterward, the interaction of organic semiconductors (OSCs) with surfaces is introduced, including the possibility of tuning these interactions through the choice of substrate. The formation of self-assembled molecular layers (SAMs) based on specific molecule–substrate interactions is then addressed. Finally, the formation of MOFs is discussed in more detail, with a focus on transition metal atoms as additional metal nodes.

### 1.1. Molecular building blocks

OSCs and  $\pi$ -conjugated molecules play a central role in modern devices such as organic light-emitting diodes (OLEDs), photovoltaics, and field-effect transistors [38–42]. Their semiconducting properties, combined with low-cost fabrication, compatibility with thin-film architectures, and mechanical flexibility, make them attractive alternatives or complements to conventional inorganic semiconductors (ISCs) [43]. In addition, molecules also act as ligands in MOFs, thereby further extending the range of accessible functionalities [44].

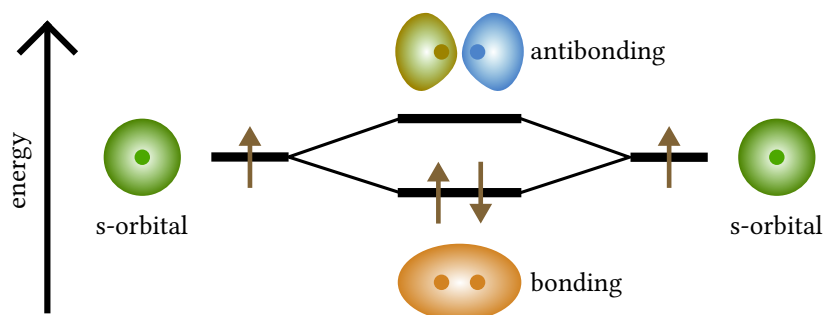


Figure 1.1.: Sketch illustrating the formation of MOs from two atomic  $s$  orbitals, resulting in bonding and antibonding states. Adapted from [45].

Molecules are formed when atoms bond, giving rise to new molecular wave functions that can be described as linear combinations of the wave functions of the interacting atoms. These combine into molecular orbitals (MOs) with bonding and antibonding character, as sketched in Figure 1.1 for two  $s$  orbitals. The bonding state lies at lower energy than the original atomic orbitals, while the antibonding state lies at higher energy. In addition to the energetic change, the spatial shape of the orbitals is modified: the electrons become delocalized between the nuclei and are shared within the chemical bond. Bonding states

exhibit an increased electron density between the nuclei as a result of constructive, in-phase interference of the wave functions, whereas antibonding states show a node between the nuclei due to destructive, out-of-phase interference. The resulting orbitals largely determine the structural, optical, and electronic properties of the molecules [2, 30, 40, 46].

Carbon, which forms the backbone of most organic molecules, gives rise to two characteristic bonding contributions in conjugated systems [38]. One bond originates from the overlap of the  $s$ ,  $p_x$ , and  $p_y$  orbitals, forming  $sp^2$ -hybrid orbitals with  $\sigma$ -bond character and a symmetry along the bond direction [38]. The second bond is formed by overlap of the  $p_z$  orbitals, resulting in a  $\pi$  bond with a symmetry perpendicular to the bond direction [38]. According to their occupation, the resulting molecular orbitals can be grouped into occupied ( $\sigma$ ,  $\pi$ ) and unoccupied ( $\sigma^*$ ,  $\pi^*$ ) states. Since the  $\pi$  orbitals are less localized between the nuclei, they are less strongly bound and therefore usually lie energetically higher than the corresponding  $\sigma$  orbitals. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is defined here as the band gap energy ( $E_g$ ), as indicated in Figure 1.2. Although the HOMO and LUMO are localized on individual molecules, they can be viewed as molecular analogs of the valence and conduction bands in conventional ISCs, respectively. The  $E_g$  of an OSC is therefore a key quantity for its interaction with light and can be tuned by modifying the chemical composition and bonding of the molecule.

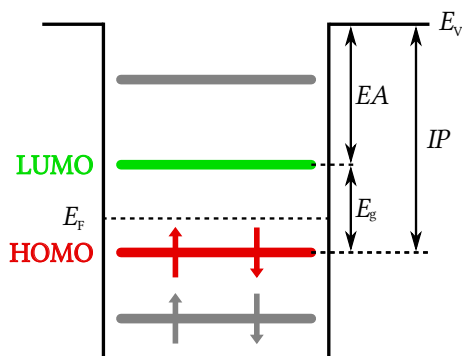


Figure 1.2.: Illustration of the effective potential well experienced by the valence electrons in a molecule. This gives rise to discrete energy levels, with the HOMO denoting the highest occupied orbital and the LUMO the lowest unoccupied orbital, separated by the band gap energy ( $E_g$ ). Each orbital can be occupied by two electrons with opposite spin. The rim of the well corresponds to the vacuum level ( $E_v$ ), while the  $IP$  and  $EA$  characterize the energetic cost or gain associated with removing or adding an electron relative to the vacuum level.

In a simplified picture, the valence electrons of a molecule can be described by an effective potential arising from the surrounding atomic cores and electrons [43]. Figure 1.2 shows an illustrative representation of such a potential well. The rim of this well corresponds to the vacuum level ( $E_v$ ), which serves as a common reference level for the MOs. Removing an electron from the HOMO into the vacuum requires the energy of the ionization potential ( $IP$ ), which is given by the energy difference between the vacuum level and the HOMO. Analogously, the electron affinity ( $EA$ ) is related to the energy difference between the vacuum level and the LUMO, and characterizes the energetic balance associated with adding an electron to the OSC.

While the valence electrons contribute to bonding within the molecule and form delocalized molecular orbitals, the more tightly bound electrons remain localized at their atomic nuclei. The binding energy of these core electrons is nevertheless influenced by the newly formed MOs, through changes in the screening of the core charge by the shared electrons and through the electrostatic potential generated by the surrounding ions. These effects are collectively described as the chemical environment.

In addition to light elements such as carbon, nitrogen, oxygen, and hydrogen, other elements can be incorporated into organic semiconductors. In particular, transition metals considerably extend the accessible range of properties and can introduce, for example, magnetism and chemical reactivity [41, 42]. These aspects are discussed below using metallated porphyrins as a model system. Furthermore, the properties of OSCs can be modified through their interaction with other materials when deposited on surfaces, as will be discussed in Section 1.2.

## Metallated porphyrins as molecular platforms

Metallated porphyrins are a class of  $\pi$ -conjugated macrocyclic molecules composed of four pyrrole rings arranged around a metal center and equipped with additional functional groups, see Figure 1.3. These compounds play important roles in biological systems, for example as heme in hemoglobin [47] or chlorophyll in photosynthesis [48, 49]. Porphyrins have also been studied extensively on surfaces and are known to self-assemble on a wide range of substrates [44, 50–53]. Their well-defined optical signatures, pronounced redox activity, and high thermal robustness make them attractive building blocks for organic electronic devices [42]. More generally, their distinct photophysical, redox, and catalytic properties, together with their ability to coordinate a wide range of metals, make porphyrins attractive for applications including catalysis, photovoltaics, sensing, and biomedical imaging [2, 30, 40].

Porphyrins belong to the family of planar  $\pi$ -conjugated tetrapyrroles. Their parent macrocycle, porphine ( $C_{20}H_{14}N_4$ ), consists of four pyrrole rings linked by four carbon atoms at the *meso* positions [48], see Figure 1.3. Their aromaticity makes porphyrins remarkably stable and allows them to withstand the sublimation procedures typically used under ultra-high vacuum (UHV) conditions. In metallated porphyrins, the nitrogen atoms of the pyrrole units coordinate the central metal ion. The *meso* carbon atoms can additionally bind peripheral substituents, which in turn may provide further coordination sites [54]. In the present case, pyridyl substituents, indicated in Figure 1.3, provide an additional nitrogen atom that can coordinate further metal atoms and thereby enable MOF formation [17, 24, 34].

Intramolecular steric repulsion and, upon adsorption, intermolecular interactions as well as molecule–substrate coupling can lead to deviations from the ideal planar geometry of the porphyrin [28, 51, 55–57]. These distortions reduce the original fourfold symmetry and can be described by  $\rho_1$  and  $\rho_2$ , the bending angles of the two pairs of opposite pyrrole rings out of the macrocycle plane, as indicated on the right-hand side of Figure 1.3. In addition, the orientation of the functional groups can be described by the twist angle  $\beta$ , corresponding to rotation around the  $\sigma$  bond connecting the substituent to the macrocycle, and by the tilt angle  $\varphi$ , which describes the out-of-plane bending of the functional group.

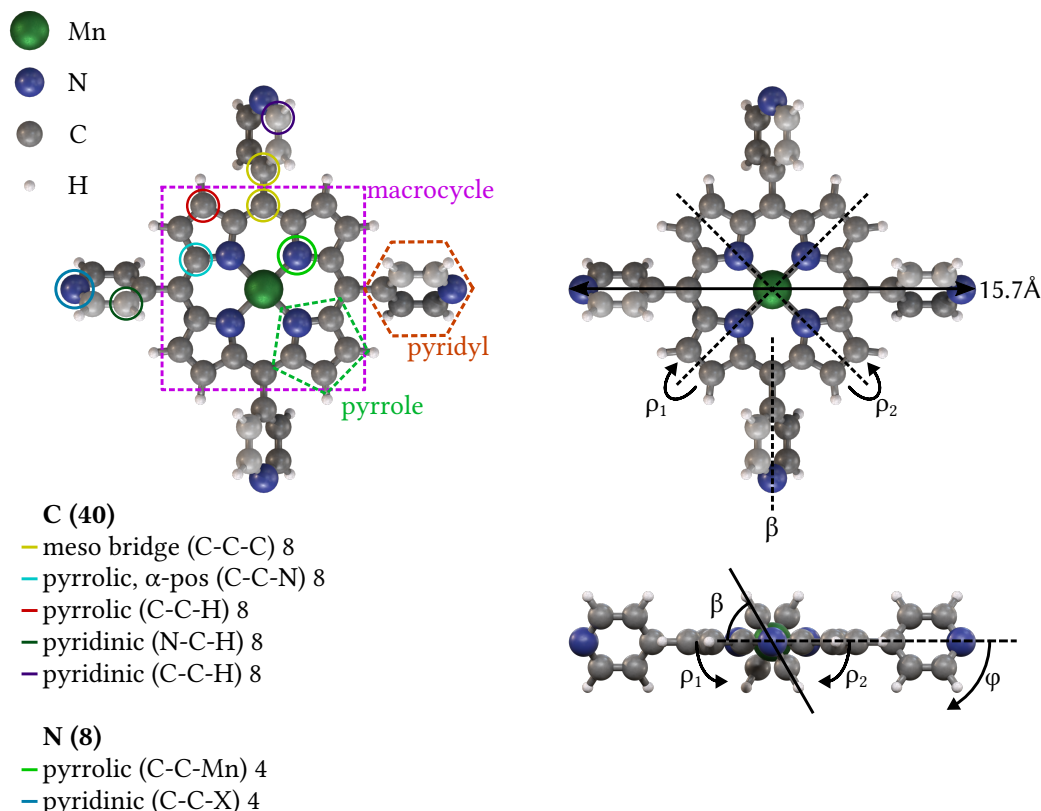


Figure 1.3.: Chemical structure of MnTPyP (left) and schematic description of its geometric parameters (right). The lower left part indicates the assignment of the elements within the molecule together with the corresponding numbers in parentheses. Further details are given in the text.

Transition metals with open  $3d$  shells are particularly attractive as porphyrin metal centers because they can provide magnetic moments, rich redox chemistry, and ionic radii that fit well into the macrocyclic cavity [19, 35, 51, 53]. As a result, the transition metal is typically incorporated approximately in the plane of the macrocycle.

In an undistorted molecule, the central metal experiences a square-planar ligand field with  $D_{4h}$  symmetry generated by the negatively charged nitrogen atoms. Whereas the five  $3d$  orbitals of a free transition metal cation are degenerate, this ligand field partially lifts the degeneracy, as illustrated in Figure 1.4 [59–61]. Placing the ion in a spherical distribution of negative charge raises the energy of all five  $3d$  orbitals equally because of the electrostatic repulsion between the ligand charges and the electron density in the  $3d$  orbitals, see Figure 1.4 (center). The square-planar ligand field of the porphyrin macrocycle then further splits the  $3d$  orbitals into subgroups, resulting in three non-degenerate orbitals and one doubly degenerate pair [61], as schematically shown on the right-hand side of Figure 1.4. These subgroups correspond to  $a_{1g}$  ( $d_{z^2}$ ),  $b_{1g}$  ( $d_{x^2-y^2}$ ),  $e_g$  ( $d_{xz}$ ,  $d_{yz}$ ), and  $b_{2g}$  ( $d_{xy}$ ) [62]. For  $D_{4h}$  symmetry, the  $d_{x^2-y^2}$  orbital points directly toward the negatively charged nitrogen atoms and therefore experiences the strongest electrostatic repulsion, which places it at the highest energy among the  $3d$  orbitals [60, 61]. The exact order and spacing of the levels depend on the ligand-field strength, for example on the bond lengths, on geometric distortions, and on the degree of hybridization with ligand states [61, 62]. Additional axial ligands, such as gas molecules or surface atoms coordinated to the metal center, can

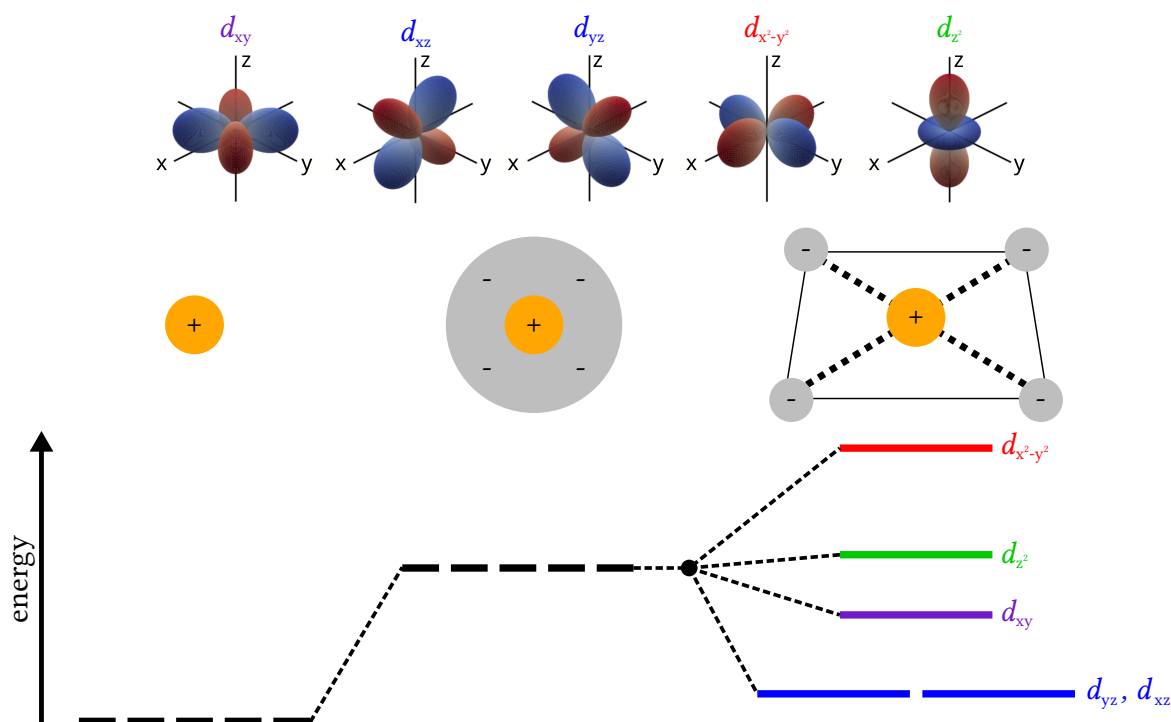


Figure 1.4.: Scheme illustrating ligand-field splitting of the 3d orbitals of a transition metal in a porphyrin macrocycle. Top: schematic representation of the  $d$  orbitals in real space. Middle (from left to right): the free metal cation, the metal cation in a spherical uniform distribution of negative charge, and the metal cation in a square-planar ligand field with  $D_{4h}$  symmetry. Bottom (from left to right): the five degenerate 3d orbitals of the free metal cation, the uniformly shifted 3d orbitals in a spherical negative charge distribution, and the ligand-field splitting pattern in square-planar  $D_{4h}$  symmetry. Top row adapted from [58].

further modify the symmetry and the strength of the ligand field and thereby induce a reorganization of the 3d orbital occupation [19, 35].

## 1.2. Adsorption-induced interactions

When organic molecules are deposited on surfaces, they interact both with the substrate and with each other through a balance of attractive and repulsive forces. Attractive interactions can originate from dispersion forces, electrostatics, or covalent bonding mediated by hybridization. Repulsive interactions arise primarily from Pauli exclusion between the molecular electrons and the substrate electron density. The resulting interface properties therefore depend sensitively on the chemical nature of the molecule and the substrate. In addition, surface reconstructions, step edges, defects, and surface states can modify the interaction strength and influence the adsorption geometry. As a consequence of the molecule–surface interaction, the electronic and geometric configurations of both components may be modified substantially relative to those of the isolated systems [34, 51, 63, 64]. This section summarizes the most important mechanisms required for interpreting the results presented in this thesis; more detailed discussions can be found elsewhere [38, 53, 65–68].

A weak interaction between substrate and molecular adlayer is commonly referred to as physisorption and is often observed on inert or weakly reactive surfaces such as graphene, Au, Cu–O, or Fe–O. By contrast, strong hybridization accompanied by chemical bond formation is described as chemisorption and typically occurs on more reactive surfaces, for example open-*d*-shell metals such as Fe, Co, Ni, or Pt. The transition between these two adsorption regimes is continuous, and one important quantity characterizing the interface is the work function (WKF) [38]. Understanding the adsorption regime is essential for describing structure, charge redistribution, energy-level alignment, and reactivity, all of which are central to applications in heterogeneous catalysis, molecular electronics, template-assisted growth, and on-surface synthesis [25]. In particular, the alignment of the electronic levels at the interface controls charge transport, chemical reactivity, and optical response.

Physisorption describes adsorption dominated by weak, non-covalent interactions. The main driving force is the van der Waals interaction (dispersion forces) while chemical bond formation is absent [69]. Electrostatic attraction between permanent or induced dipoles, as well as image-charge interactions, can also contribute. Physisorption typically occurs on inert or passivated surfaces [41], and the gas-phase electronic structure of the molecule is often largely preserved. Even in this weak-coupling regime, some charge redistribution may occur and can affect the interface WKF, for example through partial occupation of the LUMO or partial depopulation of the HOMO. Such redistribution can arise not only from electron tunneling across the surface barrier but also from polarization and rearrangement of charge in response to the surface electron density.

In contrast, chemisorption is characterized by the formation of chemical bonds between molecule and substrate. This includes hybridization between molecular orbitals and substrate bands, charge redistribution, substrate-mediated bond activation, and, in some cases, dissociation or rearrangement of the adsorbate. Non-integer charge transfer and strong hybridization manifest themselves as continuous changes in the electronic structure, and states with mixed molecule–substrate character emerge as a consequence of covalent bond formation. In addition, the molecule–substrate distance is reduced relative to the physisorption regime [70, 71]. The stronger coupling to the substrate modifies the screening of molecular excitations [71] and can lead to energetic broadening of molecular-derived states. Charge transfer from the surface toward the molecule can populate frontier molecular orbitals and even higher unoccupied states, as observed in more weakly interacting systems [63, 72]. This behavior can be understood in terms of a shift of the molecular-orbital manifold relative to the Fermi level ( $E_F$ ).

A ubiquitous consequence of adsorption is the so-called push-back, or pillow, effect. The electron density of a clean metal surface extends beyond the last atomic layer into the vacuum, whereas the positive charge density associated with the ion cores drops to zero at the surface. Adsorption of molecules, even in the absence of an intrinsic molecular dipole, pushes back part of this out-of-plane electron density because of Pauli repulsion between the electrons of the metal and those of the adsorbate [73–75]. This weakens the surface dipole and usually lowers the WKF [38]. If the molecule itself carries a permanent dipole moment, its orientation and magnitude can further decrease or increase the WKF. Charge transfer from the molecule to the substrate tends to reduce the total WKF, whereas charge transfer in the opposite direction leads to an increasing.

Adsorption generally leads to charge redistribution within both molecule and substrate, and charge transfer between the two is frequently observed [19, 35, 63]. For metallic substrates, as in the systems investigated here, the high density of electronic states near the Fermi energy interacts strongly with the molecular levels [38]. Because  $\pi$  bonds are weaker and less localized than  $\sigma$  bonds, population or depopulation of  $\pi$  and  $\pi^*$  states is more likely to occur without breaking the underlying  $\sigma$ -bond framework of the molecule, thereby preserving the molecular backbone [38]. Furthermore, the electronic structure of the adsorbed molecular layer can be insulating, semiconducting, or even metallic, and may be tailored through oxidation or reduction [38]. These electronic changes are often accompanied by geometric distortions and vibrational relaxation due to electron–phonon coupling [34, 42, 45, 51, 63, 76]. In this context, the HOMO and LUMO of the neutral molecule alone are often insufficient to describe interfacial processes. Upon charge transfer, new frontier levels, such as a singly occupied molecular orbital (SOMO), can become relevant for the description of energy-level alignment and charge injection [38].

In addition, deviations from the gas-phase geometry may arise from the competition between intramolecular strain, intermolecular repulsion, and interaction with the substrate. For example, reducing the adsorbate–substrate distance may lower the total energy, even though this can conflict with a preferred non-planar molecular geometry [42]. The final adsorption structure is therefore determined by a balance of these competing tendencies [38, 43, 67, 68]. In some cases, interaction with the substrate can even induce self-metallation, in which metal atoms are extracted from the surface and incorporated into the macrocycle of adsorbed porphyrins [77, 78]. Furthermore, molecules whose metal center has a larger ionic radius than the space available in the macrocycle, and therefore protrudes out of the macrocycle plane, may exhibit weaker metal–ligand bonding upon adsorption and can thereby facilitate demetallation [79, 80].

For metallated porphyrins, adsorption on metal substrates has a particularly strong impact on the energy alignment and occupation of the metal-centered  $3d$  levels. The square-planar ligand field imposed by the macrocycle is further perturbed by the asymmetric environment above and below the molecule, such that the substrate effectively acts as an additional axial ligand [76]. Among the  $3d$  orbitals, the  $d_{z^2}$  state is usually affected most strongly because its lobes point along the surface normal and therefore overlap most efficiently with substrate states and with any axial ligands [76, 81]. As a result, the  $d_{z^2}$ -derived level often exhibits pronounced energy shifts and broadening, and may form interface states with mixed metal–substrate character near the Fermi level [17, 19, 42, 82]. More generally, metallated porphyrins whose metal centers possess partially or completely unoccupied  $3d$  orbitals with out-of-plane character, such as  $d_{z^2}$ ,  $d_{xz}$ , or  $d_{yz}$ , tend to engage more strongly in covalent bonding with the substrate. This is the case, for example, for Mn(II) ( $d^5$ ) and Co(II) ( $d^7$ ). By contrast, ions with fully occupied out-of-plane orbitals, such as square-planar Ni(II) ( $d^8$ ), typically interact more weakly and remain more effectively decoupled from the substrate [42].

### 1.3. Self-assembled molecular layers

As a direct consequence of the interactions discussed in Section 1.2, molecules deposited on surfaces can spontaneously organize into regular patterns, a process referred to as

self-assembly and the resulting structure is referred to as a self-assembled molecular layers (SAM) [6, 44, 55]. Such layers represent a key motif in the development of two-dimensional molecular architectures. Depending on the molecular functionality, substrate symmetry, and deposition conditions, the resulting assemblies can range from close-packed monolayers to complex supramolecular networks [42, 71].

Three main contributions compete and cooperate in determining the final energetically favored structure: intermolecular interactions within the adlayer, interactions with the substrate, and the mobility of the adsorbates on the surface. Non-covalent intermolecular interactions often dominate the lateral organization within the adlayer and can drive the formation of SAMs. The main contributions are attractive van der Waals forces, steric repulsion between neighboring molecules, in particular between hydrogen atoms in large aromatic systems such as porphyrins, as well as weak hydrogen bonding,  $\pi$ - $\pi$  stacking, and dipole-dipole interactions [71]. The balance between these attractive and repulsive contributions determines the lateral packing and unit cell of the assembled structure [71, 83–85].

A second crucial factor is the interaction with the substrate and its reactivity. The kinetics and energetics of adsorption can either support or hinder self-assembly. Strong interaction, as in chemisorption, can reduce molecular mobility and thereby impede long-range ordering, whereas weak interaction, as in physisorption, is often more favorable for the formation of well-ordered SAMs. In addition, the substrate can act as a template for molecular arrangement through its lattice symmetry and surface corrugation, which define preferred adsorption sites. Surface states can mediate long-range oscillatory interactions that promote ordering, while step edges, defects, and adatoms can serve as preferential binding sites that either support or disrupt self-assembly [42, 44, 81].

Finally, molecular mobility on the surface is essential for achieving well-ordered, large-area structures. Sufficient mobility allows molecules to explore the surface and reach energetically favorable adsorption sites and configurations. This mobility can be enhanced by increasing the substrate temperature, provided that the molecular structure remains intact [71, 86]. At still higher temperatures thermal motion and rapid surface diffusion can in turn suppress long-range ordering [71]. Annealing can also promote exchange of the metal center in a metallated porphyrin with a surface atom [87].

The ordering of SAMs has been studied extensively in order to clarify the geometric structure of molecular adlayers and the influence of the substrate on the electronic and geometric properties of the adsorbed molecules [42, 71]. Non-metallated porphyrins often self-assemble on inert and weakly interacting substrates, resulting in well-ordered structures, whereas on more reactive surfaces they show less order [42, 88]. By contrast, metallated porphyrins frequently form well-ordered SAMs on inert and more strongly interacting substrates [42, 88]. In many cases, metallated porphyrins self-assemble into approximately square-like arrangements [42, 44, 63, 76, 89–91].

The versatility of available molecular systems allows different lateral arrangements and electronic structures to be realized and tailored toward specific functionalities [89, 92]. SAMs provide a route to controlling the properties of single-atom catalysts in well-defined environments and to tuning magnetic moments at the molecular scale, which is relevant for proposed data-storage concepts aiming to reduce device dimensions [18–20, 35]. The use of organic molecules composed mainly of abundant light elements further makes such



systems attractive for future miniaturized and potentially low-cost (opto-)electronic and spintronic applications [83, 93]. At the same time, SAMs provide a natural starting point for further structural and functional modification, for example through the growth of two-dimensional MOFs, which is discussed in the following section.

## 1.4. Two-dimensional metal-organic frameworks

Beyond such self-assembled molecular layers, two-dimensional (2D) metal-organic frameworks (MOFs), also referred to as metal-organic networks, extend the concept of self-assembled molecular layers by using metal atoms to interconnect neighboring molecules through open coordination sites. Connecting the molecules in this way gives rise to new properties, such as cooperative or anti-cooperative behavior of neighboring sites and a more band-like character of the electronic states [26, 30, 93, 94]. Band-like electronic properties arise from the extended periodicity of the network, which allows electrons to delocalize over the layer [5, 30, 94, 95]. By combining the structural flexibility of OSCs with a wide variety of metal species, MOFs provide attractive platforms for tailoring the band structure toward specific functionalities. In this way, band-structure engineering in MOFs complements the possibilities offered by conventional ISCs and other two-dimensional materials, such as transition metal dichalcogenides [93, 96].

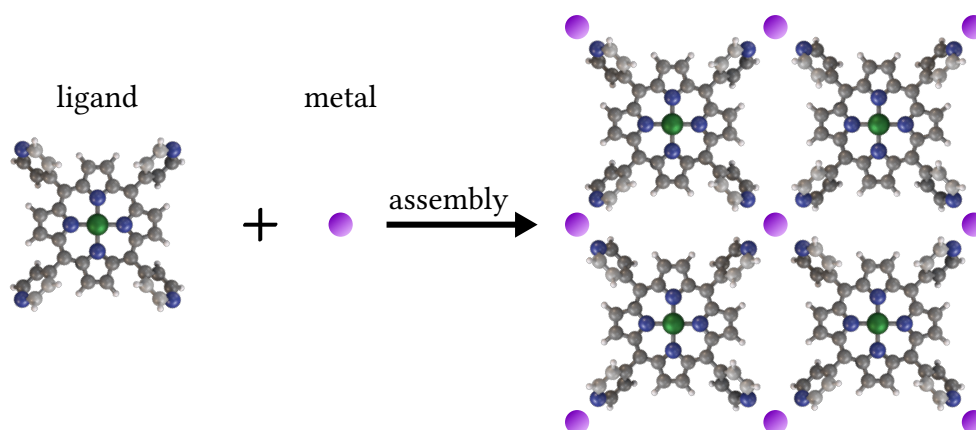


Figure 1.5.: Ingredients of a MOF: organic ligands (linkers) together with metal ions (nodes) forming an extended framework.

Although most MOFs exist in three-dimensional and two-dimensional forms, the focus here is on surface-mediated two-dimensional MOFs fabricated by on-surface synthesis [2, 5, 96, 97]. Two-dimensional MOFs can also be obtained by exfoliation of layered three-dimensional structures or by other top-down and bottom-up approaches [96]. For surface-confined 2D MOFs, well-defined single-crystal substrates with known surface symmetry are typically used [26, 34, 57, 93, 94, 98]. In a common preparation protocol, the organic molecules are first evaporated to form a SAM, after which the metal nodes are deposited, see Figure 1.5. These SAMs must provide unsaturated coordination sites so that the additional metal atoms can interconnect the molecules and form the MOFs. The number, geometry, and chemical nature of these open coordination sites largely determine the accessible network topologies [92, 99].

A widely used class of linkers for two-dimensional networks is porphyrins, which host an embedded metal center in the macrocycle while also offering additional peripheral coordination sites [17, 29, 98]. Working with metallated molecules allows two different metals to be integrated into the same framework, one in the macrocycle and one at the node sites. This can significantly increase the number and variety of potentially active metal centers compared with the corresponding SAMs of the same molecules. If the same metal is used as the central atom and as the additional node, the resulting networks are called homobimetallic. Even in such systems, the two metal sites can exhibit different oxidation states and coordination environments while sharing the same elemental composition [17, 34]. When the embedded macrocycle metal and the additional deposited metal are different, heterobimetallic networks are formed [20, 24, 28]. Such heterobimetallic MOFs are predicted to display enhanced catalytic activity compared with their homobimetallic counterparts because of synergistic effects between the different metal centers [20].

The additional metal centers in a MOF are often referred to as metal nodes, reflecting their role in connecting the organic linkers into an extended network. These nodes can be intrinsic, formed by extraction of metal atoms from the substrate, often promoted thermally, or extrinsic, introduced by co-deposition of metal species. As in the case of SAMs, weak molecule–substrate interaction, corresponding to physisorption, generally favors the formation of highly ordered 2D MOFs, whereas strong chemisorption can hinder long-range order by immobilizing the linkers or competing with metal–ligand coordination. In well-ordered networks, the lateral structure is dominated by the strong coordination bonds between the metal nodes and the organic linkers, while the molecule–substrate interaction remains relatively weak. The coordination introduces new hybridized states within the frontier-orbital manifold of the layer and modifies both the node states and the molecular states [17, 24, 29, 100]. In some cases, the deposited metal can also induce transmetalation, which exchanges the original metal center in the molecule with the added metal [101]. The distinction between coordination-node formation and metal-center exchange is crucial for the design of functional MOFs, because it provides additional control over the distribution and chemical nature of the active metal sites.

Open  $3d$  shells make transition metals particularly attractive as additional metal nodes in two-dimensional MOFs, in close analogy to their role in metallated porphyrins discussed in Section 1.1. Depending on the coordination number and geometry imposed by the organic linkers, different ligand-field symmetries, for example approximately linear, trigonal, or square-planar environments, and the corresponding splittings arise, which control the oxidation state, spin state, and degree of orbital localization [102–104]. In the MOFs investigated here, the transition metal nodes exhibit an approximately square-planar ligand field, in close analogy to the central metal ion in metallated porphyrins with  $D_{4h}$  symmetry. Nevertheless, the presence of the substrate leads to adsorption-induced changes analogous to those discussed above for the pyrrolic metal centers, resulting in energy shifts, broadening, and, in some cases, spin quenching or Kondo screening [105–108].

MOFs exhibit a wide range of promising properties that can be tuned toward specific applications through their modular design [2, 5, 96, 97]. The organic ligands can be used to adjust pore size, chemical environment, stability, and the geometric structure of the metal sites. Potential applications exploit their adsorption characteristics, for example gas sensing, gas storage, and catalytic activity, their optical response, for example light harvesting and photonics, and their magnetic behavior, for example in spintronics [5, 8, 33, 92, 96].

In contrast to traditional heterogeneous catalysts, MOFs offer a well-defined and periodic arrangement of active centers [5]. Surface-supported two-dimensional MOFs therefore combine structural control with direct accessibility by surface-science techniques and compatibility with solid–gas and solid–liquid catalytic configurations, making them a versatile platform for fundamental studies and for potential device-oriented applications [93].



# 2

## Model system

Building on the general concepts of molecules and metal–organic frameworks introduced in Chapter 1, this chapter introduces the specific model system investigated in this thesis and its key components. First, the Au(100) surface is presented, with a focus on its geometric structure, surface reconstruction, and electronic properties relevant for adsorption and interface formation. The second section discusses the MnTPyP molecules, including their geometric and electronic structure as well as their adsorption behavior on different substrates. Finally, the formation and properties of the two-dimensional coordination networks obtained by adding transition metal nodes are described.

### 2.1. The Au(100) surface as a platform for SAM and surface-grown MOF

The Au(100) surface is one of the low-index facets of gold, which crystallizes in a face-centered cubic (fcc) structure, and is frequently used as a model substrate in surface science. Gold is known to provide atomically flat and weakly interacting surfaces for many  $\pi$ -conjugated adsorbates, making it well suited to promote self-assembly and on-surface growth of two-dimensional metal–organic frameworks [38]. On such metallic substrates, the molecule–substrate interaction often favors a flat-lying adsorption geometry for planar molecules, which supports dense packing and ordered adlayers [85, 109]. For large organic molecules without specific anchoring groups, the weak interaction with gold generally does not lead to strong covalent bond formation, so that intermolecular forces dominate and drive the formation of ordered structures [38]. Furthermore, in the systems considered here, the molecules are not known to dissociate or undergo substrate-induced chemical modification upon deposition onto Au [110–112]. The low chemical reactivity of gold not only favors the formation of SAMs dominated by intermolecular interactions, but also helps ensure that linker–metal coordination in surface-grown MOFs proceeds without significant competing substrate chemistry. In addition, the resistance of gold to oxidation and other ambient-induced changes simplifies data interpretation in experiments that require long acquisition times, such as XPS, ARPES, and XAS.

The seemingly simple picture of gold as a weakly reactive substrate does not directly carry over to the reconstruction of the Au(100) surface, which has been debated for decades. All proposed models share the feature that the topmost atomic layer adopts a quasi-hexagonal arrangement, while the subsurface layers retain the square fcc-(100) stacking. Although different unit cells have been reported, such as  $(5 \times 20)$  [113, 114],  $c(26 \times 68)$  [115], incommensurate  $\begin{pmatrix} 24 \pm 3 & 0 \\ 43 \text{ or } 48 & -5 \text{ to } 0 \end{pmatrix}$  [116],  $(5 \times 28)$  [117, 118], and others [119, 120], Hammer et al. [119] carried out a comprehensive comparison of the literature and combined spot

profile analysis of low-energy electron diffraction (SPA-LEED) and STM to resolve the structure of the Au(100) surface. Together with co-workers, Hammer proposed a commensurate quasi-hexagonal  $c(28 \times 48)$  reconstruction of the Au(100) surface. In LEED, this reconstruction appears as a superposition on the unreconstructed bulk  $(1 \times 1)$  diffraction pattern. In conventional LEED images, the pattern is often described as  $(5 \times 20)$ , because spots at one-fifth of the distance between the (0,0) and (1,0) bulk spots are clearly resolved and appear in V-shaped (doublet) or W-shaped (triplet) arrangements around the bulk spots, whereas other members of the full  $c(28 \times 48)$  set are suppressed by the structure factor [119]. As a result, the electronic structure of the Au(100) surface is rather complex and contains contributions from bulk states, interface states below the reconstructed quasi-hexagonal top layer, and surface states arising from the outermost atomic layer [120]. A detailed analysis of the valence band (VB) structure of the Au(100) surface, based on a combination of ARPES measurements and density functional theory (DFT) calculations, is given by Bengió et al. [120].

Deposition of adsorbates, such as organic molecules or metal atoms, often lifts the quasi-hexagonal reconstruction and restores a square  $(1 \times 1)$  surface lattice corresponding to the unreconstructed Au(100) termination [121]. The fourfold symmetry ( $C_{4v}$ ) of the unreconstructed Au(100) surface makes it an attractive template for rectangular molecular arrangements and distinguishes it from the more commonly studied Au(111) surface. In particular, it can help suppress multiple rotational domains that tend to occur on hexagonal surfaces for molecules with approximate fourfold symmetry [17, 24, 88, 122]. The corresponding nearest-neighbor distance in the surface plane of the unreconstructed (100) surface is 2.88 Å [121, 123].

In summary, the Au(100) surface combines structural tunability, chemical inertness, and favorable symmetry, making it an excellent platform for the growth of SAMs and surface-supported MOFs built from MnTPyP.

## 2.2. MnTPyP as a molecular precursor for MOF formation

Manganese 5,10,15,20-tetra(4-pyridyl)porphyrin (MnTPyP,  $\text{MnC}_{40}\text{H}_{24}\text{N}_8$ ) is used in this thesis. Owing to its fourfold symmetry, MnTPyP is particularly well suited as a building block for ordered SAMs and surface-supported MOFs on Au(100), whose surface symmetry is also fourfold. As shown in Figure 1.3, the molecule consists of a manganese ion incorporated into the macrocycle and pyridyl substituents at the *meso* positions. The pyridyl end groups provide pyridinic nitrogen atoms that can serve as coordination sites for metal nodes and thereby enable the formation of extended networks [17, 24, 34]. As a result, two chemically distinct types of nitrogen atoms are present: four nitrogen atoms in the macrocycle coordinating the central manganese ion, and four pyridyl nitrogen atoms in the peripheral substituents.

The valence configuration of elemental manganese,  $[\text{Ar}] 3d^5 4s^2$ , gives rise to rich redox chemistry and allows for several accessible oxidation and spin states in coordination compounds. Accordingly, the partially filled 3d shell of Mn provides low-lying occupied and unoccupied states whose energies can be tuned by the ligand field and by axial ligands. This

makes MnTPyP highly sensitive to its chemical environment and particularly interesting as a catalytic center. In air, an axial chloride ligand stabilizes the +3 oxidation state of the central manganese ion and protects it against uncontrolled oxidative degradation [124, 125]. Upon deposition in vacuum and subsequent annealing to temperatures between 423 K and 525 K, the axial Cl ligand dissociates from the metal center, leaving manganese in the +2 oxidation state [20, 91, 124]. After thermal removal of Cl, exposure to O<sub>2</sub> can reoxidize the metal center in Mn(II)TPP to Mn(III) [124]. Similar behavior is expected for MnTPyP, given its close structural analogy to MnTPP. In addition, manganese phthalocyanines (MnPc) have been reported to react even with activated nitrogen species under suitable conditions, illustrating the pronounced reactivity of manganese macrocycles toward small molecules [126].

Manganese porphyrins with additional coordination sites, such as pyridyl substituents, have only recently been explored in the context of on-surface MOF formation [24, 57], whereas their phenyl-substituted analogs have long been studied as catalysts and as functional molecular units [91, 124, 125, 127]. Compared with their phenyl-substituted counterparts (TPP), the pyridyl substituents in TPyP-type molecules differ only by replacement of one carbon atom by nitrogen in each end group. This seemingly small modification already leads to pronounced changes in self-assembly and coordination behavior. For example, tetraphenylporphyrins tend to form square-like arrangements on Ag(111), whereas the corresponding tetrapyridylporphyrins assemble into herringbone structures [81]. On Au(111) and Cu(111), TPyP-type molecules can also interact strongly with the substrate: surface atoms may be incorporated either into the macrocycle or at the pyridyl end groups via covalent bonding, and metal-organic networks can form through coordination at the pyridyl nitrogen sites [57, 92]. SAMs of MnTPyP have already been studied by STM on graphene, where a quasi-rectangular unit cell of 12 Å × 25 Å was observed [24]. The formation of metal-organic networks has been demonstrated either by post-deposition of metal atoms onto pristine MnTPyP monolayers on graphene [24] or by pulling surface atoms into the pyridyl end groups on Cu(111) [57]. In both cases, heterobimetallic MOFs are obtained, with Mn in the macrocycle and Co or Cu in the pyridyl coordination nodes, respectively. Similar SAMs and MOFs have also been reported for other metallated porphyrins with pyridyl end groups, such as 2HTPyP on Cu(111) [128, 129], ZnTPyP on Au(111) [99], and CoTPyP on various substrates [20, 34, 130].

There are, however, important differences between adsorption of MnTPyP on graphene and on Au(100). First, the two substrates differ in symmetry: Au(100) exhibits fourfold surface symmetry, which matches the C<sub>4v</sub> symmetry of the adsorbed MnTPyP molecule. By contrast, graphene has hexagonal C<sub>6v</sub> symmetry, which often gives rise to multiple rotational domains in molecular overlayers. Second, graphene is widely used as an inert decoupling layer. Its relatively low density of states near the Fermi level suppresses charge transfer between adsorbates and the substrate, whereas charge transfer is more likely on metallic surfaces [19, 131]. As a consequence, MnTPyP is expected to be more strongly influenced by the substrate on Au(100) than on graphene, both in terms of energy-level alignment and possible geometric arrangement.

In summary, MnTPyP combines a conformationally flexible porphyrin macrocycle, multiple coordination sites, and a tunable electronic structure through its manganese center. On weakly to moderately interacting substrates, the macrocycle typically adsorbs

approximately parallel to the surface, while the peripheral pyridyl groups mediate intermolecular bonding and coordination to adatoms, resulting in well-ordered layers and surface-supported MOFs. These characteristics make MnTPyP a highly suitable precursor for studying the formation and electronic properties of two-dimensional MOFs, and an attractive system for investigating electronic structure and redox chemistry in both the SAM and the MOF.

### 2.3. Cobalt and nickel as metal nodes in MnTPyP-based MOF

Cobalt is a widely used transition metal in porphyrin chemistry [24, 74, 132, 133]. It has also attracted considerable attention in the formation of surface-supported two-dimensional MOFs because of its ability to coordinate strongly to nitrogen-containing ligands, such as the pyridyl groups present in MTPyP [2, 24, 29, 30, 76, 134]. Cobalt porphyrins and related complexes exhibit rich catalytic behavior in oxygen reduction, hydrogen evolution, and other energy-related reactions. This behavior is commonly attributed to the partially filled  $3d$  shell and the accessibility of multiple oxidation states,  $\text{Co}^{\text{III}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Co}^{\text{I}}$ , which can participate in electron transfer [2, 17, 19, 30, 135]. Moreover, cobalt has already been extensively used and characterized as a building block in surface-confined metal-organic networks, where it displays reactivity toward small molecules such as CO, NO, and  $\text{O}_2$  [2, 17, 29, 30, 76, 134]. In addition, heterobimetallic coordination systems are expected to show enhanced gas reactivity compared with homobimetallic networks because of synergistic effects between the different metal centers [2, 20].

On noble-metal surfaces such as Au(100), isolated Co adatoms exhibit sufficient mobility at room temperature to diffuse across terraces, but they can be efficiently trapped by strong coordination to nitrogen donors. When MnTPyP is preadsorbed, the open nitrogen sites of the pyridyl substituents act as anchor points for diffusing Co adatoms, which can then be captured to form well-ordered metal-organic networks. In these networks, cobalt atoms serve as fourfold coordination nodes that link adjacent pyridyl termini into extended grid-like architectures [6, 24]. On weakly interacting substrates such as Au(100), the Co-ligand coordination dominates over molecule-substrate bonding, so that the framework is primarily coordination-stabilized rather than substrate-stabilized [24, 33]. As a result, the node experiences a ligand field close to square-planar  $D_{4h}$  symmetry, similar to that of the transition metal ion in the macrocycle. While cobalt in the macrocycle is typically close to the +2 oxidation state [19, 59, 131], cobalt coordinated at the pyridyl substituents has been found in the +1 oxidation state [17, 24, 34]. This lower oxidation state is often more reactive toward axial ligands such as  $\text{NO}_2$  or CO than the +2 state, and this enhanced reactivity has been exploited to reversibly switch the spin state and coordination environment of cobalt porphyrins on surfaces [17, 19, 30]. Beyond their local chemical role, cobalt nodes can mediate indirect coupling between porphyrin macrocycles, giving rise to cooperative and anti-cooperative behavior in both catalysis and magnetic response [8, 30, 33, 136]. Changes in oxidation state or coordination at one cobalt site can influence neighboring sites through electronic and elastic interactions transmitted by the network, leading to nontrivial coverage-dependent adsorption energies and collective switching phenomena [17, 30]. In addition, deposition of cobalt onto preformed metallated porphyrin layers can induce



transmetallation, in which the original metal center in the macrocycle is expelled and replaced by cobalt [101].

Nickel is closely related to cobalt and is therefore also a promising candidate as a metal node in MnTPyP-based networks [35, 51, 52, 72, 137]. Nickel porphyrins can be stabilized in different oxidation states and exhibit reversible redox chemistry [35, 52, 137]. On inert substrates, Ni(II) can often be stabilized, whereas on more reactive substrates reduction to Ni(I) has been reported [138]. Furthermore, nickel has already been investigated in the formation of MOFs with tunable conformation and electronic structure [25, 26, 36]. Owing to these similarities in coordination chemistry and redox flexibility, nickel is expected to provide a meaningful comparison to cobalt in MnTPyP-based networks.

In summary, both cobalt and nickel are suitable metal nodes in MnTPyP-based MOFs because of their favorable coordination chemistry with pyridyl ligands, their ability to modify the electronic structure and spin state of the network, and their intrinsic activity toward small-molecule adsorption and activation.



# 3

## Experimental methods

This chapter introduces the experimental techniques used in this thesis to characterize the geometric and electronic structure of the investigated systems.

First, in order to establish a reliable structural basis for the investigated systems, the discussion begins with a technique that probes the periodic arrangement of atoms at surfaces. Low-energy electron diffraction (LEED) uses elastically backscattered low-energy electrons to generate diffraction patterns that provide information on the surface lattice, reconstructions, and the periodic order of adsorbate layers.

The second part of this chapter focuses on methods that probe the occupied electronic states. By irradiating the sample with photons of different energies, photoemission spectroscopy in the X-ray (XPS) and ultraviolet (UPS) regimes, including angle-resolved photoemission spectroscopy (ARPES), provides element-specific information on core states as well as detailed insight into the valence electronic structure and band dispersion of the systems.

Finally, a complementary approach is required that can simultaneously provide electronic and local structural information. X-ray absorption spectroscopy (XAS) fulfills this role by offering element- and orbital-specific sensitivity to the local coordination environment and the unoccupied electronic states. Together, these methods represent a well-established toolkit in surface science and provide a comprehensive basis for interpreting the experimental results presented in this thesis.

### 3.1. Low-energy electron diffraction

Low-energy electron diffraction (LEED) is a standard technique widely used to probe the geometric structure of crystalline surfaces [139]. In a typical LEED experiment, a monochromatic beam of low-energy electrons with kinetic energies  $E \lesssim 200$  eV is accelerated toward the surface. The corresponding de Broglie wavelengths are comparable to interatomic spacings, which makes the technique highly sensitive to periodic order in the topmost atomic layers. Electrons elastically backscattered by the surface are projected by the LEED optics onto a fluorescent screen, see Figure 3.1. Constructive and destructive interference of these elastically scattered electrons generates a diffraction pattern on the screen that directly reflects the symmetry and periodicity of the surface structure. The diffraction pattern is typically recorded with a camera, and the positions of the diffraction spots are analyzed to determine the surface unit cell and symmetry, often by comparison with simulated LEED patterns. Background intensity, the sharpness of the diffraction spots, and their relative intensities provide additional information on the surface quality, including the degree of order, defect density, and cleanliness [139, 140].

The appearance of diffraction patterns depends on two factors: the structure factor and the lattice factor. The structure factor mainly modulates the diffraction intensities and reflects the atomic arrangement and scattering factors within the unit cell, whereas the lattice factor describes the periodicity in the plane parallel to the surface [139]. For a surface with two-dimensional lattice vectors  $\vec{a}_1$  and  $\vec{a}_2$ , the diffraction pattern can be interpreted in terms of the corresponding reciprocal-lattice vectors  $\vec{b}_1$  and  $\vec{b}_2$ , defined by  $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$  [139]. Under elastic-scattering conditions, the component of the scattered wave vector parallel to the surface,  $\vec{k}_{\parallel,f}$ , differs from that of the incident beam,  $\vec{k}_{\parallel,i}$ , by an in-plane reciprocal-lattice vector  $\vec{G}_{hk} = h\vec{b}_1 + k\vec{b}_2$ , where  $h$  and  $k$  are integers (Laue equations). As a result, each diffraction spot on the screen can be indexed by  $(h, k)$ , and the set of spot positions maps out the two-dimensional reciprocal lattice of the surface. By measuring the relative positions of the diffraction spots with respect to the specular  $(0, 0)$  beam and known reference spots, for example those of the Au(100) substrate, real-space lattice constants, overlayer periodicities, and rotational domains can be determined. This makes LEED particularly powerful for analyzing coincidence lattices, reconstruction patterns, and the registry between adsorbate overlayers and the underlying substrate.

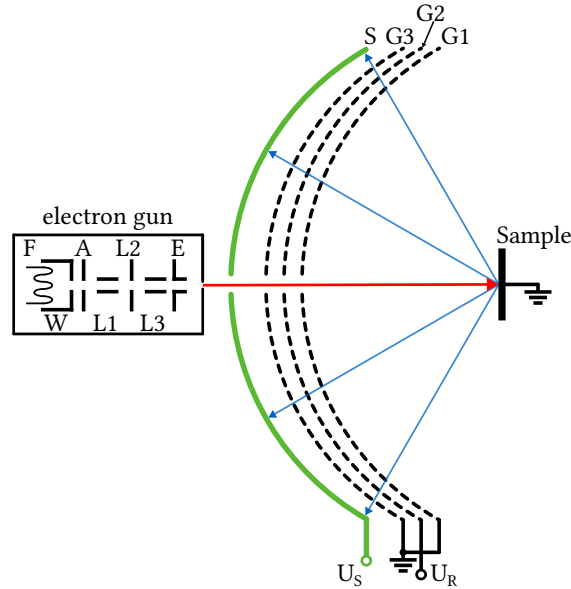


Figure 3.1.: Schematic representation of a LEED optics with the sample at the focal point. The setup includes the electron gun (F: filament, W: Wehnelt cylinder, A: anode, L1–L3: electrostatic lenses, E: accelerating field), the grids (G1–G3), and the fluorescent screen (S).  $U_R$  denotes the retarding voltage and  $U_S$  the screen acceleration voltage. The red arrow indicates the primary electron beam with kinetic energy  $E$ , while the blue arrows represent the backscattered electrons that form the diffraction pattern on the screen.

A schematic representation of the LEED optics is shown in Figure 3.1. At its center, an electron gun equipped with a filament (F), a Wehnelt cylinder (W), an anode (A), and electrostatic lenses (L1–L3) generates a monochromatic electron beam. The gun accelerates and collimates the beam, focuses it onto a small spot on the sample, and allows control over the beam divergence, which is important for spot sharpness and energy resolution. In front of the sample, a stack of grids (G1–G3) and the fluorescent screen (S) collect the scattered electrons. The first grid (G1) is usually kept at ground potential and placed closest to the sample to ensure that the electrons propagate in a field-free region between the surface

and the grid. The second grid (G2) is biased with a retarding voltage  $U_R$  and acts as an energy filter: inelastically scattered electrons, which have lost part of their kinetic energy, are largely suppressed by the counterfield, resulting in reduced background intensity. A third grid (G3), again held at ground potential, shields the electron trajectories from the strong acceleration field of the screen, which is operated at a high positive voltage  $U_S$  of a few kV.

More advanced LEED systems use a microchannel plate (MCP) placed in front of the screen, which amplifies the electron signal and allows the use of much lower primary-beam currents. This is particularly advantageous for sensitive structures, such as weakly bound adsorbates or insulating substrates, for which high beam currents could induce damage. Some setups also allow recording the intensity of individual diffraction spots as a function of electron energy, so-called  $I(V)$ -LEED, which provides more detailed structural information through quantitative comparison with dynamical LEED calculations.

## LEED setup

All LEED images shown in this work were recorded with a three-grid SPECS ErLEED 150 system. A primary-electron energy of 25 eV was used for all measurements, which provides a good compromise between surface sensitivity and diffraction-spot intensity for the clean Au(100) surface, the MnTPyP monolayer, and the Co–MnTPyP network.

## 3.2. Photoemission spectroscopy

Photoemission spectroscopy (PES) uses light to eject electrons from a sample and measures their kinetic energy. In angle-resolved modes in the valence band (VB) region, the emission direction is recorded as well and used to determine the electronic structure in momentum space. The underlying physics is based on the photoelectric effect, discovered by Heinrich Hertz in 1887 [141] and explained by Albert Einstein in 1905 [142]. This section gives a brief overview of photoemission spectroscopy and its underlying physics; more detailed discussions can be found elsewhere [143–146].

When a photon excites an electron in a solid, the electron can escape into the vacuum and be detected with a kinetic energy referenced to the vacuum level. The kinetic energy  $E_k$  depends on the photon energy  $h\nu$  and on the binding energy  $E_b$  of the electron relative to the Fermi level  $E_F$ , with  $E_b = 0$  eV at the Fermi level. It is given by

$$E_k = h\nu - \Phi - E_b, \quad (3.1)$$

where  $\Phi$  is the work function (WKF) of the sample, the energy difference between  $E_F$  and vacuum level  $E_v$  [144]. If the sample and analyzer are electrically connected, their Fermi levels align, and the analyzer WKF can be used for energy calibration. Depending on the photon energy  $h\nu$ , PES predominantly probes either core levels (X-ray photoelectron spectroscopy (XPS)) or valence states near  $E_F$  (ultraviolet photoelectron spectroscopy (UPS)). These regimes are discussed in more detail in Sections 3.2.1 and 3.2.2, respectively.

A typical PES setup consists of a photon source, a sample manipulator, an electron energy analyzer, and a detector, all housed in an ultra-high vacuum (UHV) chamber in order to suppress electron scattering by residual gas and to maintain sample cleanliness. The photon source provides photons of energy  $h\nu$  to excite the electrons, while the sample is mounted on a manipulator that allows precise positioning relative to the analyzer and photon source, as well as temperature control. As sketched in Figure 3.2, the sample is irradiated by a

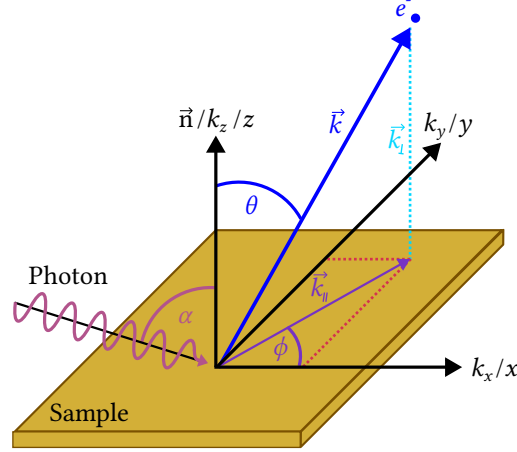


Figure 3.2.: Example of a PES geometry. A photon beam of energy  $h\nu$  impinges on the sample at an angle  $\alpha$ , and electrons are emitted with characteristic kinetic energy  $E_k$  and emission angles  $\theta$  and  $\phi$ .

monochromatic photon beam of energy  $h\nu$  at an incidence angle  $\alpha$  with respect to the surface normal  $\vec{n}$ . Common excitation sources include laboratory-based X-ray tube and ultraviolet lamps, synchrotron radiation, and laser sources, sometimes combined with high-harmonic generation. Among these, synchrotron radiation is particularly advantageous because of its high brilliance and its tunable, high-intens photon beam, which allows the excitation conditions to be optimized for a given experiment in terms of photon energy, polarization, and flux. Electrons are then emitted from the sample with kinetic energies given by Equation (3.1). After leaving the sample, they travel through a field-free region before entering the analyzer, for example a hemispherical analyzer, where they are energy-dispersed and detected as a function of kinetic energy ( $E_k$ ) and, if required, emission angle. A hemispherical analyzer energy-filters electrons by bending them through an electrostatic field between two concentric hemispheres, such that only electrons with a specific pass energy follow the central trajectory and reach the exit slit. Electrons with higher or lower kinetic energy are dispersed to different radii and are blocked by the slits. The detected electrons are characterized by a polar emission angle  $\theta$  and an azimuthal angle  $\phi$ , which determine their momentum, as indicated in Figure 3.2.

Approximating the final state of the emitted electron as free-electron-like, which is often a useful approximation in the UV and soft X-ray regimes, simplifies the analysis. The momentum component parallel to the surface can then be written as

$$k_{\parallel} = |\vec{k}_{\parallel}| = \frac{1}{\hbar} \sqrt{2m_e E_k} \sin(\theta), \quad (3.2)$$

which depends on the polar emission angle  $\theta$  and the kinetic energy  $E_k$  of the emitted electron. The momentum component perpendicular to the surface is given by

$$k_{\perp} = |\vec{k}_{\perp}| = \frac{1}{\hbar} \sqrt{2m_e(E_k \cos^2(\theta) + V_0)}, \quad (3.3)$$

where  $V_0$  is the inner potential of the crystal. In contrast to  $k_{\parallel}$ ,  $k_{\perp}$  is not strictly conserved at the surface because of the potential step at the solid–vacuum interface. Nevertheless, it can be accessed experimentally by varying the photon energy, which changes the kinetic energy of the emitted electrons. Angle-resolved photoelectron spectroscopy (ARPES) therefore allows mapping of the electronic structure as a function of  $E(k_{\parallel})$  for a fixed  $k_{\perp}$ , or, conversely, probing along  $k_{\perp}$  by tuning the photon energy. This has to be taken into account when comparing measurements with band-structure calculations, as the inner potential  $V_0$  is not directly accessible and is often treated as an adjustable parameter.

Standard XPS and UPS measurements are often performed in or close to normal emission ( $\theta \approx 0$ ) within the analyzer acceptance angle, which is the solid angle from which electrons can enter the analyzer. ARPES, by contrast, exploits the angular dependence of the emitted electrons in order to resolve the in-plane momentum  $k_{\parallel}$  of the photoelectrons. The overall energy resolution is determined by the photon source, the analyzer, and the detector, and typically ranges from a few hundred meV down to a few meV. It is additionally broadened by the thermal width of the electronic states, approximately  $\Delta E \approx 4k_B T$ , depending on the sample temperature  $T$  [144]. Because of the finite excitation spot size and analyzer acceptance, the lateral resolution of conventional PES is typically macroscopic.

PES is often described by the illustrative three-step model, shown in Figure 3.3, which decomposes the process into three conceptually separate steps:

1. **Excitation:** An electron absorbs a photon of energy  $h\nu$  and is excited from an initial state into a higher-lying final state.
2. **Transport:** The excited electron propagates toward the surface and may undergo elastic or inelastic scattering, which determines the probing depth.
3. **Escape:** The electron crosses the surface potential barrier and escapes into the vacuum, overcoming the WKF  $\Phi$ .

This three-step model was introduced by Berglund and Spicer [147, 148]. Besides this intuitive picture, a more rigorous one-step model exists that treats excitation, transport, and escape as a single quantum-mechanical scattering problem [144, 149]. However, the one-step model is computationally more demanding and less intuitive, so the three-step model is commonly used for qualitative interpretation. It should nevertheless be kept in mind that, in reality, these processes are not fully independent and that the three-step model relies on several simplifying assumptions.

In the first step, indicated by ① in Figure 3.3, an electron absorbs a photon of energy  $h\nu$  and is promoted from an initial state to a final state with energies  $E_i$  and  $E_f$ . Energy conservation requires

$$E_f = E_i + h\nu. \quad (3.4)$$

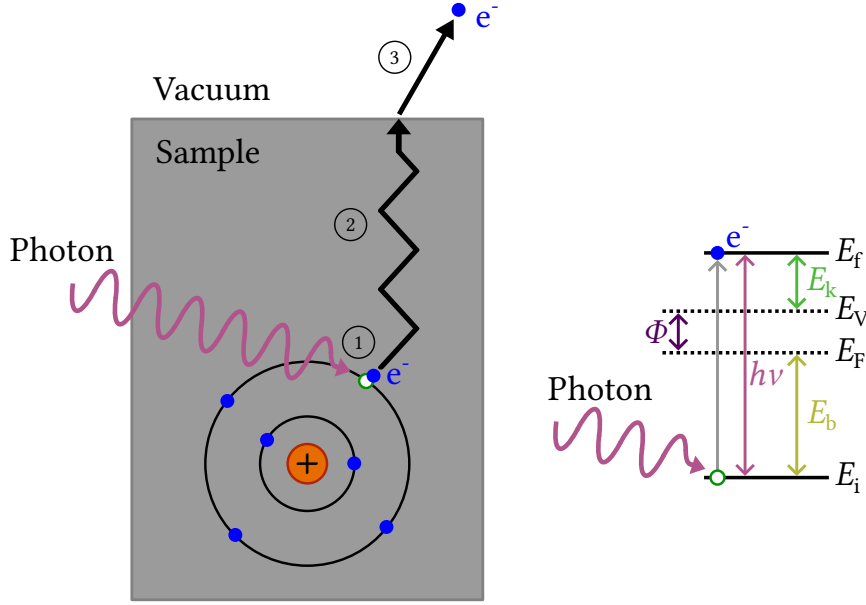


Figure 3.3.: Illustration of the three-step model (left) as described in the text: 1: excitation from the initial to the final state, 2: propagation toward the surface, where scattering may occur, 3: escape from the sample into the vacuum. The right-hand side shows the corresponding energy levels.

The corresponding crystal momenta  $\vec{k}_i$  and  $\vec{k}_f$  fulfill

$$\vec{k}_f = \vec{k}_i + \vec{G}, \quad (3.5)$$

where  $\vec{G}$  is a reciprocal-lattice vector accounting for the periodicity of the crystal lattice. In the ultraviolet and X-ray regimes, the photon momentum is typically small compared with the electron momentum and is therefore often neglected in the momentum balance [144].

In the second step, indicated by ② in Figure 3.3, the excited electrons travel toward the surface and may undergo electron–electron, electron–phonon, and electron–defect scattering, which leads to energy loss and loss of phase information. Electrons that reach the surface without inelastic scattering preserve information about their initial state and are called primary electrons, whereas inelastically scattered electrons are referred to as secondary electrons. The probability of inelastic scattering is characterized by the material-specific inelastic mean free path (IMFP)  $\lambda$ , the average distance an electron travels without inelastic scattering, which depends on the electron kinetic energy  $E_k$ . The attenuation of the photoemission intensity as a function of path length  $d$  is described by

$$I(d) = I_0 \exp\left(-\frac{d}{\lambda(E_k) \cos(\theta)}\right), \quad (3.6)$$

where  $I_0$  is the initial intensity. As a result, the surface sensitivity can be tuned by varying the photon energy or probing emission angle. For example, in the XPS regime the photon energy is often chosen such that about 95 % of the detected electrons originate from within approximately  $3\lambda$  of the surface [150]. The empirical universal curve provides a qualitative overview of  $\lambda$  [139, 151], whereas quantitative values depend on the material and the kinetic-energy range. Detailed calculations and experiments on the IMFP have been reported by



Tanuma and co-workers [152–158]. The limited escape depth makes PES intrinsically surface-sensitive, typically probing only the top few atomic layers.

In the final step, indicated by ③ in Figure 3.3, the electron must overcome the surface potential barrier defined by the WKF  $\Phi$  in order to escape into the vacuum. Because of the potential change at the surface, the momentum component perpendicular to the surface is not conserved, whereas the parallel component is conserved owing to translational symmetry parallel to the surface.

Photoemission data are typically presented as intensity  $I$  versus binding energy ( $E_b$ ), a so-called energy distribution curves (EDCs). Features in these spectra correspond to specific electronic states in the sample, superimposed on a background arising mainly from inelastically scattered electrons. The measured intensity at a given emission direction ( $\theta, \phi$ ) and kinetic energy  $E_k$  results from all allowed transitions into the corresponding final state  $\Psi_f(\theta, \phi, E_k)$  and can be written as

$$I(\theta, \phi, E_k) \propto \sum_i w_{if}, \quad (3.7)$$

where  $w_{if}$  is the transition probability from an initial state  $\Psi_i$  to a final state  $\Psi_f$  [143]. This transition probability is given by Fermi's golden rule,

$$w_{if} = \frac{2\pi}{\hbar} |\langle \Psi_f | H' | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\nu), \quad (3.8)$$

where  $H'$  is the perturbation Hamiltonian describing the light–matter interaction. The delta function enforces energy conservation for a photon of energy  $\hbar\nu$ . In first-order perturbation theory and within the dipole approximation, valid when the photon wavelength is much larger than the spatial extent of the electronic wave function, the interaction Hamiltonian can be written in velocity form as

$$H' = -\frac{e}{m_e c} \vec{A} \cdot \hat{\vec{p}}, \quad (3.9)$$

where  $\vec{A}$  is the electromagnetic vector potential of the incoming light and  $\hat{\vec{p}}$  is the electron momentum operator. In the context of photoemission, one often uses the crystal, or quasi-momentum,  $\vec{k}$  to label Bloch states, whereas the true quantum-mechanical momentum operator entering the light–matter interaction is  $\hat{\vec{p}} = -i\hbar\nabla$  [145].

The initial state is an  $N$ -electron many-body state, whereas the final state consists of an  $(N - 1)$ -electron state plus the outgoing photoelectron. The sudden approximation assumes that the photoelectron leaves the sample sufficiently rapidly that the remaining  $(N - 1)$ -electron system does not relax during the ionization process and does not interact further with the escaping electron [144]. Under this approximation, and assuming Bloch-like initial states, the photoemission intensity can be related more directly to the one-particle spectral function of the solid. In practice, relaxation and screening effects in the  $(N - 1)$ -electron system still contribute to the observed spectral shape and complicate the final-state description [144, 159]. This becomes particularly relevant for satellite features in XPS spectra, which will be discussed in more detail in the following sections.

### 3.2.1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique for investigating the chemical composition and electronic structure of materials. Because of its ability to identify elements and their chemical states, it is also referred to as electron spectroscopy for chemical analysis (ESCA). XPS employs photons in the X-ray regime, from about 100 eV up to several keV, to probe deeply bound occupied states, the core levels. These states are localized near the atomic nucleus and therefore give rise to relatively narrow features in EDCs. Since they are less influenced by the surrounding electronic structure than valence states, they are particularly well suited for elemental identification.

Core level peaks are labeled by their quantum numbers as  $nl_j$ , with the principal quantum number  $n$ , orbital angular momentum  $l$ , and total angular momentum  $j = l \pm s$ , where  $s$  is the spin angular momentum. Orbital letters are used for the angular momentum ( $s : l = 0$ ,  $p : l = 1$ ,  $d : l = 2$ , etc.). A core level with orbital angular momentum  $l > 0$  exhibits spin-orbit coupling and therefore splits into doublets, with an intensity ratio given by the degeneracy of the  $2j + 1$  states; for example,  $2p_{3/2} : 2p_{1/2} = 2 : 1$  [160, 161]. This ratio is only an approximation, since the actual intensity ratio also depends on the photon energy and polarization used [162, 163].

The binding energy of a core level depends on both the element and the orbital type. Changes in the local electron density lead to chemical shifts, typically of a few eV, with higher oxidation states appearing at higher binding energy. These shifts mainly reflect changes in the local charge density around the atom, which modify the Coulomb interaction between the core electron and the nucleus. At the same time, the absolute binding energy is also influenced by the local chemical environment and ligand geometry [164]. A well-known example is the difference between surface and bulk metal atoms, which experience different local potentials and can therefore exhibit measurable energy shifts [165, 166]. Oxidation-state assignments should therefore be made with care and are best supported by comparison to well-characterized reference compounds [167]. For some elements, especially transition metals, interpretation is further complicated by multiplet features [161], Gunnarsson–Schönhammer (GS) screening [168, 169], and other many-body effects. Nonmetallic elements are also affected by their environment and often exhibit spectra composed of several chemically shifted components. These components may arise from different bonding configurations, oxidation states, or local chemical environments of the same element within a compound, and if unresolved they often appear only as an asymmetry of the main feature [170].

As already introduced in the general discussion of PES, several physical effects influence the line shape of core level peaks in XPS spectra [144, 171]. The term *satellites* is often used as a collective term for additional spectral features with different physical origins. These include imperfections of the X-ray source, such as oxidized anodes or additional radiative transitions (“ghost lines”) [139, 144, 172]; inelastic losses such as plasmons [166, 173]; shake-up and shake-off processes [144]; and intrinsic excited-state effects such as multiplet splitting [161, 171, 174] or charge-transfer satellites [175]. Multiplet splitting originates from the interaction of the photoemission-induced core hole with the open valence shell, leading to a set of final states with different energies instead of a single unsplit line, especially for the investigated transition metals. These additional contributions can considerably complicate spectral interpretation, especially in complex materials where

features of different elements overlap or where one element occurs in several chemical environments. In such cases, peak fitting and comparison with suitable reference compounds are essential for a reliable analysis. The contribution from source-related artifacts can be reduced by using monochromatized X-rays, which also suppress Bremsstrahlung background, improve the energy resolution, and allow tighter beam focusing [166, 176].

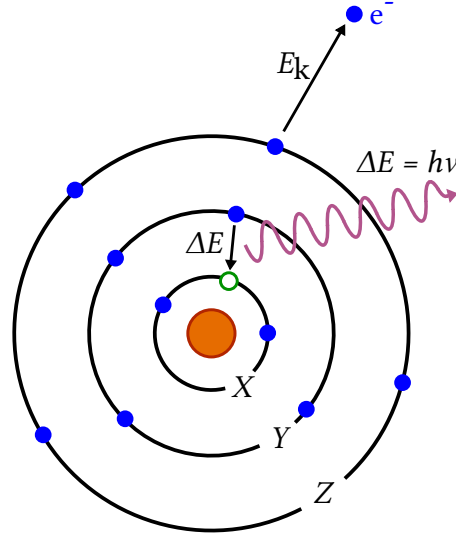


Figure 3.4.: Visualization of the Auger-Meitner and fluorescence decay processes. The core hole left after photoemission in shell X is filled by an electron from an outer shell Y. The remaining energy can be transferred to another electron Z, which then leaves the surface as an Auger electron. Alternatively, the excess energy can be released by emission of a photon  $h\nu$ .

The decay of a core-excited atom, *i.e.* the filling of the remaining core hole, can proceed via two main channels, as indicated in Figure 3.4. One is the Auger-Meitner process, in which an electron from a higher-lying occupied state Y fills the core hole X and transfers the excess energy to another electron Z. This process is denoted in XYZ notation, where the shells are given in X-ray notation ( $K \hat{=} 1s$ ,  $L_1 \hat{=} 2s$ ,  $L_2 \hat{=} 2p_{1/2}$ ,  $L_3 \hat{=} 2p_{3/2}$ , ...). The kinetic energy of the emitted Auger electron is determined by the binding energy differences of the involved states [177]:

$$E_k = E_b(X) - E_b(Y) - E_b(Z) - \Phi.$$

Spin-orbit-split states can exhibit different Auger-Meitner transitions, including (super) Coster-Kronig processes, which may lead to multiple decay channels for a given initial core hole and thus to different linewidths [166, 177]. The second decay channel is fluorescence, in which a photon is emitted instead of an electron. In the energy range relevant to this work, the decay is dominated by the Auger-Meitner processes, which can therefore generate additional spectral features.

Careful interpretation of XPS data begins already during the planning and acquisition of the experiment [167, 173, 178, 179]. Important aspects include the choice of excitation source and photon energy, the energy resolution, the measurement geometry, sample preparation and handling, and the calibration of the energy scale [180]. The photon energy determines the probing depth, as discussed in Equation 3.6, while the use of an achromatic or monochromatic X-ray source strongly influences the achievable energy

resolution. Choosing the energy resolution requires balancing signal-to-noise ratio against the ability to resolve fine spectral features, since higher energy resolution is generally accompanied by lower intensity [173]. XPS is usually performed in normal-emission geometry, with the analyzer axis aligned with the surface normal. Surface sensitivity can be enhanced by moving toward grazing emission, thereby suppressing contributions from deeper layers [181]. This can be exploited to obtain depth-dependent information from layered structures or to emphasize surface-related components. However, changing the emission angle also alters the spectral background because of scattered electrons, diffraction effects, and surface plasmon excitations [144, 181, 182].

The energy scale must also be calibrated with care. Reliable calibration is typically achieved using reference peaks such as Ag  $3d_{5/2}$ , Au  $4f_{7/2}$ , or the Fermi edge of a metallic sample [183]. Adventitious carbon is not suitable for absolute energy calibration, since its binding energy can vary with the chemical environment, although it may serve as a consistency check within a given sample series [150, 173]. For insulating samples, additional complications arise from sample charging, caused by electron emission without sufficient compensation by the drain current [184, 185]. Charging manifests itself as time-dependent peak shifts and broadening and can be mitigated by reducing the photon flux, using thin films on conductive substrates, or employing charge-compensation guns [184, 185].

To identify the elements present in an unknown sample, a survey scan is typically recorded first at moderate energy resolution and correspondingly high count rate [167, 186]; an example is shown in Figure 3.5. Peaks in this spectrum can then be assigned to specific elements and orbitals by comparison with literature or databases such as the *NIST X-Ray Photoelectron Spectroscopy Database* [187] and related reference compilations [188, 189]. In Figure 3.5, the core levels are indicated by arrows and assigned accordingly. Reliable identification requires considering all characteristic peaks of an element, not only the most intense one, since overlapping features, for example of Au and Mn or W and Ta, can otherwise lead to misinterpretation [150]. Owing to the decay processes discussed above, Auger peaks can also appear in survey spectra; they must not be confused with photoemission peaks and can be identified by their constant kinetic energy  $E_k$  when the photon energy is varied. No Auger lines are observed within the measured energy range. Towards higher binding energies, the background from secondary electrons rises strongly, although this contribution is not shown explicitly in Figure 3.5. For completeness, the Fermi level and the low-binding-energy VB region are also indicated.

Once the relevant elements have been identified, narrow scans with higher energy resolution are performed on selected peaks in order to resolve their intrinsic line shape, as shown for example in Figure 3.6. Such spectra provide more detailed information on the chemical and electronic state through their peak positions, line shapes, and relative intensities. The relative intensity of a given peak can often be enhanced by choosing a photon energy about 100 eV above the corresponding binding energy, which maximizes the photoionization cross-section [167]. Scofield [163] tabulated cross-sections for commonly used Al  $K_\alpha$  and Mg  $K_\alpha$  sources, while Yeh and Lindau [162] extended these calculations to broader photon energy ranges.

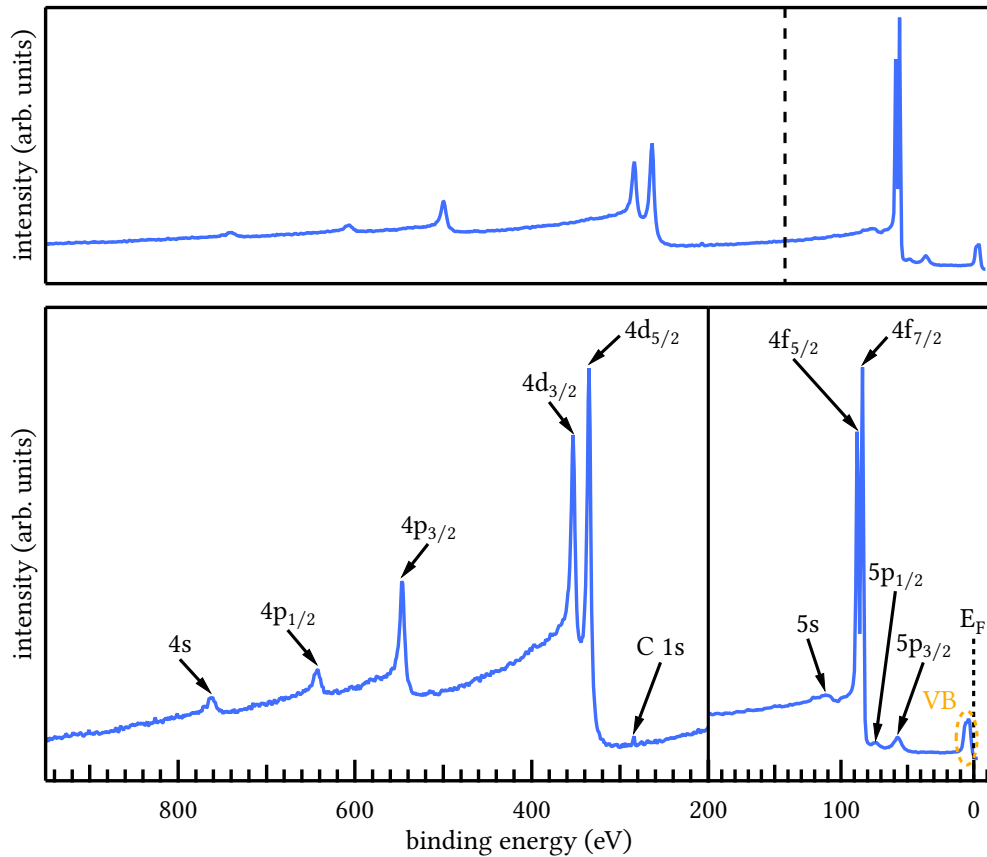


Figure 3.5.: Survey spectra of a carbon-contaminated Au(100) surface. Top: full survey spectrum illustrating the large variation in intensity across the binding energy range. Bottom: intensity-scaled view to enhance weaker contributions at higher binding energies. Labeled peaks correspond to gold core levels unless indicated otherwise. The spectrum was acquired using a near ambient pressure XPS system in UHV with a monochromatized Al  $K_{\alpha}$  source in Dortmund.

### XPS fitting and background treatment

Fitting of high-resolution XPS spectra is a common analysis tool for evaluating composition and chemical state, although it is not always necessary [166, 190, 191]. If fitting is used, a stable and physically motivated fitting procedure is essential for reliable interpretation and should incorporate prior knowledge about the system [167, 190]. This includes the expected number of components, their approximate binding energies, their intensity ratios, and their linewidths [190]. Shared broadening contributions, such as the instrumental energy resolution, can be fixed during the fitting procedure, whereas other parameters can be linked, for example the expected area ratios in a spin-orbit doublet. Appropriate boundary conditions help to obtain stable and physically meaningful fits, the mathematically best fit is not necessarily the most meaningful one [150, 190]. Effects such as X-ray photoelectron diffraction, especially in single crystals and ordered materials, or different contributions from surface and bulk layers are sometimes neglected and can lead to misinterpretation, particularly when comparing spectra recorded at different emission angles [167]. Quantitative compositions can be obtained from fitted peak areas corrected for sensitivity factors and sampling depth [183]. Because fitting procedures are often challenging and can suffer from limited reproducibility, detailed information about the fitting approach should always

be provided, including the line shapes used, the background treatment, and the applied constraints [192]. Dedicated collections and guidelines on XPS analysis and reporting are available in the literature [193–195].

The full width at half maximum (FWHM), the linewidth of a XPS signal, results from a convolution of the experimental energy resolution and the intrinsic linewidth of the investigated state [166, 171]. The natural linewidth is commonly described by a Lorentzian contribution, which is inversely proportional to the lifetime  $\tau$  of the core hole, whereas the experimental broadening contributes mainly a Gaussian component. In particular, temperature broadening, the energy resolution of the analyzer  $\Delta E$ , and the photon energy resolution  $\Delta h\nu$  all contribute to the experimental broadening [144]. The experimental broadening can be determined from the Fermi edge by fitting it with a convolution of a Gaussian and a Fermi–Dirac distribution with known temperature broadening. In this way, the width of the Fermi–Dirac distribution reflects the temperature-induced broadening, whereas the Gaussian width provides access to the instrumental resolution. Additional broadening beyond this value can be attributed to inhomogeneous effects such as vibrational disorder or local chemical variations [196, 197]. The excitation-source contribution depends on the photon source: laboratory X-ray sources usually produce photons with a Lorentzian distribution around the main photon energy, whereas synchrotron radiation introduces a predominantly Gaussian broadening around the nominal photon energy.

Electrons traveling toward the surface undergo electron–electron scattering, which produces asymmetric peak tails toward higher binding energy. This effect is most pronounced in metals, where the high density of valence states leads to strong asymmetric broadening associated with continuous electron-hole pair excitations in the valence band [144, 198]. In semiconductors and insulators, by contrast, the larger band gap leads to more discrete energy-loss structures. Consequently, metal peaks often appear asymmetric, whereas peaks from insulating systems are usually more symmetric [170]. For conductive samples, especially metals, asymmetric line shapes such as Doniach–Šunjić functions convoluted with a Gaussian [166, 171] or asymmetric pseudo-Voigt functions [171] are commonly used. For nonmetals, more symmetric Voigt or pseudo-Voigt functions are typically appropriate [171]. Voigt functions are convolutions of Gaussian and Lorentzian components and therefore account for both experimental and intrinsic broadening [190].

Just as the choice of a suitable line shape is important for describing the underlying physical processes, the choice of background function is equally important for reliable fitting. It strongly influences the evaluated peak areas and therefore the quantitative information extracted from the spectra [166, 190]. The spectral background in XPS arises primarily from inelastically scattered electrons. A common way to describe this contribution is the Shirley background. The Shirley background  $B(E)$  assumes a constant loss probability of scattering electrons and describes the background as an integral over the intensity, from higher to lower kinetic energy, resulting in a step-like background with an inflection point below each peak, as shown in Figure 3.6. It can be written as

$$B(E) = g \cdot \int_E^{\infty} I(E') dE' + b, \quad (3.10)$$

where  $I(E')$  is the measured intensity at energy  $E'$ ,  $b$  is an offset, and  $g$  is a scaling constant determining the step height [199, 200]. The background correction should be carried out

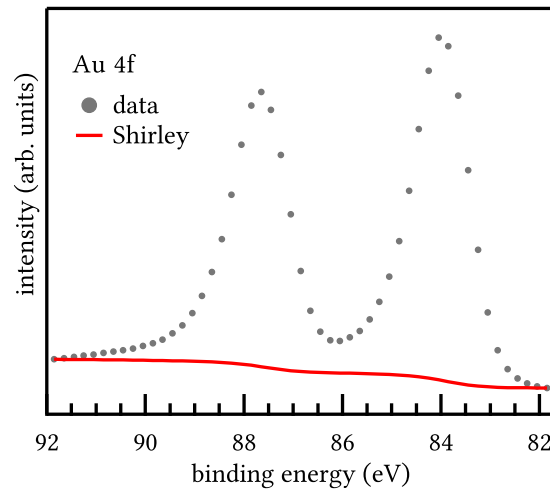


Figure 3.6.: Au 4*f* core level spectrum of a clean Au(100) surface together with the evaluated iterative Shirley background. The spectrum was acquired with a near ambient pressure XPS system in UHV using a monochromatized Al  $K_{\alpha}$  source in Dortmund.

iteratively and included in the fitting procedure together with the peak structure [190, 201]. A more sophisticated approach is the Tougaard background [202, 203], which is based on a calculated loss function and a scattering probability that depends explicitly on the electron energy [200]. The parameters used for this background are largely derived from theory, with only small adjustments made to experimental data. The Tougaard approach is well established for metals, alloys, and transition metal oxides, but it is less suitable for materials with larger band gaps. For some spectra, simpler approaches such as linear or spline-like backgrounds, or combinations of several simple background functions, may already be sufficient [167, 204–206]. Reliable determination of the background requires a sufficiently wide spectral window on both sides of the investigated peak [200]. In practice, this is not always feasible because other spectral features may appear in the same energy range, for example intrinsic core levels, source-related satellite features, or simply because acquisition time is limited.

### XPS setup

In this work, XPS experiments were performed at the University of Graz in the group of Martin Sterrer using a Phoibos 100 (SPECs GmbH) hemispherical analyzer in normal-emission geometry. An achromatic dual-anode X-ray source (SPECs XR50) with an incidence angle of  $55^{\circ}$  was employed, and a five-channel electron multiplier was used for detection. Details on the energy resolution during the different measurement periods are given in Section A.5. The energy scale was calibrated using the Au 4*f*<sub>7/2</sub> peak at 84 eV as reference [207]. From the fitting procedure, a typical statistical uncertainty in the peak positions of about  $\pm 100$  meV is obtained; this must be combined with the overall experimental energy resolution. Some measurements were acquired by Olga Resel on the same setup in Graz after the X-ray anode had been replaced and interfering radiation from the silver primer layer of the anode had been eliminated. The corresponding spectra are identified in the figure captions.

### 3.2.2. Ultraviolet photoelectron spectroscopy

UPS has become an indispensable tool in surface science and materials research. In contrast to XPS, UPS uses ultraviolet light with photon energies between 5 eV and 100 eV. Consequently, UPS focuses on the valence band (VB) region, which is directly involved in chemical bonding. The energetic and momentum distribution of the electronic states largely governs the physical and chemical properties of a material [65]. Valence band states are typically not localized around individual atomic nuclei, but are often delocalized over several atomic sites and form energy bands in crystalline solids. In EDCs, such delocalized states therefore appear as broadened features near the Fermi level rather than as sharp, discrete peaks.

Contributions from different elements and orbitals can be distinguished by calculating the projected density of states (PDOS) and comparing it with the measured spectra. In addition, spectral features often show characteristic polarization and photon energy dependences, which can provide further support for their assignment when spectra are acquired under different excitation conditions [62, 94, 145]. The relatively low photon energy used in UPS leads to low kinetic energies of the emitted electrons and therefore to high surface sensitivity, with a typical probing depth of about 0.5 nm to 2 nm [144, 208]. At the same time, the limited photon energy restricts the accessible binding energy range. For this reason, UPS is often used together with XPS to obtain a more complete picture of the electronic structure.

In addition, UPS is well suited to monitor changes in the WKF induced by different surface terminations, adsorbates, or chemical and geometric modifications [139, 209]. The sample WKF  $\Phi$  can be determined from the secondary-electron cutoff. The energy interval between the Fermi edge  $E_F$  and the secondary-electron cutoff  $E_{\text{sec}}$ , together with the incident photon energy  $h\nu$ , yields

$$\Phi = h\nu - |E_F - E_{\text{sec}}|, \quad (3.11)$$

as described in Refs. [210, 211].

UPS spectra are often measured in normal emission and therefore collect electrons from a small region around the  $\Gamma$  point of the Brillouin zone. Changing the measurement geometry probes a different region in  $k_{\parallel}$  space and can therefore reveal distinct spectral features arising from the band structure. To obtain explicit momentum-resolved information, the emission angle must also be measured. This is the basis of ARPES, which is discussed in the following section.

### 3.2.3. Angle-resolved photoelectron spectroscopy

ARPES extends UPS by additionally detecting the emission angle of the photoelectrons. Within the usual approximations discussed above, the crystal momentum of the initial electronic states can then be accessed from the emission angle using Equations 3.2 and 3.3. In this way, ARPES provides momentum-resolved information on the electronic band structure and the Fermi surface, and thereby offers unique insight into dispersive states, many-body interactions, and electron-correlation effects [139, 144, 159].



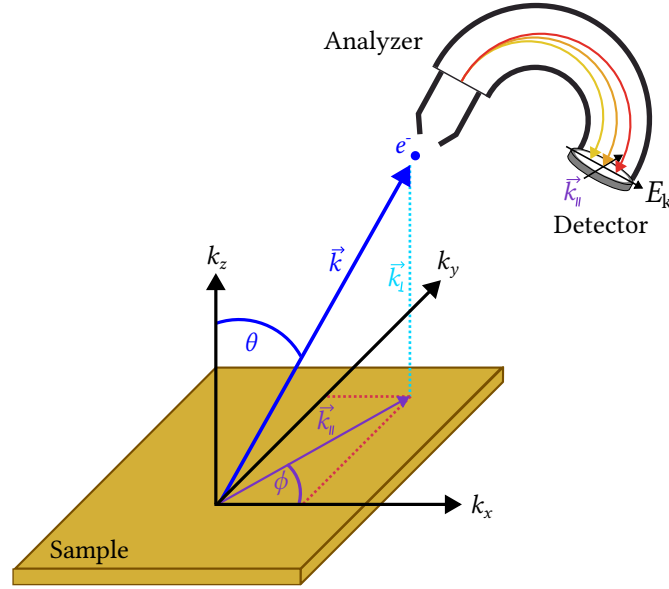


Figure 3.7.: ARPES measurement geometry: electrons emitted at  $\theta$  and  $\phi$  are accepted by the hemispherical analyzer and energy-dispersed onto the detector, providing  $I(E_k, k_{||})$  with  $k_{||} = (k_x, k_y)^T$ .

In contrast to XPS and angle-integrated UPS, ARPES employs a two-dimensional detector. One detector axis corresponds to the energy-dispersion direction, while the other covers a certain range of  $k_{||}$ , depending on the alignment of the analyzer relative to the sample, as indicated in Figure 3.7. Each spectrum recorded at a fixed angular setting of the analyzer therefore represents a one-dimensional cut through the band structure along a specific direction in reciprocal space, typically within an angular acceptance range of about  $\pm 20^\circ$ . Recording the intensity as a function of kinetic energy and emission angle yields a two-dimensional image in which the intensity is mapped as a function of energy and momentum. Such representations are referred to as band maps (BMs), an example of which is shown in Figure 3.8b. By scanning over different emission angles, a full three-dimensional data set can be assembled, as illustrated in Figure 3.8c. The resulting angle- and energy-dependent spectra directly reveal the electronic dispersion.

Furthermore,  $k_{||}$  from Equation 3.2 can be decomposed into its Cartesian components,

$$k_x = k_{||} \cdot \cos(\phi), \quad (3.12)$$

$$k_y = k_{||} \cdot \sin(\phi), \quad (3.13)$$

where  $\phi$  is the azimuthal emission angle. In order to analyze the electronic structure, three types of data extraction from the three-dimensional data set are commonly considered: EDCs, BMs, and constant-energy maps, as visualized in Figure 3.8.

Integration over a defined region in the measured momentum range yields angle-integrated EDCs as shown in Figure 3.8a. These resemble conventional UPS spectra, but with the advantage that a specific region of interest in reciprocal space can be selected. EDCs are useful for analyzing non-dispersive features and for comparison with density of states (DOS) calculations, although they mix contributions from all bands present within the selected momentum range.

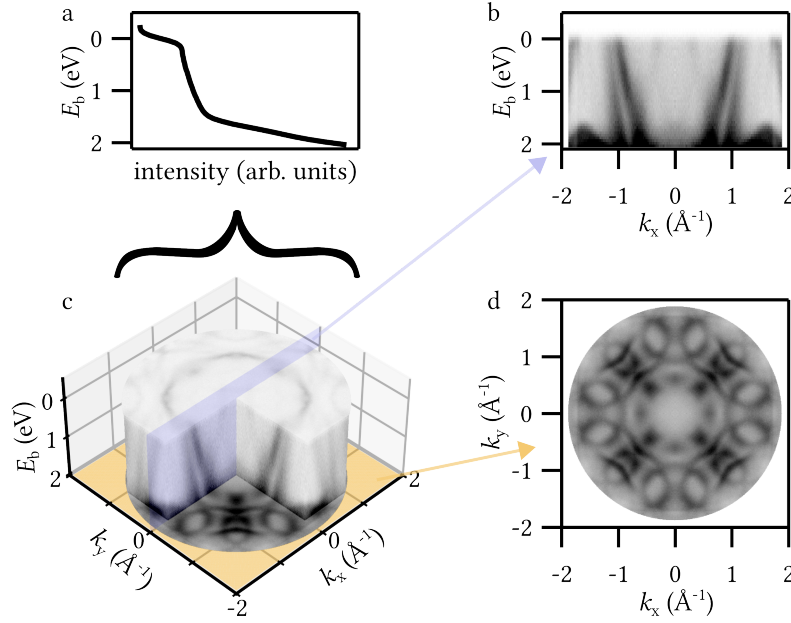


Figure 3.8.: Visualization of the data extraction from the three-dimensional data cube shown in panel (c). (a) EDC obtained by integrating over momentum space. (b) BM cut along  $k_y = 0$ , indicated by the light-blue plane in panel (c). (c) Three-dimensional data cube in  $(E, k_x, k_y)$ . (d) Constant-energy layer extracted from the data cube, indicated by the light-orange plane in panel (c).

In addition to EDCs, BMs can be extracted by selecting a narrow momentum range and plotting the intensity as a function of momentum and binding energy. Figure 3.8b presents such a BM, extracted along the blue plane in panel (c). They are particularly useful for analyzing dispersive features.

The data can also be sliced at fixed energy over a two-dimensional momentum range to generate constant-energy maps, also referred to as momentum maps. These maps visualize the distribution of spectral weight in  $\vec{k}$ -space at a given energy, as shown in Figure 3.8d.

ARPES experiments can be performed both at synchrotron radiation facilities and in laboratories using gas-discharge lamps or laser sources. Synchrotron-based ARPES offers several important advantages. The photon energy can be tuned continuously, which allows one to select a specific  $k_{\perp}$  and to optimize the photoionization cross-sections. While laboratory systems can also provide different photon energies, this is usually possible only with considerably greater effort and only at discrete energies. In addition, the polarization of the light can be adjusted more flexibly at synchrotrons, typically allowing access to different linear and circular polarizations. This can be used to investigate orbital symmetries, since the polarization modifies the dipole matrix elements and thus the measured intensity distribution in momentum space [145, 212]. The high photon flux available at synchrotrons also enables the investigation of weakly dispersive states and subtle many-body effects, because sufficient signal-to-noise ratio can be achieved within reasonable acquisition times. Modern ARPES setups reach energy resolutions of about 10 meV [139], and in specialized cases down to 1.5 meV [213], allowing very detailed studies of complex materials. Hemispherical-analyzer-based systems can furthermore achieve angular resolutions on the order of  $0.1^\circ$ , corresponding to about  $0.0004 \text{ \AA}^{-1}$  in momentum space [214].

### 3.2.4. Momentum microscopy

Momentum microscopy (MM) simplifies ARPES measurements by largely avoiding the need to mechanically rotate the sample during data acquisition. It relies on a cathode (immersion) lens, which applies a high extraction voltage, typically 10 kV to 15 kV, between the sample and the first lens element (extractor). This allows photoelectrons emitted into a very large angular range above the sample to be collected. In practice, the maximum acceptance angle depends on the lens settings, the kinetic energy, and the selected apertures, and can extend to angles close to  $\theta = \pm 90^\circ$  [215]. Owing to the symmetry of the extraction field, the lens preserves the angular distribution of the emitted photoelectrons and thereby allows reconstruction of their in-plane momentum distribution.

After acceleration away from the sample, the electrons pass through a lens column consisting of electrostatic lenses that maps the electron distribution onto the analyzer entrance, as sketched in Figure 3.9. The electrons then enter an energy analyzer, typically either a hemispherical analyzer or a time-of-flight (TOF) analyzer, which sorts them according to their kinetic energy. A second lens column then projects the resulting two-dimensional electron distribution onto the detector.

MM can be operated in two complementary modes, namely real-space imaging and momentum-space imaging, by using the electron distribution in the back-focal plane of the cathode lens. In real-space mode, the spatial distribution of photoelectrons emitted from the surface is imaged onto the detector, providing information on the surface morphology and, depending on the selected kinetic energy, chemical contrast with high lateral resolution. In momentum-space mode, the angular distribution of the photoelectrons is imaged, yielding the momentum maps shown in Figure 3.8d. This allows reconstruction of the electronic band structure and the Fermi surface. Switching between these modes is achieved by changing the electrostatic lens settings, enabling complementary access to both structural and electronic properties. In the context of organic materials, MM provides direct information on the occupied valence electronic structure, including the energetic position of the highest occupied molecular orbital (HOMO) levels in organic semiconductors (OSCs) and thin films, whose signatures often extend to comparatively high momenta. It also gives access to band alignment at interfaces, which is crucial for the performance of devices such as photovoltaics and organic light-emitting diodes (OLEDs) [216].

As illustrated in Figure 3.9, apertures are used to restrict either the probed area in real space, via the field aperture (FA) in an image plane, or the accepted momentum range, via the contrast aperture (CA) in the back-focal plane. The FA defines the size and location of the probed surface region, whereas the CA selects specific emission angles and can therefore enhance contrast in real-space images by suppressing undesired momentum channels. Since the probed real-space region can be reduced to several  $\mu\text{m}$  [215], the method is often also referred to as  $\mu$ -ARPES.

Reconstruction of the in-plane crystal momentum  $k_{\parallel}$  follows the same principle as in ARPES, using Equation 3.2. In practice, calibration of momentum space is commonly performed using a reference sample with known band features, for example gold surface states, and/or characteristic intensity distributions of secondary electrons. Secondary electrons parabolic dispersion can be used directly for momentum calibration. Fitting this parabola provides a practical conversion from detector pixels to  $\text{\AA}^{-1}$  for momentum images. The overall energy

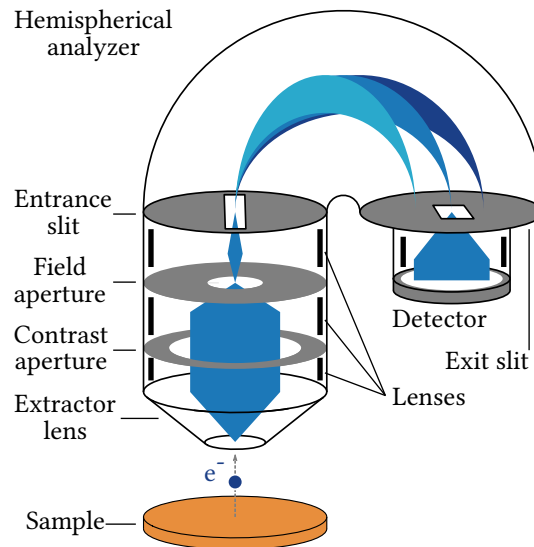


Figure 3.9.: Sketch of the layout of the KREIOS MM from SPECS GmbH. The image shows the lens column consisting of the extractor lens, electrostatic lenses, the CA in the back-focal plane, and the FA in the image plane. The lens column is followed by the hemispherical analyzer, where the electrons are separated according to their  $E_k$ . Finally, a second set of electrostatic lenses projects the two-dimensional electron distribution onto the detection unit. Figure adapted from [217].

resolution of a momentum microscope is limited by the settings of the energy analyzer, the photon bandwidth, space-charge effects, and the sample temperature.

The resulting measurement is a three-dimensional data cube with the two momentum components ( $k_x, k_y$ ) parallel to the surface and the binding energy ( $E_b$ ) along the third axis, as illustrated in Figure 3.8c. In the case of a hemispherical analyzer, a two-dimensional  $k_{||}$  image is recorded within a selected energy window, yielding a momentum map as shown in Figure 3.8d. The full three-dimensional data cube is then obtained by scanning the kinetic energy [218]. In contrast, a TOF analyzer determines the kinetic energy from the flight-time delay of the individual electrons. It can therefore record the entire three-dimensional stack in a single shot, although it is restricted to pulsed light sources.

The main advantage of MM over conventional ARPES is the ability to capture the full in-plane momentum space simultaneously. This considerably simplifies the measurement, since one does not need to account for changing light-incidence conditions, matrix-element variations, or changes in the illuminated area caused by mechanical sample rotation, as is often the case in conventional ARPES. This gain in acquisition efficiency comes at the expense of reduced energy and momentum resolution compared with state-of-the-art hemispherical ARPES setups. MMs can reach momentum resolutions of about  $0.005 \text{ \AA}^{-1}$  [219]. Owing to this high acquisition efficiency, MM is increasingly applied to molecular systems, whose orbitals often produce spectral intensity at relatively large  $k_{||}$ . At the same time, the requirement of a homogeneous extraction field restricts the method to sufficiently flat and conductive samples. Furthermore, the maximum usable count rate in momentum microscopes is limited by space-charge effects, caused by strongly focused electrons inside the lens system. High local count rates can lead to Coulomb interactions between photoelectrons, which broaden the energy distribution and smear out the momentum images [220]. For conventional ARPES setups this limit is typically

reached at much higher count rates [221]. Together with the generally higher resolution and the broader availability of conventional analyzers, this explains why standard ARPES remains more widely used in many laboratories.

### Momentum microscope setup

The MM measurements were carried out on a KREIOS 150 momentum microscope (SPECS GmbH) at TU Dortmund, equipped with a hemispherical energy analyzer. The electrons passing through the lens system and the energy analyzer were multiplied by a MCP and projected onto a fluorescence screen, which was recorded with a two-dimensional CMOS camera. The system can achieve an energy resolution down to 25 meV and a  $k_{\parallel}$  resolution down to  $0.008 \text{ \AA}^{-1}$  [217, 222]. In this thesis, the MM was operated at a pass energy of 50 eV, with an extractor voltage of 10 keV applied. No CA or FA was inserted, and the magnification was set to 2, resulting in a field of view of about  $\pm 2 \text{ \AA}^{-1}$ . Entrance slit 5, with dimensions of  $0.5 \text{ mm} \times 1.0 \text{ mm}$ , was used. As excitation source, a monochromatized He I $_{\alpha}$  gas-discharge lamp ( $h\nu = 21.2 \text{ eV}$ ) was used. This source provides predominantly p-polarized light at an incidence angle of  $\alpha = 68^\circ$ . During the experiments, the samples were kept at room temperature and the base pressure was about  $3 \times 10^{-10} \text{ mbar}$ .

### 3.2.5. Photoemission orbital tomography

Photoemission orbital tomography (POT) is a method for identifying molecular orbital (MO) contributions in photoemission spectra by comparing experimentally measured momentum maps with theoretically calculated momentum distributions. The method was first introduced by Puschnig et al. [223] and requires ordered molecular layers in which the molecules share a common azimuthal orientation. Without such ordering, the characteristic patterns in the momentum maps would be averaged out.

The calculation of theoretical momentum distributions proceeds in three steps and assumes a plane-wave-like final state. First, density functional theory (DFT) is used to calculate the molecular structure, including the bond lengths and overall geometry, as well as the molecular orbitals and their occupation, as illustrated in Figure 3.10a. Second, the orbital wave functions are Fourier transformed to reciprocal space, as shown in Figure 3.10b. Finally, the resulting three-dimensional momentum distribution is cut at constant kinetic energy to obtain simulated momentum maps that can be compared directly with experiment, Figure 3.10c and d.

This makes it possible to assign spectral features that are typically broad and weak in EDCs to their molecular-orbital origin, even in cases where charge-transfer effects or hybridization are relevant. As a result, POT can also provide information on the interaction strength between molecules and the substrate, for example when gas-phase lowest unoccupied molecular orbitals (LUMOs) become occupied and identified through their momentum pattern.

In the plane-wave final-state approximation, the photoelectron intensity for orbital  $i$  can be written as

$$I_i(\theta, \phi) \propto |\vec{A} \cdot \vec{k}|^2 |\tilde{\psi}_i(\vec{k})|^2, \quad (3.14)$$

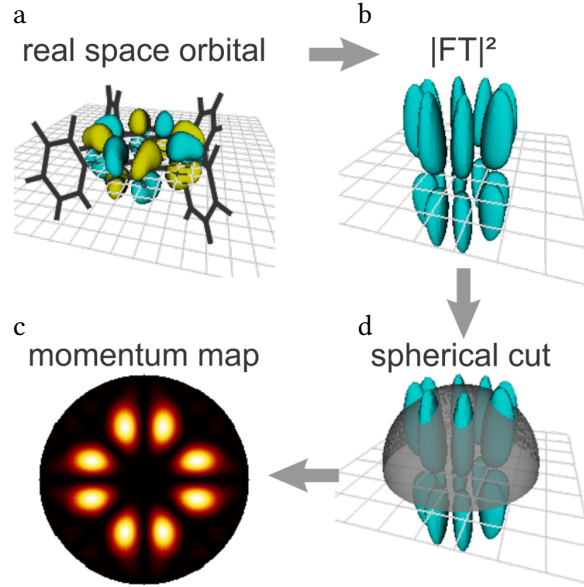


Figure 3.10.: Illustrative scheme of how momentum distributions are calculated theoretically. (a) Real-space orbitals are calculated for the relaxed molecular structure. (b) Fourier transformation of the molecular orbital. (c) Final momentum distribution. (d) Spherical cut at constant kinetic energy. Adapted with permission from [224].

where  $\tilde{\Psi}_i(\vec{k})$  is the Fourier-transformed initial-state wave function. The factor  $|\tilde{\Psi}_i(\vec{k})|^2$  encodes the shape of the molecular orbital and therefore determines the characteristic intensity distribution, whereas the term  $|\vec{A} \cdot \vec{k}|^2$  introduces a polarization dependence set by the experimental geometry. In practice, degenerate or quasi-degenerate orbitals that lie within the experimental energy resolution must be summed. Furthermore, substrate-related features must be considered in order to isolate the molecular contribution, and a presence of multiple rotational domains has to be taken into account when comparing experiment and theory. Beyond confirming the involvement of specific molecular orbitals in the electronic structure, POT can also provide information on adsorption geometry and molecular conformation. For example, POT has been used to determine the tilt angle of pentacene in multilayer films [225] and to detect saddle-shaped deformations in porphyrins [51].

### 3.3. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) provides information complementary to photoemission techniques by probing unoccupied electronic states and their orientation. In contrast to XPS and UPS, where the photon energy is typically fixed, XAS requires tunable photon energies in the X-ray range, only available at synchrotron radiation facilities. By scanning the photon energy across an absorption edge and measuring the corresponding absorption signal, one gains access to both the electronic structure and the local geometric arrangement of atoms or molecular orbitals.

The attenuation of light intensity in matter follows the Beer–Lambert law,

$$I(z) = I_0 e^{-\mu(h\nu)z}, \quad (3.15)$$

with the initial intensity  $I_0$ , the path length  $z$ , and the absorption coefficient  $\mu(h\nu)$ , which depends on both the material and the photon energy. In general, the absorption decreases with increasing photon energy, approximately following a  $(h\nu)^{-3}$  dependence [226]. Near the absorption edges of specific elements, however,  $\mu(h\nu)$  increases strongly due to excitations of core electrons into unoccupied states above the Fermi level. In the soft X-ray regime, the absorption coefficient is dominated by the photoelectric effect, and the dipole approximation introduced in Equation 3.9 is valid in the energy range of about 150 eV to 2000 eV [104, 138]. Thus, when the photon energy  $h\nu$  matches the energy difference between an initial core state  $E_i$  and a final unoccupied state  $E_f$ , a resonant excitation occurs, and the absorption probability is strongly enhanced. Sharp resonances in the absorption spectrum reflect discrete bound unoccupied states, whereas a step-like increase corresponds to the ionization threshold, at which the excited electron is promoted into the continuum. At higher energies, these resonances can overlap with scattering-related features arising from interference between the outgoing photoelectron wave and waves scattered by neighboring atoms. Because the initial state in XAS is a core level, it allows selective probing of individual elements in complex materials.

The XAS signal can be detected either directly, by measuring the transmitted intensity, or indirectly via secondary processes. Direct transmission measurements are only feasible for sufficiently thin samples, such as foils or gases, and require detectors before and after the sample to measure the incident and transmitted intensities. Gas cells with capacitor-like electrodes are often used as detectors by measuring the ionization current of the gas, which is proportional to the intensity. More commonly in surface science, XAS is measured via secondary processes, namely fluorescence yield (FY), partial electron yield (PEY), and total electron yield (TEY). FY relies on photons emitted during core-hole decay; because of the long escape depth of these photons, the technique is relatively bulk-sensitive. In contrast, electron-yield techniques detect electrons generated during the absorption and decay processes. X-ray absorption can lead to the emission of primary photoelectrons, while the subsequent decay process can generate Auger electrons and secondary electrons. Both PEY and TEY are therefore more surface-sensitive because of the limited IMFP of electrons, similar to PES (Equation 3.6) [227]. PEY employs a retarding field or an energy analyzer to select electrons above a defined kinetic-energy threshold or specific Auger lines. In contrast, TEY collects all emitted electrons, including primary photoelectrons, Auger electrons, and secondary electrons, by measuring the resulting drain current. In the soft X-ray regime, the fluorescence yield is relatively low, so electron-yield modes are often preferred, in particular TEY [228].

The TEY mode used in this thesis is based on measuring the current flowing from ground to the sample, which compensates for the electrons emitted into the vacuum. This current is proportional to the number of absorbed photons and thus to  $\mu(h\nu)$ . To evaluate the absorption signal quantitatively, the incident photon flux  $I_0$  must be monitored. This is typically done using a grid in front of the sample or by measuring the drain current of the last mirror before the sample. Both signals can be used to normalize the measured TEY and thereby eliminate fluctuations in photon flux caused by variations in storage-ring current or beamline efficiency.

Because different physical processes dominate in different energy ranges around an ionization threshold, X-ray absorption spectra are commonly divided into two regions, each of which contains rich information on the electronic structure and local geometry. The

region near the absorption edge is known as the near-edge region and is often referred to as near-edge X-ray absorption fine structure (NEXAFS) or X-ray absorption near-edge structure (XANES); it extends from below the edge to a few tens of eV above it. The sharp resonances in this region result from transitions into bound unoccupied states and depend strongly on the symmetry of the initial and final states, as described by the dipole transition probability in Equation 3.8. These near-edge features are sensitive to the chemical species and its local environment, since both affect the energy levels and the density of unoccupied states. Just above the ionization threshold, electrons are promoted into continuum-like states, leading to a step-like increase in absorption. At higher energies, typically 50 eV to 1000 eV above the edge, the spectrum is dominated by oscillatory features arising from interference between the outgoing photoelectron wave and waves scattered by neighboring atoms. This region is known as extended X-ray absorption fine structure (EXAFS) and provides information about the local atomic arrangement, including bond lengths and coordination numbers [229].

In the NEXAFS region, the absorption probes unoccupied states of well-defined symmetry, and the dipole selection rules must be considered. For electric-dipole transitions, the change in orbital angular momentum is restricted to  $\Delta l = \pm 1$ , while the spin remains unchanged ( $\Delta s = 0$ ) [174]. Transitions from a given core shell are denoted by capital letters according to the principal quantum number  $n$ : K for  $n = 1$ , L for  $n = 2$ , M for  $n = 3$ , and so on. While the K-edge involves transitions from 1s core levels, spin-orbit coupling splits the L-edge into subshells; for transition metals, the  $L_3$  and  $L_2$  edges correspond to the  $2p_{3/2}$  and  $2p_{1/2}$  core levels, respectively, while  $L_1$  denotes the 2s level. The final states in the valence region participate in bonding and are therefore often complex: depending on the system, the near-edge features may be associated with atomic-like orbitals, molecular orbitals, or band states in solids. In a coordination environment, additional splitting arises from ligand-field effects, which lift orbital degeneracies and can produce multiplet structures. Although the dipole selection rules reduce the number of allowed transitions, the remaining transitions can still lead to complicated line shapes in the absorption spectrum [229]. Distinguishing different species of the same element can nevertheless remain challenging, because XAS probes a macroscopic area and therefore averages over multiple sites.

Polarization-dependent K-edge NEXAFS is frequently used to extract geometric information and molecular conformation of adsorbates [104]. The K-edge probes transitions from the 1s ( $l = 0$ ) core level into  $2p$ -like final states ( $l = 1$ ) [104] and thus provides access to unoccupied molecular orbitals. Because the transition probability depends on the projection of the electric-field vector onto the symmetry axis of the final state, polarization-dependent measurements directly relate spectral intensity to orbital orientation and therefore to adsorption geometry.

For planar  $\pi$ -conjugated molecules such as porphyrins, this makes it possible to distinguish  $\pi^*$  and  $\sigma^*$  resonances. The  $\pi^*$  orbitals have electron density perpendicular to the local bond direction and typically out of the molecular plane, whereas  $\sigma^*$  orbitals are oriented along the bond direction. Accordingly, at grazing incidence with linearly polarized X-rays, p-polarized light couples strongly to out-of-plane  $\pi^*$  orbitals, while transitions into in-plane  $\sigma^*$  orbitals are suppressed; the opposite tendency is obtained for geometries in which the electric field lies predominantly in the surface plane, as illustrated in Figure 3.11.



If  $\vec{O}$  denotes the symmetry direction of the final-state orbital and  $\vec{E}$  the electric-field vector of the incident light, the absorption intensity can be written as

$$I \propto |\vec{E} \cdot \vec{O}|^2 \propto \cos^2(\theta), \quad (3.16)$$

where  $\theta$  is the angle between  $\vec{E}$  and  $\vec{O}$ . The absorption is therefore maximal when both are parallel (Figure 3.11b) and strongly reduced when they are perpendicular (Figure 3.11c) [230]. Equivalent information can be obtained either by switching between p- and s-polarized light or by varying the incidence angle  $\alpha$  of p-polarized light, which changes the projection of  $\vec{E}$  onto the surface normal  $\vec{n}$ . The resulting difference in spectral intensity is referred to as X-ray linear dichroism (XLD) and can be used to assign orbital symmetries as well as to determine molecular tilt angles and adsorption geometries [228].

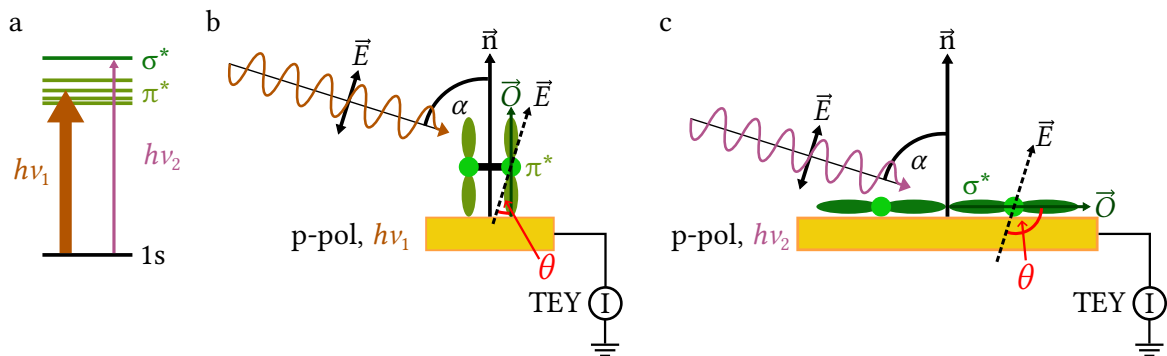


Figure 3.11.: Schematic illustration of the polarization dependence of K-edge NEXAFS. (a) Transitions from the 1s core level into  $\pi^*$  and  $\sigma^*$  final states, where the arrow thickness represents the relative absorption probability, corresponding to the alignment in b and c. (b) Strong coupling for a  $\pi^*$  orbital whose symmetry axis has a large projection onto the electric-field vector  $\vec{E}$ . (c) Suppressed absorption for a  $\sigma^*$  orbital when  $\vec{E}$  is largely orthogonal to the orbital direction.

L-edges are commonly used to probe the oxidation state and orbital orientation of transition metals [226]. In this case, the XLD signal originates from the different orientations and symmetries of the  $d$ -derived valence orbitals involved in bonding. Because the five  $d$  levels split in a ligand or crystal field, as discussed in Section 1.1, the spectra exhibit multiple features that can be described by transitions of the type

$$2p^6 3d^n \rightarrow 2p^5 3d^{n+1}.$$

If oxidation states are determined by comparison with reference spectra, only systems with similar local symmetry and coordination should be used, because differences in crystal-field splitting can strongly modify the spectra [226]. In general, higher oxidation states shift the edge position toward higher photon energies [226].

For transition metals, where predominantly  $d$  orbitals are probed, the spin state influences the spectral-weight distribution because only unoccupied or partially occupied  $d$  orbitals contribute to the absorption. In a high-spin (HS) configuration, the maximum possible number of  $d$  orbitals is singly occupied, whereas in a low-spin (LS) configuration some orbitals are fully occupied while others remain completely empty. This leads to characteristic changes in the intensity distribution across the L-edge features.

In summary, XAS can reveal the orientation and symmetry of unoccupied orbitals, for example molecular tilt angles and adsorption geometries, probe oxidation states through the number and energy of unoccupied states, and provide information on ligand-field strength and symmetry, as well as indications of the spin state of transition metal centers [228, 229, 231].

## BOREAS beamline

The XAS measurements presented in this work were performed at the BOREAS beamline at the ALBA synchrotron facility in Barcelona, Spain, using soft X-rays. Total electron yield mode was employed by measuring the sample drain current and normalizing it to the drain current of a freshly evaporated gold grid in front of the sample. NEXAFS spectra were recorded in grazing incidence, with an angle of  $\alpha = 70^\circ$  relative to the surface normal, using both linear-horizontal and linear-vertical polarization. A defocused beam with a size of  $800 \times 300 \mu\text{m}^2$  and a photon flux of about  $\sim 10^{12}$  photons/s was used in order to minimize beam-induced damage to the molecular layers. In addition, a small magnetic field of about 50 mT, applied parallel to the light-incidence direction, was used to reduce noise in the spectra. Table 3.1 gives an overview of the magnetic fields and temperatures used for the different samples and absorption edges. The experimental beamline setup is described in more detail elsewhere [232].

| absorption edge | sample    | temperature (K) | magnetic field (T) |
|-----------------|-----------|-----------------|--------------------|
| N K-edge        | MnTPyP    | 300             | 0.05               |
|                 | Co-MnTPyP | 300             | 0                  |
| Mn L-edge       | MnTPyP    | 300             | 0.05               |
|                 | Co-MnTPyP | 300             | 0.05               |
| Co L-edge       | Co-MnTPyP | 4.5             | 6                  |

Table 3.1.: Experimental conditions used for the XAS measurements, listing the sample temperature and applied magnetic field for each absorption edge and sample.

Nitrogen absorption spectra were calibrated using the absorption signal at the last mirror by measuring its drain current and aligning the corresponding feature to the reference value of 398.45 eV, which had been calibrated using the  $\text{N}_2$  gas absorption spectrum at the ALOISA beamline in Trieste, Italy [233]. Since this was only possible for the first sample, the characteristic first peak of the subsequent nitrogen spectra was set to 398.6 eV, matching that of the first measurement. Small deviations between different metal centers are expected, but the mirror reference was available only during the first measurements; therefore, a potentially small transmetallation-related shift was neglected. The manganese and cobalt L-edges were calibrated by measuring a CoO reference sample and shifting the photon energy scale to match the reference spectra reported by Regan et al. [234], more specifically by setting the main Co resonance to 776.08 eV. Background removal was performed separately for each polarization and spectrum by subtracting a cubic-spline background function, and the spectra were interpolated to equal photon energy steps for further analysis.

# 4

## Formation and properties of the Co–MnTPyP MOF

This chapter addresses the preparation of the MnTPyP self-assembled molecular layers (SAM) and the Co–MnTPyP metal–organic framework (MOF) and focuses on both their geometric and electronic structure. The discussion emphasizes the changes induced by coordination and is organized according to the experimental methods. First, the sample preparation is described in Section 4.1, while Section 4.2 focuses on the geometric structure as determined by LEED and nitrogen K-edge NEXAFS. The electronic structure is discussed in Section 4.3, combining XPS, NEXAFS, and MM. As will be shown, the data indicate that Mn is replaced by Co after cobalt deposition onto the pristine MnTPyP layer. To investigate the electronic structure in more detail, reference systems based on CoTPyP and Co–CoTPyP are introduced where appropriate and discussed in the corresponding sections. Nevertheless, the nomenclature Co–MnTPyP is retained in order to distinguish this MOF from the one prepared from CoTPyP with additional Co, referred to as Co–CoTPyP. Data analysis in this chapter was carried out with Spot Plotter [235] for LEED, Python for XPS, and IGOR Pro 8 [236] for XPS, NEXAFS, and MM.

### 4.1. Sample preparation and coverage calibration

Prior to network formation, the Au(100) substrate was cleaned by repeated cycles of Ar<sup>+</sup> ion sputtering at 2 keV and subsequent annealing at 750 K. Surface cleanliness was verified by LEED through the well-known c(28 × 48) reconstruction of Au(100) [119], shown in Figure 4.1a. The clear fourfold symmetry of the surface is apparent from the main spots of the square unit cell of the unreconstructed surface, marked in green. The assignment of the LEED spots of gold to the corresponding high-symmetry real-space directions was taken from Reference [119]. Where available, the absence of surface contamination (*i.e.*, O, N, and C) was additionally verified by XPS.

The pristine MnTPyP monolayer (ML) was prepared by sublimation of commercially available Mn(III) *meso*-tetra(4-pyridyl)porphine chloride (MnClTPyP, Frontier Specialty Chemicals) onto a clean Au(100) single crystal held at room temperature from a Knudsen cell kept at 660 K. Prior to deposition, the molecules were outgassed for several hours at 520 K in order to remove residual organic contamination. It should be noted that Cl dissociates during the deposition and outgassing process, as discussed in Section 4.3.1; accordingly, the notation MnTPyP is used in the following. The molecules were deposited stepwise until a full ML was reached. Upon completion of a full monolayer, the LEED pattern of the surface reconstruction was suppressed and additional sharp diffraction spots appeared, see Figure 4.1b. When the coverage exceeded one monolayer, these spots became blurred, indicating the formation of a disordered second layer. The calibration of one full monolayer was performed once in Dortmund by tracking the deposition rate ( $\sim 0.12 \text{ \AA}/\text{min}$ ) with a quartz crystal microbalance (QCM). Consistency of the sample preparation across different

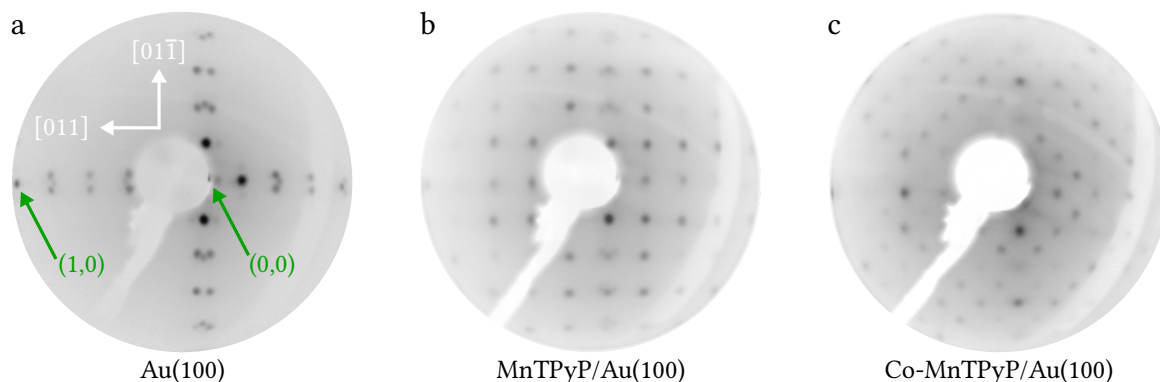


Figure 4.1.: LEED image of (a) the clean Au(100) surface, (b) the MnTPyP SAM, and (c) the Co–MnTPyP MOF, all recorded at a kinetic energy of 25 eV. In (a), the high-symmetry directions of the Au(100) surface are indicated by white arrows, together with the first-order diffraction spots of the unreconstructed Au(100) surface, marked in green.

experimental setups was then ensured by adjusting the deposition time according to the measured evaporation rate. In addition, the appropriate coverage was always supported by the appearance of sharp LEED spots.

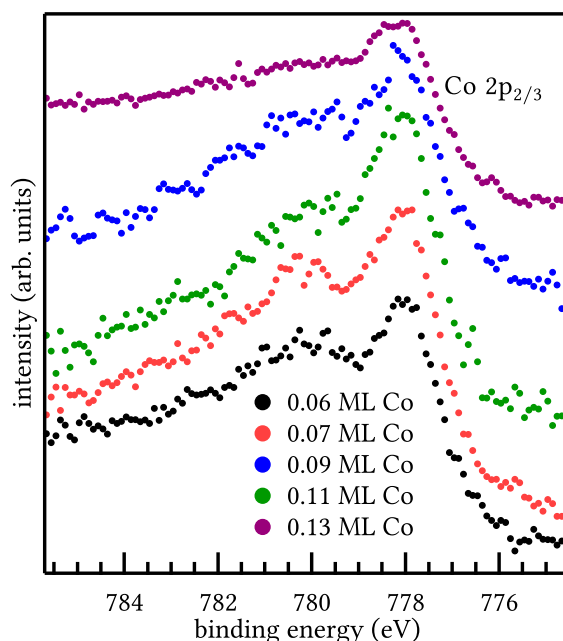


Figure 4.2.: Co  $2p_{3/2}$  core level spectra for the stepwise deposition of Co onto a MnTPyP ML; after each step, the sample was briefly annealed to about 420 K. The background was subtracted as described in Section A.8.

MOF synthesis was carried out by evaporating cobalt atoms onto pristine MnTPyP/Au(100) at about 420 K or, depending on the available setup, by depositing cobalt at room temperature followed by post-annealing at the same temperature. To determine a suitable cobalt coverage, the metal was deposited stepwise in a dedicated calibration experiment. After each Co deposition step, XPS and LEED were recorded until the sharp LEED pattern associated with network formation became visible, see Figure 4.1c. As in the case of the molecular layer, the appropriate Co coverage is reflected by sharp diffraction spots in the

LEED image. The corresponding XPS spectra are shown in Figure 4.2. Starting from low coverages, two peaks develop and initially increase in intensity together. Once saturation is reached, only the first peak at lower binding energy continues to grow, indicating the formation of metallic Co clusters on top of the network. From the combined LEED and XPS results, in particular the evolution of the Co  $2p_{3/2}$  core level, a coverage of 0.11 ML was identified as appropriate for MOF formation. The used metal evaporator is equipped with a flux monitor whose ion current is used as feedback during deposition to ensure a constant evaporation rate and is proportional to the deposited flux. Together with the deposition time, it can therefore be used as a relative measure of the deposited thickness. This calibration was quantified independently from the attenuation of the Au  $4f$  core level, as described below. In addition, the cobalt deposition rate was monitored with a QCM in order to reproduce the calibrated coverage on different setups. Minor deviations from the described preparation procedure may occur depending on the techniques available at the respective experimental setups.

## Co coverage calibration

The nominal Co coverage was calibrated by XPS from the attenuation of the Au  $4f$  core level. For this purpose, a reference amount corresponding to ten times the Co coverage required for MOF formation was deposited onto the clean Au(100) substrate. The attenuation of the Au  $4f$  intensity follows Equation 3.6, so that the effective film thickness can be written as

$$d = -\lambda(E) \cdot \ln \left( \frac{I(d)}{I_0} \right). \quad (4.1)$$

The corresponding peak areas were obtained from fits of the Au  $4f$  core level, as described in Section A.5. For the clean surface, the fitted area of the Au  $4f_{7/2}$  peak is  $(405\,526 \pm 1610)$  arb. units, see Figure 4.3a. After Co deposition, the Au  $4f_{7/2}$  intensity is attenuated to  $(371\,530 \pm 1783)$  arb. units, see Figure 4.3b. For electrons emitted from the Au  $4f_{7/2}$  core level and traveling through cobalt, an inelastic mean free path of  $\lambda_{\text{Co}} = 16.49 \text{ \AA}$  is obtained from Equation (7) in Reference [156]. The thickness of the deposited Co film is therefore estimated as

$$d = -\lambda(E) \cdot \ln \left( \frac{I(d)}{I_0} \right) = -16.49 \text{ \AA} \cdot \ln \left( \frac{371\,530 \text{ arb. units}}{405\,526 \text{ arb. units}} \right) = 1.44 \text{ \AA}.$$

This value should be regarded as an estimate, since the exact growth mode is not known and influences the attenuation of the substrate signal [167, 237]. The uncertainty of the fitted peak areas already provides a lower bound for the accuracy of about  $\pm 0.1 \text{ \AA}$ . In addition, Equation 3.6 may not be sufficiently accurate for films in this thickness range. For this reason, two alternative approaches for the calibration of the deposited Co are presented in Section A.1. The quoted coverage should therefore be regarded as an upper estimate, since both alternative approaches yield somewhat lower values.

The evaluated thickness must then be converted into a 1:1 coverage with the Au(100) surface atom density, the here used definition of 1 ML. One Au surface atom on Au(100) covers an area of  $a/\sqrt{2} \cdot a/\sqrt{2} = a^2/2$  with  $a_{\text{Au}} = 4.078 \text{ \AA}$  [123], corresponding to a surface

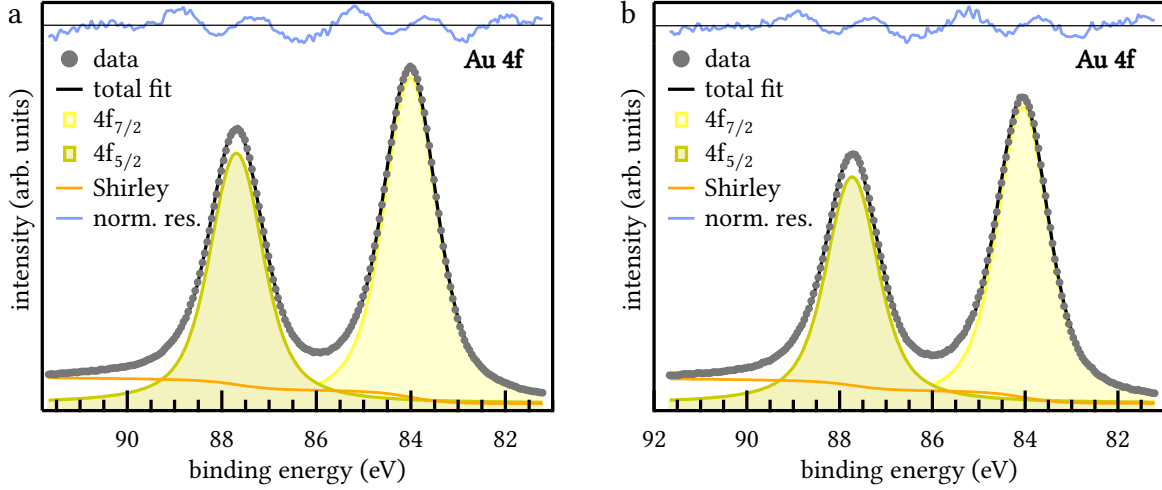


Figure 4.3.: Fits of the Au 4f core level used for the Co coverage calibration. (a) Clean Au(100) surface and (b) after deposition of 1.09 ML Co. The fitting parameters are given in Tables A.1 and A.2, respectively. Both plots share the same y-axis.

atom density of  $n_{\text{sub}} = 2/a^2 = 0.12 \text{ \AA}^{-2}$ . To convert the thickness of  $1.44 \text{ \AA}$  of Co into ML coverage, the different lattice constants of the substrate and the cobalt overlayer must be taken into account. The ML coverage is then obtained from

$$t = d \cdot \frac{\rho_{\text{Co}} N_{\text{A}}}{n_{\text{sub}} M_{\text{Co}}}, \quad (4.2)$$

with the density of cobalt  $\rho_{\text{Co}} = 8.90 \text{ g/cm}^3$  [238], the Avogadro constant  $N_{\text{A}}$  [239], and the atomic weight of cobalt  $M_{\text{Co}} = (58.933 194 \pm 0.000 003) \text{ g/mol}$  [240], resulting in a coverage of 1.09 ML. This ML definition is used throughout the thesis for the additionally deposited transition metals, whereas 1 ML of molecules corresponds to 0.04 ML in this notation.

Accordingly, the experimentally identified dose for MOF formation corresponds to 0.11 ML Co. Given the uncertainties in both the molecular coverage and the metal calibration, this value is reasonably close to the ideal coverage of 0.08 ML, which corresponds to two Co atoms per MnTPyP molecule rather than one Co atom (0.04 ML) in the hypothetical case without transmetallation. With the preparation procedure and coverage calibration established, the geometric structure of the molecular layer and the Co–MnTPyP network can now be addressed.

## 4.2. Geometric structure characterization

This section addresses the geometric arrangement of the Co–MnTPyP network on the Au(100) surface. LEED is used to determine the geometric periodicity of the molecular layer and the network relative to the gold substrate, while nitrogen K-edge NEXAFS provides insight into deformation of the molecules themselves.



### 4.2.1. Long-range order from LEED

As already described in Section 4.1, the cleanliness of the sample is supported by the well-known  $c(28 \times 48)$  reconstruction of Au(100) visible in the LEED image in Figure 4.1a [119].

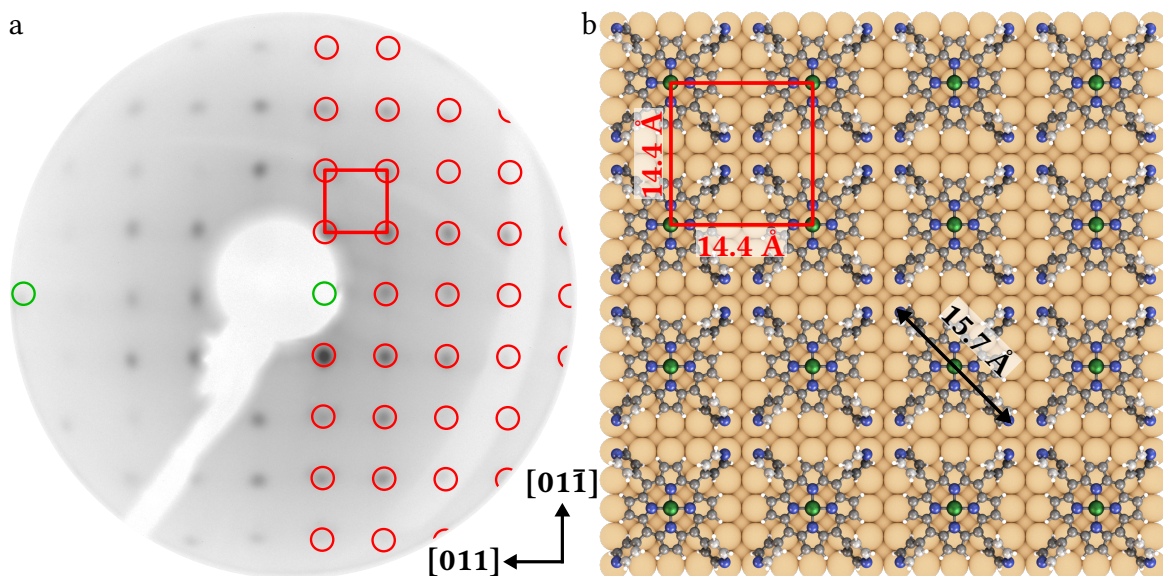


Figure 4.4.: (a) LEED image of the MnTPyP SAM on Au(100). Red markers indicate the superstructure of the molecular adlayer, determined with Spot Plotter [235]. Green markers denote the (1,0) and (0,0) diffraction spots of the unreconstructed Au(100) surface. The kinetic energy of the primary electrons was 25 eV. (b) Corresponding real-space structure of the SAM with a  $14.4 \text{ \AA} \times 14.4 \text{ \AA}$  unit cell. Geometric structure based on a creation by Mira Arndt, TU Dortmund.

**MnTPyP SAM** After deposition of one monolayer of MnTPyP onto clean Au(100), the surface reconstruction is lifted and new sharp diffraction spots appear. In the LEED image shown in Figure 4.4a, these spots are marked by red circles in one half of the image. Their sharpness indicates the formation of an ordered molecular adlayer. By analyzing the additional spot positions with Spot Plotter [235], a

$$\begin{pmatrix} 5 & 0 \\ 0 & 5 \end{pmatrix}$$

superstructure is obtained relative to the unit cell of the unreconstructed Au(100) surface (green markers). A corresponding LEED pattern is also observed for pristine CoTPyP on Au(100), supporting that the reference compound adopt the same square commensurate SAM structure (Figure A.2a).

Although LEED is sensitive only to geometric periodicity, simple geometric considerations allow a real-space structural model to be proposed, as shown in Figure 4.4b. First, the substrate and the molecule both exhibit fourfold symmetry, and the surface reconstruction disappears upon molecular adsorption. Furthermore, the superstructure is commensurate with the substrate [241], so the symmetry of both is expected to coincide. In reciprocal space, the spot distances are reduced by a factor of five; in real space, the periodicity is therefore five times larger than the nearest-neighbor distance of the Au atoms on the (100) surface,

2.88 Å [121]. This yields a lateral unit-cell size of  $5 \times 2.88 \text{ Å} = 14.4 \text{ Å}$ . Given the size of the MnTPyP molecule along the pyridyl groups, 15.7 Å [57], the molecules can be arranged along the diagonal of the square unit cell (20.4 Å), which leads to the conclusion that each square-like unit cell contains one molecule. Consequently, the molecular N–Mn–N axes are aligned with the substrate [110] directions. Only minor azimuthal deviations, caused by steric repulsion between the hydrogen atoms of the pyridyl groups and the macrocycle of neighboring molecules, are expected. Other highly symmetric orientations would lead to a physical overlap of the pyridyl end groups and can therefore be excluded.

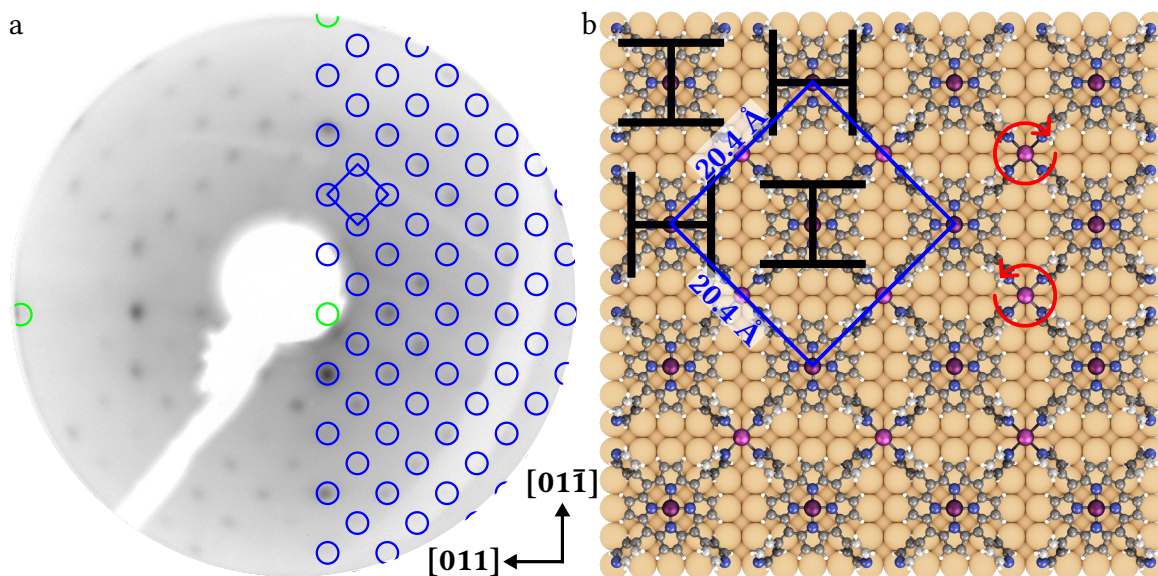


Figure 4.5.: (a) LEED image of the Co–MnTPyP MOF on Au(100) at 25 eV. Blue markers indicate the superstructure of the network layer, determined with Spot Plotter [235]. (b) Corresponding real-space structure with a 20.4 Å × 20.4 Å unit cell. Geometric structure based on a creation by Mira Arndt, TU Dortmund.

**Co–MnTPyP MOF** Deposition of cobalt leads to additional spots, rotated by 45° and shifted by a factor of  $\sqrt{2}$  with respect to the pristine SAM, as shown in Figure 4.5a. The resulting

$$\begin{pmatrix} 5 & -5 \\ 5 & 5 \end{pmatrix}$$

superstructure is indicated by blue circles in Figure 4.5a. The enlarged unit cell cannot be explained simply by coordination of additional Co atoms to the pyridyl end groups of the square-ordered MnTPyP layer, since such coordination alone would not alter the periodicity. As discussed later, analysis of the N 1s core level (Section 4.3.5) and interpretation of the nitrogen K-edge NEXAFS data (Section 4.2.2) support the conclusion that the additional cobalt is coordinated by the pyridyl end groups. An explanation based on saturation of only every second coordination site can likewise be excluded, since the nitrogen 1s core level indicates that all pyridyl groups are coordinated. Because the square-like order is preserved and all matrix elements are rational numbers, the superstructure remains commensurate with the substrate geometry [241]; the enlarged unit cell must therefore have a different origin. The same superstructure is found for the reference Co–CoTPyP network on Au(100) (Figure A.2b), indicating that both preparation routes lead to the same long-range lateral



arrangement.

In reciprocal space, the unit cell in Figure 4.5a is half the size of that in Figure 4.4a, corresponding to a real-space unit cell that is twice as large as that of the pristine MnTPyP layer. The framework unit cell therefore contains two molecules. In addition, the unit cell is rotated by 45° relative to the high-symmetry directions of the substrate. The most plausible explanation is that neighboring molecules are not equivalent, as already observed by scanning tunneling microscopy (STM) for Co–CoTPyP and for Co–MnTPyP on graphene [24, 34]. An alternating clockwise and counterclockwise rotation of the pyridyl end groups around the bond to the macrocycle (angle  $\beta$  in Figure 1.3) leads to an “H”-shaped appearance in STM images [24, 34]. In addition, a relative rotation of neighboring molecules by 90° accounts for the observed enlarged unit cell. Each Co atom coordinated by the pyridyl groups is then surrounded by four pyridyl end groups rotated in the same direction. This structural model is illustrated in Figure 4.5b. The rotation of the pyridyl end groups is consistent with the nitrogen K-edge NEXAFS results discussed in Section 4.2.2. Figure 4.5b already anticipates another important result, namely replacement of the macrocyclic Mn by Co, which will be addressed in the following section.

**Summary** Both the self-assembled MnTPyP layer and the final Co–MnTPyP MOF exhibit commensurate square unit cells relative to the substrate. In the SAM, the unit cell contains one MnTPyP molecule and 25 surface Au atoms. Upon MOF formation, the unit cell doubles and contains two non-equivalent molecules, rotated by 90° relative to each other and exhibiting an alternating rotation of the pyridyl substituents. The corresponding real-space model further suggests that the two embedded metal atoms, namely the one in the macrocycle and the one coordinated by four neighboring pyridyl substituents, occupy different adsorption sites relative to the substrate.

#### 4.2.2. Molecular deformation and coordination from nitrogen K-edge NEXAFS

Complementary NEXAFS measurements at the nitrogen K-edge provide information on molecular deformation as well as on coordination of the pyridyl end groups upon cobalt deposition. Figure 4.6 shows the nitrogen K-edge NEXAFS spectra of the pristine molecular layer (bottom) and the MOF (top). The features labeled by capital letters are assigned by comparison with previous studies on related systems. A major advantage for the assignments is that typical  $\pi^*$  orbitals lie below the vacuum level, whereas  $\sigma^*$  orbitals remain above the absorption threshold [72, 104, 242]. Accordingly, states below 405 eV, *i.e.* below the absorption threshold, can be attributed to unoccupied  $\pi^*$  orbitals, while states above this energy arise from unoccupied  $\sigma^*$  orbitals. Furthermore, transitions into  $\pi^*$  orbitals usually appear as sharp resonances, whereas transitions into  $\sigma^*$  states give broader spectral features. For the assignment of the spectral features, it is important to note that MnTPyP contains two non-equivalent nitrogen species: the nitrogen atoms of the macrocycle coordinated to Mn, and the pyridyl nitrogen atoms. Studies on pyridine and on isolated metallated tetraphenylporphyrins, which do not contain both nitrogen species simultaneously, serve as useful references for disentangling the individual contributions. This makes it possible to assess deformation of the macrocycle and rotation of the substituents separately. Since the

energy calibration in the literature is not always consistent, small rigid shifts were applied where necessary for comparison. A summary of the assignments is given in Table 4.1.

**MnTPyP SAM** The NEXAFS spectra of the pristine molecular film (Figure 4.6, bottom) show four prominent features in p-polarization at 398.6 eV (A), 400.5 eV (C), 401.3 eV (D), and 402.6 eV (E). In addition, a broad feature appears at 408 eV (G), which also persists in s-polarization at slightly lower photon energy, namely 406.7 eV (F). Apart from this, resonances A and E remain visible in s-polarization, and a new feature at 399.8 eV (B) emerges.

According to previous studies, the broad resonances F and G originate from  $\sigma^*$  states of both nitrogen species, *i.e.* the macrocycle nitrogen atoms and the pyridyl nitrogen atoms [28, 90, 128, 243–246]. This assignment is further supported by their appearance as broad features above the absorption threshold and by their larger spectral weight in s-polarization than in p-polarization [104, 242].

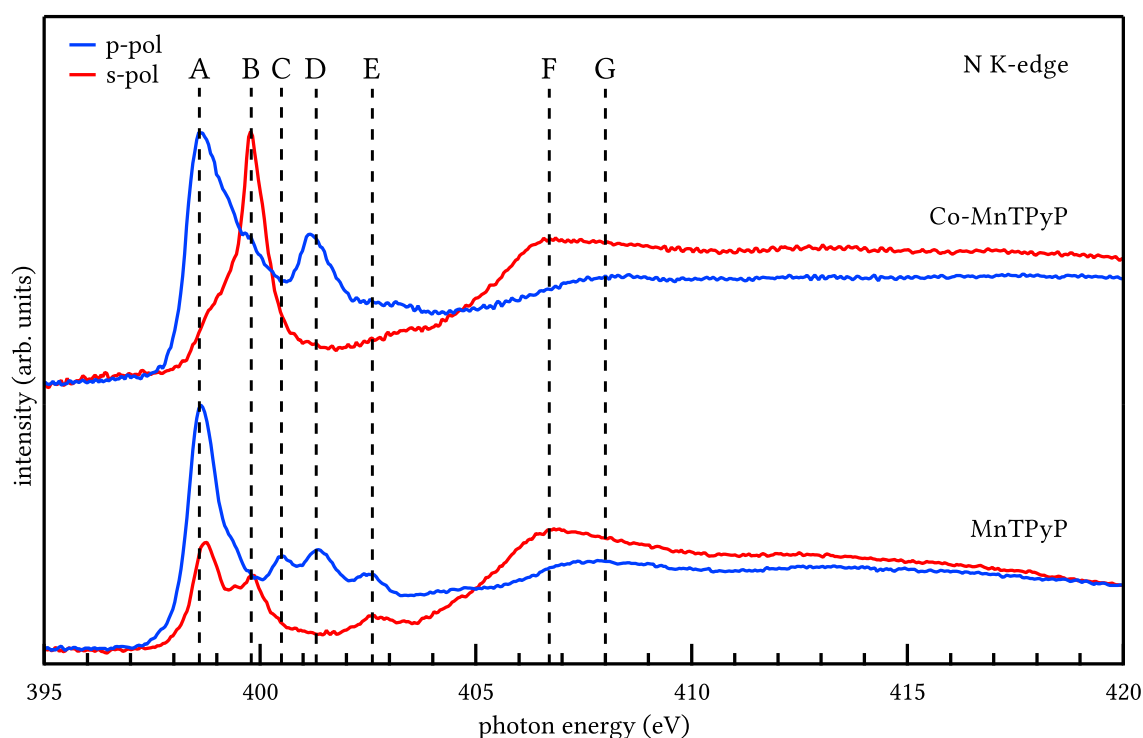


Figure 4.6.: NEXAFS spectra at the nitrogen K-edge for the molecular layer (bottom) and after MOF formation (top). The spectra were measured in grazing incidence ( $\alpha = 70^\circ$ ) using p-polarized (blue) and s-polarized (red) light.

At 402.6 eV, resonance E is visible in both polarizations, with higher intensity in p-polarization. Its energetic position agrees well with that expected for pyridinic  $\pi^*$  orbitals [28, 244–246]. The occurrence of feature E in both p- and s-polarization implies that the pyridyl groups are rotated out of the surface plane. Such rotations, already reported in the literature for related systems [24, 28, 34], are driven by steric repulsion between hydrogen atoms of neighboring pyridyl groups and those attached to the pyrrole units of the macrocycle [42].

Resonance D exhibits its highest intensity in p-polarization, with only a minor residual contribution in s-polarization. Its energetic position at 401.3 eV is characteristic of a macrocyclic  $\pi^*$  orbital formed by hybridization between N and C states within the pyrrole rings [24, 28, 90, 242, 243, 247, 248]. The pronounced polarization dependence therefore indicates that the macrocycle is flat and oriented parallel to the surface plane [72, 137].

Using p-polarized light, a further resonance, labeled C, appears at 400.5 eV. It also shows a small but detectable intensity in s-polarization, slightly larger than that of resonance D in the same polarization. A possible explanation for this polarization dependence was proposed by Petraki et al. for phthalocyanines [249]: the feature originates from transitions into macrocyclic  $\pi^*$  states hybridized with in-plane components of the metal  $d$  states. This interpretation was further supported by Peisert et al., who measured the N K-edge of phthalocyanines with central transition metals spanning  $d^5$  to  $d^9$  configurations; whereas Cu, Ni, Co, and Fe complexes exhibit very similar spectral shapes, MnPc shows additional features [59]. By analogy, resonance C can be attributed to transitions from the 1s level into unoccupied states of the flat macrocycle that are influenced by the presence of the Mn center [77, 247, 249, 250].

The origin and dichroism of peak B at 399.8 eV, which has nearly equal intensity for both polarizations, can be assigned to pyridyl end groups rotated out of the surface plane, as already anticipated from feature E [245, 246]. Its spectral position is consistent with adsorbed or coordinated pyridyl moieties, for which small energy shifts between non-interacting (gas-phase or multilayer) and surface-interacting pyridyl species are expected [245, 251]. A related splitting is also observed in the N 1s core level after network formation, where it appears as a distinct fingerprint of coordination [197, 227].

Finally, resonance A at 398.6 eV can be assigned to overlapping contributions from macrocyclic and pyridyl  $\pi^*$  orbitals [28, 90, 128, 137, 243, 244, 252]. According to the literature, the energetic separation of these two contributions is less than 0.15 eV [244, 247]. This overlap is consistent with the N 1s core level (Section 4.3.5), which shows only a single peak for the pristine molecular layer, even though the final states of XPS and NEXAFS differ [197, 227]. Because of the mixed contributions from both molecular subunits, this resonance alone does not permit conclusions about structural changes. However, in combination with the polarization dependence of the other features, it can be concluded that the macrocycle only contributes to p-polarization, as evident from resonance D, whereas the pyridyl contributes to both polarizations, similar to resonances E and B.

In summary, for the pristine molecular layer the MnTPyP macrocycle is flat and oriented parallel to the surface plane, while the pyridyl groups are rotated out of this plane around their bond axis to the macrocycle. This configuration was already assumed in Section 4.2.1 to construct the structural model in Figure 4.4b. A quantitative determination of the pyridyl tilt angle would require incidence-angle-dependent NEXAFS measurements.

**Co–MnTPyP MOF** After network formation, the spectral weight is redistributed among the resonances (Figure 4.6, top). Resonances A and B now show comparable intensity, but with opposite polarization dependence: A dominates in p-polarization, whereas B dominates in s-polarization. Resonance A retains only a small residual intensity in s-polarization, while B still carries a certain amount of intensity in p-polarization. Signatures

| resonance | energy                | assignment                                          | reference                            |
|-----------|-----------------------|-----------------------------------------------------|--------------------------------------|
| A         | 398.6 eV              | macrocycle $\pi^*$<br>uncoordinated pyridyl $\pi^*$ | [28, 90, 128, 137,<br>243, 244, 252] |
| B         | 399.8 eV              | coordinated<br>pyridyl $\pi^*$                      | [245, 246, 251]                      |
| C         | 400.5 eV              | macrocycle $\pi^*$ or mixed<br>with Mn $d$ orbitals | [77, 247, 249,<br>250]               |
| D         | 401.3 eV              | macrocycle $\pi^*$                                  | [24, 28, 90, 242,<br>243, 247, 248]  |
| E         | 402.6 eV              | pyridyl $\pi^*$                                     | [28, 244–246]                        |
| F/G       | 406.7 eV to<br>408 eV | macrocycle $\sigma^*$<br>pyridyl $\sigma^*$         | [28, 90, 104, 128,<br>242–246]       |

Table 4.1.: Assignment of the resonances in the nitrogen K-edge measurements in Figure 4.6.

C and E disappear, whereas D remains visible in p-polarization. In contrast, features F and G near the absorption threshold remain largely unchanged.

As discussed above, cobalt deposition leads to displacement of Mn from the macrocycle, which is subsequently replaced by Co, as will be further supported in Section 4.3.2. This replacement is expected to induce a small energetic shift of resonance A, because the central metal atom influences its position [59, 247]. Here, this shift is neglected, since peak A was used as the reference for photon energy calibration and fixed at equivalent photon energy. As in the pristine molecular layer, the Co–MnTPyP layer contains two non-equivalent nitrogen species; after network formation, both are coordinated to Co, one within the macrocycle and one at the pyridyl groups.

Resonances F and G, previously assigned to transitions into  $\sigma^*$  states of both the macrocycle and the pyridyl groups, are only weakly affected by MOF formation. This indicates that the  $\sigma^*$  states do not play a major role in cobalt coordination and network formation.

In contrast, resonance E is completely quenched in both polarizations. Since it was attributed to a pyridinic  $\pi^*$  orbital, its disappearance indicates that this state participates directly in the interaction with Co and becomes either occupied, strongly broadened, or shifted in energy such that it is no longer resolved as a distinct peak. A similar quenching of a  $\pi^*$  resonance was reported for the transition from gas-phase pyridine to a monolayer of pyridine adsorbed on Pt(111) [245].

Resonance D, originating from a macrocyclic  $\pi^*$  orbital, remains almost unchanged, indicating that the macrocycle is still flat and aligned parallel to the surface. Its relatively enhanced intensity in p-polarization, compared with the neighboring features, is largely a consequence of the quenching of resonances C and E.

The complete suppression of resonance C upon network formation supports its assignment in the SAM to a mixed state involving Mn  $d$  orbitals and macrocyclic  $\pi^*$  states: once Mn is removed from the macrocycle, this hybridization channel is closed (compare Section 4.3.2).

Resonance B shows pronounced dichroism after MOF formation, with some remaining intensity visible in p-polarization. Its origin was already associated with interacting pyridyl groups. Upon coordination of additional Co within the pyridyl functional groups, the intensity of B increases significantly, accompanied by a decrease of the contribution to resonance A. The stronger dichroism of B compared with that of E and B in the molecular film indicates that the pyridyl tilt out of the surface plane increases upon coordination.

Strong dichroism is also observed for resonance A, which shows only minor intensity in s-polarization. Unlike in the molecular film, the contributions from the macrocycle and the pyridyl groups are now energetically separated and can be distinguished. The initial state of the transition likewise shows two separated contributions in XPS, associated with MOF formation (Section 4.3.5) [197, 227]. Moreover, the strongly reduced s-polarized intensity on the low-energy side of the spectrum indicates that nearly all pyridyl end groups are coordinated by Co, resulting in a pronounced local modification of the electronic structure. This feature therefore predominantly originates from transitions into macrocyclic  $\pi^*$  orbitals, which remain oriented parallel to the surface.

Taken together, and as already observed for the pristine molecular layer, the macrocycle remains flat relative to the surface plane after MOF formation, whereas the pyridyl groups are rotated around their bonds to the macrocycle. Further, the shifted spectral weight from resonance A to B indicates the coordination of the pyridyl motifs, while the disappearance of C can be associated with the transmetallation.

Overall, these results highlight the role of network formation in reshaping the local electronic structure, particularly at the pyridyl end groups, where cobalt coordination is directly reflected in the N K-edge spectra. In contrast, the resonances associated with the macrocycle are only weakly affected, indicating that the macrocyclic backbone remains largely unchanged.

**Summary** In the SAM, the macrocycle is adsorbed in a flat geometry, while the pyridyl substituents are rotated out of the molecular plane. Upon MOF formation, the macrocycle remains flat, whereas the substituents undergo additional rotation. A precise determination of the pyridyl rotation would require further STM measurements to confirm the alternating tilt, as well as incidence-angle-dependent NEXAFS measurements to extract the exact tilt angle. In other systems, the steric repulsion responsible for pyridyl rotation can also induce a saddling distortion of the macrocycle [42, 51], which is not observed here. Furthermore, the deposited Co adatoms are coordinated by the pyridyl substituents, and the vanishing resonance, associated with the hybridization with Mn, points towards transmetallation. This will be further addressed in the following by the electronic structure.

### 4.3. Electronic structure characterization

To gain insight into the electronic structure of the MnTPyP SAM and the Co–MnTPyP MOF, complementary XPS, NEXAFS, and MM measurements were carried out. While XPS provides access to strongly bound core states and their chemical shifts, NEXAFS probes element-specific unoccupied states and local coordination environments. MM, in

turn, extends the analysis to the occupied valence states and their momentum-dependent character. The discussion begins with the role of the manganese center and the question of chloride dissociation, then turns to the core level signatures of the molecular layer and the coordinated network, and finally addresses the changes in the valence electronic structure induced by network formation.

### 4.3.1. Chloride dissociation and oxidation-state change

Before turning to the manganese centers in the layers, the role of the axial chloride ligand has to be considered. In air, the MnTPyP molecules are stabilized as MnClTPyP by an axial Cl ligand, which maintains manganese in the +3 oxidation state [91, 125], as discussed in Section 2.2. To assess whether chloride is still present in the prepared molecular film, XPS was applied to the Cl 2*p* core level of a powder sample and a thin evaporated film. In principle, the expected change in manganese oxidation state upon Cl release could also be monitored by the Mn 2*p*<sub>3/2</sub> core level. For the molecular film on gold this is not feasible, since the binding energies of the Mn 2*p* core levels (2*p*<sub>3/2</sub> ≈ 639 eV, 2*p*<sub>1/2</sub> ≈ 650 eV) overlap with the intense Au 4*p*<sub>1/2</sub> core level at 643 eV. Given that the Mn coverage in a monolayer is only about 4 % of the surface Au atom density, and that approximately 13 Au bulk layers contribute to the signal, the manganese emission is overwhelmed by the much stronger gold signal. Therefore, the Mn 2*p*<sub>3/2</sub> core level was investigated only for the powder sample.

In a first step, MnClTPyP powder was pressed onto a sample plate using double-sided conductive carbon tape and investigated by XPS at both the Cl 2*p* and Mn 2*p*<sub>3/2</sub> core levels, as shown in Figure 4.7a and b, respectively.

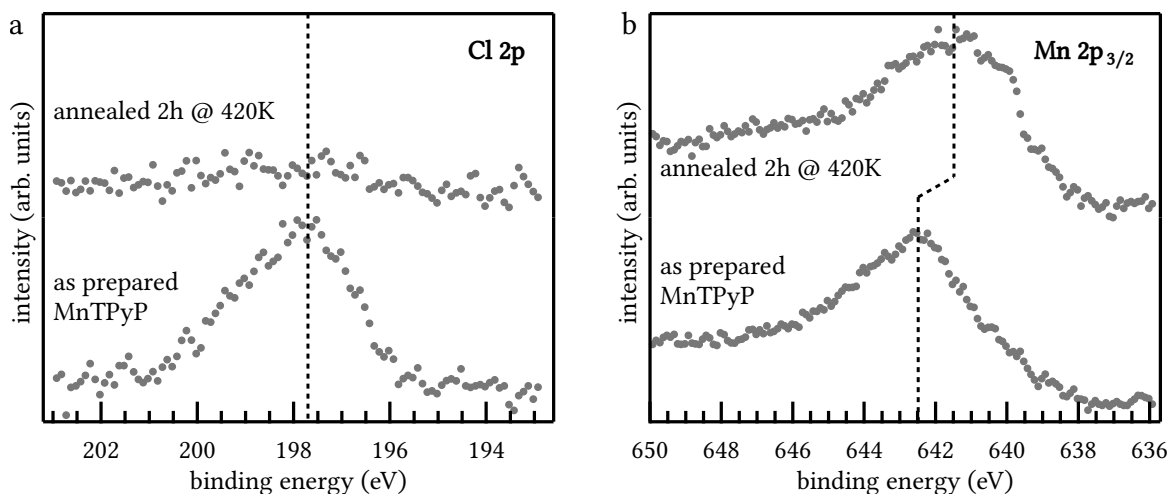


Figure 4.7.: (a) Cl 2*p* core level spectra of the MnClTPyP powder sample before and after annealing to 420 K. (b) Corresponding Mn 2*p*<sub>3/2</sub> core level spectra. Measurements performed by Olga Resel.

The Cl 2*p* region shows a clear feature centered around 197.5 eV, with an asymmetry toward higher binding energy caused by the unresolved spin-orbit components (see also Figure A.3a). After annealing the sample to 420 K, which is also the temperature used for MOF formation, the intensity of this feature decreases strongly, consistent with dissociation

of Cl from the molecules. Since the integration time and analyzer settings were identical before and after annealing, the upper and lower spectra in Figure 4.7a share the same intensity scale. Similar thermal dissociation of chloride ligands has been reported for related manganese porphyrin derivatives annealed between 423 K and 525 K [20, 91, 124].

The Mn  $2p_{3/2}$  core level of the pristine powder sample in Figure 4.7b (bottom) exhibits a broad line shape centered around 642.5 eV, with an asymmetry toward higher binding energy. This asymmetry arises from the open-shell configuration of Mn, giving rise to characteristic, here unresolved, multiplet splitting [24, 91, 253, 254]. The main intensity of the as-prepared powder sample is located at 642.5 eV (see also Figure A.3b), in agreement with reported values for Mn in the +3 oxidation state [255]. After annealing to 420 K and release of Cl, the spectrum shifts by 1.3 eV toward lower binding energy to 641.2 eV, as shown in Figure 4.7b. This shift indicates conversion to the +2 oxidation state [255], consistent with previous reports [20, 124].

In a second experiment, 2.4 ML of MnTPyP were deposited in UHV from a Knudsen cell onto the Au(100) surface, following the same procedure used to prepare the SAM. The Cl  $2p$  core level region was then compared between the clean Au(100) surface and the thin MnTPyP film, as shown in Figure 4.8. A small residual Cl contribution may still be present after deposition of MnTPyP, with the Cl  $2p_{3/2}$  feature around 198.5 eV [91, 124].

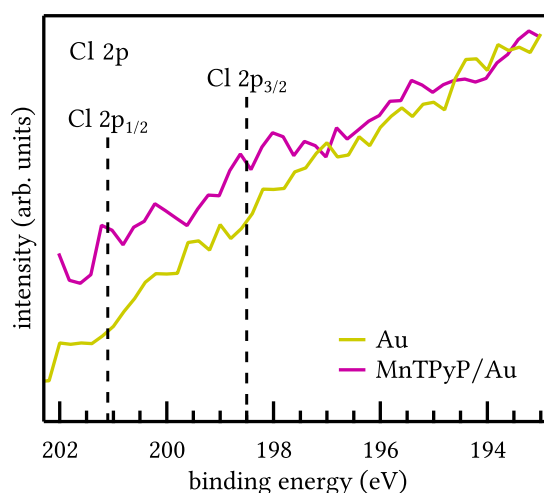


Figure 4.8.: Cl  $2p$  core level region of the clean Au(100) surface (yellow) and after deposition of  $\sim 2.4$  ML MnTPyP (purple). Acquired by Olga Resel and Giovanni Zamborlini.

Overall, the observations of chloride release upon annealing, the accompanying change in manganese oxidation state, and the possible presence of a small residual chloride contribution in the as-prepared MnTPyP film are consistent with the literature, where Cl is reported to dissociate from the porphyrin metal center during or after deposition [24, 30, 34, 228]. In some studies, Cl loss occurs only upon post-annealing in the range 423 K to 525 K [20, 91, 124]. From the present data, it cannot be fully excluded that a small amount of residual Cl remains bound in the SAM immediately after deposition. Nevertheless, at the annealing temperature employed for network formation (420 K), the powder measurements clearly demonstrate that Cl is removed from the Mn center.

### 4.3.2. Transmetallation probed at the manganese L<sub>3</sub>-edge

To assess the oxidation state of manganese, XPS would in principle be the most direct approach. However, the Mn 2*p* photoemission spectrum of MnTPyP on Au(100) cannot be evaluated reliably because it overlaps with the intense Au 4*p*<sub>1/2</sub> core level, as discussed in the previous section. In XPS, the manganese-related signal is therefore superimposed on much stronger gold emission, whereas in NEXAFS the gold contribution appears only as a smooth background. The Mn L-edge NEXAFS thus provides selective access to the 2*p* → 3*d* transitions, in particular the L<sub>3</sub>-edge, corresponding to excitations from the 2*p*<sub>3/2</sub> (*l* = 1) core level into the unoccupied 3*d* (*l* = 2) states.

Within the molecule, Mn experiences an approximately square-planar ligand field, which lifts the degeneracy of the Mn 3*d* orbitals, as discussed in Section 1.1 [62]. Upon adsorption of a monolayer on Au(100), the overall molecule–substrate complex is formally of C<sub>4v</sub> symmetry, but for the local ligand field at the metal center it remains a reasonable approximation to use a D<sub>4h</sub> description, as is commonly done for related systems [124, 249]. Because Mn in the relevant oxidation states, Mn(II) and Mn(III), has five or fewer electrons in the 3*d* shell, a considerable number of 3*d*-derived states remains unoccupied and contributes to the L<sub>3</sub>-edge spectrum [59]. In the following, the discussion focuses on qualitative changes in spectral shape, dichroism, and overall energy position rather than on a detailed assignment of the individual multiplet features.

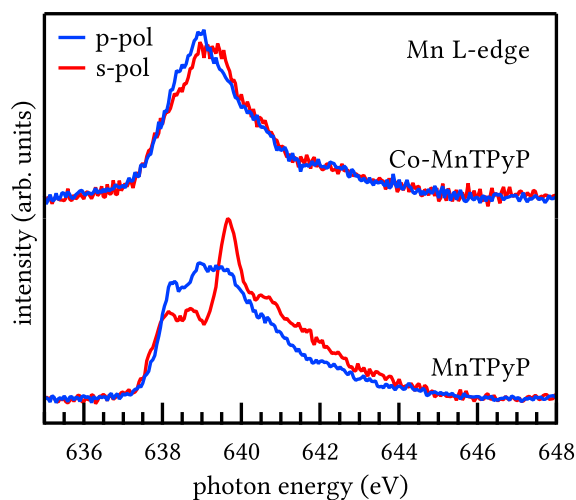


Figure 4.9.: NEXAFS spectra at the Mn L<sub>3</sub>-edge for the MnTPyP ML (bottom) and after formation of the Co-MnTPyP network (top). The spectra were measured in grazing incidence ( $\alpha = 70^\circ$ ) using p-polarized (blue) and s-polarized (red) light.

**MnTPyP SAM** Figure 4.9 (bottom) shows the Mn L<sub>3</sub>-edge of the MnTPyP SAM. Several well-separated resonances with pronounced linear dichroism are observed, as expected for transition metal centers in porphyrins and phthalocyanines [62, 228, 256]. The occurrence of distinct spectral features indicates that Mn is incorporated into the macrocycle and experiences a well-defined ligand field imposed by the four nitrogen donors. From the dichroic response, a preferred orientation of the associated 3*d* orbitals can be inferred: resonances enhanced in p-polarization are predominantly associated with out-of-plane 3*d*-like orbitals, whereas features stronger in s-polarization mainly reflect in-plane character.



A comparison with reference systems is instructive. For MnClTPP multilayers, a  $3d^4$  high-spin configuration, corresponding to Mn(III), has been reported, whereas in the monolayer the interaction with the substrate reduces Mn to the +2 oxidation state ( $3d^5$  high-spin), attributed to release of the axial Cl ligand [127]. The Mn  $L_3$ -edge spectrum of the MnTPyP SAM on Au(100) resembles the monolayer spectra assigned to Mn(II) more closely than the multilayer spectra characteristic of Mn(III) [102, 124, 228, 257]. In particular, the three-peak multiplet structure commonly reported for Mn(III) in chlorinated porphyrins and phthalocyanines is more spread out in energy than in the present SAM spectrum [228]. This assignment is further supported by the fact that most of the Cl stabilizing Mn(III) in air is already dissociated during deposition (Section 4.3.1). Additional consistency is found with thin MnPc layers on Au(100) and Ag(111), where charge transfer and metal–ligand hybridization lead to an effective Mn(II) configuration [59, 249, 258]. Similar metal–ligand hybridization is also found here, as reflected by resonance C in the nitrogen K-edge (Section 4.2.2). Overall, the Mn center is therefore assigned to a +2 oxidation state, or to a state very close to +2, possibly with a small non-integer charge transfer to the macrocycle.

**Co–MnTPyP MOF** After cobalt deposition and mild annealing at 420 K, the Co–MnTPyP network is formed, and the Mn  $L_3$ -edge spectrum changes drastically (Figure 4.9, top). An almost featureless resonance is observed, without the previously well-resolved multiplet structure. The loss of distinct multiplet peaks indicates that Mn is no longer located in the well-defined ligand field of the porphyrin macrocycle [101, 102]. Such a broad line shape is more reminiscent of metallic Mn [259], and can not be simply explained by the release of remaining Cl. In addition, the absence of linear dichroism points to an isotropic coordination environment without a preferred orbital orientation. In other words, the Mn atoms are no longer bound within the planar macrocycle but instead reside in a more disordered or cluster-like environment.

This interpretation is fully consistent with the changes observed at the nitrogen K-edge (Section 4.2.2), where resonances C and E vanish upon network formation. Resonance C had been attributed to a state with mixed macrocycle–Mn  $3d$  character; its disappearance after Co deposition therefore provides strong evidence for the loss of Mn from the macrocycle. Additional experimental support for transmetallation comes from the N 1s core level spectra (Section 4.3.5), where the binding energy of the pyrrolic nitrogen shifts upon Co deposition. A similar on-surface transmetallation process has been reported for FeTPP on Au(111) after Co deposition [101]. In contrast, no transmetallation occurs for MnTPyP on graphene under comparable conditions [24], suggesting that the interaction with the Au substrate plays a crucial role in enabling Mn/Co exchange.

**Summary** In the MnTPyP SAM on Au(100), the Mn center is coordinated within the macrocycle in a ligand field consistent with an effective +2 oxidation state, or a state very close to it. After Co deposition and annealing at 420 K, Mn is expelled from the macrocycle and replaced by Co. Further evidence for this picture is provided in the following section through core level spectroscopy.

### 4.3.3. XPS fitting strategy and experimental constraints

Before discussing the XPS results, several experimental and data-treatment aspects should be highlighted. The X-ray source is a non-monochromatized dual-anode system that produces the main  $K_{\alpha 1,2}$  lines together with several higher-energy satellites,  $K_{\alpha 3}, K_{\alpha 4}, \dots, K_{\beta}$ . Most of these satellites lie outside the narrow scan windows used for individual core levels, but they still contribute to the overall background. The expected satellite energies and intensities are summarized in Table 4.2. Because their photon energies differ from that of  $K_{\alpha 1}$ , these lines give rise to weak replica features shifted in apparent binding energy relative to the main peak. In particular, they contribute additional intensity on the low-binding-energy side of the spectrum, while the closely spaced  $K_{\alpha 2}$  component mainly broadens and slightly distorts the high-binding-energy side. An example of their effect is visible in the extended Au 4f spectrum in Figure 4.10.

|                      | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\alpha_5$ | $\alpha_6$ | $\beta$ |
|----------------------|------------|------------|------------|------------|------------|------------|---------|
| Mg displacement (eV) | 0          | -0.25      | 8.4        | 10.1       | 17.6       | 20.6       | 48.7    |
| relative height (%)  | 100        | 50         | 8.0        | 4.1        | 0.6        | 0.5        | 0.5     |

Table 4.2.: Relative intensities and displacements of satellites in achromatic Mg X-ray sources to the  $K_{\alpha 1}$ -line [188, 260, 261].

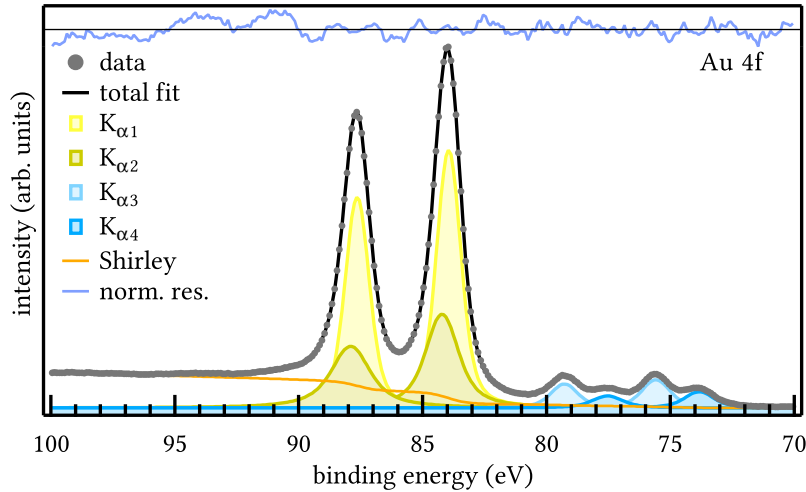


Figure 4.10.: Fit of the Au 4f core level over an extended energy range, illustrating the contribution of X-ray satellites to the background. The spectrum was measured with  $E_{\text{pass}} = 20$  eV. Corresponding fitting parameters are summarized in Table A.7. Data acquisition was performed by Olga Resel.

The core level line shapes are further affected by the intrinsic linewidth of the X-ray source. For the Mg anode, the  $K_{\alpha 1}$  line dominates, while the  $K_{\alpha 2}$  component is shifted by only about 0.25 eV to lower photon energy and contributes with roughly half the intensity of  $K_{\alpha 1}$  [161, 172, 260, 261]. This doublet structure produces an asymmetric broadening of the photoelectron lines and contributes significantly to the overall linewidth. The intrinsic source-limited linewidth is about 680 meV for non-monochromatized Mg  $K_{\alpha}$  radiation [176]. Moreover, the non-monochromatized X-ray source produces an increased background due to Bremsstrahlung [161]. Since the Shirley background approximates the integrated spectral intensity, it naturally accounts for such smoothly varying backgrounds and asymmetries;

empirically, it provided the most robust description in the present case.

The measured lines are additionally broadened by the experimental resolution. Because of the low density of metal centers in the molecular and MOF layers, and the limited acquisition time, the pass energy of the analyzer could not be minimized without losing too much intensity. Consequently, a compromise between counting statistics and energy resolution was chosen and must be taken into account in the analysis.

For metallic core levels such as Au 4*f*, a combination of a Doniach–Šunjić (DS) line shape and a Tougaard background would, in principle, best capture the intrinsic asymmetry of the metallic line [196]. In practice, this asymmetry is further convoluted with the asymmetric contribution of the X-ray source. Within the present resolution regime, a Shirley background together with a symmetric Voigt profile provides an adequate effective description while maintaining a consistent set of constraints for the analysis of the other core levels. In addition, at the kinetic energies relevant for the Au 4*f* electrons, the surface contribution is below about 5 %, and the corresponding surface core level shift of approximately 0.28 eV toward lower binding energy [165] can be neglected in the fits. Further details on the fitting procedure for the Au 4*f* core level are given in Section A.5.

Taken together, the finite experimental resolution, the non-trivial X-ray-induced line shape, the intrinsic asymmetry of metallic states, the presence of multiple chemical species, and the multiplet structure expected for transition metal centers would require very elaborate models. Given the low signal-to-noise ratio and the aim of extracting reliable trends in binding energies, relative areas, and the number of distinct components, a simplified fitting procedure based on Voigt line shapes and Shirley backgrounds was adopted [196]. Multiplet effects of transition metal core levels are effectively accounted for by including a single Gaussian satellite peak rather than resolving the full multiplet structure explicitly. Because different core levels were acquired with different analyzer settings and with different Mg X-ray anodes, each dataset was accompanied by a reference Au 4*f* spectrum, which provides the corresponding set of constraints, such as the Gaussian width; see Section A.5.

#### 4.3.4. Global electronic shifts in the C 1s region

To monitor changes in the overall electronic structure between the SAM and the network, the C 1s core level was recorded, since carbon is not directly involved in the MOF formation. As shown in Figure 1.3, the MnTPyP molecule contains up to five chemically distinct carbon species. Previous studies on related tetrapyrroles have described the C 1s region using between two and four components, in some cases including explicit shake-up satellites [62, 90, 91, 138, 250, 254, 262]. Given the limited energy resolution and the small energy separations reported in the literature, the individual components cannot be resolved here. Fitting the spectra with a single Voigt line shape is therefore a pragmatic approach appropriate for the present resolution. Additional details on the fitting procedure are given in Section A.6.

Figure 4.11a shows the C 1s spectra and corresponding fits for the MnTPyP ML (bottom) and the Co–MnTPyP network (top). For the pristine MnTPyP layer, a single peak is found at 284.44 eV. After network formation, the peak shifts toward higher binding energy by about 0.49 eV and exhibits a slight additional broadening. The reference system CoTPyP

behaves similarly, see Figure 4.11b. The pristine CoTPyP ML spectrum (bottom) shows a broad C 1s peak at 284.48 eV, in very good agreement with the MnTPyP value. Its broader appearance in the CoTPyP case is mainly due to the higher pass energy used for that dataset. Upon Co deposition, the peak shifts toward higher binding energy by 0.39 eV, again accompanied by modest broadening. Shake-up satellites commonly reported around 288 eV and 292 eV for related systems [254, 263] are not clearly resolved here. They may either be absent or hidden in the background because of their intrinsic width and the additional broadening introduced by the experimental conditions. In the CoTPyP case, some residual intensity is visible in the difference spectrum around these energies, but only at the level of the overall noise.

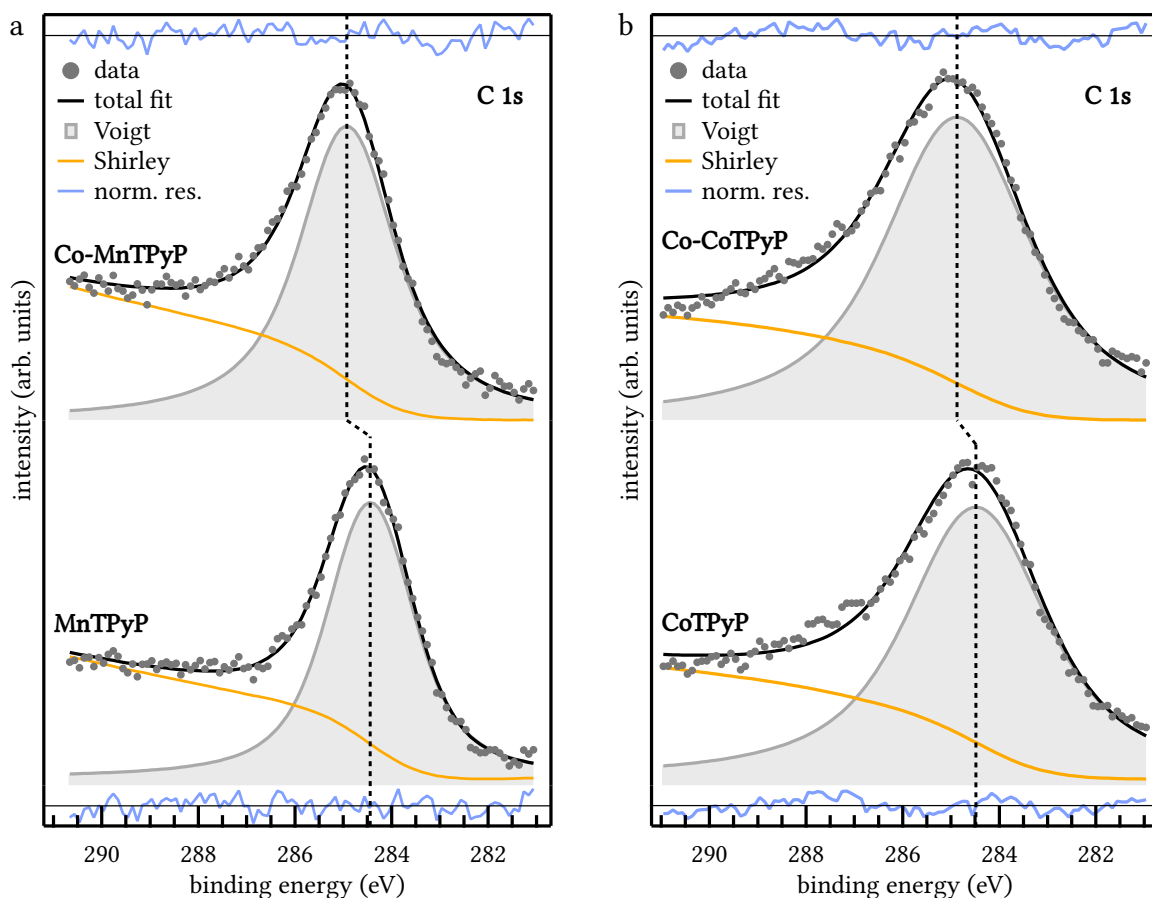


Figure 4.11.: XPS spectra of the carbon 1s core level for the pure molecular layers (bottom) and the corresponding network layers (top). (a) MnTPyP and Co–MnTPyP, (b) CoTPyP and Co–CoTPyP. For both systems 0.11 ML Co was deposited. The corresponding fitting parameters can be found in Tables A.13 to A.16, respectively. Panel (a) was acquired with a pass energy of 20 eV, panel (b) with 50 eV. CoTPyP-related spectra were acquired by Olga Resel.

The C 1s feature of the MnTPyP SAM at 284.44 eV is consistent with reported values for manganese-containing porphyrins and phthalocyanines [91, 264]. It has been shown that changing the metal center in the macrocycle can cause substantial shifts of the C 1s binding energy [62]. However, since the C 1s positions of the MnTPyP and CoTPyP MLs are nearly identical within the experimental uncertainty, the shift observed after Co deposition on the MnTPyP SAM cannot primarily be attributed to the transmetallation of Mn by Co in the

macrocycle. Moreover, the initial-state configuration of the carbon atoms in MnTPyP and CoTPyP is almost identical. In the MnTPyP-based network, some residual Mn remains on the sample, which may contribute to the small difference of about 0.1 eV between the core level shifts observed for the two network systems. As will be shown below, the observed shifts are, within the experimental resolution, similar for all investigated core levels and therefore point to a global change in the electronic landscape of the adlayer rather than to local chemical changes at specific atoms.

The shift of roughly 0.4 eV and 0.5 eV toward higher binding energy upon network formation in both systems can have two, not mutually exclusive, origins. First, such an almost rigid shift can be attributed to a change in the interface dipole and, consequently, in the WKF of the molecular adlayer [100]. Positively charged metal centers in the network can partly quench the surface dipole and modify the local electrostatic potential at the adsorbate sites [100]. A change of the overall WKF between the pristine MnTPyP SAM and the final Co–MnTPyP MOF of about 490 meV is indeed observed in Section 4.3.8, in very good agreement with the C 1s shift.

Second, the increased binding energy upon Co deposition can be interpreted in terms of reduced final-state screening due to an increased average distance of the molecules from the metal surface. This distance is strongly correlated with the rotation of the pyridyl substituents: as observed from the nitrogen K-edge NEXAFS (Section 4.2.2), the pyridyl twist in the network layer is larger than in the molecular layer, which effectively lifts parts of the molecule further away from the Au substrate. This leads to a larger average molecule–surface distance in the MOF than in the SAM. Beggan et al. reported a 400 meV shift toward lower binding energy from a multilayer to a ML of MnTPP on Ag(111), which they attributed to enhanced final-state screening in the ML, where core holes in the molecules are more efficiently screened by substrate electrons [91]. A similar effect was also found for CoTPP on Ag(100) [90].

A change in screening probability should, in principle, also be reflected in the intrinsic linewidth: lower screening efficiency corresponds to a longer core-hole lifetime and thus to a narrower Lorentzian component. In the fits the Lorentzian linewidth of the final network layers (Co–MnTPyP and Co–CoTPyP) is slightly larger than in the initial SAMs, while the Gaussian broadening remains almost unchanged. This small broadening may indicate that additional relaxation channels are introduced upon network formation, for example via the Co nodes that connect neighboring molecules. Given the limited resolution and the small absolute change in linewidth, these trends should not be overinterpreted.

**Summary** For both MnTPyP and CoTPyP, a shift of around 500 meV and 400 meV of the C 1s core level is observed after MOF formation. This shift cannot be unambiguously separated into contributions from the WKF change, *i.e.* the interface dipole, and modified final-state screening. Both mechanisms are naturally correlated: an increased molecule–surface distance not only reduces screening but also affects the interface dipole and hence the effective WKF. Other subtle effects may also contribute. In the following, it will be shown that the direction and magnitude of the binding energy shifts are consistent across the different core levels, supporting the interpretation in terms of a global modification of the electrostatic potential and screening environment upon Co-driven network formation.

### 4.3.5. Chemical-state changes in the N 1s region

Investigating the nitrogen species by XPS provides direct access to the chemical-state changes that occur when the uncoordinated MnTPyP SAM is transformed into the coordinated Co–MnTPyP network. Figure 4.12a (bottom) shows the N 1s spectrum of the pristine MnTPyP SAM. A single asymmetric feature with a tail toward higher binding energy is observed. Upon Co deposition, the overall intensity shifts toward higher binding energy and the spectrum becomes broader, see Figure 4.12a (top). As established in Section 4.3.2, the final network contains Co instead of Mn in the macrocycle. Therefore, a SAM of CoTPyP was also investigated as a reference, see Figure 4.12b (bottom). In this case, the N 1s feature is considerably narrower than for the MnTPyP layer. Post-deposition of Co onto the CoTPyP SAM leads to a shift toward higher binding energy and to the appearance of an additional component, visible as a shoulder on the high-binding-energy side (Figure 4.12b, top).

To extract quantitative information from the N 1s region, the spectra were fitted, and the results are summarized in Table 4.3. Metallated TPyP molecules contain two non-equivalent nitrogen species: pyrrolic nitrogen in the macrocycle, coordinating either Mn or Co, and pyridinic nitrogen in the meso-substituents, which serve as coordination sites for the additional cobalt atoms. For the SAM, the ratio of pyrrolic to pyridinic nitrogen is fixed at 1:1. In the final network, however, the ratio of coordinated to uncoordinated pyridyl nitrogen depends on the coverage of the added metal nodes and cannot be fixed a priori. In principle, up to four configurations could be present in the MnTPyP-based network: uncoordinated pyridyl, coordinated pyridyl–Co, pyrrolic–Mn, and pyrrolic–Co. However, given the experimental energy resolution and the expected energy differences of around 100 meV and 350 meV, a four-component fit would not be statistically robust and would likely overfit the data. To ensure that only two chemically distinct nitrogen species are present, an excess amount of Co was deposited so that all pyridyl sites are saturated and transmetallation is complete. This again makes it possible to fix the area ratio at 1:1. Figures A.8 and A.10 show the evolution of the N 1s line shape of MnTPyP and CoTPyP, respectively, as a function of increasing Co coverage. Accordingly, all N 1s spectra were fitted with two Voigt components together with a Shirley background and a pre-subtracted background. Details of the procedure and the specific constraints are given in Section A.7; the resulting fit parameters and constraints are summarized in the corresponding tables.

**MnTPyP SAM** The fit of the MnTPyP SAM N 1s spectrum yields one peak at 397.95 eV with a total width of 1.17 eV, and a second component at 398.74 eV with a width of 1.47 eV. The feature at 398.74 eV can be assigned to uncoordinated pyridinic nitrogen, which is typically found at slightly higher binding energy than the metallated pyrrolic component [24, 28]. This assignment is consistent with reported values for pyridyl-substituted porphyrins on metal surfaces, which generally place pyridinic nitrogen in the upper part of the 398.3 eV to 399.1 eV range, depending on substrate interaction [24, 28, 93, 100, 265, 266]. The comparatively broad pyridinic contribution likely reflects two unresolved subcomponents: a dominant fraction of uncoordinated pyridyl groups and a smaller fraction that interacts with the Au surface [250], consistent with the NEXAFS observation of peak B in the nitrogen K-edge of the SAM (Section 4.2.2).

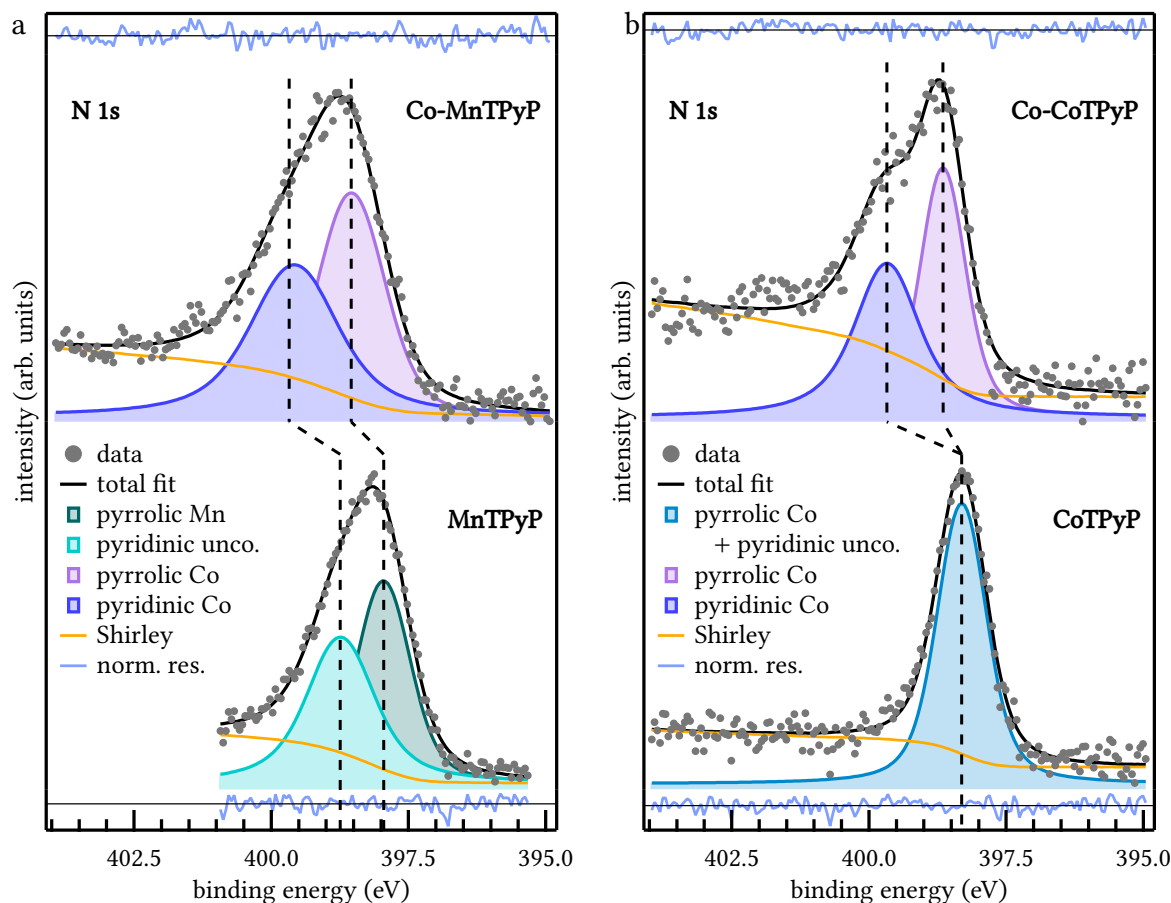


Figure 4.12.: N 1s XPS spectra. (a) Pure molecular layer MnTPyP (bottom) and the network layer after depositing 0.15 ML Co (top). (b) Analogous measurements for a ML of CoTPyP (bottom) and after 0.11 ML Co deposition (top). The resulting fitting parameters are reported in Tables A.17 to A.20. Measurements were performed by Olga Resel.

By assigning the component at 398.74 eV to pyridinic nitrogen, the second component at 397.95 eV can be attributed to the macrocycle. Comparison with the literature shows that the binding energy of pyrrolic nitrogen depends on both the embedded transition metal and the substrate, since both influence the oxidation state of the central metal and thus the metal–nitrogen bond [24, 62, 263, 267]. Reported values for manganese-containing porphyrins are comparatively scarce, but the present value agrees well with MnTPyP on graphene (397.8 eV) and lies within the range reported for related manganese tetrapyrroles (397.8 eV to 398.9 eV) [24, 242, 254].

**CoTPyP SAM** In contrast to MnTPyP, the CoTPyP SAM exhibits a much narrower N 1s feature. A fit with two Voigt components, constrained to equal areas and Gaussian widths, yields peaks at 398.14 eV and 398.55 eV, see Figure A.9. Given the limited energy resolution and the small expected separation, this likely does not reflect the true physical situation, since both the pyrrolic and pyridinic contributions are expected in this energy range [24, 28, 100]. Fitting the spectrum with a single Voigt line yields a peak at 398.31 eV, which better reflects the experimental non-separability of the two actual components. Both approaches result in similar reduced  $\chi^2$  values of 4.46 and 4.76, respectively, meaning that neither model significantly improves the fit. Therefore, in the following, the single-peak position

| system    | pyrrolic–Mn | pyrrolic–Co | pyridinic | pyridinic–Co |
|-----------|-------------|-------------|-----------|--------------|
| MnTPyP    | 397.95      | -           | 398.74    | -            |
| Co–MnTPyP | (398.44)    | 398.54      | (399.23)  | 399.58       |
| CoTPyP    | -           | 398.31      | -         | -            |
| Co–CoTPyP | -           | 398.65      | (398.69)  | 399.67       |

Table 4.3.: Assignment of the features in the N 1s spectra, with their positions given in eV. Values in parentheses are estimated from the shift of the C 1s binding energy upon network formation. In the case of Co–CoTPyP, the parenthetical value corresponds to the unresolved average position of the pyrrolic and pyridinic components, which coincide in pristine CoTPyP.

at 398.31 eV is used as an effective average for the pyrrolic and pyridinic nitrogen species in CoTPyP.

This average value is consistent with the literature for both nitrogen environments in cobalt porphyrin systems. Reported N 1s binding energies for pyrrolic nitrogen in CoTPP/CoTPyP-type systems span a relatively broad range, approximately 398.1 eV to 398.95 eV, depending on substrate and coordination environment [19, 28, 268]. The pyridinic contribution is likewise expected in a very similar energy range and has been reported to vary with the central transition metal and the molecule–substrate interaction [24, 28, 100]. The fact that the two nitrogen species are not resolved here is therefore fully consistent with their small intrinsic energy separation.

The higher effective binding energy of the CoTPyP N 1s signal relative to the pyrrolic component of MnTPyP is consistent with the known dependence of the macrocyclic nitrogen binding energy on the incorporated transition metal [62, 263, 267]. At the same time, small shifts of the pyridinic contribution between MnTPyP and CoTPyP may reflect differences in molecule–substrate distance and interaction, as observed for related systems on graphene [24, 28]. A further difference is found in the linewidth: the CoTPyP feature is narrower than the pyrrolic component in MnTPyP. This can be attributed to stronger hybridization between pyrrolic N and Mn *d* states in the manganese case, as evidenced by the nitrogen K-edge NEXAFS (Section 4.2.2). A similar broadening of the pyrrolic peak was previously observed for MnPc [264].

**MOF layers** After assigning the components in the SAMs, the same strategy can be applied to the network layers. After deposition of 0.15 ML Co onto the MnTPyP SAM, the N 1s features shift to 398.54 eV and 399.58 eV, with widths of 1.4 eV and 1.9 eV, respectively. For the CoTPyP-based network, deposition of 0.11 ML Co, again exceeding the stoichiometric coverage of 0.04 ML, leads to peaks at 398.65 eV and 399.67 eV, with widths of 0.98 eV and 1.42 eV, respectively. The Co–CoTPyP spectrum displays a barely visible additional feature around 401.5 eV, which is attributed to a HOMO–LUMO shake-up process [24, 100, 171]. When this feature was included as an additional component in the fit, no meaningful convergence could be achieved.

In both final network structures, the N 1s features shift to higher binding energy relative to the pristine SAM. For Co–CoTPyP, the two components are shifted by 0.34 eV and 1.36 eV, respectively, relative to the single-peak position of the SAM. The lower-binding-energy component exhibits a shift similar to the C 1s core level shift of 0.39 eV and to the 0.41 eV



shift later observed for the Co  $2p_{3/2}$  core level. Therefore, the component at 398.65 eV is still assigned to the pyrrolic nitrogen. The second component shows a much larger shift, within the range reported for coordination of pyridinic nitrogen to additional metal centers [24, 28, 266]. Thus, the higher-binding-energy feature at 399.67 eV is assigned to coordinated pyridyl nitrogen.

By analogy, since the same final MOF structure is expected independent of whether the precursor is MnTPyP or CoTPyP, Co–CoTPyP serves as the reference for the assignments in the Co–MnTPyP system. Accordingly, the lower-binding-energy feature at 398.54 eV in the Co–MnTPyP spectrum is assigned to pyrrolic nitrogen coordinated to Co, and the second component at 399.58 eV to pyridyl nitrogen coordinated to the Co nodes. Thus, in the MnTPyP-based network the pyrrolic component is shifted by about 600 meV relative to the pyrrolic–Mn position in the SAM. This shift is larger than the previously identified C 1s core level shift of 0.49 eV, which was attributed mainly to modified screening and interface energetics (Section 4.3.4). The same screening-related contribution is expected to be present here as well [267], but an additional chemical shift must also be considered. This additional contribution is naturally explained by transmetallation, *i.e.* by replacement of Mn by Co in the macrocycle, since the pyrrolic binding energy depends on the central metal. The pyridinic component is shifted by 0.84 eV, a magnitude similar to that found for the CoTPyP case and to reported values upon pyridyl coordination [24, 28].

In the present case, the N 1s features also broaden upon network formation, in agreement with the behavior of the C 1s line. This broadening corresponds to a reduced core-hole lifetime, *i.e.* a larger Lorentzian width, and therefore indicates a change in the decay channels. Since the MOF layer is located farther from the metal substrate than the SAM, substrate-mediated screening of the core hole is expected to decrease. The observed broadening is therefore more naturally attributed to additional intralayer decay channels introduced by the network connectivity and the presence of multiple Co centers. In other words, the molecules can now partially relax each other's core holes via the Co nodes, partly overcompensating the reduced substrate relaxation channels. Previously reported screening-related asymmetries induced by additional metal centers [197] may be hidden by the limited energy resolution and by the asymmetry introduced experimentally by the X-ray source. Any remaining asymmetry is further absorbed by the Shirley background used in the fit.

**Summary** In the pristine SAMs, distinct pyrrolic and pyridinic nitrogen contributions are observed, and their positions depend on both the central metal and the molecule–substrate interaction. The pyrrolic component is shifted between MnTPyP and CoTPyP, in agreement with the literature on transition metal porphyrins. For the pyridinic species, the picture is less straightforward, but the non-identical binding energies in the two SAMs are consistent with different geometries and interactions, as reported previously. In the final networks, both nitrogen components, namely pyrrolic–Co in the macrocycle and coordinated pyridyl–Co, appear at essentially the same binding energies within experimental uncertainty for the two different precursors, supporting the conclusion that the final coordination environment is the same. The somewhat sharper line shape of the Co–CoTPyP network compared to Co–MnTPyP may reflect residual Mn-related species or a small fraction of uncoordinated pyridyl sites in the latter. In both networks, the nitrogen

peaks are broader than in the pristine SAMs, which can be linked to enhanced screening channels introduced upon coordination.

#### 4.3.6. Cobalt oxidation states from the Co $2p_{3/2}$ core level

To obtain detailed information on the oxidation state of the cobalt centers in the network, the Co  $2p_{3/2}$  core level was investigated by XPS. To assign the features observed for Co-MnTPyP, spectra of the reference systems CoTPyP and Co-CoTPyP were analyzed in parallel. Figure 4.13 shows the Co  $2p_{3/2}$  spectra of CoTPyP, Co-CoTPyP, and Co-MnTPyP, together with the corresponding fits. The peak assignment is summarized in Table 4.4.

The Co  $2p_{3/2}$  core level is well known to be complex even for a single oxidation state because of the open  $3d$  shell, which gives rise to multiplet structure, shake-up satellites [24, 269], and screened final-state contributions such as GS features [24, 28]. In a square-planar ligand field, Co(II) ( $3d^7$ ) typically exhibits pronounced multiplet structure, whereas Co(I) ( $3d^8$ , usually low spin) shows substantially weaker multiplet signatures [19, 76, 131, 257, 267, 270]. Even metallic Co can display an asymmetric line shape with weak satellite intensity in the submonolayer regime (Figure A.13), attributed to interactions between Co  $d$  states and substrate  $sp$  states [271]. In addition, X-ray source satellites ( $K_{\alpha 3}$ ,  $K_{\alpha 4}$ , etc.; see Section 4.3.3) mirror intensity from the Co  $2p_{1/2}$  region into the Co  $2p_{3/2}$  window. Given the low cobalt concentration and the broad intrinsic line shape, together with the limited analyzer resolution and non-monochromatized X-ray source, a full decomposition of all these contributions is not feasible here. A simplified but internally consistent fitting approach was therefore adopted. After linear background subtraction in the pre-peak region (Section A.8), the spectra were fitted using a Shirley background and Voigt line shapes: one Voigt peak for the CoTPyP SAM and two Voigt peaks for the MOFs, with a shared Gaussian width to account for the experimental resolution. In addition, a broad Gaussian was included to describe satellite intensity and thus to effectively capture unresolved multiplet and shake-up contributions. Further details on the fitting strategy and background treatment are given in Section A.8.

**CoTPyP SAM** In CoTPyP, only one cobalt species is present, namely Co in the macrocycle. The corresponding spectrum in Figure 4.13a exhibits a single dominant feature at 779.65 eV. Its asymmetric and broadened line shape indicates unresolved multiplet structure. Accordingly, the weak satellite-like peak included in the fit should be regarded as an effective description of the high-binding-energy tail rather than as a literal one-to-one representation of individual multiplet components.

By comparison with related systems, the feature at 779.65 eV is assigned to Co(II) in the macrocycle. For cobalt porphyrins, the Co(II)  $2p_{3/2}$  peak is commonly reported close to 780 eV in multilayers [76, 131], while somewhat lower values, down to about 779.25 eV, have been observed for monolayers [19]. On graphene, CoTPyP shows a pronounced multiplet structure with the main peak around 780.1 eV, likewise assigned to Co(II) [28, 169]. The slightly lower value observed here is therefore fully consistent with a Co(II) species in a monolayer interacting with the Au(100) substrate.

A screened final-state (Gunnarsson–Schönhammer) contribution at lower binding energy, as reported for related systems [24, 28, 169], could in principle be present but is not resolved here. Tests including an explicit GS component do not significantly change the extracted main peak position (changes  $< 0.05$  eV), but they introduce unacceptably large uncertainties in the fit parameters. Within the present resolution, a distinct GS component in CoTPyP therefore cannot be extracted reliably and is not considered further.

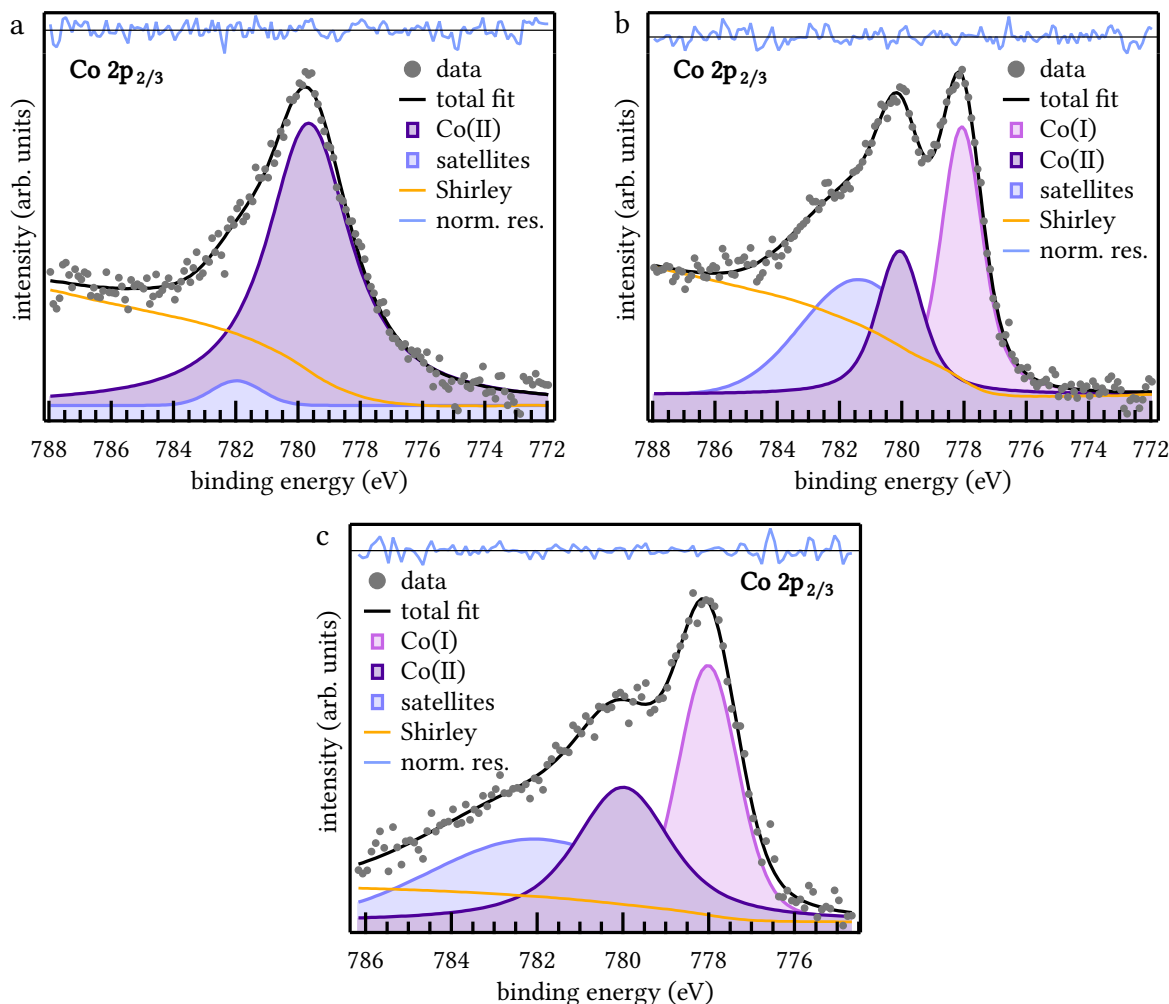


Figure 4.13.: Co  $2p_{3/2}$  core level spectra for (a) CoTPyP, (b) Co-CoTPyP, and (c) Co-MnTPyP. The corresponding fitting parameters are given in Tables A.22, A.23, and A.26. For the network layer, 0.11 ML Co was deposited. The spectra of CoTPyP and Co-CoTPyP were measured by Olga Resel.

**Co-CoTPyP MOF** Upon network formation by deposition of 0.11 ML Co and annealing to 420 K, the Co  $2p_{3/2}$  spectrum changes markedly (Figure 4.13b). A new component appears at lower binding energy (778.07 eV), while additional intensity develops on the high-binding-energy side.

The low-binding-energy peak at 778.07 eV is consistent with Co(I). Similar energies have been reported for Co(I) in cobalt porphyrins and phthalocyanines on surfaces [19, 76, 270], as well as for Co(I) coordinated by pyridyl moieties in MTPyP-based MOFs on graphene [17,

24]. The low-binding-energy component in the Co-CoTPyP network is therefore assigned to Co(I) at the pyridyl coordination nodes.

| system    | pyridinic-Co | pyrrolic-Co | satellite |
|-----------|--------------|-------------|-----------|
| CoTPyP    | –            | 779.65      | 782       |
| Co-CoTPyP | 778.07       | 780.06      | 781.4     |
| Co-MnTPyP | 778.01       | 779.99      | 782       |

Table 4.4.: Assignment of the features in the Co  $2p_{3/2}$  spectra. All values are given in eV.

The macrocycle-related component shifts by about 0.41 eV toward higher binding energy upon network formation, from 779.65 eV to 780.06 eV. This shift is comparable to those observed for the C 1s and N 1s core levels (Sections 4.3.4 and 4.3.5). As discussed there, such a shift can be related to changes in interface energetics and final-state screening [76, 91, 131]. The cobalt center in the macrocycle therefore remains Co(II), and its slightly higher binding energy places it closer to the values commonly reported for multilayer Co(II) porphyrins around 780 eV [76, 131]. A Co(III) state in a porphyrin environment would be expected at substantially higher binding energy, around 781.4 eV in related systems [17], and would moreover require stronger oxidizing ligands such as NO<sub>2</sub> [19], which are absent here.

The high-binding-energy shoulder is assigned to a superposition of unresolved multiplet and shake-up intensity from both cobalt species. Changes in the shape and intensity of the broad Gaussian used to represent this part of the spectrum are therefore indicative of modifications in the valence configuration of the cobalt centers [28], which will be discussed in Section 4.3.8.

The coexistence of Co(II) in the macrocycle and Co(I) at the pyridyl nodes can be rationalized by differences in local coordination geometry and Co–N bond length [24, 272]. In CoTPP and CoTPyP, Co–N bond lengths within the macrocycle are typically around 1.9 Å [17, 273, 274]. In the Co-MTPyP frameworks on graphene, longer Co–N distances around 2.3 Å, have been reported for the node site [17, 24]. A weaker ligand field at the pyridyl node is consistent with stabilization of a Co(I) center. In addition, the commensurate network on Au(100) implies that the macrocycle-centered and node-centered cobalt atoms may occupy different adsorption registries, which can further modulate their effective charge state. A more detailed analysis of such site-specific effects would require complementary STM and scanning tunneling spectroscopy (STS) measurements.

The appearance of a low-binding-energy peak does not, by itself, prove a distinct oxidation state, since screened final states (GS) and metallic Co can also produce intensity on that side of the main line [131, 168, 267]. Such screening contributions depend sensitively on the valence-level alignment and may therefore change upon network formation. However, comparison of the normalized spectra of CoTPyP and Co-CoTPyP (Figure A.12) supports the presence of a genuine second chemical species: if the additional Co atoms had the same chemical environment as the cobalt ions already present in the macrocycle, the main peak near 779.65 eV would be expected simply to scale in intensity, without the appearance of a distinct new peak. Instead, the additional intensity is concentrated at 778.07 eV. A contribution from metallic Co clusters must also be considered, since the deposited coverage of 0.11 ML exceeds the stoichiometric value of 0.04 ML. However, the low-binding-energy peak in the network is sharper and more intense than the signal

observed for metallic Co reference deposits (Figure A.13), indicating that it cannot be explained solely by Co(0) clusters. A minor admixture of screened final-state intensity to this component, as discussed for related Co–MTPyP networks [24, 28], cannot be excluded but cannot be quantified reliably here.

**Co–MnTPyP MOF** The Co  $2p_{3/2}$  spectrum of Co–MnTPyP (Figure 4.13c) closely resembles that of Co–CoTPyP, although the individual components are less clearly resolved, similar to the situation found for the N 1s region (Section 4.3.5). This is most likely related to residual Mn on the surface and to less favorable experimental conditions. In particular, the Co–MnTPyP spectrum was acquired during an earlier measurement period with a more heavily used anode, resulting in lower X-ray flux, increased background, and additional radiation from the Ag primer of the anode.

This similarity between Co–MnTPyP and Co–CoTPyP is structurally expected, since both precursors ultimately yield the same final MOF, with cobalt occupying the macrocycle and the pyridyl coordination sites. For detailed analysis, the spectrum measured at 0.11 ML Co is shown here, corresponding to the coverage used for most core level experiments. Metallic Co clusters are expected to be less relevant here than in the CoTPyP case, because 0.11 ML is close to the ideal stoichiometric coverage of 0.08 ML, corresponding to two Co atoms per MnTPyP molecule.

The fit of the Co–MnTPyP spectrum yields two main components at 778.01 eV and 779.99 eV, together with a broad Gaussian at 782 eV representing unresolved satellite intensity. These values are very close to those found for Co–CoTPyP (Table 4.4) and lead to the same assignment: Co in the macrocycle remains in the +2 oxidation state, while Co at the pyridyl coordination nodes is in the +1 oxidation state.

To further probe the evolution of the two contributions, an additional series of Co dosing experiments on MnTPyP was carried out, as already introduced in Section 4.1. More details about it can be found in Section A.8.

**Summary** In both network systems, Co–CoTPyP and Co–MnTPyP, cobalt in the macrocycle is assigned to the +2 oxidation state, whereas cobalt coordinated at the pyridyl nitrogen sites is assigned to the +1 oxidation state. This is fully consistent with previous studies on Co–CoTPyP and related MTPyP-based frameworks on graphene [24, 34]. In those systems, the same pattern was observed: Co(II) in the macrocycle and Co(I) at the nodes, with the latter being significantly more chemically reactive [30, 34, 275]. That distinction will become directly relevant for the gas-adsorption experiments discussed in Section 6.1.

### 4.3.7. Ligand-field signatures at the cobalt L<sub>3</sub>-edge

To further support the coordination of the deposited Co atoms on top of the MnTPyP ML, complementary NEXAFS measurements were performed at the Co L<sub>3</sub>-edge. As shown in Section 4.2.2, the pyridyl groups participate directly in coordination to the additional Co. In addition, Section 4.3.2 demonstrated that Mn in the macrocycle is replaced by Co through transmetallation. The Co 2p<sub>3/2</sub> analysis in Section 4.3.6 further showed that two cobalt species are present in the final framework: Co(I) (3d<sup>8</sup>) at the pyridyl coordination nodes and Co(II) (3d<sup>7</sup>) in the macrocycle. In contrast to XPS, which resolves chemically shifted core levels, NEXAFS probes transitions into unoccupied states and therefore reflects the combined unoccupied 3d manifold of all Co species within the probed area. Because both Co sites are coordinated by nitrogen in an approximately square-planar environment, their ligand-field splittings are expected to be similar and their spectral contributions to overlap strongly.

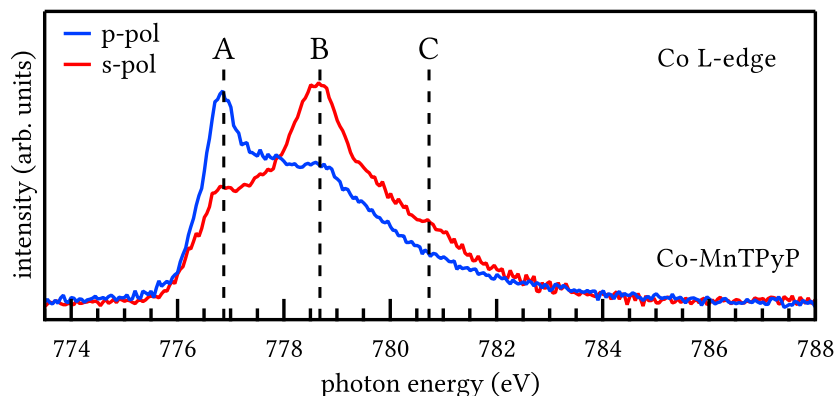


Figure 4.14.: NEXAFS spectra at the Co L<sub>3</sub>-edge for the Co–MnTPyP network. The spectra were measured with p-polarized (blue) and s-polarized (red) light at an incidence angle of  $\alpha = 70^\circ$ .

The Co L<sub>3</sub>-edge absorption spectrum of the Co–MnTPyP MOF is shown in Figure 4.14 for p- and s-polarized light. Two main resonances are observed at 776.87 eV (A) and 778.68 eV (B), together with a weak shoulder at 780.73 eV (C). A clear linear dichroism is present: resonance A is enhanced in p-polarization, whereas B and C gain intensity in s-polarization. This dichroic response directly evidences a ligand field around the cobalt atoms and therefore supports that the deposited Co is predominantly coordinated rather than purely metallic [101, 257, 276]. A small residual contribution from uncoordinated Co in clusters, due to the slight excess of deposited cobalt, cannot be excluded.

Compared with the Mn L<sub>3</sub> spectrum, the Co L<sub>3</sub> spectrum is less structured and narrower. This is consistent with the smaller number of unoccupied 3d states for Co(I) and Co(II) compared with Mn(II), leading to generally weaker multiplet structure for 3d<sup>8</sup> and 3d<sup>7</sup> configurations than for 3d<sup>5</sup> systems [59, 228].

According to the consensus in the literature, the first resonance A is predominantly associated with transitions into the Co  $a_{1g}$  ( $d_{z^2}$ ) orbital, consistent with its enhancement in p-polarization [132, 270, 277]. The second resonance B is assigned mainly to transitions into the  $b_{1g}$  ( $d_{x^2-y^2}$ ) orbital, which is stronger in s-polarization [132, 270, 277]. The weak shoulder C has likewise been attributed to additional  $b_{1g}$ -derived transitions and is often

more pronounced in thicker films, while its intensity decreases when substrate interaction and charge transfer become more important [270].

In comparing the present spectra with literature data, it should be noted that the absolute photon energy calibration is not always fully consistent between different studies. Relative peak separations and the overall spectral shape are therefore more reliable comparison criteria than absolute energy positions. Small differences in relative intensities and peak positions can be rationalized by variations in Co–N bond lengths, substrate interaction, ligand-field strength, and polarization degree [132, 228]. Overall, the spectra in Figure 4.14 most closely resemble those reported for Co in a  $D_{4h}$  ligand field formed by nitrogen ligands in the +2 oxidation state [132, 277]. This interpretation is further supported by gas-phase CoPc data and corresponding multiplet ligand-field calculations [278]. In addition, a qualitatively similar double-peak structure was observed after on-surface replacement of Fe by Co in FeTPP on Au(111), where only a single Co environment in the macrocycle is expected [101].

An alternative interpretation discussed in the literature is a mixed-valence scenario arising from charge-transfer hopping between Co  $3d_{z^2}$  and Au  $sp$  bands [279]. In the present case, the XPS results of the previous subsection already establish the coexistence of Co(I) and Co(II) in the framework. The relevant question is therefore not whether mixed valence may occur in a broader sense, but rather how the two chemically identified cobalt species contribute to the measured NEXAFS spectrum

Literature on related systems suggests that the low-energy resonance A is strongly associated with Co(II) and becomes strongly suppressed when the cobalt center is reduced to Co(I) [19]. A similar correlation between the weakening of resonance A and reduction from Co(II) to Co(I) has been reported in other systems, while resonance B remains much less affected [132, 277]. The disappearance or strong reduction of A has been linked to increased occupation or hybridization of the Co  $d_{z^2}$  orbital, for example through stronger substrate interaction [270]. Since Co(I) carries one additional  $3d$  electron relative to Co(II), its contribution to transitions into  $d_{z^2}$ -derived final states is expected to be smaller. This is consistent with resonance A being dominated by Co(II) even though Co(I) is also present in the framework. In this picture, resonance A is primarily associated with Co(II) in the macrocycle, where the  $d_{z^2}$  orbital points out of the molecular plane and remains sufficiently localized. Resonance B, by contrast, is expected to contain contributions from both Co(II) and Co(I). Resonance C can also be assigned to additional  $b_{1g}$ -like transitions, predominantly associated with the Co(II) species [132, 270, 277].

Based on electron counting alone, one might expect resonance B, which receives contributions from both oxidation states, to be substantially more intense than A. This is not observed in the present data, and two geometric effects may contribute to this. First, the  $d_{z^2}$  orbital associated with resonance A is oriented along the surface normal and is therefore comparatively insensitive to the in-plane azimuthal orientation of the molecules relative to the incident polarization. By contrast, the  $d_{x^2-y^2}$  orbital associated with resonance B lies in the molecular plane, and its projection onto the electric-field vector depends strongly on the azimuthal orientation. In the network, the N–Co–N axes of the macrocycle-centered Co and the pyridyl-coordinated Co are rotated by  $45^\circ$  with respect to each other and to the substrate high-symmetry directions (see Figure 4.5b). Since the sample was not azimuthally aligned during the NEXAFS measurement, the in-plane anisotropy of the  $d_{x^2-y^2}$ -derived

intensity is partially averaged out, whereas the out-of-plane  $d_{z^2}$ -derived intensity remains efficiently probed in p-polarization. Second, the pyridyl groups are rotated out of the molecular plane after MOF formation, as shown by the nitrogen K-edge data (Section 4.2.2). Hybridization between the cobalt  $d$  orbitals and the tilted pyridyl  $\pi$  system can alter the effective orientation and admixture of the  $d_{x^2-y^2}$ -like states, thereby modifying their dichroism relative to reference systems with flatter ligands. The macrocycle-centered Co, in contrast, remains embedded in a flatter environment that is more similar to the porphyrin and phthalocyanine reference systems.

As an additional remark, the Co  $L_3$ -edge spectra were acquired at 6 T and 4.5 K with high statistics and were compared with spectra measured at room temperature and zero magnetic field. Within the experimental noise, no significant differences in line shape were detected. This indicates that the Co  $L_3$ -edge spectra reflect the electronic ground state of the cobalt centers and are not measurably modified by field-induced spin-state changes under the present conditions [257].

**Summary** In summary, the dichroism at the Co  $L_3$ -edge shows that the deposited cobalt is located in a ligand field and therefore supports coordinated, rather than purely metallic, cobalt species. After MOF formation, Co is incorporated both into the macrocycle through transmetallation and at the pyridyl coordination nodes. Because Co(I) and Co(II) share a similar square-planar coordination and their spectral contributions overlap strongly, the Co  $L_3$ -edge alone cannot disentangle the two oxidation states quantitatively. The low-energy resonance A is characteristic of Co(II) in a  $D_{4h}$ -like ligand field and thus clearly supports the presence of Co(II) in the network. Resonance B likely contains contributions from both Co(II) and Co(I) and therefore does not allow an independent quantification of the Co(I) fraction. In this sense, the Co  $L_3$ -edge NEXAFS is fully consistent with the two-species picture derived from XPS, but by itself it primarily supports the presence of coordinated Co(II) and does not independently prove the presence of Co(I).

#### 4.3.8. Molecular orbitals and band formation from MM

After establishing the formation of the coordination network, the focus now shifts to changes in the valence band (VB) region induced by network formation, since the occupied states determine many of the electronic properties of the system [2, 30, 40, 46]. First, the momentum-integrated EDCs are discussed together with the corresponding momentum maps of the observed features. BMs are then used to analyze the dispersion of these states as a function of  $k_{\parallel}$  and  $E_b$ . Finally, MM also provides access to the samples' WKF, which allows the experimentally observed states to be compared with calculated molecular-orbital energies.

**MnTPyP** Figure 4.15a shows the angle-integrated VB spectra of the clean Au(100) substrate and the MnTPyP SAM, together with the corresponding difference spectrum (top). The difference spectrum highlights two features located at 1.15 eV (①) and 1.50 eV (②), with feature ① being more intense than feature ②. To identify their origin, the corresponding momentum maps are shown in the upper half of Figure 4.15b and c, respectively.



The lower half of Figure 4.15b and c shows the calculated momentum distributions of the gas-phase HOMO-1 and HOMO-2 of MnTPyP [280]; other molecular orbitals are compiled in Figure A.17. Since the molecular-orbital intensities are comparatively weak and their spectral signatures rather broad, the momentum maps were integrated over an energy window of 150 meV around the respective peak maxima. To highlight the molecular contributions, the momentum maps of the clean Au(100) substrate (Figure A.16) were subtracted, as described in detail in Section A.9.1. For comparison with theory, the experimental data were symmetrized according to the  $D_{4h}$  symmetry of the substrate surface in order to reduce polarization-related effects. The calculated maps were symmetrized by summing four maps rotated by  $90^\circ$ , accounting for the rotational domains imposed by the substrate symmetry. In addition, the calculated maps were rotated by a common azimuthal angle to match the experimentally observed molecular fingerprints in momentum space. They were generated using the Python tool *kmap.py* [281] for a kinetic energy of 15 eV, based on orbitals from the molecular-orbital database [282].

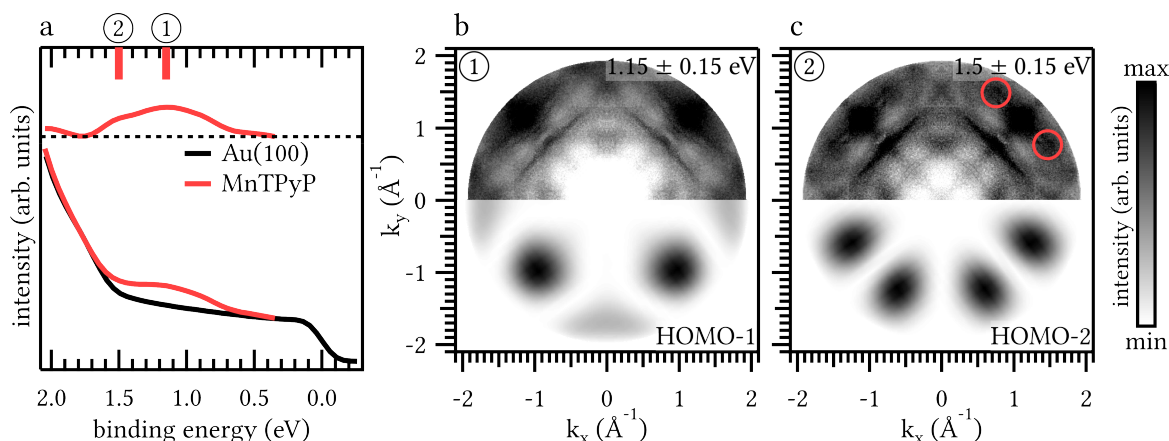


Figure 4.15.: (a) EDCs of the VB region of the clean Au(100) substrate (black) and the MnTPyP SAM (red). (b, c) Momentum maps of the features at 1.15 eV (b) and 1.50 eV (c), integrated over an energy window of  $\pm 0.15$  eV (top), and the corresponding calculated momentum distributions of gas-phase MnTPyP orbitals at a kinetic energy of 15 eV (bottom). The measurements were performed with a photon energy of 21.2 eV. Data of the theoretical orbitals from [280, 281].

The identified double-peak structure in the EDC is characteristic of metallated porphyrins and phthalocyanines, whereas non-metallated molecules typically exhibit only a single dominant feature [51, 59, 131, 262, 267]. POT provides direct access to the molecular-orbital origin of these features. The momentum pattern of feature 1 in Figure 4.15b closely resembles the calculated HOMO-1 of gas-phase MnTPyP. Feature 2 in Figure 4.15c still shows a pronounced HOMO-1 fingerprint, but with an additional contribution from the HOMO-2. This mixed assignment is consistent with the calculated energy separation of only about 150 meV between HOMO-1 and HOMO-2 and with the intrinsic broadening of the experimental spectral features. Remaining differences between experiment and theory may arise from background subtraction, the adsorption geometry, and the fact that the calculations refer to the gas-phase molecule [51, 283].

A quantitative comparison can be made using the calculated orbital energies (see Table A.27) of gas-phase MnTPyP [280] together with the measured WKF of the SAM, 4.61 eV. Within this picture, feature 1 is expected to receive contributions from the spin-up HOMO,

HOMO-1, and HOMO-2, as well as from the spin-down HOMO-1 and HOMO-2. A clear fingerprint of the HOMO itself is not observed in the momentum maps. This can be rationalized by the low photoemission cross-section of Mn 3*d* states at the employed photon energy of 21.2 eV, compared with the significantly larger cross-sections of C and N 2*p* states [62] and the location of the HOMO on the metal core [280]. Feature ② shows a stronger HOMO-2 contribution in its momentum map, consistent with the calculated energetic ordering. The different intensities of features ① and ② are therefore more plausibly explained by the number and character of the contributing orbitals than by cross-section arguments alone. The relative intensity may further be influenced by the experimental geometry, since mainly p-polarized light impinges on the sample at an angle of 68°, which enhances photoemission from states with out-of-plane character [94].

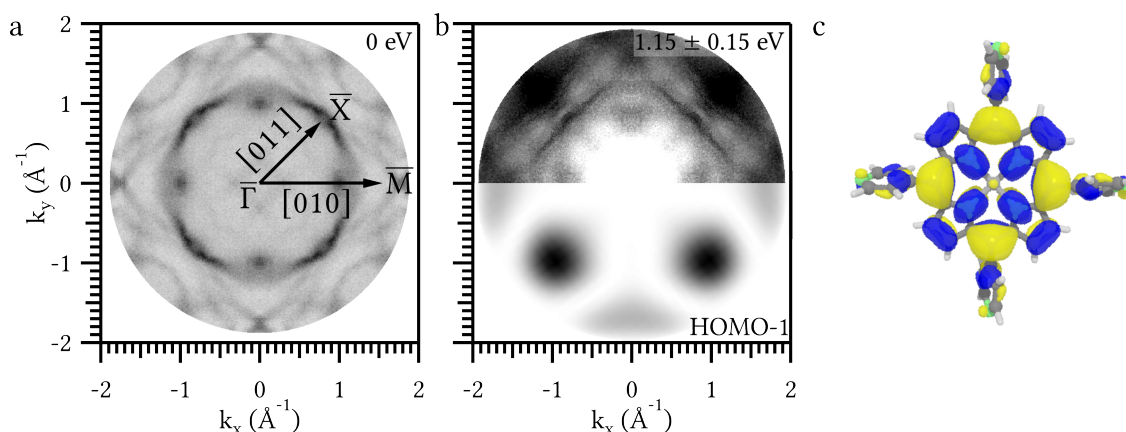


Figure 4.16.: Identification of the azimuthal orientation of the molecules relative to the substrate. (a) Fermi surface of the clean Au(100) substrate. The arrows indicate the high-symmetry directions  $[120]$ . (b) Experimental (top) and theoretical (bottom) momentum-resolved electron distribution of the identified MnTPyP HOMO-1 from Figure 4.15b. (c) Corresponding real-space distribution of the HOMO-1, adapted from [280]. Data of the theoretical orbital from [280, 281].

Before discussing the MOF features, the alignment of the molecular symmetry axes relative to the high-symmetry directions of the substrate is considered, as illustrated in Figure 4.16. From the Fermi surface of Au(100) in Figure 4.16a, the high-symmetry directions in momentum space can be identified and related to the corresponding real-space directions [119, 120]. The  $\bar{X}$  direction corresponds to the  $[011]$  direction in real space. Panel b of Figure 4.16 shows the momentum pattern of the identified HOMO-1; its four main lobes are aligned along the  $[011]$  direction of the substrate. The corresponding real-space molecular-orbital distribution is shown in panel c [280]. It follows that the N-Mn-N bond directions of MnTPyP are aligned with the  $[011]$  directions of the substrate. This is fully consistent with the real-space model proposed in Figure 4.4b.

**Co-MnTPyP** Figure 4.17a shows the EDCs of the clean Au(100) substrate, the MnTPyP SAM, and the Co-MnTPyP MOF; the upper part again displays the corresponding background-subtracted spectra of the SAM and MOF. The double-peak signature (① and ②) identified for the SAM shifts by about 350 meV toward higher binding energy upon network formation, giving rise to features ④ and ⑤. In addition, a new feature appears at 0.45 eV (③). The overall double-peak structure is preserved, but with increased intensity. Figure 4.17b

shows the momentum pattern of feature ④ at 1.5 eV (top), while the momentum map of feature ⑤ at 1.85 eV is displayed in Figure 4.17c (top). The lower halves of these panels show the corresponding calculated momentum distributions of the HOMO and HOMO-2 of gas-phase CoTPP, respectively. The momentum map of the newly emerged feature ③ at 0.45 eV is presented separately in Figure 4.18. As before, the experimental momentum maps were extracted from the background-corrected data (Section A.9.1) and integrated over an energy window of  $\pm 0.15$  eV.

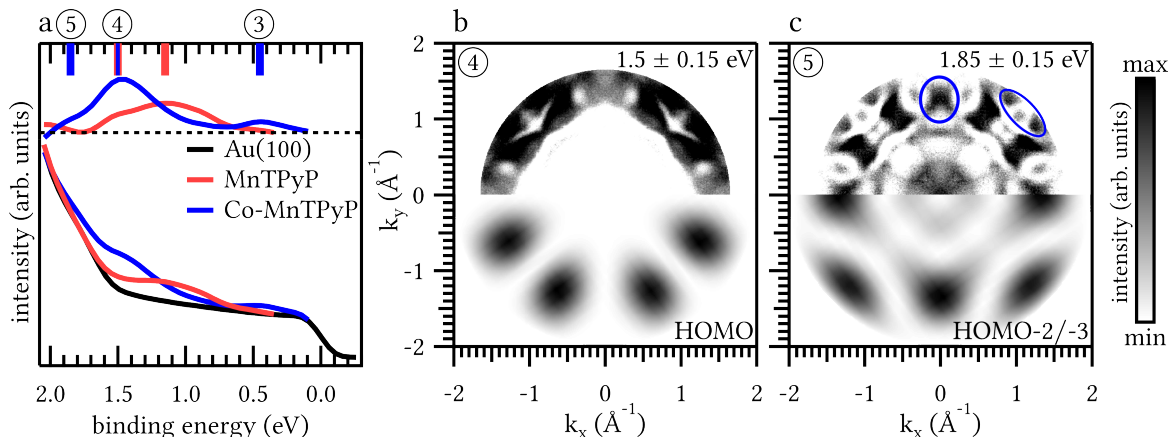


Figure 4.17.: (a) EDCs of the VB region for the clean Au(100) substrate (black), the MnTPyP SAM (red), and the Co-MnTPyP MOF (blue), measured with a photon energy of 21.2 eV. (b, c) Momentum maps of the features at 1.5 eV (b) and 1.85 eV (c), integrated over an energy window of  $\pm 0.15$  eV (top), and the corresponding calculated momentum distributions of gas-phase CoTPP orbitals at a kinetic energy of 15 eV (bottom). Data of the theoretical orbitals from [281, 284].

Since network formation leads to replacement of Mn by Co in the macrocycle (Section 4.3.2), gas-phase CoTPP provides the closest available orbital reference in the database [282]. It should be kept in mind that this reference does not include the second Co species at the pyridyl coordination nodes, whose local square-planar environment is rotated by  $45^\circ$  with respect to the N-Co-N axis in the macrocycle. Nevertheless, feature ④ closely resembles the calculated momentum distribution of the HOMO of CoTPP, as shown in Figure 4.17b. Feature ⑤ still carries a residual HOMO-like pattern, but additional intensity appears that is consistent with contributions from the HOMO-2 and HOMO-3, which are degenerate in the calculations.

A comparison with the calculated orbital energies of gas-phase CoTPP, referenced to the measured WKF of the framework (4.12 eV), supports this assignment. Within this scheme, feature ④ is consistent with the HOMO, whereas feature ⑤ falls into the energy range expected for HOMO-2 and HOMO-3. At the same time, the calculated manifold requires a rigid shift of about 0.5 eV relative to experiment. This indicates that the gas-phase reference captures the main momentum fingerprints, but not the full energetic renormalization caused by coordination, substrate interaction, and the coexistence of Co(I) and Co(II) in the network. In particular, feature ③ at 0.45 eV cannot be assigned to any gas-phase CoTPP orbital.

The fact that feature ③ has no counterpart in the gas-phase CoTPP momentum maps suggests that it is induced by network formation. Its absence in pristine MnTPyP and its

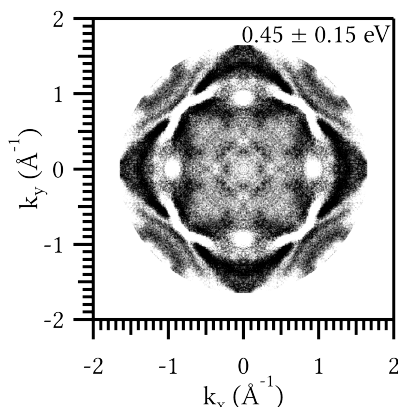


Figure 4.18.: Momentum map of the feature at 0.45 eV, integrated over an energy window of  $\pm 0.15$  eV. The measurement was performed with a photon energy of 21.2 eV. Data of the theoretical orbitals from [281, 284].

appearance in related coordinated cobalt porphyrin systems indicate that it is associated with the cobalt-containing network rather than with the uncoordinated precursor layer. In particular, similar low-binding-energy spectral weight has been discussed for Co-CoTPyP and related systems on graphene [17, 24], where it was linked to the modified electronic structure after coordination. In the present case, feature ③ may originate from a state with substantial transition metal character, possibly involving hybridization between the pyrrolic Co  $3d_{z^2}$  states and the Au-derived  $sp$  states, analogous to observations for CoPc on Au(111) [279]. Its comparatively low intensity in the EDC is consistent with such a more strongly metal-centered character at 21.2 eV, where the photoemission cross-section of transition metal  $d$  states is relatively low. The experimental geometry should also be kept in mind here: the predominantly p-polarized light incident at  $68^\circ$  favors contributions from states with out-of-plane character and may therefore enhance such a feature relative to more purely in-plane molecular states [94].

BM provides access to the dispersion of the identified features. Figure 4.19 shows the BMs of the clean Au(100) substrate (left), the MnTPyP SAM (middle), and the Co-MnTPyP MOF (right). The top row displays cuts along the  $\overline{\Gamma M}$  direction of the gold surface, as indicated in the Fermi surface of Au(100) in Figure 4.16a. The corresponding cuts along  $\overline{\Gamma X}$  are shown in the bottom row. For the SAM and MOF, the BMs were extracted from background-subtracted data, and red and blue markers on one half of each panel highlight the molecular features discussed in the text. Panels (a) and (d) show the clean gold substrate as reference; its band-structure signatures are also visible, though reduced in intensity, in the molecular-layer panels. For each BM, an interval of  $\pm 0.017 \text{ \AA}^{-1}$  was integrated perpendicular to the cut direction.

**MnTPyP** For the pristine MnTPyP layer, enhanced intensity is observed around 1.15 eV binding energy in both the  $\overline{\Gamma M}$  and  $\overline{\Gamma X}$  cuts in Figure 4.19b and e, respectively. As already seen in the momentum maps, the intensity is more pronounced along  $\overline{\Gamma X}$  than along  $\overline{\Gamma M}$ , consistent with the molecular alignment discussed above. The molecular states do not show any detectable dispersion in the MnTPyP layer, but instead appear as broad, non-dispersive features with an energy width of about 400 meV. Residual intensity from the gold band structure remains visible as a faint V-shaped signature across the full energy range.

Additional molecular states at higher binding energies contribute to the enhanced intensity around 2 eV. This combination of broad, non-dispersive features at larger  $|k_{\parallel}|$  and the absence of clear band dispersion is characteristic of molecular states in weakly interacting organic layers, where intermolecular overlap and molecule–substrate hybridization are limited [26, 285].

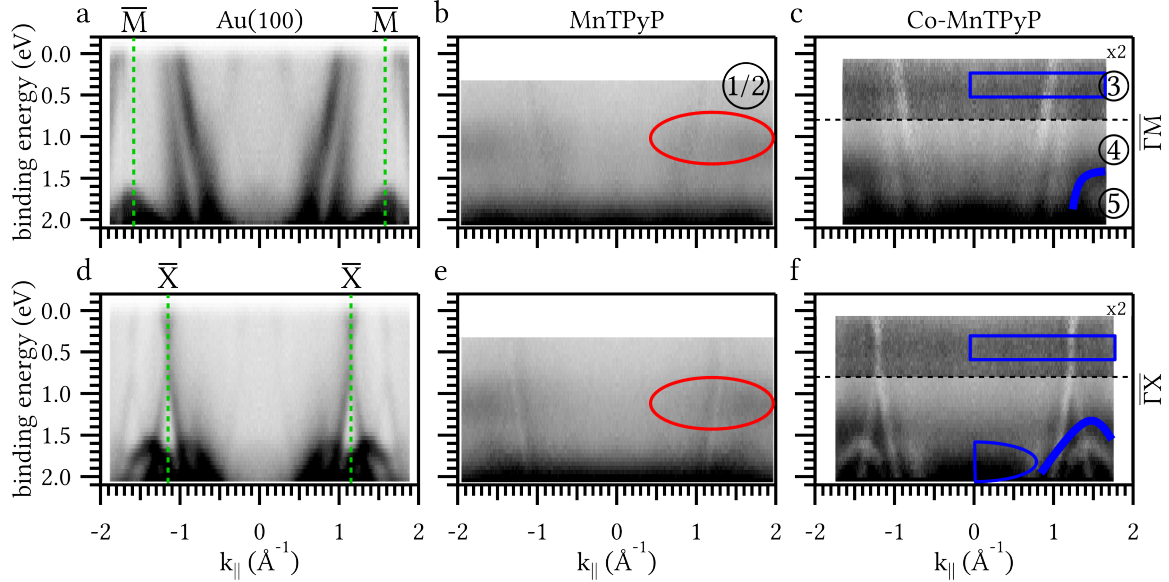


Figure 4.19.: BMs for the clean Au(100) substrate (left), the MnTPyP ML (middle), and the Co–MnTPyP network (right). The top row shows the BMs along the  $\overline{\Gamma M}$  direction of the substrate, while the bottom row displays the corresponding BMs along  $\overline{\Gamma X}$ . Dashed green lines in panels (a) and (d) highlight the high-symmetry points  $\overline{M}$  and  $\overline{X}$  of the Au(100) surface, respectively. For the BMs of the MOF, the upper part (above 0.8 eV) is multiplied by a factor of two to enhance the contributions in this energy range.

**Co–MnTPyP** Upon Co deposition and network formation, additional intensity appears closer to the Brillouin-zone center, as shown on the right-hand side of Figure 4.19. Compared with the pristine molecular layer, the molecular features are shifted to higher binding energy. Residual contributions from the Au(100) band structure remain visible, but the overall molecular intensity is clearly enhanced, which can be associated with increased intermolecular coupling within the coordination network. In both cuts, along  $\overline{\Gamma M}$  and  $\overline{\Gamma X}$ , the strongest molecular intensity is still found at  $|k_{\parallel}| > 1 \text{ Å}^{-1}$  and around 1.5 eV, while weaker contributions also appear near the center of the surface Brillouin zone. After enhancing the intensity above 0.8 eV by a factor of two, feature ③ is seen to extend across essentially the full accessible momentum range in both cuts (panels (c) and (f) of Figure 4.19). Such a broad momentum-space distribution is compatible with a state that is partially delocalized due to hybridization between delocalized Au *sp* bands and localized metal 3*d* orbitals. A similar behavior has been reported for the Co–CoTPyP network on graphene [17] and is indicative of band-like features in two-dimensional MOFs [94]. This feature becomes even more apparent in the image-curvature representation [286], shown in Figure A.22c and f. In addition, the BMs along the high-symmetry directions reveal dispersion for features ④ and ⑤ along both the energy and momentum axes, highlighted in blue on the right-hand side of Figure 4.19c and f. Such band-like behavior is naturally explained by intermolecu-

lar coupling mediated by the transition metal nodes at the pyridyl linkers [26, 94]. The angle-resolved EDCs of the Co-MnTPyP network in Figure A.20 support the separation into distinct contributions, even though these partially overlap in energy because of their intrinsic linewidths. The additional spectral weight at higher binding energies can again be associated with higher occupied molecular orbitals of the coordinated molecules.

**Work function** The overall modification of the electronic structure is further quantified through the system work function  $\Phi$ . From the position of the secondary-electron cutoff, the photon energy (21.2 eV), and the Fermi-edge position, the WKF can be determined using Equation 3.11. The 5.28 eV WKF of clean Au(100) is reduced to 4.61 eV after deposition of a ML of MnTPyP. This reduction can be associated with the push-back (or pillow) effect discussed in Section 1.2 [73–75]. Upon additional cobalt deposition, the WKF is further lowered to 4.12 eV, corresponding to a shift of 0.49 eV relative to the SAM. A similar reduction has been associated with the presence of Co in the +1 oxidation state, where occupation of the  $d_{z^2}$  orbital plays an important role [270], consistent with a reduced interface dipole induced by the additional positively charged metal centers in the coordination network [100]. This WKF change, which was already invoked to explain the core level shifts observed by XPS, is thus independently confirmed by the MM measurements.

**Summary** MM was used to investigate the VB region of the MnTPyP ML and the Co-MnTPyP network on Au(100), thereby providing both energetic and momentum-resolved information on the occupied states. The EDC of the SAM exhibits two prominent features, assigned on the basis of their momentum fingerprints to gas-phase MO of MnTPyP. Upon network formation, the spectral weight shifts to higher binding energy and an additional low-binding-energy feature emerges at 0.45 eV. The momentum maps show that the MOF retains molecular fingerprints but also develops additional, more extended spectral weight that is absent in the pristine SAM. The BMs reveal broad, non-dispersive molecular features in the SAM, characteristic of localized molecular states with weak intermolecular coupling. By contrast, the MOF exhibits band-like dispersive features, indicating electronic interconnection of the molecules within the framework. The additional low-binding-energy feature at 0.45 eV extends over the full accessible momentum range and is consistent with a hybridized state involving molecular 3d levels and Au  $sp$  bands. Deposition of the MnTPyP SAM already reduces the surface dipole, resulting in a WKF of 4.61 eV, and network formation induces a further WKF shift of 490 meV, in agreement with the core level shifts observed by XPS.

## 4.4. Summary

Combining LEED, NEXAFS, XPS, and MM yields a consistent microscopic picture of the structural and electronic differences between the MnTPyP SAM and the Co-MnTPyP coordination network on Au(100). LEED reveals a commensurate unit cell containing one MnTPyP molecule and 25 surface Au atoms for the SAM, whereas the MOF exhibits an enlarged commensurate unit cell containing two molecules rotated by 90° relative to each other. Together with the azimuthal orientation extracted from MM, this shows that the



macrocycles are aligned such that the N–Mn–N axes follow the [011] directions of the Au(100) surface.

Nitrogen K-edge NEXAFS shows that, in the MnTPyP SAM, the macrocycle lies flat and parallel to the surface, while the pyridyl groups are rotated out of the molecular plane. The spectra further support hybrid states involving both Mn 3*d* and N 2*p* orbitals, as well as a small fraction of pyridyl nitrogen already interacting with the substrate in the SAM. Upon Co deposition and mild annealing, a two-dimensional coordination network forms in which Co binds to the pyridyl termini of neighboring molecules. In this network, the additional Co is coordinated by four pyridyl groups, and the pyridyl tilt increases relative to the pristine molecular layer. At the Mn L<sub>3</sub>-edge, the MnTPyP SAM exhibits a well-resolved multiplet structure with pronounced dichroism, characteristic of Mn in a square-planar ligand field. Comparison with reference spectra indicates that Mn is in a high-spin configuration close to the +2 oxidation state, with significant ligand-field splitting and hybridization with the macrocyclic nitrogen states. After network formation, this dichroism vanishes and the multiplet structure collapses, providing clear evidence for transmetallation, the replacement of Mn by Co in the macrocycle.

XPS corroborates this interpretation. Core level spectroscopy reveals nearly rigid shifts across all investigated species upon network formation. These shifts match the WKF decrease of 490 meV measured by MM and are therefore attributed primarily to changes in the interface dipole and the overall electrostatic potential landscape, rather than to purely local chemical effects. Whereas in the SAMs the two nitrogen species are only weakly separated, after MOF formation both systems exhibit two clearly distinct N components: a lower-binding-energy pyrrolic contribution coordinated to Co and a higher-binding-energy pyridyl contribution associated with coordination to the additional Co nodes. The increased linewidths in the network are consistent with enhanced screening channels introduced by the connectivity within the MOF. In addition, Co(I) at the pyridyl coordination nodes and Co(II) in the macrocycle are identified from the Co 2*p*<sub>3/2</sub> core level. NEXAFS at the Co L<sub>3</sub>-edge further supports the presence of coordinated Co in a square-planar ligand field. The two main resonances are consistent with transitions into states of predominantly *d*<sub>z<sup>2</sup></sub> and *d*<sub>x<sup>2</sup>-y<sup>2</sup></sub> character for Co(II) in a D<sub>4h</sub>-like environment, with additional overlap from the Co(I) species and possibly a minor contribution from metallic Co clusters due to excess deposition.

MM connects these structural and core level results to the VB electronic structure. The main molecular features in the EDCs can be assigned to specific MOs by comparison with gas-phase calculations and their momentum fingerprints. The MnTPyP SAM exhibits two dominant features assigned mainly to the HOMO-1 and HOMO-2. In the Co–MnTPyP network, these features shift to higher binding energy and gain intensity, while an additional low-binding-energy state emerges at 0.45 eV. The preserved molecular fingerprints are consistent with the CoTPP HOMO and HOMO-2/-3, whereas the feature at 0.45 eV cannot be assigned to a specific gas-phase MO and is instead attributed to a network-induced state with strong involvement of metal-substrate interaction. BMs along  $\overline{\Gamma\text{M}}$  and  $\overline{\Gamma\text{X}}$  further show that, within the present resolution, the molecular states are largely non-dispersive in the SAM, but develop band-like behavior in the coordinated network.

Overall, the combined spectroscopic and momentum-resolved data lead to the following picture. The MnTPyP SAM on Au(100) consists of flat-lying macrocycles containing Mn(II)

in a ligand field close to  $D_{4h}$  symmetry and pyridyl substituents tilted out of the molecular plane, with the valence band dominated by ligand-based  $\pi$  states weakly hybridized with Mn  $3d$  orbitals. Upon Co deposition and annealing, transmetallation replaces Mn by Co(II) in the macrocycle and yields a two-dimensional coordination network in which Co(I) nodes are bound to the pyridyl groups. This structural reorganization increases the pyridyl tilt, slightly decouples the organic layer from the substrate, lowers the work function, and introduces an additional interface-related valence feature associated with the coordinated cobalt network.



# 5

## Formation and properties of the Ni–MnTPyP MOF

After the detailed discussion of the Co–MnTPyP system, including the Co–CoTPyP reference, a second transition metal is now introduced to further explore the properties of two-dimensional surface-confined MOFs. The preparation of the Ni–MnTPyP MOF was carried out analogously to that of the Co–MnTPyP MOF described in Section 4.1. As in the cobalt case, the notation Ni–MnTPyP will be retained throughout the thesis, although transmetallation of Mn by Ni may also occur.

For the network preparation, a Ni rod was used in the metal evaporator, and the thickness calibration was performed in the same way as for cobalt. First, different Ni coverages on the MnTPyP SAM were characterized by LEED and by following the evolution of the Ni  $2p_{3/2}$  core level. The behavior of the LEED pattern upon Ni deposition is identical to that observed for Co, and the Ni  $2p_{3/2}$  core level likewise exhibits two distinct features, as shown in Figure 5.1. From both observations, an evaporation of 0.07 ML was identified as the appropriate coverage.

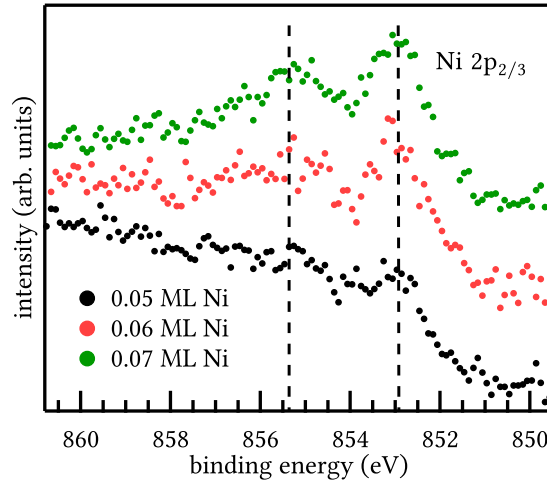


Figure 5.1.: Ni  $2p_{3/2}$  core level spectra for different Ni coverages on the MnTPyP SAM after background subtraction. After each deposition step, the sample was annealed to 420 K to promote the transmetallation process.

The deposited thickness of Ni was refined via attenuation of the Au  $4f_{7/2}$  core level, using the inelastic mean free path  $\lambda_{\text{Ni}} = 16.90 \text{ \AA}$  [156]. Evaporation of ten times the Ni coverage needed for the MOF reduces the Au  $4f_{7/2}$  intensity to an area of  $(382\,694 \pm 1535) \text{ arb. units}$ , see Figure 5.2. The film thickness can then be estimated as

$$d = -\lambda(E) \cdot \ln\left(\frac{I(d)}{I_0}\right) = -16.90 \text{ \AA} \cdot \ln\left(\frac{382\,694 \text{ arb. units}}{405\,526 \text{ arb. units}}\right) = 0.98 \text{ \AA}.$$

Thus, a coverage corresponds to  $0.98 \text{ \AA}$  of deposited Ni, again representing an upper limit and carrying a lower uncertainty bound of about  $\pm 0.1 \text{ \AA}$ , as already discussed for the cobalt calibration. Using Equation 4.2, this thickness can be converted into a Ni coverage of  $0.74 \text{ ML}$  ( $\rho_{\text{Ni}} = 8.902 \text{ g/cm}^3$  [287] and  $M_{\text{Ni}} = (58.6934 \pm 0.0004) \text{ g/mol}$  [240]). From this, the appropriate coverage Ni corresponds to  $0.07 \text{ ML}$ . This value is again larger than the  $0.04 \text{ ML}$  required to saturate only the pyridyl coordination sites and is close to the optimal coverage determined for transmetallation in the Co-MnTPyP MOF.

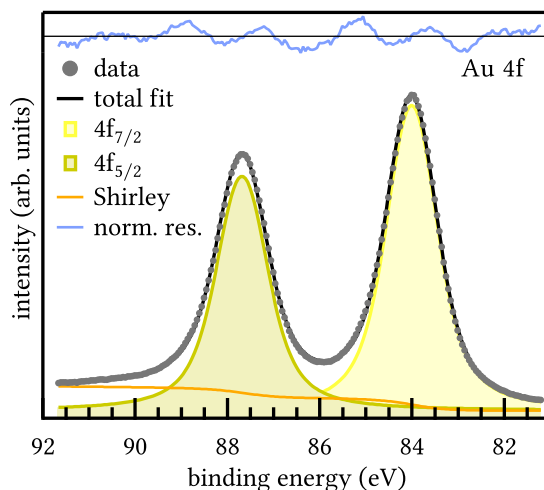


Figure 5.2.: Au  $4f$  core level spectrum used for the Ni coverage calibration after  $0.74 \text{ ML}$  Ni deposition. The reference spectrum of the clean surface is shown in Figure 4.3a. Fit parameters are listed in Table A.30.

## 5.1. Geometric structure characterization

As in the Co-MnTPyP case, the Ni-MnTPyP network is formed by depositing additional Ni onto the MnTPyP SAM and annealing the sample to  $420 \text{ K}$ . The resulting LEED pattern in Figure 5.3 is identical to that of the Co-MnTPyP network (Figure 4.5a) and the Co-CoTPyP network (Figure A.2).

In contrast to the Co-MnTPyP case, faint traces of the Au(100) surface reconstruction persist in the LEED pattern, highlighted in light green on the right-hand side of Figure 5.3. This likely indicates that the initial MnTPyP SAM does not completely cover the substrate, which is also apparent in the STM image in Figure 5.4a. However, the persistence of the surface reconstruction below the network cannot be ruled out completely, since the LEED and STM measurements were performed on different sample sets. Nevertheless, the final network structure is consistent with the real-space model in Figure 4.5b and is further corroborated by the following STM measurements.

Additional insight into the geometric arrangement is obtained from STM measurements of the occupied states of the final Ni-MnTPyP network, see Figure 5.4. The STM measurements were performed by Michele Capra. The reconstruction of the uncovered Au(100) surface appears as rows along the  $[011]$  direction, see Figure 5.4a. These rows are separated perpendicular to the row direction by five times the nearest-neighbor atomic spacing, *i.e.*

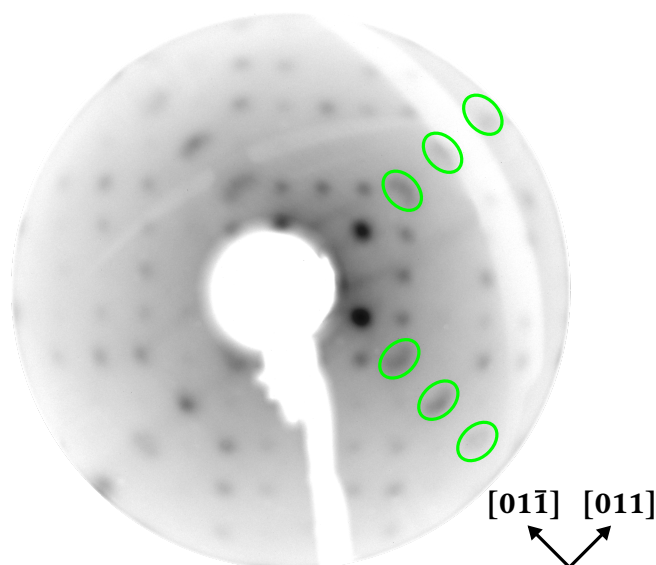


Figure 5.3.: LEED pattern at a primary electron energy of 25 eV for the Ni-MnTPyP network layer after deposition of 0.07 ML Ni.

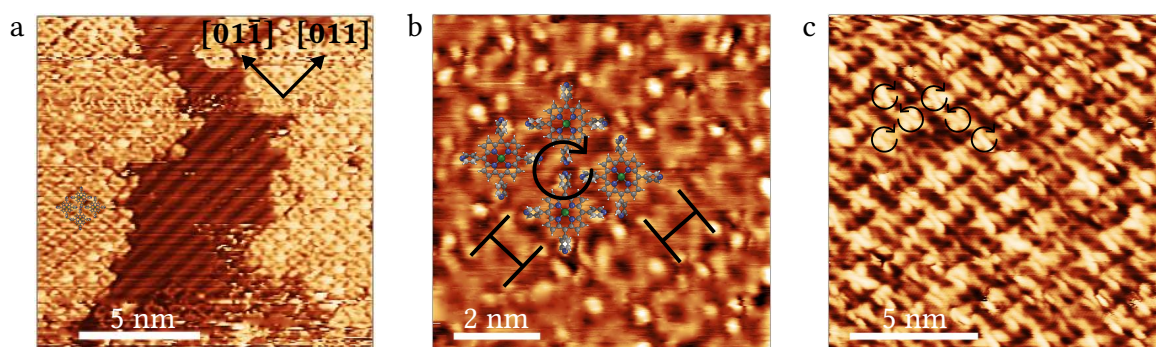


Figure 5.4.: STM images of the Ni-MnTPyP network. (a) Large-scale image showing MOF islands and row-like Au(100) surface reconstruction along the  $[011]$  direction. (b) High-resolution image with superimposed schematic molecules indicating the molecular arrangement. (c) Highlighting the rotation of the pyridyl substituents, which gives rise to the H-shaped molecular contrast in (b). Bias voltages: (a)  $-1500$  meV, (b)  $-238$  meV, (c)  $-1300$  meV. Measurements performed by Michele Capra.

$14.4 \text{ \AA}$  [119, 121]. The reconstruction rows were also used as a length reference. Because they appear only along one diagonal direction and the row separation is sensitive to the step size [288], a precise calibration is difficult, and absolute distances should therefore be treated with some caution. Nevertheless, the images are fully sufficient to determine the molecular arrangement and adsorption geometry. The molecular alignment relative to the substrate high-symmetry axes, deduced from MM on Co-MnTPyP, is consistent with the STM data: the N-M-N axes of the macrocycle are aligned along the  $[011]$  directions.

In the high-resolution image in Figure 5.4b, the molecular structure of the MTPyP units is clearly resolved. The macrocycle and the four pyridyl substituents are visible, forming a square-like network. A depression in the center of the macrocycle is observed, consistent with previous STM studies of MnTPP and NiTPP [91, 268]. This indicates that the frontier MO probed at the applied bias has only a minor contribution from the central metal  $d_{z^2}$  orbital [91]. Thus, the depression at the center of the macrocycle does not contradict

transmetallation, even though in the case of Ni(II) the  $d_{z^2}$  orbital is occupied, whereas it would remain unoccupied for Mn(II). For NiTPP on Cu(100), the Ni(I) center in a  $D_{4h}$  ligand field appears as a depression over a wide bias range due to the strong rotation of the phenyl substituents and their increased apparent height [35, 63, 283]. Consequently, the Ni(I) nodes at the pyridyl sites are not expected to exhibit a distinct localized contrast in the STM images, since the local environment around the metal resembles that in NiTPP.

The molecules appear with a characteristic H-shape in Figure 5.4b, as already proposed for the Co–MnTPyP case and previously observed for Co–MTPyP on graphene [24, 34]. This contrast arises from the alternating rotation of the pyridyl substituents within each molecule. Moreover, neighboring molecules are rotated by  $90^\circ$  relative to one another, so that each Ni node is surrounded by four pyridyl groups with the same rotation sense, visible as chiral spiral-like motifs in Figure 5.4c. The presence of two enantiomorphic spirals reflects the two possible rotation directions of the pyridyl substituents. These two non-equivalent molecular orientations explain why the unit cell contains two molecules and why additional superstructure spots appear in the LEED patterns after Ni/Co deposition.

## 5.2. Electronic structure characterization

After establishing the geometric structure, the discussion now turns to the electronic properties of the network. As in the cobalt-based systems, the C 1s core level serves as a reference for global changes in the electronic structure.

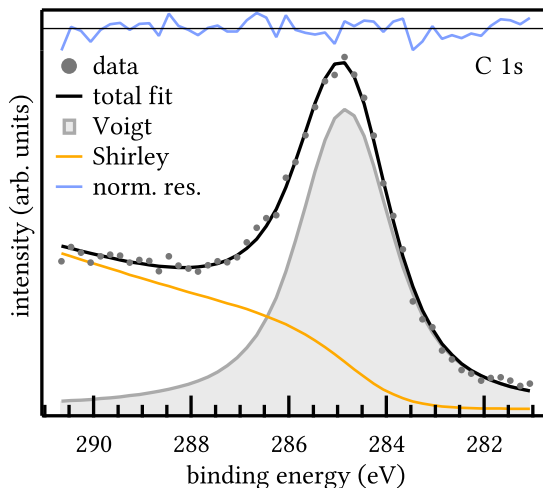


Figure 5.5.: C 1s spectrum after 0.07 ML Ni deposition on MnTPyP. The corresponding fit parameters are listed in Table A.31. The pure MnTPyP SAM in Figure 4.11a (bottom) serves as reference.

The C 1s core level is found at 284.84 eV after deposition of 0.07 ML Ni and formation of the Ni–MnTPyP network (Figure 5.5). Compared with the C 1s spectrum of the pristine MnTPyP ML (Figure 4.11a, bottom), this corresponds to a shift of about 400 meV toward higher binding energy. This is analogous to the shifts observed after formation of Co–MnTPyP and Co–CoTPyP, and again points to a similar change in the overall electronic structure of the layer.

The Ni  $2p_{3/2}$  spectrum of the Ni–MnTPyP network after deposition of 0.07 ML Ni, shown in Figure 5.6, exhibits two distinct peaks, closely resembling the situation in the Co  $2p_{3/2}$  spectra of the cobalt-based networks. Although XAS measurements at the Ni L-edge are not available, the presence of two well-separated components in the Ni  $2p_{3/2}$  region strongly supports a scenario analogous to Co–MnTPyP, in which transmetallation and pyridyl coordination lead to two non-equivalent species.

Prior to fitting, a background subtraction identical to that used for the Co  $2p_{3/2}$  analysis was applied. The spectrum was then modeled with two Voigt line shapes on top of a Shirley background. In contrast to cobalt, no additional broad Gaussian component was included to account for satellites, since previous studies did not report strong satellite features close to the main peaks for similar Ni systems [137]. Shake-up satellites are typically expected at about 6 eV higher binding energy [289], outside the scanned energy window.

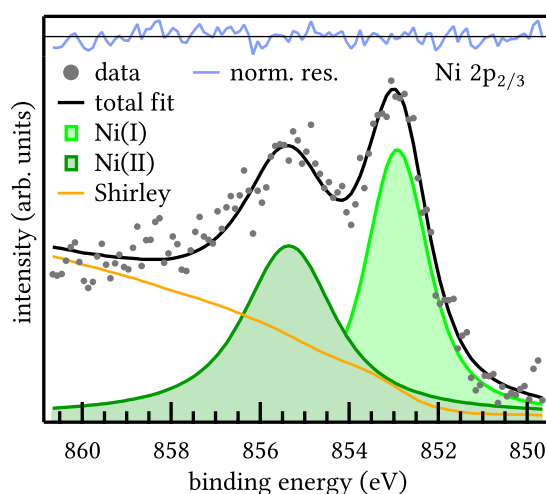


Figure 5.6.: Ni  $2p_{3/2}$  core level spectrum for the final Ni–MnTPyP MOF structure. Fit parameters are given in Table A.32.

The fit yields two components at 852.92 eV and 855.36 eV, which increase in intensity roughly equally with increasing Ni coverage, see Figure 5.1. The lower-binding-energy feature at 852.92 eV is assigned to Ni(I) [35, 137], most likely located at the pyridyl coordination sites. Earlier work had attributed a similar binding energy to Ni(0) [263]. However, this can be ruled out in the present case, since a thin metallic Ni film used for the coverage calibration (Figure A.24) shows a single asymmetric peak at about 851.8 eV. The presence of two non-equivalent nickel species, together with the absence of a dominant metallic Ni contribution, is fully consistent with a transmetallation-driven network formation similar to the cobalt case.

Consequently, the second component at 855.36 eV is assigned to Ni(II), as commonly observed for NiTPP multilayers and for monolayers on weakly interacting substrates such as Au or oxygen-passivated Cu [87, 137, 263, 268, 290]. This species is most plausibly located in the porphyrin macrocycle, mirroring the situation of Co(II) in the Co–MnTPyP network.

### 5.3. Summary

In summary, the structural model shown in Figure 4.5b, with its square unit cell, is also valid for the Ni–MnTPyP system. The central depression in the macrocycle observed in STM at negative bias is consistent with an occupied Ni(II)  $d_{z^2}$ -derived state that contributes only weakly to the tunneling current, which is dominated by the molecular  $\pi$  system [268], and thus does not contradict transmetallation of Mn by Ni. While the first peak in the Ni  $2p_{3/2}$  spectrum is assigned to Ni(I) at the pyridyl coordination nodes, the second peak originates from Ni(II) in the macrocycle. Thus, the Ni–MnTPyP network follows the same qualitative electronic and geometric scheme as the cobalt-based system.



# 6

## Gas-induced changes in the electronic structure of the coordination networks

Tailoring the 2D MOF structures toward functionality, a natural target application is their use in gas sensing and catalysis. Therefore, the reactivity of the Co–MnTPyP and Ni–MnTPyP networks toward NO<sub>2</sub> and CO was investigated at room temperature under UHV conditions. In both cases, the samples were exposed to increasing gas doses. Here, only the (nearly) saturated exposures are presented, as they most clearly highlight the impact on the electronic structure.

For each experiment, the pristine network was first characterized and fitted. The system was then incrementally exposed to the respective gas, and spectra were recorded until no further spectral changes could be detected. Subsequently, the sample was annealed stepwise to increasing temperatures until the initial spectral shape of the network was recovered. At each dosing and annealing step, LEED was recorded and did not show any detectable changes in the lateral periodicity of the MOFs. Due to the limited measurement time and the low concentration of the gas species, comparable to the concentration of the metal adatoms, it was not possible to obtain meaningful gas-induced changes in the N 1s, C 1s, and O 1s regions. In addition, the molecular N and C signals exceed the expected gas-related contributions by factors of approximately 8 and 40, respectively.

In the following, the two systems are discussed separately, each subsection addressing the response to the two gases. The main text focuses on the quantitative analysis based on fits. For direct visual comparison of the spectral-weight redistribution, the area-normalized spectra are shown in the Section A.11. The spectra were fitted after subtraction of a linear background as described in Section A.8. The final Section 6.3 summarizes the findings for both systems and discusses their potential for gas sensing and catalysis.

### 6.1. Reactivity of the Co–MnTPyP network

A nominal coverage of 0.11 ML Co is incorporated in the final MOF, which splits into equal amounts of Co(I) at 778.01 eV and Co(II) at 779.99 eV, as discussed in Section 4.3.6. The fitted Co 2p<sub>3/2</sub> spectra for the gas-dosing experiments are shown in Figure 6.1, while the corresponding area-normalized spectra for direct visual comparison are provided in Figure A.25. A pressure of  $7 \times 10^{-8}$  mbar was used for the NO<sub>2</sub> exposure on the Co–MnTPyP system, whereas pressures up to  $4 \times 10^{-6}$  mbar were used for CO.

For a quantitative analysis, the spectra were fitted in the same way as in Figure 4.13c. In each data set, the peak positions, Gaussian and Lorentzian widths, and relative line-shape parameters were fixed to those obtained for the pristine MOF, and only the peak areas and background parameters were allowed to vary. Thus, the spectrum of the clean Co–MnTPyP layer prior to CO dosing serves as reference, and the corresponding fit parameters were

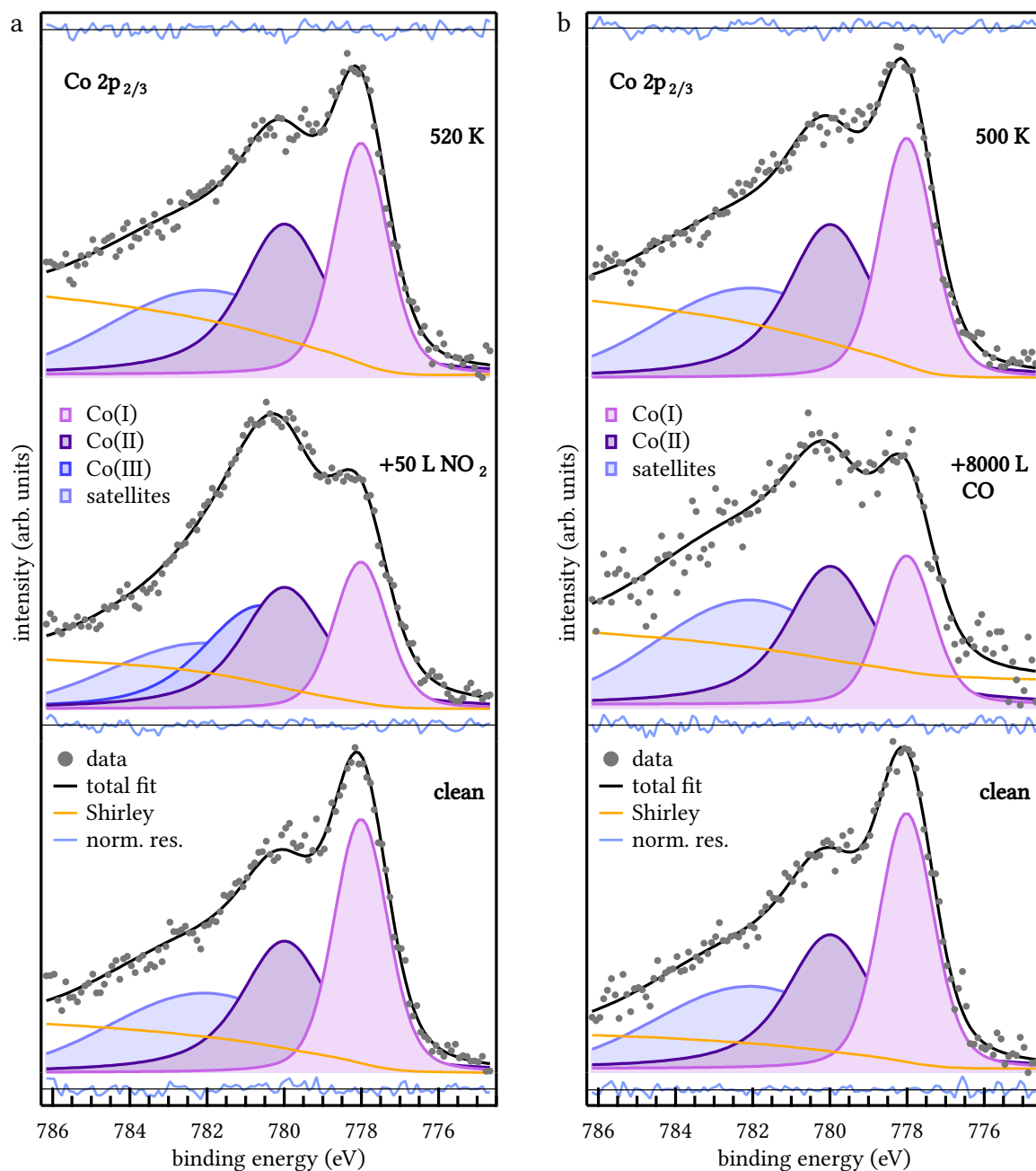


Figure 6.1.: Co  $2p_{3/2}$  core level for  $\text{NO}_2$  dosing (a) and CO dosing (b), together with the corresponding fits. Bottom: Pristine Co–MnTPyP network layer before gas exposure. Middle: After dosing 50 L  $\text{NO}_2$  and 8000 L CO, respectively. Top: Restored initial structure after annealing the samples to 520 K and 500 K, respectively. The corresponding fitting parameters can be found in Tables A.26 and A.34 to A.39, respectively. The corresponding area-normalized spectra are shown in Figure A.25.



used as constraints for all subsequent fits; this spectrum is identical to the one shown in Figure 4.13c. For the pristine layers, the areas of the Co(I) and Co(II) components and their Gaussian widths were constrained to be equal, consistent with the 1:1 ratio inferred from the coverage analysis.

**NO<sub>2</sub>** As the pristine network layer has already been discussed in Section 4.3.6, the following focuses on the changes induced by NO<sub>2</sub> adsorption. Figure 6.1 (left column) shows the corresponding Co 2p<sub>3/2</sub> spectra and fits. Dosing 50 L NO<sub>2</sub> quenches the Co(I) signal that dominates the low-binding-energy side of the pristine spectrum. A fit using only the two Voigt components and the broad Gaussian satellite from the pristine network leads to a pronounced increase in the Gaussian contribution and a poor overall reproduction of the line shape; a clear residual peak remains in the difference spectrum, see Figure 6.2. An additional Voigt peak was introduced to account for a possible higher oxidation state. The resulting fit, shown in the middle panel of Figure 6.1a, reduces the reduced  $X^2$  by about a factor of two. A new component at 780.6 eV is obtained and assigned to Co(III), in analogy to CoTPP on Cu(100) after NO<sub>2</sub> exposure [19]. The change induced by adsorbed NO<sub>2</sub> at the Co(I) sites is fully reversible: annealing at 520 K restores the initial spectral shape, and no additional fourth peak is required to describe the data.

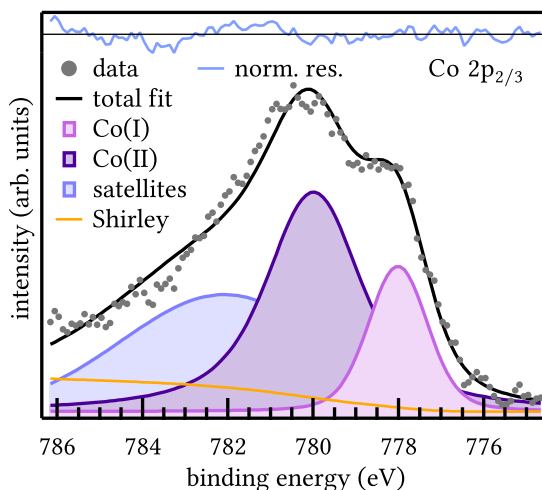


Figure 6.2.: Co 2p<sub>3/2</sub> spectrum after NO<sub>2</sub> dosing fitted with only three peaks (two main components and one broad satellite). The fit parameters are given in Table A.35.

**CO** For CO exposure (Figure 6.1b), the quenching of the Co(I) signal is somewhat weaker than for NO<sub>2</sub>, and the overall statistics of the spectra are poorer. Nevertheless, a similar enhancement of the broad Gaussian component is observed, indicating a modified satellite structure. Because the expected Co(III) contribution would be separated by only about 600 meV from the Co(II) peak in the present system and the signal-to-noise ratio is lower, it is not possible to resolve an additional Co(III)-related peak unambiguously. As in the NO<sub>2</sub> case, annealing to 500 K restores the original spectrum of the Co–MnTPyP network.

The residual low-binding-energy intensity after gas dosing in both cases is attributed to excess Co that was already present in the pristine MOF preparation and is not directly involved in the reversible redox chemistry at the Co(I)/Co(III) sites. Another explanation for

the residual low-binding-energy intensity could be (anti)cooperative behavior, as observed for Co–CoTPyP on graphene under near-ambient-pressure CO dosing at room temperature [30]. There, charge redistribution and geometric distortions of the metal–organic network modified the adsorption energies, resulting in higher pressures being required for saturation [30]. If only every second Co(I) species adsorbed an additional gas molecule, the periodicity would remain identical to that of the initial MOF and no corresponding change would be expected in the LEED pattern.

## 6.2. Reactivity of the Ni–MnTPyP network

The fitted Ni  $2p_{3/2}$  spectra for NO<sub>2</sub> and CO dosing on the Ni–MnTPyP MOF are shown in Figure 6.3, while the corresponding area-normalized spectra for direct visual comparison are provided in Figure A.26. The pristine spectrum exhibits two features, assigned in Section 5.2 to Ni(I) at 852.92 eV and Ni(II) at 855.36 eV (see Section 5.2). For the gas exposure, pressures of  $7 \times 10^{-8}$  mbar (NO<sub>2</sub>) and  $2 \times 10^{-6}$  mbar (CO) were used.

For quantitative comparison, the spectra were fitted using the same procedure as for Co. The fit parameters for the pristine Ni–MnTPyP layer (Figure 5.6) are reproduced in the bottom row of Figure 6.3a. These parameters were then kept fixed for the gas-exposed and annealed spectra, while only the peak areas and background parameters were allowed to vary. In the pristine case, the Gaussian widths were constrained to be identical for Ni(I) and Ni(II), reflecting the common experimental resolution, and the areas were initially constrained to be equal.

**NO<sub>2</sub>** The left column of Figure 6.3 shows the Ni  $2p_{3/2}$  spectra for NO<sub>2</sub> exposure. After dosing 10 L NO<sub>2</sub>, the intensity of the Ni(I) component is strongly reduced, while the Ni(II) component gains intensity. This behavior is consistent with literature on NiTPP/Cu(100), where NO<sub>2</sub> adsorption shifts the Ni(I) ( $S = 1/2$ ) component at 852.9 eV toward a Ni(II) (HS,  $S = 1$ ) component at 854.6 eV [35]. Thus, the reported Ni(II) (HS) value would lie in between the two components of the pristine spectrum. However, the residuum after fitting with only the two constrained components does not show any systematic structure that would indicate an additional component in this energy range. Annealing for a few minutes at 510 K restores the initial spectral shape, demonstrating the reversibility of the reaction.

**CO** For CO exposure (Figure 6.3b), the behavior is very similar to the NO<sub>2</sub> case. After dosing 1000 L CO, most of the intensity of the Ni(I) component is transferred to the Ni(II) component, leaving less than 10 % of the original Ni(I) intensity. Again, annealing at 480 K restores the original spectral shape with two components.

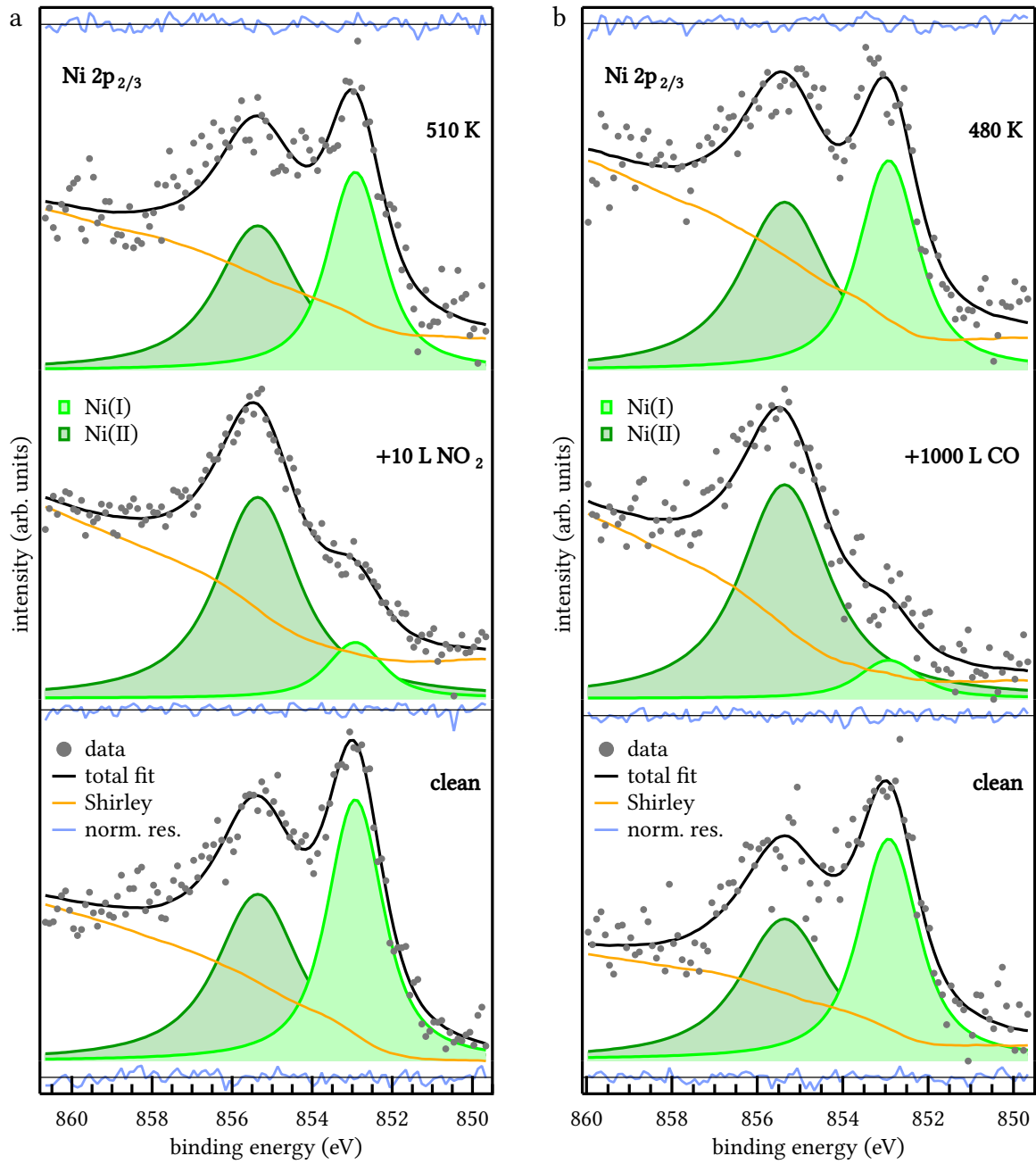


Figure 6.3.: Ni  $2p_{3/2}$  core level of the Ni-MnTPyP MOF with the corresponding fits. (a)  $\text{NO}_2$  dosing; (b) CO dosing. Bottom: Pristine network layer before gas exposure. Middle: After dosing 10 L  $\text{NO}_2$  and 1000 L CO. Top: After annealing to 510 K and 480 K. Tables A.32 and A.40 to A.44 summarize the fitting parameters. The corresponding area-normalized spectra are shown in Figure A.26.

### 6.3. Comparative discussion and summary

In summary, both Co–MnTPyP and Ni–MnTPyP networks exhibit very similar qualitative behavior upon NO<sub>2</sub> and CO exposure: the low-binding-energy peak in the Co 2*p*<sub>3/2</sub> and Ni 2*p*<sub>3/2</sub> spectra, assigned to the +1 oxidation state, is suppressed, while intensity shifts toward a higher oxidation state. For the Co–MnTPyP MOF exposed to NO<sub>2</sub>, the intensity of the +1 oxidation state is transferred to a Co(III) component, whereas for the other cases the feature associated with the +2 state gains intensity. Thus, for both transition metals only the +1 oxidation state acts as the reactive center toward the offered gaseous ligands, whereas the +2 oxidation state remains essentially inert, in line with previous studies [17, 19, 35, 137].

Quantitatively, the required gas doses differ between the two systems. The Ni-containing network requires smaller doses of both NO<sub>2</sub> and CO than the Co-containing network to achieve a comparable quenching of the +1 species. Taking into account the different coverages (nominal 0.11 ML Co vs. 0.07 ML Ni), the Co network requires a factor of

$$\frac{50 \text{ L}}{10 \text{ L}} \cdot 0.68 = 3.38$$

more NO<sub>2</sub> and

$$\frac{8000 \text{ L}}{1000 \text{ L}} \cdot 0.68 = 5.41$$

more CO than the Ni network. These factors are in fact lower bounds, because the Co–MnTPyP MOF is further away from ideal saturation, either due to fractions of non-reactive metallic clusters or anti-cooperative behavior, as observed previously [30]. Instead, the Ni coverage of 0.07 ML is closer to the optimal value of 0.08 ML. This implies that Ni–MnTPyP is more easily oxidized, and thus more sensitive, under the same dosing conditions, while Co–MnTPyP shows clearer spectroscopic fingerprints of a full +1 → +3 oxidation in the case of NO<sub>2</sub>. Furthermore, restoring the original spectra after NO<sub>2</sub> exposure requires a higher temperature than after CO exposure, indicating stronger adsorption.

However, both systems operate reversibly, adsorbing at room temperature and desorbing after mild annealing. This makes them promising platforms for switchable gas sensing or catalysis based on the redox-active +1 centers. The formation of an additional axial ligand in trans position modifies the substrate–metal bond length, which increases upon gas adsorption and thus affects both the local coordination environment and the electronic coupling to the substrate [76].

# 7

## Conclusion and outlook

This thesis demonstrates that MnTPyP-derived two-dimensional coordination networks on Au(100) form a structurally well-ordered and chemically addressable platform in which metal incorporation, oxidation states, and interface energetics can be tuned and tracked by surface-sensitive spectroscopy and diffraction. By combining LEED, STM, polarization-dependent NEXAFS, XPS, and momentum-resolved photoemission (MM), a consistent microscopic picture is established across long-range order, local coordination chemistry, and the occupied and unoccupied electronic structure.

A central outcome is the strong substrate influence on on-surface metal exchange. On Au(100), the deposited metal does not merely occupy the pyridyl coordination nodes, but also replaces Mn in the porphyrin macrocycle, yielding homo metallic Co–CoTPyP and Ni–NiTPyP networks. This on-surface transmetallation contrasts with graphene-supported systems, where such behavior was not observed under comparable conditions [24]. Moreover, for the gold-supported network, a Co(II) macrocycle center is identified, whereas Co(III) macrocycle centers have been reported for related graphene-supported networks [17]. In contrast, the reduced node species, Co(I) at the pyridyl coordination sites, is a shared motif across platforms [17, 24]. Likewise, for the Ni-terminated MOF, the macrocycle-bound Ni was assigned to the +2 oxidation state, while the metal node exhibits a +1 oxidation state, emphasizing that the node environment stabilizes a chemically distinct and redox-active metal state.

The real-space order was found to be square both in the pristine SAM of MnTPyP and in the final MOFs. In all cases, the macrocycle is adsorbed flat with respect to the substrate, while the pyridyl substituents are rotated out of the molecular plane and exhibit a larger rotation in the MOF structures. Furthermore, the MOF structures exhibit an enlarged unit cell containing two molecules, which arises from the alternating rotation of the molecules and their substituents.

Network formation has a clear electronic signature beyond local chemical shifts. Across the investigated sample series, the C 1s core level shifts by about 0.5 eV toward higher binding energy upon MOF formation, indicating an overall change in the interface energetics rather than a purely site-specific effect. Together with the work function changes discussed in this thesis, these shifts highlight that coordination and metal exchange reshape the interface dipole and the electrostatic potential landscape. In addition, the occupied electronic structure accessed by MM shows the development of band-like features for the Co–MnTPyP MOF, supporting the electronic interconnection of the individual molecules within the network.

Finally, the gas-exposure experiments identify the chemically active center of the networks. Upon dosing with NO<sub>2</sub> and CO, the node species, M(I) at the pyridyl substituents, is suppressed in XPS, while intensity shifts toward higher oxidation states, demonstrating that the coordination nodes constitute the redox-responsive sites, whereas the macrocycle-bound

M(II) component remains comparatively inert under the applied conditions. The comparison between Co- and Ni-based networks further shows that the node metal tunes the switching threshold: the Ni network requires smaller doses to quench the Ni(I) component than are needed to quench Co(I) in the cobalt network. Both systems exhibit reversibility by desorption upon mild annealing, underscoring their relevance as surface-confined, switchable redox platforms.

## Key findings

- **Substrate control:** Au(100) promotes on-surface transmetallation and stabilizes homo metallic Co–CoTPyP networks, in contrast to graphene-supported reference systems [24].
- **Two metal sites, two valence states:** Macrocycle centers and pyridyl nodes host chemically distinct metal species; M(I) nodes are a general motif and constitute the redox-active sites [17, 24].
- **Interface energetics:** MOF formation induces an overall electronic shift, for example about 0.5 eV in C 1s, consistent with modified interface dipoles and band alignment. In addition, Co–MnTPyP exhibits band-like features in the valence band.
- **Tunable switching:** Ni nodes respond at lower doses than Co nodes, providing a handle to tune redox susceptibility via the choice of node metal.

## Outlook

The results of this thesis identify MnTPyP-derived coordination networks on Au(100) as a versatile model platform for studying how substrate symmetry, on-surface coordination chemistry, and metal-center exchange determine the structure and functionality of two-dimensional metal–organic frameworks. Beyond the specific Co- and Ni-based systems investigated here, the present findings suggest a broader design principle: substrate, macrocycle metal, and node metal can be tuned as largely independent parameters in order to control long-range order, oxidation state, and chemical reactivity. In this sense, the studied networks are not only well-defined model systems, but also a promising starting point for the rational design of functional surface-confined architectures.

A central conclusion of this work is that the supporting substrate is not merely a passive template. On Au(100), it promotes both structural ordering and on-surface transmetallation, thereby stabilizing chemically distinct metal sites in the final network. An important next step will therefore be to clarify how general this substrate control is. A systematic comparison with other weakly interacting but structurally different supports, for example Ag(100) or Au(111), could reveal which substrate properties primarily govern metal exchange, node formation, and the stabilization of reduced node species. Such studies would also provide a realistic route toward preserving heterobimetallic frameworks, which are of particular interest because macrocycle and node sites could then be tuned independently and may enable cooperative or synergistic functionality [2, 20].

A second key direction concerns the preparation and structural quality of the networks. Although the present work demonstrates ordered and chemically addressable phases, possible residual metallic species still limit a fully quantitative analysis of the active node sites. Further optimization of the deposition protocol, in particular the deposition rate, substrate temperature, and annealing procedure, should improve stoichiometric network formation and suppress metallic cluster contributions. Complementary STM studies would then be highly valuable to quantify domain size, defect density, and local motif variations, and to test more directly the interpretation of the characteristic H-shaped intramolecular contrast associated with rotated pyridyl substituents. Together, such efforts would strengthen the structural basis on which the electronic and chemical conclusions are built.

From the perspective of functionality, the most promising result of this thesis is the identification of the reduced node species as the redox-active center of the networks. This makes the present systems attractive model platforms for studying single-site chemistry in a periodic and structurally well-defined environment. The next step is therefore to move from the qualitative demonstration of reversible gas-induced switching toward a more quantitative description of adsorption energetics and reaction pathways. Systematic gas-dosing experiments combined with stepwise annealing should allow the extraction of comparative desorption temperatures and adsorption strengths for different gases and node metals. At the same time, higher-resolution core-level spectroscopy, ideally using monochromatized laboratory sources or synchrotron radiation, should make it possible to track correlated changes in the N 1s, C 1s, and O 1s regions and to distinguish more clearly between axial ligation, charge transfer, and possible side reactions. Such studies would advance the present systems from switchable redox networks toward quantitatively understood model catalysts and gas-responsive interfaces.

A further perspective lies in the magnetic and spin-dependent properties of these coordination networks. Porphyrin-based metal-organic frameworks with open-shell transition-metal centers are attractive candidates for molecular spintronics because they combine localized magnetic moments with long-range structural order and chemically tunable coordination environments [21, 22]. In particular, the coexistence of distinct oxidation states and ligand fields at macrocycle and node sites suggests that these systems may provide access to switchable magnetic functionality triggered by coordination or gas adsorption. Related studies have already shown that ligation can reversibly modify the spin state of transition-metal porphyrins on surfaces [35], and functional molecular spin-switching architectures have been identified as promising building blocks for future nanoscale devices [18]. For the present systems, this opens the perspective that the chemically active node species may act not only as redox centers, but also as externally addressable spin centers embedded in an ordered two-dimensional lattice. Future work combining gas exposure with element-specific magnetic probes, for example X-ray magnetic circular dichroism (XMCD), would therefore be particularly interesting.

Finally, the present work also points toward the need for a closer connection between experiment and theory. For the occupied states, momentum-resolved photoemission already indicates the emergence of more delocalized, band-like features upon network formation. To understand these states in a more quantitative way, future calculations should move beyond gas-phase reference molecules and explicitly include the coordinated network on the substrate. Such calculations, together with photon-energy-dependent UPS and momentum microscopy, would help to disentangle ligand-derived states, node-related

states, and interface-induced hybridization. In a broader sense, this would allow the present systems to be linked more directly to the general goals outlined in the introduction of this thesis: the development of low-dimensional metal–organic materials with tunable electronic, catalytic, and magnetic properties [1, 5, 8].

Overall, the results presented here show that surface-supported porphyrin-based coordination networks on Au(100) provide a well-defined platform in which structure, oxidation state, and functionality are intimately connected. Future work should build on this foundation by improving structural control, extending the spectroscopic toolbox, and exploring substrate, metal, and ligand combinations beyond the systems studied here. In this way, the present model networks may evolve into a broader class of tunable two-dimensional architectures relevant not only for fundamental surface science, but also for catalysis, sensing, and molecular spintronic applications.





## Appendix

### A.1. Coverage calibration

An alternative approach to calibrating the thickness follows the procedure proposed by Shard [167] for coverages below one full monolayer. In this definition, 1 ML corresponds to a fully closed Co layer rather than to a 1:1 correspondence with the surface atom density of Au, as used in the main text. The coverage is given by

$$C = \frac{1 - \frac{I}{I_0}}{1 - \exp(-d/\lambda)}, \quad (\text{A.1})$$

where  $C$  denotes the coverage ( $0 \leq C \leq 1$ ),  $I$  the attenuated signal intensity, and  $I_0$  the initial intensity. Here,  $d$  is the layer spacing, which for a fcc(100) surface is given by  $a/2$ , and  $\lambda$  is the inelastic mean free path. For Co, this approach yields a coverage of 0.82 ML for the deposited Co film, corresponding to approximately 0.94 ML in the convention used in the main text, i.e.  $a_{\text{Au}}/a_{\text{Co}} \cdot 0.82$  ML, with  $a_{\text{Au}} = 4.078 \text{ \AA}$  [123] and  $a_{\text{Co}} = 3.5446 \text{ \AA}$  [291].

A second approach to coverage calibration is based on the work of Fadley [211], as summarized by Zemlyanov et al. [292]. Using the expression given in part 1d of the supplementary information, the fractional ML coverage

$$C \equiv \frac{s_L}{s_S} = \frac{I_L(\theta)}{I_S(\theta)} \cdot \frac{D_0(E_S)\Omega_0(E_S)A_0(E_S)}{D_0(E_L)\Omega_0(E_L)A_0(E_L)} \cdot \frac{\frac{d\sigma_S}{d\Omega} \cdot \lambda_S(E_S) \cos(\theta)}{\frac{d\sigma_L}{d\Omega} \cdot d_S}, \quad (\text{A.2})$$

can be calculated. Here,  $s_L$  and  $s_S$  are the mean surface atomic densities of the overlayer (L) and substrate (S), respectively.  $I_L$  and  $I_S$  are the integrated areas of the corresponding core levels. For the constant pass energy used for both signals, the detector efficiency  $D_0(E_k)$  is identical [292]. For the lens setting used in this experiment, the source area  $A_0(E_k)$  and the solid angle  $\Omega_0(E_k)$  at the analyzer entrance are assumed to remain constant [293]. As the spectra were measured with an incidence angle close to the magic angle ( $\alpha = 54.74^\circ$ ),  $\frac{d\sigma}{d\Omega}$  can be approximated by  $\sigma/4\pi$  using the cross-sections  $\sigma$  reported by Scofield [163].  $\lambda_S(E_S)$  is the inelastic mean free path of the electron in the substrate at the kinetic energy of the substrate reference core level, here Au  $4f_{7/2}$ . Furthermore, the spectra were acquired at normal emission ( $\theta = 0^\circ$ ), and  $d_S$  denotes the layer spacing of the substrate. Based on the data presented in Figures 4.3b and A.1, the coverage can be calculated as

$$C \equiv \frac{113\,281 \text{ arb. units}}{174\,427 \text{ arb. units}} \cdot \frac{0.217\,338 \text{ Mb} \cdot 15.11 \text{ \AA} \cos(0^\circ)}{0.270\,84 \text{ Mb} \cdot 2.04 \text{ \AA}} \cdot \frac{10}{50} = 0.77 \text{ ML}, \quad (\text{A.3})$$

where the last factor accounts for the different acquisition times. The area of the Co  $2p_{3/2}$  core level was estimated as 113 281 arb. units from peaks 1 and 2 in Figure A.1. The complex line shape and the identified satellite structure of Co make it challenging to determine the true area of the Co  $2p_{3/2}$  core level accurately, and it was therefore not used as the main reference [271, 294, 295]. This method provides an accuracy of approximately  $\pm 10\%$  [211]. In addition, the cross-sections used were derived for non-ordered layers, whereas an ordered layer may differ significantly from

this approximation, and the single-crystalline substrate can further introduce anisotropy into the measured intensity [211]. A more accurate calibration would therefore require angle-resolved XPS measurements [295].

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0115 | 0.0012 | free        | -                    |
| area           | 405 526 | 1610   | free        | -                    |
| sigma          | 0.370   | 0.004  | free        | -                    |
| gamma          | 0.371   | 0.005  | free        | -                    |
| FWHM           | 1.333   | 0.010  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.6897 | 0.0015 | constrained | peak1_center + shift |
| area           | 313 597 | 1220   | constrained | ratio * peak1_area   |
| sigma          | 0.370   | 0.004  | constrained | peak1_sigma          |
| gamma          | 0.376   | 0.005  | free        | -                    |
| FWHM           | 1.340   | 0.010  | -           | calculated           |
| shift          | 3.6782  | 0.0019 | free        | -                    |
| ratio          | 0.773   | 0.003  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 37 339  | 257    | free        | -                    |
| k              | 0.0257  | 0.0004 | free        | -                    |

Table A.1.: Fit parameters of the Au 4*f* core level of the clean Au substrate in the first measurement period, as shown in Figure 4.3a. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

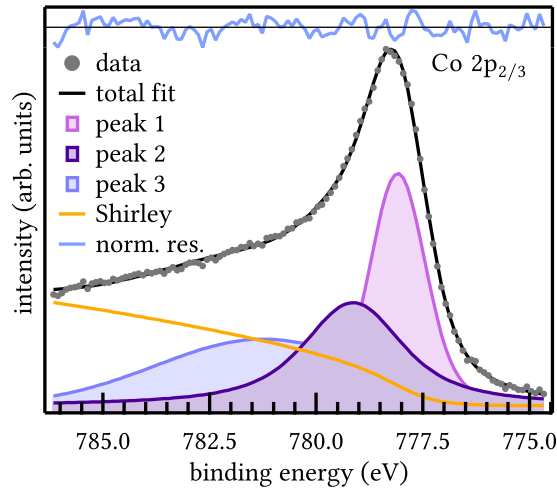


Figure A.1.: Co 2*p*<sub>3/2</sub> core level spectrum of a thin pure Co layer on Au(100) after 1.09 ML of Co deposition. The spectrum was acquired with the same parameters as the Au 4*f* core level shown in Figure 4.3b. These data are used for the coverage calibration.

All samples used for the core level investigations were prepared with a nominal 0.11 ML Co coverage, except for the sample series in which the N 1*s* core level, which was evaluated as a function of Co coverage. For the samples used in the NEXAFS and MM measurements, a similar coverage was

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0515 | 0.0015 | free        | -                    |
| area           | 174 427 | 837    | free        | -                    |
| sigma          | 0.360   | 0.004  | free        | -                    |
| gamma          | 0.386   | 0.006  | free        | -                    |
| FWHM           | 1.333   | 0.012  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.7291 | 0.0018 | constrained | peak1_center + shift |
| area           | 134 095 | 639    | constrained | ratio * peak1_area   |
| sigma          | 0.360   | 0.004  | constrained | peak1_sigma          |
| gamma          | 0.389   | 0.006  | free        | -                    |
| FWHM           | 1.338   | 0.012  | -           | calculated           |
| shift          | 3.678   | 0.002  | free        | -                    |
| ratio          | 0.769   | 0.004  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 17 599  | 133    | free        | -                    |
| k              | 0.0267  | 0.0004 | free        | -                    |

Table A.2.: Fit parameters of the Au 4*f* core level used for the Co coverage calibration after deposition of 1.09 ML of Co, as shown in Figure 4.3b. Relative to the clean Au signal in Figure 4.3a, a scaling factor of 2.13, evaluated in the pre-peak region, has to be taken into account. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

employed, estimated from a comparison of QCM readings and LEED images.

| parameter      | value   | error  | variable    | expression  |
|----------------|---------|--------|-------------|-------------|
| <b>peak 1</b>  |         |        |             |             |
| center         | 778.09  | 0.04   | free        | -           |
| area           | 57 463  | 19 868 | free        | -           |
| sigma          | 0.56    | 0.04   | free        | -           |
| gamma          | 0.20    | 0.09   | free        | -           |
| FWHM           | 1.54    | 0.14   | -           | calculated  |
| <b>peak 2</b>  |         |        |             |             |
| center         | 779.1   | 0.5    | free        | -           |
| area           | 55 818  | 78 193 | free        | -           |
| sigma          | 0.56    | 0.04   | constrained | peak1_sigma |
| gamma          | 1.1     | 0.8    | free        | -           |
| FWHM           | 3       | 1      | -           | calculated  |
| <b>peak 3</b>  |         |        |             |             |
| center         | 781     | 1      | free        | -           |
| area           | 56 999  | 47 235 | free        | -           |
| sigma          | 2.5     | 0.8    | free        | -           |
| FWHM           | 6       | 2      | -           | calculated  |
| <b>Shirley</b> |         |        |             |             |
| constant       | 159 367 | 853    | free        | -           |
| k              | 0.063   | 0.004  | free        | -           |

Table A.3.: Fit parameters of the Co  $2p_{3/2}$  core level after depositing 1.09 ML of Co. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

## A.2. Co–CoTPyP LEED

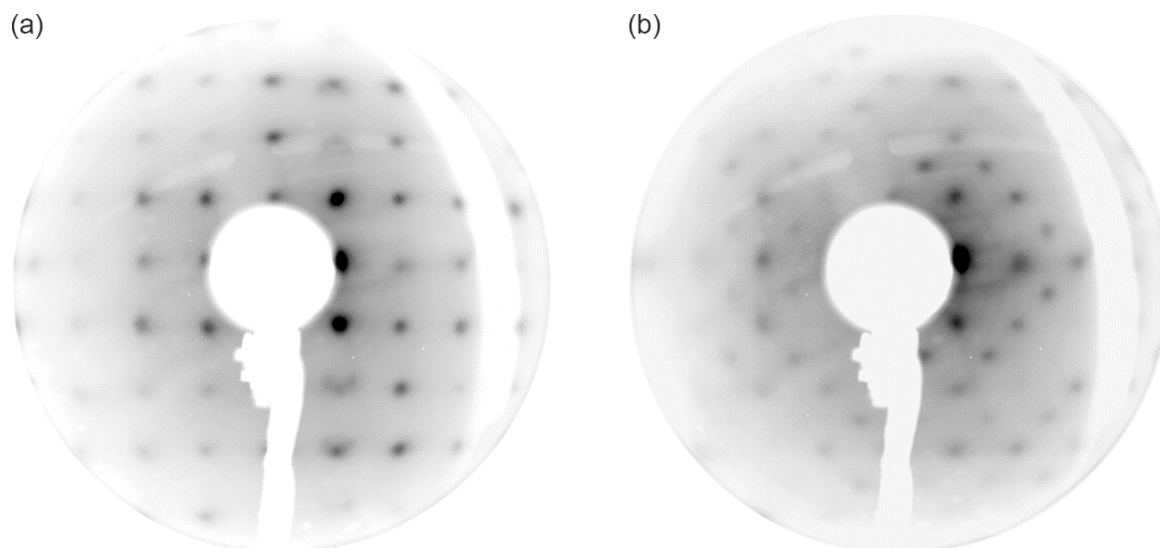


Figure A.2.: LEED patterns recorded at a kinetic energy of 25 eV for the pristine CoTPyP layer (a) and the network layer Co–CoTPyP (b). Images acquired by Olga Resel.

Figure A.2 shows the corresponding LEED patterns of the pristine CoTPyP layer (a) and the final Co–CoTPyP network layer (b). These patterns are identical to those found for the MnTPyP SAM

(Figure 4.4a) and after Co deposition on MnTPyP (Figure 4.5a), respectively. Therefore, the same real-space model as shown in Figures 4.4b and 4.5b can be assumed.

### A.3. Powder reference measurements

The Cl  $2p$  and Mn  $2p_{3/2}$  core levels mainly serve as references for chloride desorption. In both cases, single broadened Voigt profiles are sufficient to fit the spin-orbit components, and no attempt is made to resolve the multiplet contributions.

| parameter      | value  | error | variable    | expression         |
|----------------|--------|-------|-------------|--------------------|
| <b>peak 1</b>  |        |       |             |                    |
| center         | 197.52 | 0.12  | free        | -                  |
| area           | 1396   | 363   | free        | -                  |
| sigma          | 0.72   | 0.13  | free        | -                  |
| gamma          | 0.3    | 0.2   | free        | -                  |
| FWHM           | 2.0    | 0.4   | -           | calculated         |
| <b>peak 2</b>  |        |       |             |                    |
| center         | 199.1  | 0.3   | constrained | peak1_center+shift |
| area           | 768    | 604   | constrained | peak1_area*ratio   |
| sigma          | 0.72   | 0.13  | constrained | peak1_sigma        |
| gamma          | 0.3    | 0.4   | free        | -                  |
| FWHM           | 2.1    | 0.6   | -           | calculated         |
| shift          | 1.56   | 0.16  | free        | -                  |
| ratio          | 0.5    | 0.3   | free        | -                  |
| <b>Shirley</b> |        |       |             |                    |
| constant       | 2521   | 17    | free        | -                  |
| k              | 0.017  | 0.010 | free        | -                  |

Table A.4.: Fit parameters of the Cl  $2p$  core level of the powder sample before annealing, as shown in Figure A.3a. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value  | error  | variable | expression |
|----------------|--------|--------|----------|------------|
| center         | 642.47 | 0.02   | free     | -          |
| area           | 37 287 | 1979   | free     | -          |
| sigma          | 0.6    | 0.3    | free     | -          |
| gamma          | 2.00   | 0.16   | free     | -          |
| FWHM           | 4.5    | 0.5    | -        | calculated |
| <b>Shirley</b> |        |        |          |            |
| constant       | 32 342 | 101    | free     | -          |
| k              | 0.0720 | 0.0016 | free     | -          |

Table A.5.: Fit parameters of the Mn  $2p_{3/2}$  core level of the powder sample before annealing, as shown in Figure A.3b (bottom). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

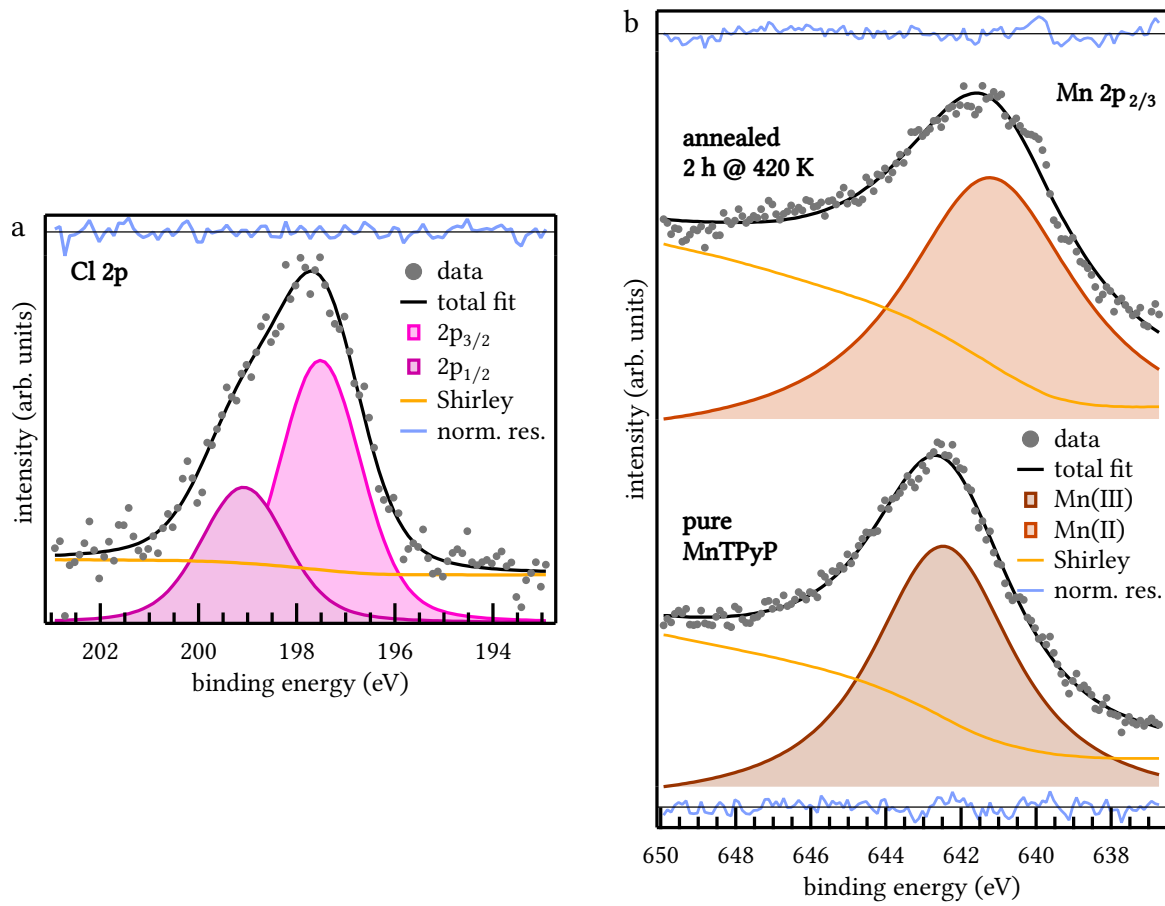


Figure A.3.: Fits to the Cl  $2p$  and Mn  $2p_{3/2}$  core levels shown in Figure 4.7 for the powder sample. Spectra acquired by Olga Resel.

| parameter      | value  | error | variable | expression |
|----------------|--------|-------|----------|------------|
| center         | 641.23 | 0.05  | free     | -          |
| area           | 50 694 | 6389  | free     | -          |
| sigma          | 0.4    | 0.3   | free     | -          |
| gamma          | 2.8    | 0.4   | free     | -          |
| FWHM           | 5.7    | 0.8   | -        | calculated |
| <b>Shirley</b> |        |       |          |            |
| constant       | 31 318 | 312   | free     | -          |
| k              | 0.106  | 0.006 | free     | -          |

Table A.6.: Fit parameters of the Mn  $2p_{3/2}$  core level of the powder sample after annealing for 2 h at 420 K, as shown in Figure A.3b (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

## A.4. General fitting procedure

All fits were performed with the Python package *lmfit*, using a least-squares optimization. The statistical weights were taken as the Poisson standard deviation,  $1/\sqrt{M}$ , of the count rate  $M$ .

All spectra were fitted using a Shirley background (see Equation 3.10), represented here as

$$bkg_i = k \cdot \left( \sum_{j=i}^N (y_j - y_0) \right) \cdot \Delta x + \text{constant}, \quad (\text{A.4})$$

where only the parameters  $k$  and *constant* were optimized during the fitting procedure. Here,  $\Delta x$  denotes the step size of the kinetic-energy scale,  $y_j$  the measured data point, and  $bkg_i$  the resulting background value for each of the  $N$  data points.

Depending on the spectrum, a varying number of Voigt profiles from the *lmfit* package was used to represent the peak shapes. The FWHM values listed in the fitting-parameter tables correspond to the Voigt FWHM, calculated from the Lorentzian width parameter  $\gamma$  and the Gaussian width parameter  $\sigma$  according to

$$\begin{aligned} \Gamma_{\text{Voigt}} &= 0.5343 \cdot \Gamma_{\text{Lorentzian}} + \sqrt{0.2169 \cdot \Gamma_{\text{Lorentzian}}^2 + \Gamma_{\text{Gaussian}}^2}, \\ \Gamma_{\text{Lorentzian}} &= 2\gamma, \\ \Gamma_{\text{Gaussian}} &= \sqrt{8 \ln(2)} \cdot \sigma. \end{aligned}$$

Because the elemental concentrations and photoionization cross-sections differ strongly between the investigated core levels, the signal intensities vary substantially. To make efficient use of the available measurement time and to obtain a balanced signal-to-noise ratio, the number of summed scans and the step sizes were adjusted individually for the different spectra.

The fits of the Au 4*f* core level provide the main constraints for the experimental energy resolution, in particular the lower bounds of the Gaussian contribution and, where appropriate, of the Lorentzian width. The Lorentzian contribution contains both the intrinsic core-hole lifetime broadening and the linewidth of the X-ray source. These reference fits were used to define suitable starting values and lower bounds for other core levels measured under identical conditions.

Linked fit parameters are listed together with their dependencies in the column *Expression* in the fitting tables. Vanishing parameter errors in the tables indicate that the corresponding quantities were fixed during the fitting procedure. The parameter *ratio* denotes the spin-orbit area ratio of the two components, while *shift* gives their relative energy separation.

## A.5. Energy resolution

For the wide-range spectrum shown in Figure 4.10, a fit with eight Voigt profiles was performed to account for the different photon energies generated by the X-ray source. The most relevant resulting parameters are summarized in Table A.7. The parameter *shift* denotes the spin-orbit splitting of the Au 4*f* core level, while the additional shifts correspond to the different photon energies referenced to  $K_{\alpha 1}$ . Likewise, the parameter *ratio* represents the relative intensity contributions, in area, of the spin-orbit components and of the different radiation lines, respectively. The resulting energy shifts and relative intensities are consistent with the values summarized in Table 4.2.

| parameter     | value   | variable    | expression            |
|---------------|---------|-------------|-----------------------|
| <b>peak 1</b> |         |             |                       |
| center        | 83.95   | free        | -                     |
| area          | 287 053 | free        | -                     |
| FWHM          | 1.17    | -           | calculated            |
| <b>peak 2</b> |         |             |                       |
| center        | 87.64   | constrained | peak1_center + shift  |
| area          | 231 375 | constrained | ratio * peak1_area    |
| FWHM          | 1.16    | -           | calculated            |
| <b>peak 3</b> |         |             |                       |
| center        | 84.21   | constrained | peak1_center + shift1 |
| area          | 157 879 | constrained | ratio1 * peak1_area   |
| FWHM          | 1.60    | -           | calculated            |
| <b>peak 4</b> |         |             |                       |
| center        | 87.90   | constrained | peak2_center + shift1 |
| area          | 127 256 | constrained | ratio1 * peak2_area   |
| FWHM          | 1.89    | -           | calculated            |
| <b>peak 5</b> |         |             |                       |
| center        | 75.58   | constrained | peak1_center + shift2 |
| area          | 39 181  | constrained | ratio2 * peak1_area   |
| FWHM          | 1.37    | -           | calculated            |
| <b>peak 6</b> |         |             |                       |
| center        | 79.28   | constrained | peak2_center + shift2 |
| area          | 31 581  | constrained | ratio * peak5_area    |
| FWHM          | 1.32    | -           | calculated            |
| <b>peak 7</b> |         |             |                       |
| center        | 73.84   | constrained | peak1_center + shift3 |
| area          | 23 449  | constrained | ratio3 * peak1_area   |
| FWHM          | 1.41    | -           | calculated            |
| <b>peak 8</b> |         |             |                       |
| center        | 77.53   | constrained | peak2_center + shift3 |
| area          | 18 901  | constrained | ratio * peak7_area    |
| FWHM          | 1.50    | -           | calculated            |
| shift         | 3.69    | free        | -                     |
| ratio         | 0.81    | free        | -                     |
| shift1        | 0.27    | free        | -                     |
| ratio1        | 0.55    | free        | -                     |
| shift2        | -8.36   | free        | -                     |
| ratio2        | 0.136   | free        | -                     |
| shift3        | -10.10  | free        | -                     |
| ratio3        | 0.082   | free        | -                     |

Table A.7.: Most important fit parameters of the wide-range Au 4*f* core-level fit, as shown in Figure 4.10. All parameters are given in eV except for the area and the ratio. All peaks share the same  $\sigma$ , which accounts for the analyzer resolution. The Shirley background yields a constant of 21 980 and  $k = 0.021\,98$ . The pass energy was 20 eV.



In the following, narrower energy windows are considered, which exclude the contributions from  $K_{\alpha 3}$  and higher-order lines in order to reduce acquisition time. For completeness, the narrow energy range of the Au 4*f* core level was fitted with four Voigt profiles to account explicitly for the  $K_{\alpha 1}$  and  $K_{\alpha 2}$  splitting, as discussed in the main text and shown in Figure A.4. The corresponding fitting parameters are summarized in Table A.8. A contribution from the surface-shifted core level to the overall line shape is expected to be below 5 % and was therefore neglected. This is justified by the high kinetic energy of approximately 1400 eV and the correspondingly low surface sensitivity. Such a procedure is only practical for the Au 4*f* core level, where only one chemical species is present and the signal intensity is high. For other core levels with lower intensity and multiple chemical contributions, resolving the  $K_{\alpha 1}/K_{\alpha 2}$  splitting is not practical and leads to unstable fits.

To compare the minimum linewidth and fit quality, the same Au 4*f* dataset was also fitted with only two Voigt profiles, as shown in Figure A.5a, since this simplified approach is later used as the reference for constraining other core levels. Using four peaks to represent both radiation contributions yields a reduced  $\chi^2$  of 4.01, approximately four times smaller than the value obtained for the unresolved  $K_{\alpha 1}/K_{\alpha 2}$  fit, for which a reduced  $\chi^2$  of 16.16 is obtained. At the same time, the two-peak approach is used as the reference for the energy calibration. This introduces an uncertainty of approximately 100 meV in the energy scale, in addition to the overall experimental energy resolution.

For each measurement period, the corresponding Au 4*f* core level was therefore recorded to determine the appropriate energy calibration, which can vary over time and in particular after bake-outs. Accordingly, the Au 4*f*<sub>7/2</sub> core level was referenced to a binding energy of  $E_B = 84.0$  eV. Small shifts caused by different pass energies can be neglected within the overall moderate energy resolution (compare Tables A.9 and A.10). Although the overall peak areas and intensities are well reproduced, residual deviations remain, particularly on the high-binding-energy side.

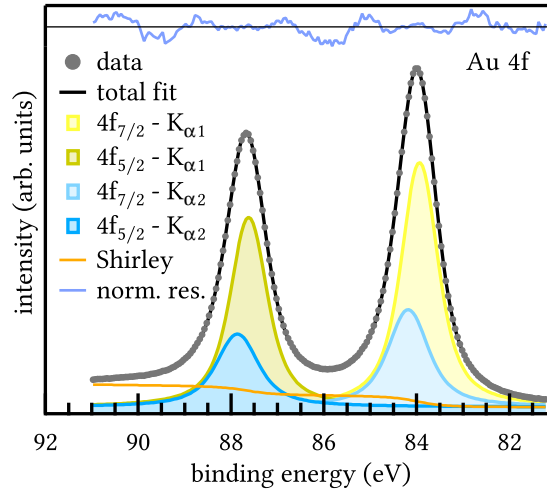


Figure A.4.: Fit of the Au 4*f* core level with four Voigt profiles to account for the  $K_{\alpha 1}/K_{\alpha 2}$  splitting, resulting in a reduced  $\chi^2$  of 4.01. The spectrum was acquired by Olga Resel at the University of Graz during the second measurement period with  $E_{\text{Pass}} = 10$  eV and is reused in Figure A.5a.

| parameter      | value    | error    | variable    | expression            |
|----------------|----------|----------|-------------|-----------------------|
| <b>peak 1</b>  |          |          |             |                       |
| center         | 83.936   | 0.016    | free        | -                     |
| area           | 452 036  | 58 589   | free        | -                     |
| sigma          | 0.226    | 0.006    | free        | -                     |
| gamma          | 0.318    | 0.007    | free        | -                     |
| FWHM           | 0.949    | 0.017    | -           | calculated            |
| <b>peak 2</b>  |          |          |             |                       |
| center         | 87.617   | 0.016    | constrained | peak1_center + shift  |
| area           | 351 372  | 45 588   | constrained | ratio * peak1_area    |
| sigma          | 0.226    | 0.006    | constrained | peak1_sigma           |
| gamma          | 0.320    | 0.009    | free        | -                     |
| FWHM           | 0.951    | 0.018    | -           | calculated            |
| <b>peak 3</b>  |          |          |             |                       |
| center         | 84.18    | 0.04     | constrained | peak1_center + shift1 |
| area           | 203 416  | 35 923   | constrained | peak1_area*ratio1     |
| sigma          | 0.226    | 0.006    | constrained | peak1_sigma           |
| gamma          | 0.382    | 0.009    | free        | -                     |
| FWHM           | 1.048    | 0.019    | -           | calculated            |
| <b>peak 4</b>  |          |          |             |                       |
| center         | 87.86    | 0.04     | constrained | peak2_center + shift1 |
| area           | 158 117  | 27 944   | constrained | peak2_area*ratio1     |
| sigma          | 0.226    | 0.006    | constrained | peak1_sigma           |
| gamma          | 0.402    | 0.012    | free        | -                     |
| FWHM           | 1.08     | 0.02     | -           | calculated            |
| shift          | 3.6809   | 0.0011   | free        | -                     |
| ratio          | 0.7773   | 0.0014   | free        | -                     |
| shift1         | 0.25     | 0.03     | free        | -                     |
| ratio1         | 0.45     | 0.02     | free        | -                     |
| <b>Shirley</b> |          |          |             |                       |
| constant       | 45 328   | 177      | free        | -                     |
| k              | 0.026 96 | 0.000 17 | free        | -                     |

Table A.8.: Fit parameters of the Au 4*f* core level in the second measurement period, fitted with four Voigt profiles, as shown in Figure A.4. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

### A.5.1. First measurement period

The measurements in the first period were conducted using a magnesium anode that had already been extensively used and therefore showed a contribution from silver radiation originating from the underlying anode coating. A total power of 300 W at an acceleration voltage of 15 kV was applied. The analyzer was operated in fixed analyzer transmission mode with a  $7 \times 20$  mm entrance slit, an open exit slit, an iris diameter of 10 mm, large-area mode, a lens range of 1500 V, and a pass energy of 20 eV. Figure 4.3a shows the Au 4*f* core level together with the corresponding fit, which was used to determine the energy resolution and to define constraints for the other fits. The corresponding fitting parameters are listed in Table A.1.

During this period, the Co and Ni coverage-dependent studies as well as the gas exposure studies were performed. Due to the contribution of Ag radiation, the N 1s core level could not be recorded because of overlap with a gold-related feature. In addition, the low photon flux limited the detection of low concentrations after gas exposure. As a result, only changes in the metallic  $2p_{3/2}$  core levels were monitored, although even these measurements required acquisition times of several hours. Possible additional contributions from O, N, and C were not accessible because of their low concentrations, the limited flux, and the smaller photoionization cross-sections of the corresponding core levels compared with those of Co and Ni.

### A.5.2. Second measurement period

During the second measurement period, the experiments on the powder sample as well as the N 1s measurements on the Co–MnTPyP samples were performed. The worn anode of the X-ray source was replaced, and a new sample-heating system was installed. In contrast to the earlier measurements, the iris diameter was set to 25 mm, and the pass energy was set to 20 eV for the Co  $2p_{3/2}$  core level and to 10 eV for all other core levels. For both pass energies, the Au 4f core level was additionally measured to evaluate the energy resolution, as shown in Figure A.5. The resulting fitting parameters are listed in Tables A.9 and A.10, respectively.

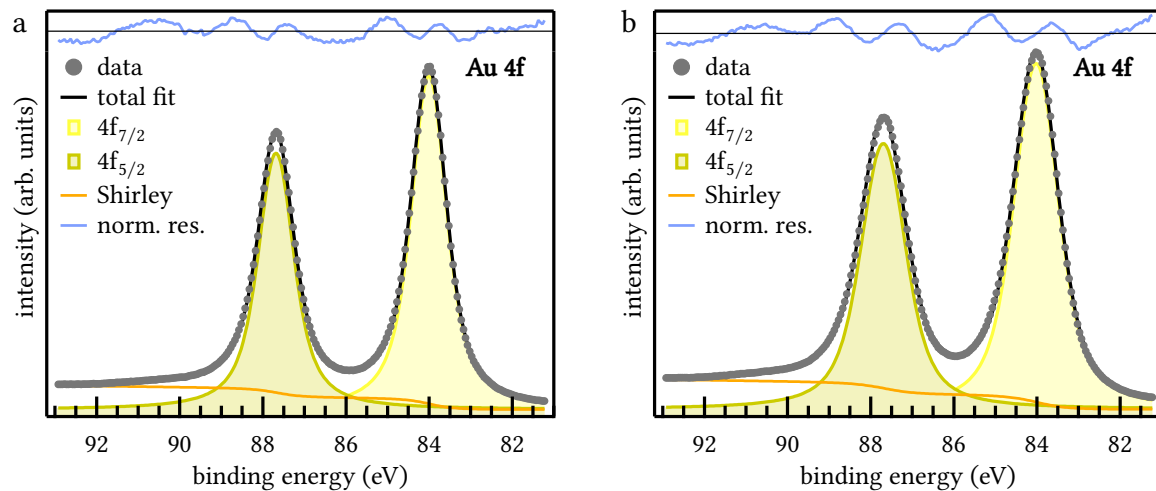


Figure A.5.: Fit of the Au 4f core level recorded with a pass energy of 10 eV (a), corresponding to the same dataset as in Figure A.4, and with a pass energy of 20 eV (b). The corresponding fitting parameters are listed in Tables A.9 and A.10, respectively. The spectra were acquired by Olga Resel at the University of Graz on a MnTPyP ML-coated Au(100) substrate.

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0031 | 0.0008 | free        | -                    |
| area           | 661 028 | 1768   | free        | -                    |
| sigma          | 0.240   | 0.002  | free        | -                    |
| gamma          | 0.347   | 0.003  | free        | -                    |
| FWHM           | 1.023   | 0.006  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.6824 | 0.0010 | constrained | peak1_center + shift |
| area           | 514 396 | 1330   | constrained | ratio * peak1_area   |
| sigma          | 0.240   | 0.002  | constrained | peak1_sigma          |
| gamma          | 0.355   | 0.002  | free        | -                    |
| FWHM           | 1.034   | 0.006  | -           | calculated           |
| shift          | 3.6793  | 0.0013 | free        | -                    |
| ratio          | 0.778   | 0.002  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 44 080  | 293    | free        | -                    |
| k              | 0.0274  | 0.0002 | free        | -                    |

Table A.9.: Fit parameters of the Au 4*f* core level in the second measurement period, as shown in Figure A.5a. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV. The fit yields a reduced  $\chi^2$  of 16.16.

| parameter      | value     | error  | variable    | expression           |
|----------------|-----------|--------|-------------|----------------------|
| <b>peak 1</b>  |           |        |             |                      |
| center         | 84.0162   | 0.0015 | free        | -                    |
| area           | 1 226 763 | 5480   | free        | -                    |
| sigma          | 0.351     | 0.004  | free        | -                    |
| gamma          | 0.368     | 0.005  | free        | -                    |
| FWHM           | 1.288     | 0.012  | -           | calculated           |
| <b>peak 2</b>  |           |        |             |                      |
| center         | 87.6942   | 0.0018 | constrained | peak1_center + shift |
| area           | 953 223   | 3844   | constrained | ratio * peak1_area   |
| sigma          | 0.351     | 0.004  | constrained | peak1_sigma          |
| gamma          | 0.376     | 0.005  | free        | -                    |
| FWHM           | 1.299     | 0.011  | -           | calculated           |
| shift          | 3.678     | 0.002  | free        | -                    |
| ratio          | 0.777     | 0.004  | free        | -                    |
| <b>Shirley</b> |           |        |             |                      |
| constant       | 62 544    | 851    | free        | -                    |
| k              | 0.0277    | 0.0004 | free        | -                    |

Table A.10.: Fit parameters of the Au 4*f* core level in the second measurement period, as shown in Figure A.5b. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

### A.5.3. Third measurement period

In the final measurement period, the control experiments on the CoTPyP and Co–CoTPyP samples were conducted. The analyzer settings were identical to those used in the second measurement period and therefore correspond to the same minimum-linewidth constraints. The corresponding reference fits are shown in Figure A.6.

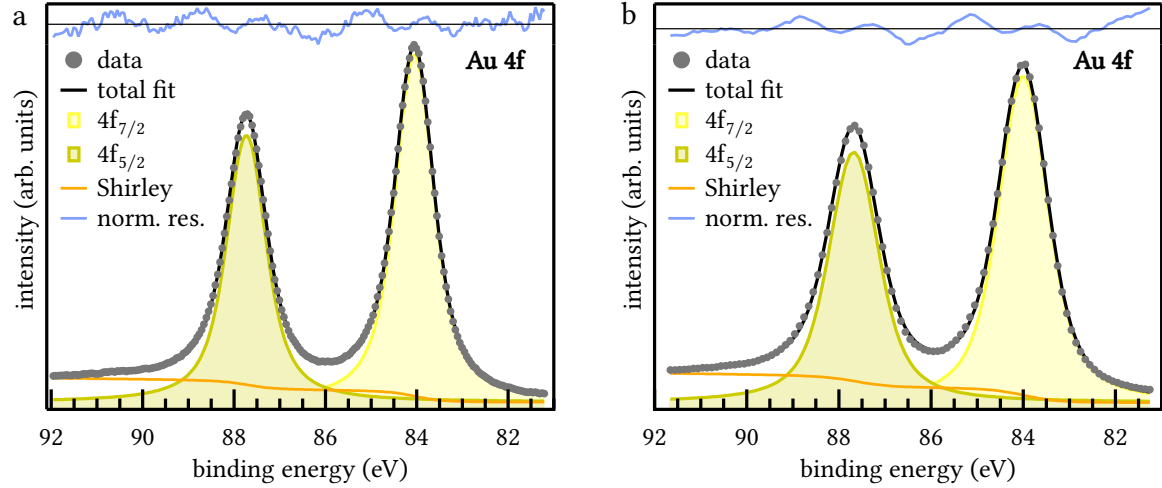


Figure A.6.: Fit of the Au 4*f* core level recorded with a pass energy of 10 eV (a) on a Co-coated Au(100) substrate and with a pass energy of 20 eV (b) on an Au(100) crystal coated with one ML of CoTPyP. The corresponding fitting parameters are listed in Tables A.11 and A.12, respectively. The spectrum in panel (b) was acquired by Olga Resel.

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0485 | 0.0008 | free        | -                    |
| area           | 154 352 | 392    | free        | -                    |
| sigma          | 0.244   | 0.002  | free        | -                    |
| gamma          | 0.345   | 0.002  | free        | -                    |
| FWHM           | 1.027   | 0.006  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.7287 | 0.0010 | constrained | peak1_center + shift |
| area           | 119 856 | 316    | constrained | ratio * peak1_area   |
| sigma          | 0.244   | 0.002  | constrained | peak1_sigma          |
| gamma          | 0.351   | 0.002  | free        | -                    |
| FWHM           | 1.036   | 0.006  | -           | calculated           |
| shift          | 3.6802  | 0.0012 | free        | -                    |
| ratio          | 0.777   | 0.002  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 10 937  | 64     | free        | -                    |
| k              | 0.0269  | 0.0002 | free        | -                    |

Table A.11.: Fit parameters of the Au 4*f* core level in the third measurement period, as shown in Figure A.6a. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0002 | 0.0018 | free        | -                    |
| area           | 452 691 | 3927   | free        | -                    |
| sigma          | 0.348   | 0.006  | free        | -                    |
| gamma          | 0.373   | 0.009  | free        | -                    |
| FWHM           | 1.289   | 0.019  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.676  | 0.002  | constrained | peak1_center + shift |
| area           | 347 489 | 2872   | constrained | ratio * peak1_area   |
| sigma          | 0.348   | 0.006  | constrained | peak1_sigma          |
| gamma          | 0.373   | 0.009  | free        | -                    |
| FWHM           | 1.290   | 0.019  | -           | calculated           |
| shift          | 3.676   | 0.003  | free        | -                    |
| ratio          | 0.768   | 0.006  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 23 323  | 725    | free        | -                    |
| k              | 0.0297  | 0.0009 | free        | -                    |

Table A.12.: Fit parameters of the Au 4*f* core level in the third measurement period, as shown in Figure A.6b. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

## A.6. Fitting the C 1s core level

The C 1s core level was fitted with a single Voigt profile and used primarily as a reference for the overall electronic shift between the pristine molecular layers and the corresponding coordination networks.

| parameter      | value   | error | variable | expression |
|----------------|---------|-------|----------|------------|
| center         | 284.438 | 0.011 | free     | -          |
| area           | 56 618  | 2568  | free     | -          |
| sigma          | 0.56    | 0.05  | free     | -          |
| gamma          | 0.64    | 0.08  | free     | -          |
| FWHM           | 2.13    | 0.16  | -        | calculated |
| <b>Shirley</b> |         |       |          |            |
| constant       | 324 493 | 274   | free     | -          |
| k              | 0.120   | 0.003 | free     | -          |

Table A.13.: Fit parameters of the C 1s core level of the pristine MnTPyP layer, as shown in Figure 4.11a. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

For the CoTPyP-based samples, the C 1s spectra were acquired with a pass energy of 50 eV. At this pass energy, the energy resolution is approximately twice as broad as at 20 eV. Since no corresponding Au 4*f* reference spectrum was recorded at 50 eV, the energy resolution could not be

| parameter      | value   | error | variable | expression |
|----------------|---------|-------|----------|------------|
| center         | 284.924 | 0.012 | free     | -          |
| area           | 74 121  | 3542  | free     | -          |
| sigma          | 0.45    | 0.08  | free     | -          |
| gamma          | 0.95    | 0.09  | free     | -          |
| FWHM           | 2.4     | 0.2   | -        | calculated |
| <b>Shirley</b> |         |       |          |            |
| constant       | 383 560 | 311   | free     | -          |
| k              | 0.111   | 0.003 | free     | -          |

Table A.14.: Fit parameters of the C 1s core level of the Co–MnTPyP layer after deposition of 0.109 ML of Co, as shown in Figure 4.11a. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

determined directly from a reference fit. The fits were therefore constrained to a minimum Gaussian width of  $\sigma = 720$  meV, corresponding to twice the value used for spectra acquired at  $E_{\text{pass}} = 20$  eV.

| parameter      | value   | error  | variable | expression  |
|----------------|---------|--------|----------|-------------|
| center         | 284.48  | 0.03   | free     | -           |
| area           | 107 038 | 10 509 | free     | -           |
| sigma          | 0.72    | 0.07   | free     | lower limit |
| gamma          | 1.3     | 0.2    | free     | -           |
| FWHM           | 3.4     | 0.4    | -        | calculated  |
| <b>Shirley</b> |         |        |          |             |
| constant       | 248 881 | 800    | free     | -           |
| k              | 0.095   | 0.006  | free     | -           |

Table A.15.: Fit parameters of the C 1s core level of the pristine CoTPyP layer, as shown in Figure 4.11b. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 50 eV.

| parameter      | value   | error | variable | expression  |
|----------------|---------|-------|----------|-------------|
| center         | 284.87  | 0.02  | free     | -           |
| area           | 112 233 | 9445  | free     | -           |
| sigma          | 0.7     | 0.5   | free     | lower limit |
| gamma          | 1.4     | 0.2   | free     | -           |
| FWHM           | 3.6     | 1.0   | -        | calculated  |
| <b>Shirley</b> |         |       |          |             |
| constant       | 260 797 | 639   | free     | -           |
| k              | 0.084   | 0.004 | free     | -           |

Table A.16.: Fit parameters of the C 1s core level of the Co–CoTPyP layer after deposition of 0.109 ML of Co, as shown in Figure 4.11b. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 50 eV.

## A.7. Fitting the N 1s core level

Prior to the actual fit, a linear background was determined from the pre-peak region, extrapolated over the full spectral range, and subtracted from the original data, following [205]. An example for the MnTPyP layer is shown in Figure A.7. The linear background was described by

$$y = a + b \cdot x, \quad (\text{A.5})$$

with fitted parameters  $a = (33.697\,40 \pm 2.372\,44) \times 10^5$  arb. units and  $b = (-3698 \pm 599) \text{ eV}^{-1}$ . After subtraction of the linear background, the spectra were fitted with one or two peaks together with a Shirley background.

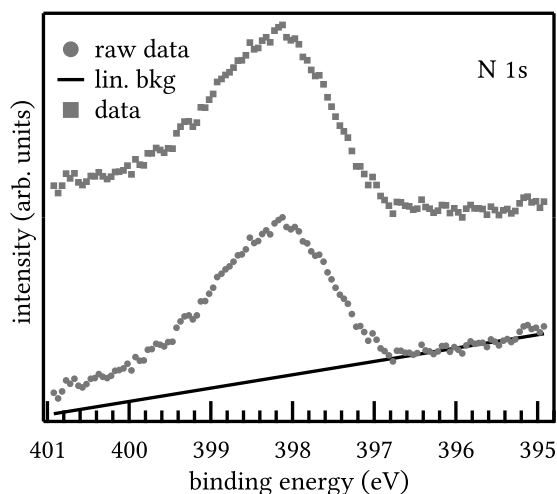


Figure A.7.: Fit of the pre-peak region used for subtraction of the linear background. The spectrum was acquired by Olga Resel.

All N 1s core levels were measured with a pass energy of 10 eV. According to the literature, N 1s spectra often show a comparatively strong Gaussian contribution, largely attributed to phonon screening in organic materials [197]. In addition, differences in local chemical environment, adsorption site, and surface roughness are frequently represented in terms of Gaussian broadening. Nevertheless, the Gaussian width was constrained to be equal for all fitted components, as it was assumed to be dominated primarily by the experimental resolution. Although this constraint is not necessarily the most rigorous in physical terms, it improves the stability of the fit. The minimum Lorentzian width was set to 0.2 eV. If two peaks were used, their areas were constrained to be equal.

### A.7.1. MnTPyP

For the pristine molecular layer, two peaks were used in accordance with the atomic stoichiometry. Upon Co deposition, two additional contributions would in principle be expected: one associated with transmetallation, i.e. the macrocyclic nitrogen coordinated to Co instead of Mn, and one associated with Co-coordinated pyridyl nitrogen. From the CoTPyP N 1s spectrum in Figure 4.12b (bottom), it is evident that the contributions from uncoordinated pyridyl nitrogen and pyrrolic nitrogen bound to Co overlap and cannot be clearly resolved.



| parameter      | value   | error | variable    | expression  |
|----------------|---------|-------|-------------|-------------|
| <b>peak 1</b>  |         |       |             |             |
| center         | 397.954 | 0.016 | free        | -           |
| area           | 42 938  | 2179  | free        | -           |
| sigma          | 0.40    | 0.05  | free        | -           |
| gamma          | 0.20    | 0.05  | free        | -           |
| FWHM           | 1.17    | 0.13  | -           | calculated  |
| <b>peak 2</b>  |         |       |             |             |
| center         | 398.74  | 0.03  | free        | -           |
| area           | 42 938  | 2179  | constrained | peak1_area  |
| sigma          | 0.40    | 0.05  | constrained | peak1_sigma |
| gamma          | 0.43    | 0.07  | free        | -           |
| FWHM           | 1.47    | 0.14  | -           | calculated  |
| <b>Shirley</b> |         |       |             |             |
| constant       | 98 133  | 542   | free        | -           |
| k              | 0.079   | 0.005 | free        | -           |

Table A.17.: Fit parameters of the N 1s core level of the pristine MnTPyP ML, as shown in Figure 4.12a (bottom). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

| parameter      | value   | error | variable    | expression  |
|----------------|---------|-------|-------------|-------------|
| <b>peak 1</b>  |         |       |             |             |
| center         | 398.540 | 0.019 | free        | -           |
| area           | 32 903  | 1520  | free        | -           |
| sigma          | 0.52    | 0.06  | free        | -           |
| gamma          | 0.20    | 0.16  | free        | -           |
| FWHM           | 1.4     | 0.2   | -           | calculated  |
| <b>peak 2</b>  |         |       |             |             |
| center         | 399.58  | 0.04  | free        | -           |
| area           | 32 903  | 1520  | constrained | peak1_area  |
| sigma          | 0.52    | 0.06  | constrained | peak1_sigma |
| gamma          | 0.54    | 0.08  | free        | -           |
| FWHM           | 1.90    | 0.17  | -           | calculated  |
| <b>Shirley</b> |         |       |             |             |
| constant       | 99 002  | 322   | free        | -           |
| k              | 0.064   | 0.003 | free        | -           |

Table A.18.: Fit parameters of the N 1s core level of the Co–MnTPyP layer after deposition of 0.15 ML of Co, as shown in Figure 4.12b (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

Figure A.8 shows the N 1s spectra normalized by area, which should remain constant as long as the total number of nitrogen atoms does not change. Because of the narrow energy window used for the MnTPyP layer, an additional overall scaling factor of 0.5 was applied to the intensity, determined from the pre-peak region. Only minor spectral changes are observed upon increasing the Co coverage from 0.11 ML to the more closely analyzed 0.15 ML sample shown in Figure 4.12a (top). It should be noted that modifications to the chamber were made between measurements, and therefore the actual deposited thickness may differ slightly from the calibrated value.

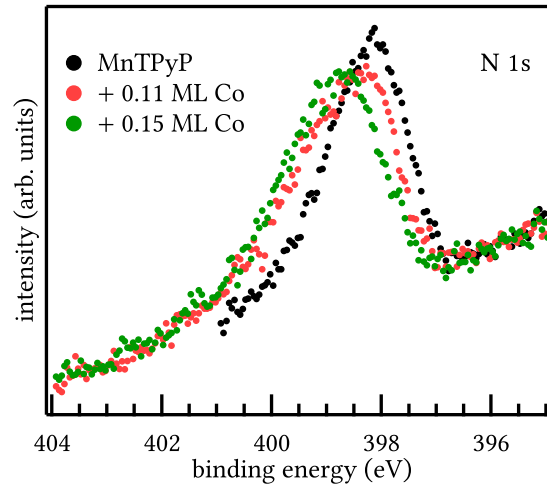


Figure A.8.: Area-normalized N 1s spectra for different Co coverages on MnTPyP. Measurements were performed by Olga Resel.

### A.7.2. CoTPyP

Although the chemical stoichiometry would suggest the use of two peaks for pristine CoTPyP, the small linewidth and the small energy separation between the expected components indicate that a single-peak description is more appropriate. Further details are discussed in the main text. Fitting the CoTPyP spectrum with a single Voigt profile yields an FWHM of  $(1.07 \pm 0.09)$  eV, similar to the corresponding Au 4f linewidth of  $(1.03 \pm 0.01)$  eV. The peak is located at  $(398.31 \pm 0.01)$  eV, with  $\gamma = (0.21 \pm 0.05)$  eV and  $\sigma = (0.35 \pm 0.03)$  eV; see Figure 4.12b (bottom) and Table A.19.

| parameter      | value   | error | variable | expression |
|----------------|---------|-------|----------|------------|
| center         | 398.308 | 0.008 | free     | -          |
| area           | 22 182  | 894   | free     | -          |
| sigma          | 0.35    | 0.03  | free     | -          |
| gamma          | 0.21    | 0.05  | free     | -          |
| FWHM           | 1.07    | 0.09  | -        | calculated |
| <b>Shirley</b> |         |       |          |            |
| constant       | 99 558  | 145   | free     | -          |
| k              | 0.079   | 0.006 | free     | -          |

Table A.19.: Fit parameters of the N 1s core level of the pristine CoTPyP ML, fitted with a single Voigt profile, as shown in Figure 4.12b (bottom). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

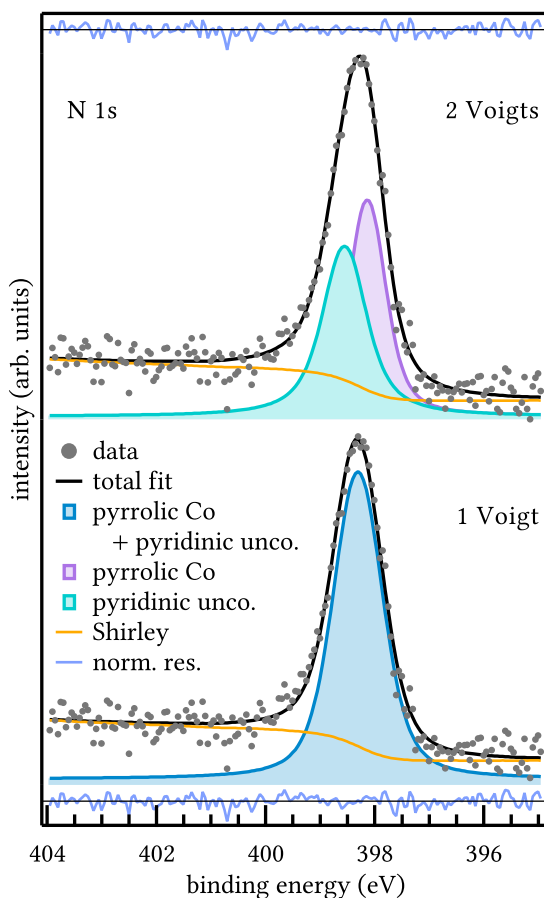


Figure A.9.: Direct comparison of the N 1s core level of pristine CoTPyP, fitted with one Voigt profile (bottom) and with two Voigt profiles (top). The corresponding values are listed in Tables A.19 and A.21, respectively. Measurements were performed by Olga Resel.

Since the single-peak approach provides the more stable fit for pristine CoTPyP, the additional coordinated pyridyl species in the MOF was represented by a second Voigt profile. The first peak accounts for the unresolved contribution of pyrrolic nitrogen bound to Co together with uncoordinated pyridyl nitrogen and was fixed in its FWHM parameters, while the remaining parameters were left free. An energy shift upon network formation was already visible in the C 1s region; accordingly, the peak position was not fixed here. The resulting fit is shown in the top panel of Figure 4.12b, and the corresponding parameters are summarized in Table A.20.

Figure A.10 shows the N 1s core level of CoTPyP for different Co depositions, normalized to the total area under the curve. No significant difference is observed between the samples with 0.11 ML and 0.22 ML of deposited Co, indicating that the lower coverage already exceeds the amount required for network formation, estimated as 0.04 ML. Since one CoTPyP molecule occupies approximately 25 surface atoms, one additional Co atom per molecule corresponds to  $1/25$ , i.e. 0.04 ML.

| parameter      | value   | error | variable    | expression  |
|----------------|---------|-------|-------------|-------------|
| <b>peak 1</b>  |         |       |             |             |
| center         | 398.650 | 0.013 | free        | -           |
| area           | 12 057  | 575   | free        | -           |
| sigma          | 0.32    | 0.04  | free        | -           |
| gamma          | 0.20    | 0.05  | free        | -           |
| FWHM           | 0.98    | 0.12  | -           | calculated  |
| <b>peak 2</b>  |         |       |             |             |
| center         | 399.67  | 0.03  | free        | -           |
| area           | 12 057  | 575   | constrained | peak1_area  |
| sigma          | 0.32    | 0.04  | constrained | peak1_sigma |
| gamma          | 0.50    | 0.07  | free        | -           |
| FWHM           | 1.42    | 0.14  | -           | calculated  |
| <b>Shirley</b> |         |       |             |             |
| constant       | 99 591  | 139   | free        | -           |
| k              | 0.108   | 0.004 | free        | -           |

Table A.20.: Fit parameters of the N 1s core level of the Co–CoTPyP layer after deposition of 0.11 ML of Co, as shown in Figure 4.12b (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

| parameter      | value  | error | variable    | expression  |
|----------------|--------|-------|-------------|-------------|
| <b>peak 1</b>  |        |       |             |             |
| center         | 398.14 | 0.03  | free        | -           |
| area           | 11 441 | 457   | free        | -           |
| sigma          | 0.24   | 0.06  | free        | -           |
| gamma          | 0.20   | 0.14  | free        | -           |
| FWHM           | 0.8    | 0.2   | -           | calculated  |
| <b>peak 2</b>  |        |       |             |             |
| center         | 398.55 | 0.03  | free        | -           |
| area           | 11 441 | 457   | constrained | peak1_area  |
| sigma          | 0.24   | 0.06  | constrained | peak1_sigma |
| gamma          | 0.31   | 0.04  | free        | -           |
| FWHM           | 0.97   | 0.14  | -           | calculated  |
| <b>Shirley</b> |        |       |             |             |
| constant       | 99 553 | 153   | free        | -           |
| k              | 0.075  | 0.006 | free        | -           |

Table A.21.: Fit parameters of the N 1s core level of the pristine CoTPyP ML, fitted with two Voigt profiles, as shown in Figure A.9 (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 10 eV.

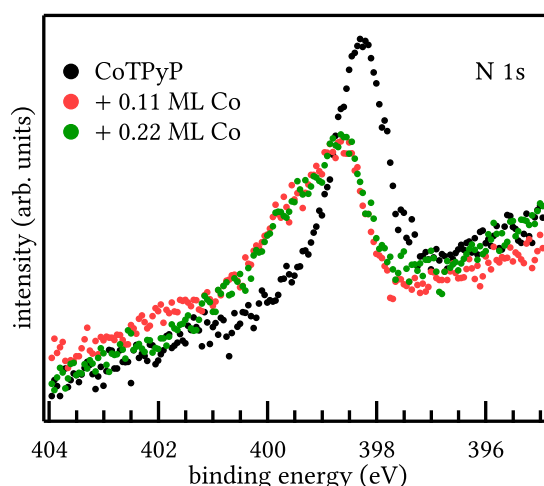


Figure A.10.: N 1s core level of pristine CoTPyP and after different Co coverages. The spectra were acquired by Olga Resel at the University of Graz, normalized by area, and vertically offset in the pre-peak region.

## A.8. Fitting the Co $2p_{3/2}$

A pass energy of 20 eV was used throughout. Although the Co deposition was calibrated with great care, the relative Co:MnTPyP coverages may still deviate from the nominal 1:1 and 2:1 ratios, because the molecular deposition flux can decrease over time and the actual MnTPyP coverage may therefore differ slightly between samples. The molecular coverage was assessed only by LEED, while additional characterization techniques such as STM were not available for all samples.

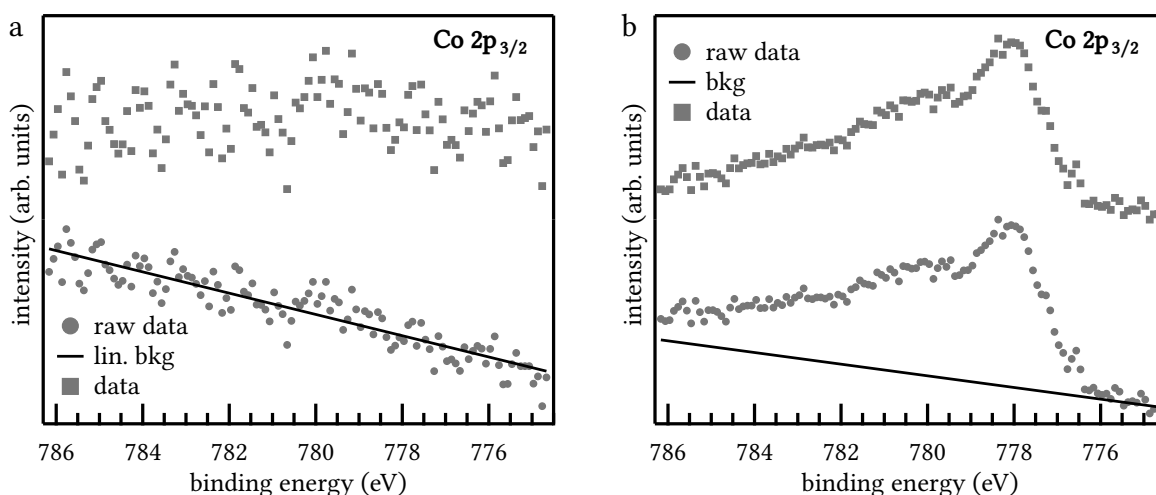


Figure A.11.: Background-removal procedure for the Co  $2p_{3/2}$  core level. (a) Clean MnTPyP, used to determine the linear background. (b) Co–MnTPyP after deposition of 0.11 ML of Co. In each panel, the lower spectrum shows the raw data together with the fitted or subtracted background, while the upper spectrum shows the corrected data.

For the molecular samples, the spectra already exhibit a linear background, as visible in Figure A.11a, which was recorded over the Co  $2p_{3/2}$  transition metal level region on the MnTPyP SAM. To account for this contribution, a linear background was first fitted over the same energy range on the pristine MnTPyP sample, as shown in Figure A.11a. The linear background was calculated according to Equation A.5, yielding  $a = (623\,812 \pm 12\,613)$  arb. units and  $b = (396 \pm 16)$  eV $^{-1}$ . This linear

background was then subtracted from the original Co  $2p_{3/2}$  spectra, as illustrated in Figure A.11b, with the final scaling adjusted in the individual pre-peak region.

### A.8.1. CoTPyP and Co–CoTPyP

For the CoTPyP and Co–CoTPyP layers, the background may differ because the X-ray anode had been exchanged. However, no dedicated background spectrum was recorded for these samples. Therefore, the same background procedure was applied, which resulted in a flat pre-peak region.

| parameter      | value     | error  | variable | expression |
|----------------|-----------|--------|----------|------------|
| <b>peak 1</b>  |           |        |          |            |
| center         | 779.65    | 0.06   | free     | -          |
| area           | 144 925   | 8760   | free     | -          |
| sigma          | 0.36      | 0.14   | free     | -          |
| gamma          | 1.49      | 0.16   | free     | -          |
| FWHM           | 3.2       | 0.3    | -        | calculated |
| <b>peak 2</b>  |           |        |          |            |
| center         | 782.0     | 0.3    | free     | -          |
| area           | 5192      | 3072   | free     | -          |
| sigma          | 0.8       | 0.3    | free     | -          |
| FWHM           | 1.9       | 0.7    | -        | calculated |
| <b>Shirley</b> |           |        |          |            |
| constant       | 1 903 790 | 384    | free     | -          |
| k              | 0.0683    | 0.0018 | free     | -          |

Table A.22.: Fit parameters of the Co  $2p_{3/2}$  core level of the pristine CoTPyP SAM, as shown in Figure 4.13a. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

Figure A.12 shows a direct comparison of the Co  $2p_{3/2}$  spectra of CoTPyP before and after deposition of 0.11 ML of Co.

### A.8.2. Cobalt

As a reference, a thin Co film on Au(100) was measured during the third measurement period. The corresponding spectrum is shown in Figure A.13. Already in the raw data, two components are visible, and an additional Gaussian peak was included to account for unresolved multiplet structure and asymmetry. This once more underlines the difficulty of fitting the Co  $2p_{3/2}$  core level, since even submonolayer Co coverages (0.29 ML) already exhibit multiple spectral contributions in the absence of additional coordination partners.

### A.8.3. Co–MnTPyP

It should first be noted that the Co  $2p_{3/2}$  spectra of the Co–MnTPyP layer were acquired on a different sample set than the corresponding N 1s spectra. Since the N 1s measurements were carried out in

| parameter      | value     | error  | variable    | expression  |
|----------------|-----------|--------|-------------|-------------|
| <b>peak 1</b>  |           |        |             |             |
| center         | 778.066   | 0.019  | free        | -           |
| area           | 89 952    | 11 331 | free        | -           |
| sigma          | 0.47      | 0.06   | free        | -           |
| gamma          | 0.39      | 0.09   | free        | -           |
| FWHM           | 1.57      | 0.19   | -           | calculated  |
| <b>peak 2</b>  |           |        |             |             |
| center         | 780.06    | 0.04   | free        | -           |
| area           | 54 781    | 33 784 | free        | -           |
| sigma          | 0.47      | 0.06   | constrained | peak1_sigma |
| gamma          | 0.5       | 0.3    | free        | -           |
| FWHM           | 1.7       | 0.4    | -           | calculated  |
| <b>peak 3</b>  |           |        |             |             |
| center         | 781.4     | 0.7    | free        | -           |
| area           | 86 745    | 37 648 | free        | -           |
| sigma          | 1.8       | 0.3    | free        | -           |
| FWHM           | 4.2       | 0.7    | -           | calculated  |
| <b>Shirley</b> |           |        |             |             |
| constant       | 2 611 699 | 504    | free        | -           |
| k              | 0.0640    | 0.0019 | free        | -           |

Table A.23.: Fit parameters of the Co 2p<sub>3/2</sub> core level after deposition of 0.11 ML of Co on the CoTPyP SAM, as shown in Figure 4.13b. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

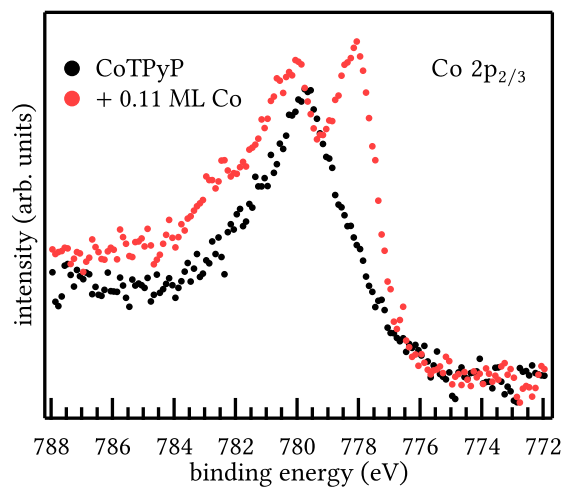


Figure A.12.: Direct comparison of the Co 2p<sub>3/2</sub> core level of pristine CoTPyP and after Co deposition, normalized in the pre-peak region. Measurements were performed by Olga Resel.

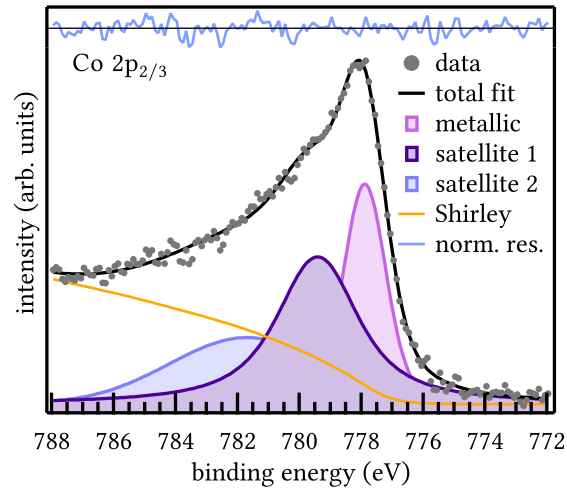


Figure A.13.: Co  $2p_{3/2}$  core level of a pure 0.29 ML Co film on Au(100).

| parameter      | value     | error  | variable    | expression  |
|----------------|-----------|--------|-------------|-------------|
| <b>peak 1</b>  |           |        |             |             |
| center         | 777.88    | 0.03   | free        | -           |
| area           | 72 633    | 16 490 | free        | -           |
| sigma          | 0.59      | 0.04   | free        | -           |
| gamma          | 0.20      | 0.14   | free        | -           |
| FWHM           | 1.62      | 0.19   | -           | calculated  |
| <b>peak 2</b>  |           |        |             |             |
| center         | 779.41    | 0.18   | free        | -           |
| area           | 115 698   | 92 570 | free        | -           |
| sigma          | 0.59      | 0.04   | constrained | peak1_sigma |
| gamma          | 1.2       | 0.6    | free        | -           |
| FWHM           | 3.1       | 0.9    | -           | calculated  |
| <b>peak 3</b>  |           |        |             |             |
| center         | 782       | 2      | free        | -           |
| area           | 72 320    | 66 044 | free        | -           |
| sigma          | 2.5       | 0.9    | free        | -           |
| FWHM           | 6         | 2      | -           | calculated  |
| <b>Shirley</b> |           |        |             |             |
| constant       | 2 147 491 | 1223   | free        | -           |
| k              | 0.059     | 0.004  | free        | -           |

Table A.24.: Fit parameters of the Co  $2p_{3/2}$  core level of a 0.29 ML Co film on Au(100), as shown in Figure A.13. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.



the second measurement period, a separate set of samples had to be prepared because the degraded X-ray source in the first period did not provide sufficient conditions for these measurements, as mentioned in the main text.

As discussed in the main text, two different Co coverages, namely 0.06 ML in Figure A.14 and 0.11 ML in Figure 4.13c, were investigated in detail in order to identify the most suitable coverage. The resulting fitting parameters are listed in Tables A.25 and A.26. Despite the higher statistics and improved signal-to-noise ratio, the fit obtained for the lower Co coverage is less stable than that for the higher coverage, as reflected by the larger parameter uncertainties. These fits are not fully stable; in particular, the low-binding-energy component tends to dominate unless additional constraints are imposed. To extract robust trends, the areas of the two components were therefore constrained to be equal.

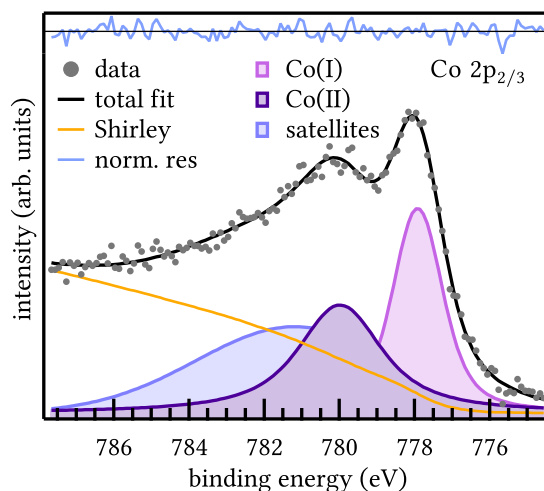


Figure A.14.: Co  $2p_{3/2}$  spectrum of MnTPyP after deposition of 0.06 ML of Co. The corresponding fitting parameters are listed in Table A.25.

| parameter      | value   | error  | variable    | expression  |
|----------------|---------|--------|-------------|-------------|
| <b>peak 1</b>  |         |        |             |             |
| center         | 777.915 | 0.019  | free        | -           |
| area           | 82 365  | 49 582 | free        | -           |
| sigma          | 0       | 3      | free        | -           |
| gamma          | 0.4     | 0.5    | free        | -           |
| FWHM           | 2       | 6      | -           | calculated  |
| <b>peak 2</b>  |         |        |             |             |
| center         | 779.98  | 0.08   | free        | -           |
| area           | 82 365  | 49 582 | constrained | peak1_area  |
| sigma          | 0       | 3      | constrained | peak1_sigma |
| gamma          | 1.1     | 0.5    | free        | -           |
| FWHM           | 3       | 5      | -           | calculated  |
| <b>peak 3</b>  |         |        |             |             |
| center         | 781     | 2      | free        | -           |
| area           | 111 140 | 90 893 | free        | -           |
| sigma          | 2.6     | 0.8    | free        | -           |
| FWHM           | 6       | 2      | -           | calculated  |
| <b>Shirley</b> |         |        |             |             |
| constant       | 96 027  | 1154   | free        | -           |
| k              | 0.070   | 0.003  | free        | -           |

Table A.25.: Fit parameters of the Co  $2p_{3/2}$  core level of Co–MnTPyP after deposition of 0.06 ML of Co, as shown in Figure A.14. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value  | error  | variable    | expression  |
|----------------|--------|--------|-------------|-------------|
| <b>peak 1</b>  |        |        |             |             |
| center         | 778.01 | 0.03   | free        | -           |
| area           | 17 827 | 6686   | free        | -           |
| sigma          | 0.60   | 0.10   | free        | -           |
| gamma          | 0.2    | 0.3    | free        | -           |
| FWHM           | 1.7    | 0.4    | -           | calculated  |
| <b>peak 2</b>  |        |        |             |             |
| center         | 779.99 | 0.13   | free        | -           |
| area           | 17 827 | 6686   | constrained | peak1_area  |
| sigma          | 0.60   | 0.10   | constrained | peak1_sigma |
| gamma          | 0.9    | 0.2    | free        | -           |
| FWHM           | 2.6    | 0.4    | -           | calculated  |
| <b>peak 3</b>  |        |        |             |             |
| center         | 782    | 1      | free        | -           |
| area           | 17 743 | 18 847 | free        | -           |
| sigma          | 2      | 1      | free        | -           |
| FWHM           | 5      | 2      | -           | calculated  |
| <b>Shirley</b> |        |        |             |             |
| constant       | 4808   | 257    | free        | -           |
| k              | 0.02   | 0.02   | free        | -           |

Table A.26.: Fit parameters of the Co  $2p_{3/2}$  core level of Co–MnTPyP after deposition of 0.11 ML of Co, as shown in Figure 4.13c. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

## A.9. Additional analysis of momentum microscopy data

All EDCs were normalized close to the Fermi edge, i.e. at the lowest accessible binding energies. Spectra covering a wider energy range, but with lower  $k$  resolution, are shown in Figure A.21 and exhibit the same features as those presented in Figures 4.15a and 4.17a in the main text. The EDCs shown in this work were extracted from momentum-resolved stack and therefore correspond to VB spectra integrated over the full measured  $k$  space. This differs from conventional UPS, where typically only electrons emitted close to normal emission are collected.

### A.9.1. Background subtraction

The background subtraction followed the procedure described in the supplementary information of [51]. As a first step, the  $k_{\parallel}$  scaling was adjusted between the clean Au substrate and the MnTPyP/Co-MnTPyP datasets. This correction is required because different microscope settings lead to different pixel-to-1/Å conversions. For this purpose, a momentum map with negligible molecular contributions was selected, and line profiles parallel to the  $k_x$  axis were compared. The procedure is illustrated schematically in Figure A.15. For the MOF layer, the gold-related features in the momentum maps are broadened due to the presence of the adsorbed overlayer. Before substrate subtraction, an averaging filter with a kernel size of 23 was therefore applied to the clean-substrate data in order to broaden the gold features and match their appearance in the MOF maps. In addition, the same line profile was used to determine a scaling factor for the subtraction of the substrate background. To this end, the maxima and minima were aligned with the corresponding features in the molecular-adlayer spectrum.

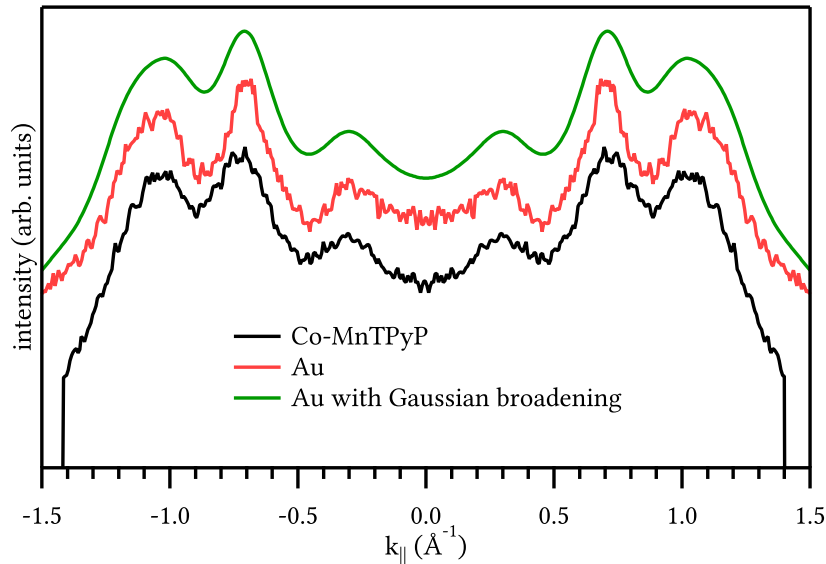


Figure A.15.: Schematic illustration of the alignment of the  $k$ -space features. For clarity, the spectra are shown with an offset; in the actual procedure, the corresponding features were aligned directly.

### A.9.2. Feature identification

Only the spin-down channel of the calculated momentum distributions is shown here, since in the relevant energy range the spin-up and spin-down orbitals exhibit very similar momentum-space fingerprints. For CoTPP, this includes orbitals from HOMO-4 to HOMO; for MnTPyP, orbitals from HOMO-2 to HOMO are considered. Tables A.27 and A.28 show that the two spin channels may appear at different energies, as discussed in the main text. Following the assumption of Bai et al. [267], the WKF was subtracted from the gas-phase energies so that experimental and calculated values are referenced to  $E_F$ . Furthermore, CoTPP and MnTPyP exhibit similar fingerprints for some orbitals, although not always in the same energetic order. Table A.29 summarizes the corresponding orbital pairs. Since some theoretical orbital energies are very close to one another, several orbitals may contribute to a single experimental photoemission feature, as illustrated in the bottom panels of Figures A.17 and A.18.

|        | spin-up |                              | spin-down |                              |
|--------|---------|------------------------------|-----------|------------------------------|
|        | theory  | theory - $\Phi_{\text{SAM}}$ | theory    | theory - $\Phi_{\text{SAM}}$ |
| HOMO-4 | 6.16    | 1.55                         | 7.11      | 2.5                          |
| HOMO-3 | 6.16    | 1.55                         | 7.00      | 2.39                         |
| HOMO-2 | 5.73    | 1.12                         | 5.64      | 1.03                         |
| HOMO-1 | 5.58    | 0.97                         | 5.62      | 1.01                         |
| HOMO   | 5.58    | 0.97                         | 3.98      | -0.63                        |
| LUMO   | 2.61    | -2.01                        | 2.78      | -1.83                        |
| LUMO+1 | 2.61    | -2.01                        | 2.78      | -1.83                        |
| LUMO+2 | 1.17    | -3.44                        | 1.15      | -3.46                        |
| LUMO+3 | 0.92    | -3.69                        | 0.94      | -3.67                        |

Table A.27.: Theoretical gas-phase orbital energies of MnTPyP, referenced to the vacuum level ( $E_v$ ), taken from [280], and after subtraction of the WKF of the SAM (4.61 eV). All values are given in eV. Data of the theoretical orbitals from [280].

|        | spin-up |                              | spin-down |                              |
|--------|---------|------------------------------|-----------|------------------------------|
|        | theory  | theory - $\Phi_{\text{MOF}}$ | theory    | theory - $\Phi_{\text{MOF}}$ |
| HOMO-4 | 6.23    | 2.11                         | 6.47      | 2.35                         |
| HOMO-3 | 5.36    | 1.24                         | 5.71      | 1.59                         |
| HOMO-2 | 5.36    | 1.24                         | 5.71      | 1.59                         |
| HOMO-1 | 5.07    | 0.95                         | 5.07      | 0.95                         |
| HOMO   | 5.07    | 0.95                         | 5.06      | 0.94                         |
| LUMO   | 1.96    | -2.16                        | 1.97      | -2.15                        |
| LUMO+1 | 1.96    | -2.16                        | 1.97      | -2.15                        |
| LUMO+2 | 1.20    | -2.92                        | 0.41      | -3.71                        |
| LUMO+3 | 0.39    | -3.73                        | 0.38      | -3.74                        |

Table A.28.: Theoretical gas-phase orbital energies of CoTPP, referenced to the vacuum level ( $E_v$ ), taken from [284], and after subtraction of the WKF of the MOF (4.12 eV). All values are given in eV. Data of the theoretical orbitals from [284].

For MnTPyP, contributions from spin-up HOMO-3 and HOMO-4 to feature ② can be neglected, since feature ① is already shifted by about 200 meV relative to the theoretical values, implying that these deeper orbitals would be expected at still higher binding energies. Additional support

| MnTPyP | CoTPP  |
|--------|--------|
| LUMO+1 | LUMO+1 |
| LUMO   | LUMO   |
| HOMO   | LUMO+2 |
| HOMO-1 | HOMO-1 |
| HOMO-2 | HOMO   |

Table A.29.: Direct comparison of orbitals of MnTPyP and CoTPP with similar momentum-space fingerprints.

for this assignment is provided by the absence of the corresponding momentum pattern in the experimental maps. Small discrepancies between the calculated energies (see Table A.27) and the experimental values may arise from differences between the gas-phase geometry used in the calculations and the actual adsorbed structure. In addition, coupling to the metal substrate is neglected in the calculations and may lead to an energy-level realignment and modified orbital occupation. Orbitals with stronger out-of-plane character couple more strongly to the substrate electrons and are therefore expected to shift more strongly in energy.

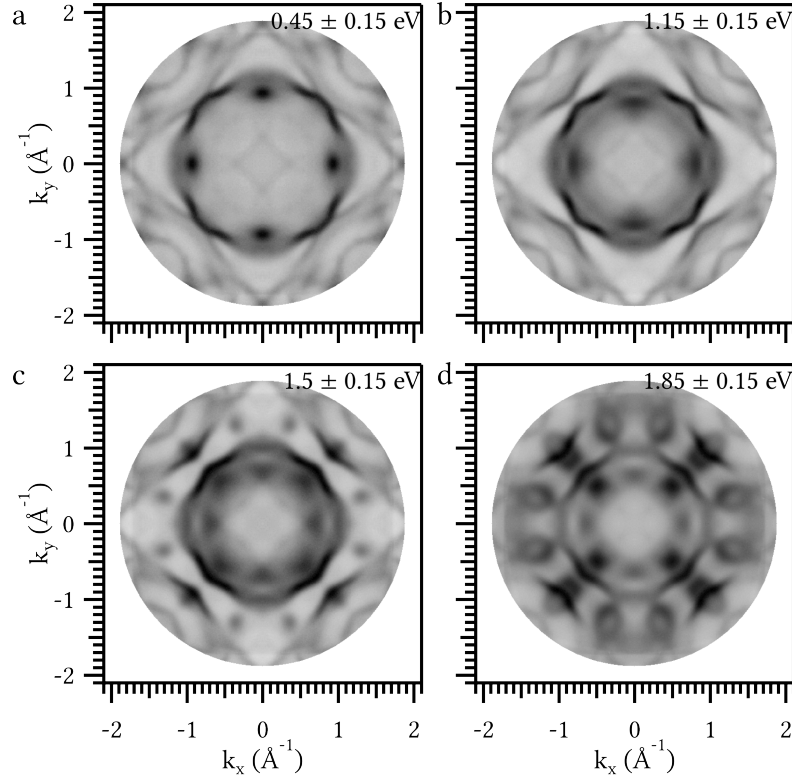


Figure A.16.: Momentum maps of the clean Au(100) substrate used as reference. (a)  $E_B = 0.45$  eV, (b)  $E_B = 1.15$  eV, (c)  $E_B = 1.5$  eV, and (d)  $E_B = 1.85$  eV.

Further support for the emerging spectral features is provided by the angle-resolved EDCs shown in Figure A.20. Although the clean Au substrate exhibits similar features at shifted energies, the observed signatures are unlikely to originate solely from the clean Au substrate for two reasons. First, the Au(100) substrate contribution was subtracted. Second, as shown in the wide-range EDC scan, the remaining gold-related features stay at the same energy and therefore cannot be explained by a global shift of the substrate spectrum; see Figure A.21. Nevertheless, these contributions originate from Au states hybridized with the metal centers in the MOF, as also discussed in the main text.

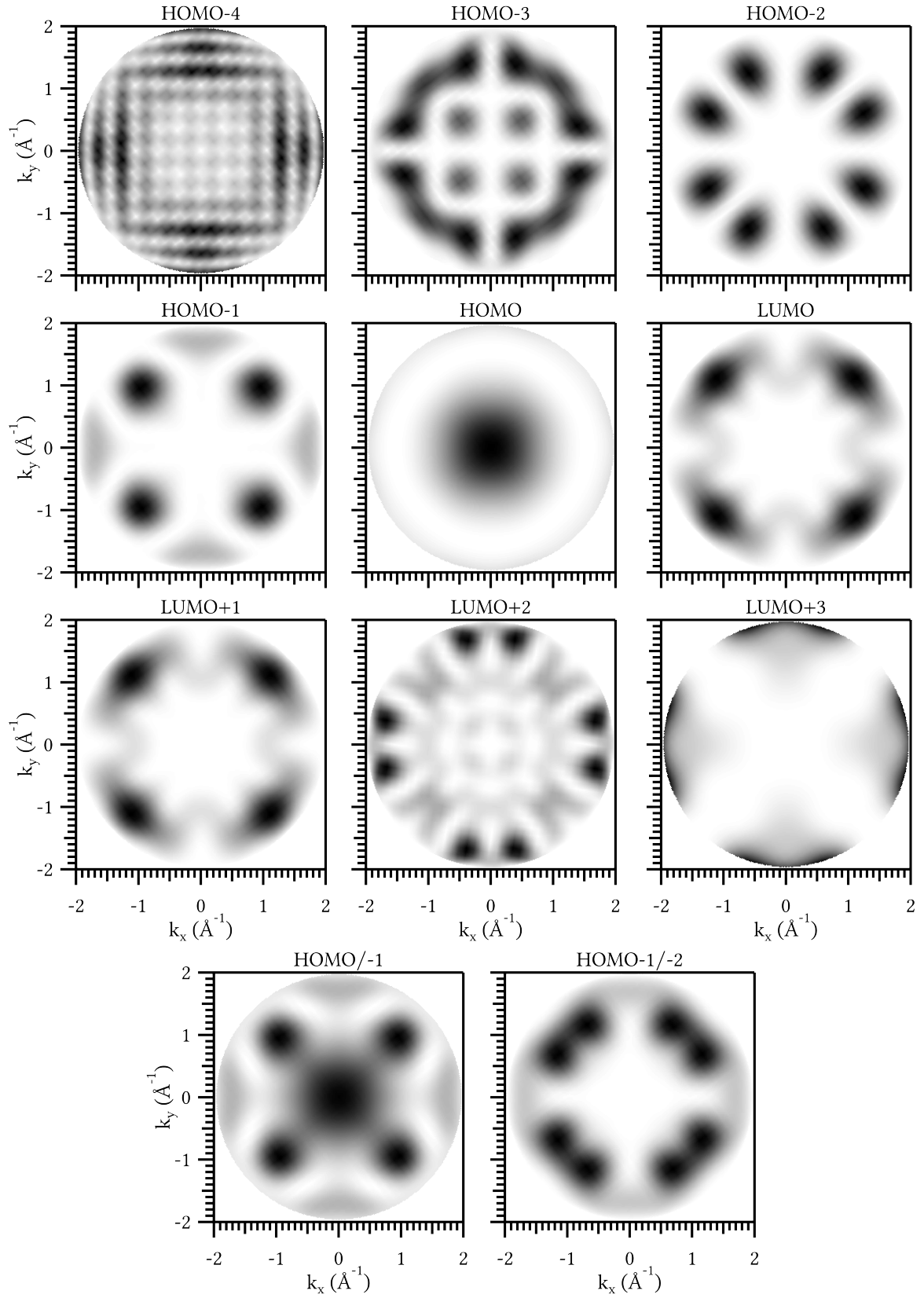


Figure A.17.: Calculated momentum maps for the spin-down channel of MnTPyP at a kinetic energy of 15 eV. Data for the theoretical orbitals from [280, 281].

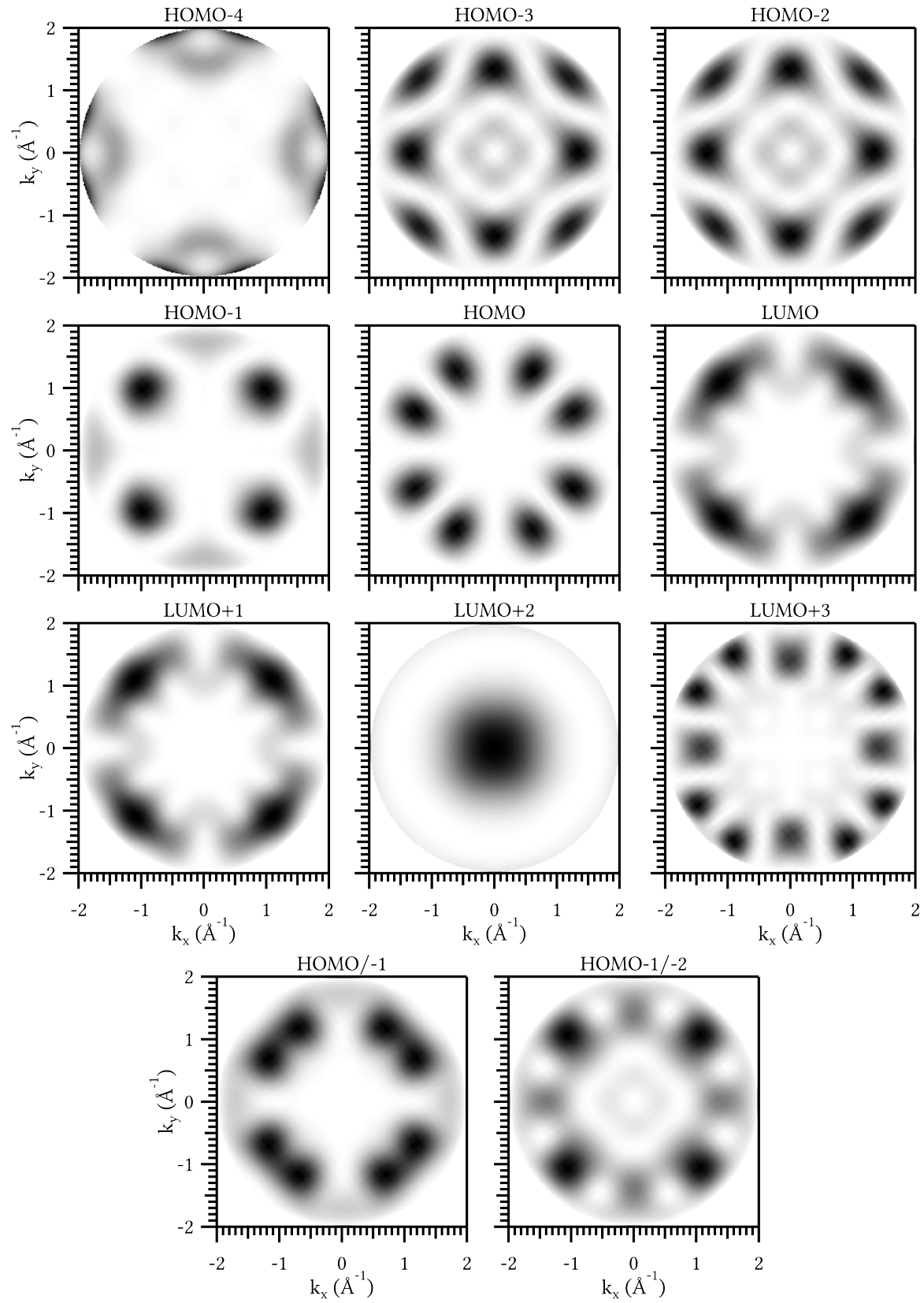


Figure A.18.: Calculated momentum maps for the spin-down channel of CoTPP at a kinetic energy of 15 eV. Data for the theoretical orbitals from [281, 284].



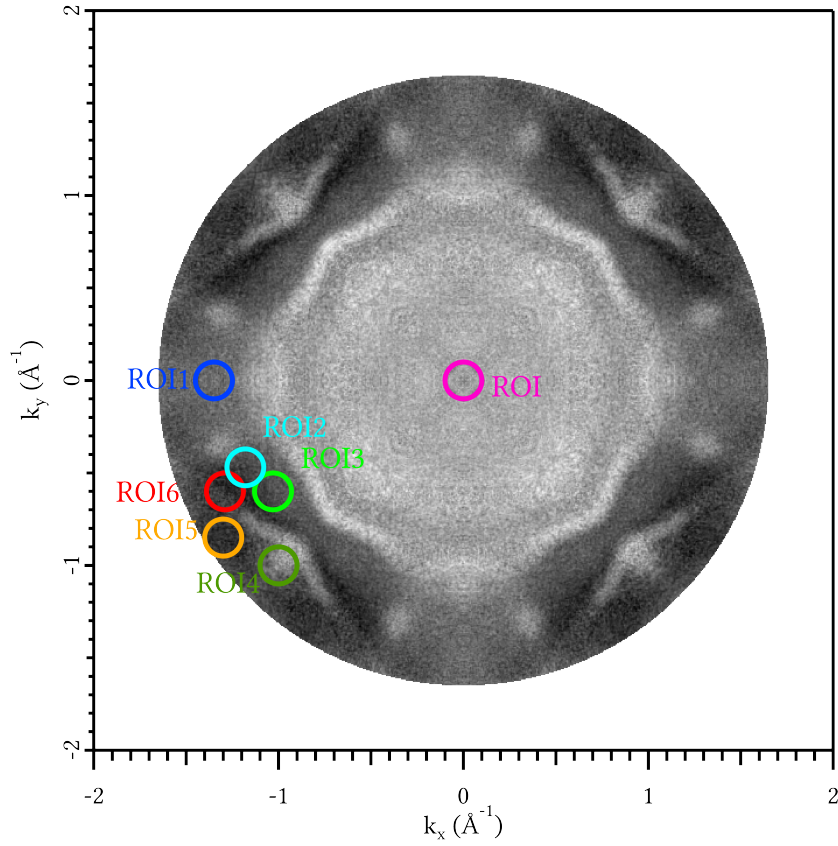


Figure A.19.: Momentum map of Co-MnTPyP after background subtraction at 1.54 eV. The regions from which the angle-resolved EDCs shown in Figure A.20 were extracted are indicated. A radius of  $0.1 \text{ \AA}^{-1}$  was used.

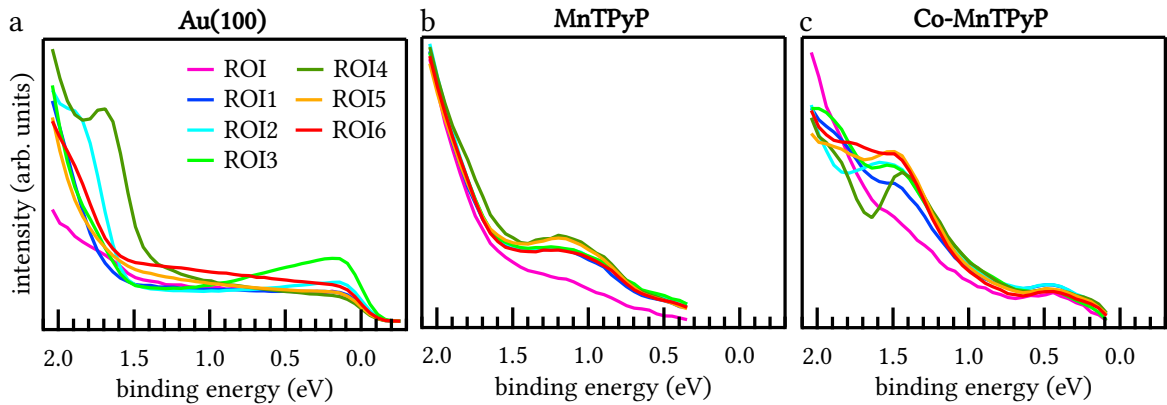


Figure A.20.: Angle-resolved EDCs, shown for Au (left), MnTPyP (middle), and Co-MnTPyP (right). The EDCs for the SAM and MOF were extracted after background subtraction. The integration regions are indicated in Figure A.19.

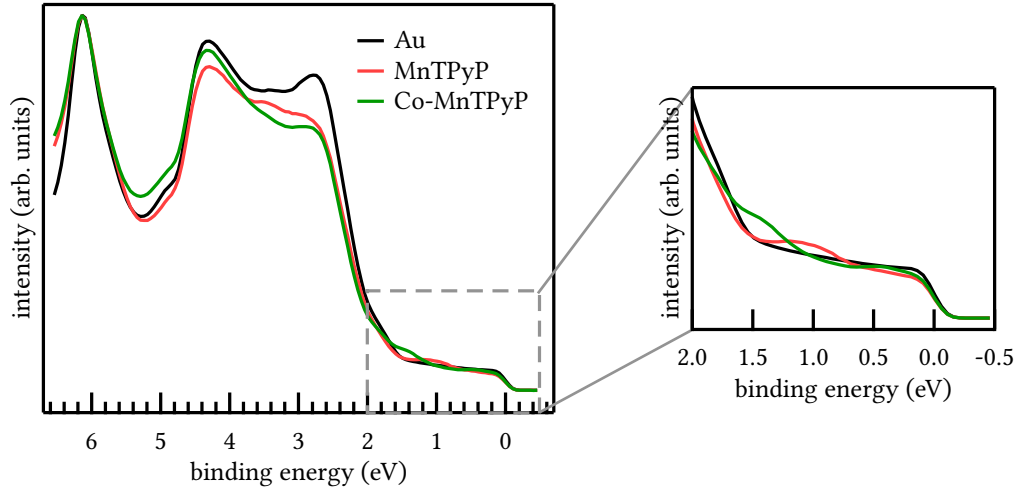


Figure A.21.: Wide-range, angle-integrated EDCs, normalized at the feature located at 6.14 eV. The right panel shows a zoom into the Fermi-edge region.

In addition, the curvature analysis shown in Figure A.22 highlights the dispersion of feature ③, whereas the other features are not represented as clearly. This is attributed to the influence of the subtracted Au background on the derivative-based analysis, which can lead to distortions in the representation.

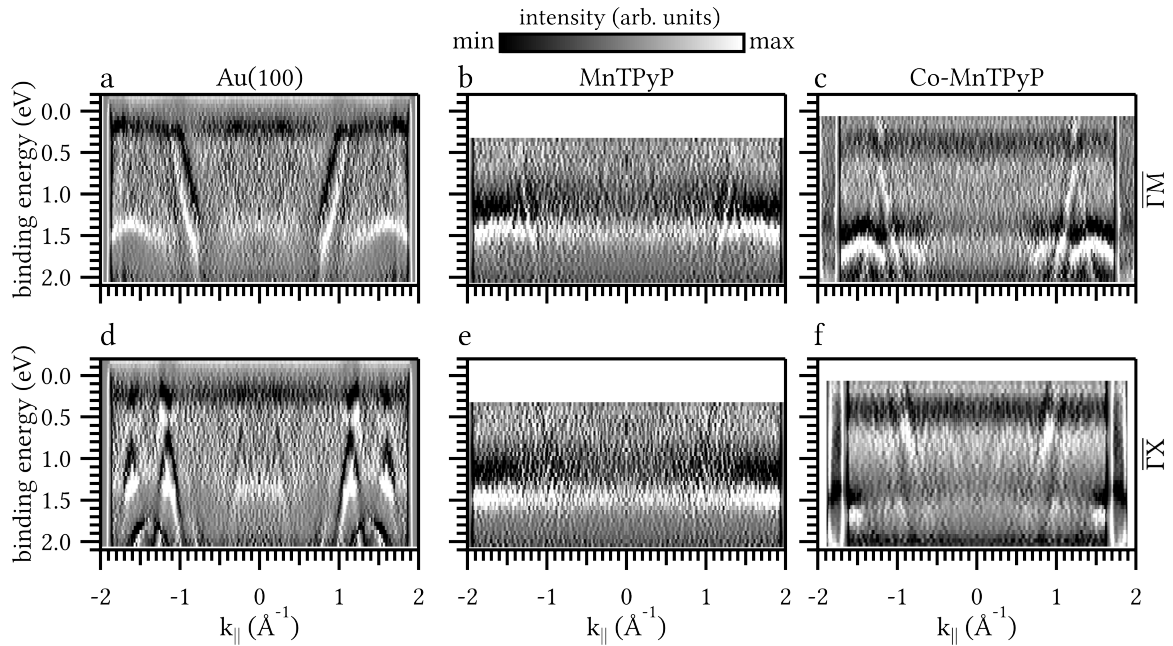


Figure A.22.: Curvature analysis [286] applied to the BMs shown in Figure 4.19. All images were processed using the same curvature parameters.

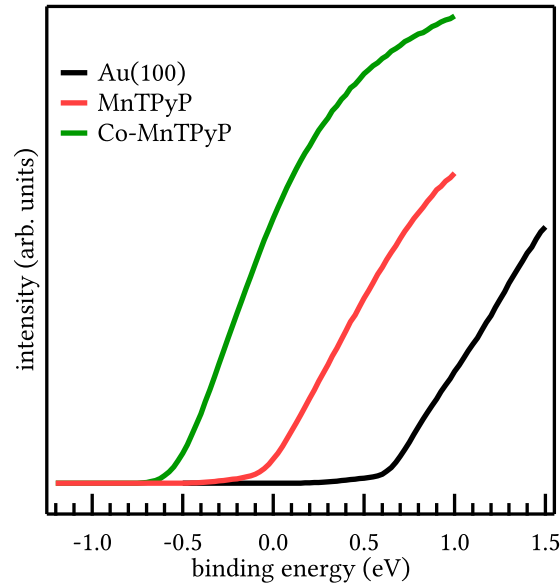


Figure A.23.: Secondary-electron cut-off used to determine the system WKF. The WKF of the clean Au(100) substrate was determined to be 5.28 eV, close to the literature value of 5.4 eV for Au(100) [109].

## A.10. Additional data for Ni–MnTPyP

Applying the approach of Shard [167] yields a coverage of 0.57 ML Ni, which corresponds to 0.66 ML in the convention used in the main text ( $a_{\text{Ni}} = 3.5238 \text{ \AA}$  [296]).

The fitting of the C 1s and Ni  $2p_{3/2}$  core levels was performed analogously to the case of Co–MnTPyP, including the same background-removal procedure.

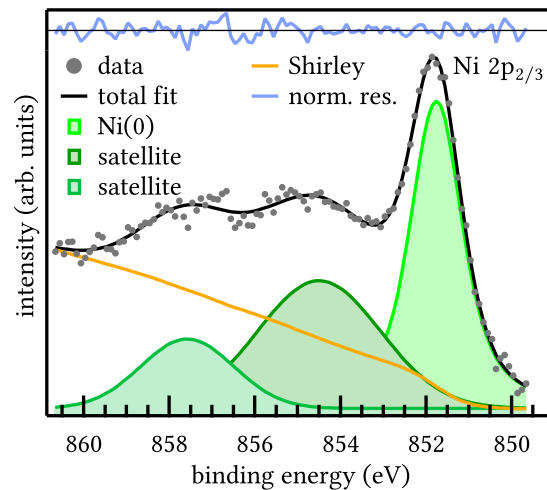


Figure A.24.: Ni  $2p_{3/2}$  core level of metallic Ni after deposition of 0.74 ML of Ni on Au(100). The corresponding fitting parameters are listed in Table A.33.

| parameter      | value   | error  | variable    | expression           |
|----------------|---------|--------|-------------|----------------------|
| <b>peak 1</b>  |         |        |             |                      |
| center         | 84.0058 | 0.0012 | free        | -                    |
| area           | 364 470 | 1462   | free        | -                    |
| sigma          | 0.365   | 0.004  | free        | -                    |
| gamma          | 0.376   | 0.005  | free        | -                    |
| FWHM           | 1.331   | 0.010  | -           | calculated           |
| <b>peak 2</b>  |         |        |             |                      |
| center         | 87.6834 | 0.0015 | constrained | peak1_center + shift |
| area           | 282 101 | 1104   | constrained | ratio * peak1_area   |
| sigma          | 0.365   | 0.004  | constrained | peak1_sigma          |
| gamma          | 0.382   | 0.005  | free        | -                    |
| FWHM           | 1.339   | 0.010  | -           | calculated           |
| shift          | 3.6776  | 0.0019 | free        | -                    |
| ratio          | 0.774   | 0.003  | free        | -                    |
| <b>Shirley</b> |         |        |             |                      |
| constant       | 35 998  | 235    | free        | -                    |
| k              | 0.0259  | 0.0004 | free        | -                    |

Table A.30.: Fit parameters correspond to Figure 5.2 for the Au 4*f* core level after 0.74 ML deposition of Ni. To compare to the clean Au 4*f* core level in Figure 4.3a, a scaling factor of 1.05 must be applied. The pass energy was set to 20 eV. All parameters are given in eV except for the area, the Shirley parameters, and the ratio. The area and the Shirley constant are given in arb. units.

| parameter      | value   | error | variable | expression |
|----------------|---------|-------|----------|------------|
| center         | 284.843 | 0.013 | free     | -          |
| area           | 102 279 | 5198  | free     | -          |
| sigma          | 0.49    | 0.08  | free     | -          |
| gamma          | 0.82    | 0.09  | free     | -          |
| FWHM           | 2.3     | 0.2   | -        | calculated |
| <b>Shirley</b> |         |       |          |            |
| constant       | 674 006 | 494   | free     | -          |
| k              | 0.120   | 0.003 | free     | -          |

Table A.31.: Fit parameters of the C 1*s* core level of the Ni–MnTPyP layer, as shown in Figure 5.5. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value  | error | variable    | expression  |
|----------------|--------|-------|-------------|-------------|
| <b>peak 1</b>  |        |       |             |             |
| center         | 852.92 | 0.03  | free        | -           |
| area           | 62 525 | 7764  | free        | -           |
| sigma          | 0.4    | 0.3   | free        | -           |
| gamma          | 0.6    | 0.3   | free        | -           |
| FWHM           | 1.7    | 0.8   | -           | calculated  |
| <b>peak 2</b>  |        |       |             |             |
| center         | 855.36 | 0.05  | free        | -           |
| area           | 62 525 | 7764  | constrained | peak1_area  |
| sigma          | 0.4    | 0.3   | constrained | peak1_sigma |
| gamma          | 1.1    | 0.3   | free        | -           |
| FWHM           | 2.4    | 0.7   | -           | calculated  |
| <b>Shirley</b> |        |       |             |             |
| constant       | 97 069 | 1208  | free        | -           |
| k              | 0.090  | 0.005 | free        | -           |

Table A.32.: Fit parameters of the Ni  $2p_{3/2}$  core level of the Ni–MnTPyP network before CO treatment, as shown in Figure 5.6 and Figure 6.3b (bottom). An incorporated Ni coverage of 0.07 ML was obtained for the network. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value   | error | variable | expression |
|----------------|---------|-------|----------|------------|
| <b>peak 1</b>  |         |       |          |            |
| center         | 851.759 | 0.012 | free     | -          |
| area           | 35 516  | 6735  | free     | -          |
| sigma          | 0.36    | 0.05  | free     | -          |
| gamma          | 0.47    | 0.16  | free     | -          |
| FWHM           | 1.5     | 0.3   | -        | calculated |
| <b>peak 2</b>  |         |       |          |            |
| center         | 854.50  | 0.10  | free     | -          |
| area           | 26 355  | 3427  | free     | -          |
| sigma          | 1.43    | 0.19  | free     | -          |
| FWHM           | 3.4     | 0.4   | -        | calculated |
| <b>peak 3</b>  |         |       |          |            |
| center         | 857.58  | 0.18  | free     | -          |
| area           | 10 873  | 2930  | free     | -          |
| sigma          | 1.09    | 0.14  | free     | -          |
| FWHM           | 2.6     | 0.3   | -        | calculated |
| <b>Shirley</b> |         |       |          |            |
| constant       | 368 415 | 752   | free     | -          |
| k              | 0.088   | 0.007 | free     | -          |

Table A.33.: Fit parameters of the Ni  $2p_{3/2}$  core level of the 0.74 ML thick Ni film on Au(100), as shown in Figure A.24. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

## A.11. Additional analysis of catalytic gas exposure

In principle, one may impose the additional constraint that the Co(II) contribution equals the sum of the Co(I) and Co(III) contributions. In practice, this leads to an unstable fit, which is attributed to the limited energy resolution and the unresolved multiplet structure of the Co(II) component overlapping with the Co(III) contribution.

For the CO-exposed Co–MnTPyP spectrum, a shoulder appears around 776 eV. Therefore, the background parameters were taken from the fit of the pristine Co–MnTPyP layer and adapted for the present analysis, resulting in  $a = 38\,500$  arb. units and  $b = 160\text{ eV}^{-1}$ .

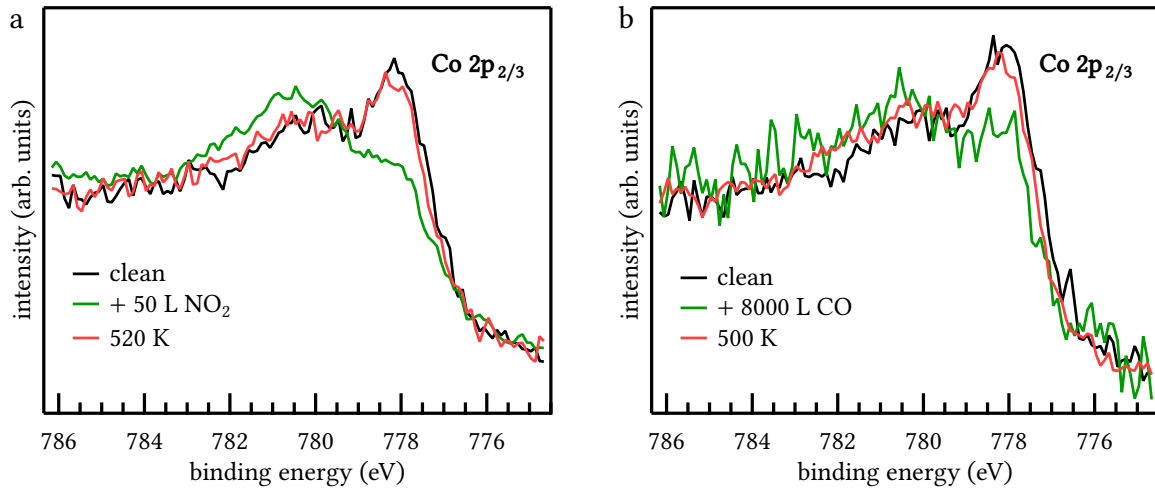


Figure A.25.: Area-normalized Co 2p<sub>3/2</sub> spectra of Co–MnTPyP in the gas exposure series. (a) Pristine layer, after dosing 50 L NO<sub>2</sub>, and after annealing to 520 K. (b) Pristine layer, after dosing 8000 L CO, and after annealing to 500 K.

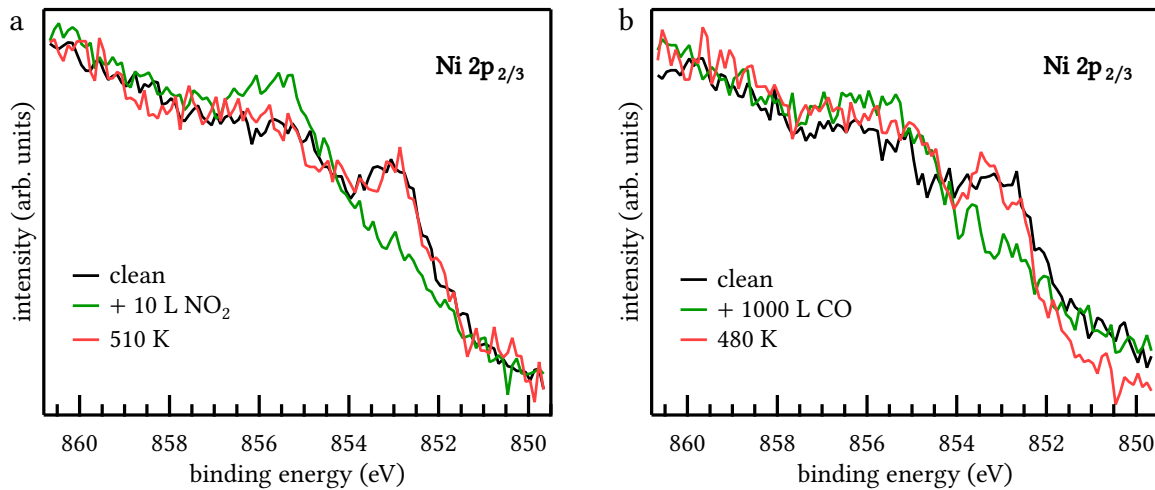


Figure A.26.: Area-normalized Ni 2p<sub>3/2</sub> spectra of the Ni–MnTPyP MOF. (a) Before NO<sub>2</sub> exposure, after dosing 10 L NO<sub>2</sub>, and after annealing the exposed sample to 510 K. (b) Before CO exposure, after dosing 1000 L CO, and after annealing the exposed sample to 480 K.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 778.01   | 0     | constrained | -           |
| area           | 33 760   | 457   | free        | -           |
| sigma          | 0.6      | 0     | constrained | -           |
| gamma          | 0.2      | 0     | constrained | -           |
| FWHM           | 1.638 84 | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 779.99   | 0     | constrained | -           |
| area           | 33 760   | 457   | constrained | peak1_area  |
| sigma          | 0.6      | 0     | constrained | peak1_sigma |
| gamma          | 0.92     | 0     | constrained | -           |
| FWHM           | 2.635 56 | 0     | -           | calculated  |
| <b>peak 3</b>  |          |       |             |             |
| center         | 782.08   | 0     | constrained | -           |
| area           | 33 215   | 1813  | free        | -           |
| sigma          | 2.41     | 0     | constrained | -           |
| FWHM           | 5.675 12 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 99 086   | 162   | free        | -           |
| k              | 0.030    | 0.003 | free        | -           |

Table A.34.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample before NO<sub>2</sub> dosing, as shown in Figure 6.1a (bottom). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 778.01   | 0     | constrained | -           |
| area           | 45 629   | 1576  | free        | -           |
| sigma          | 0.6      | 0     | constrained | -           |
| gamma          | 0.2      | 0     | constrained | -           |
| FWHM           | 1.638 84 | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 779.99   | 0     | constrained | -           |
| area           | 132 641  | 3274  | free        | -           |
| sigma          | 0.6      | 0     | constrained | peak1_sigma |
| gamma          | 0.92     | 0     | constrained | -           |
| FWHM           | 2.635 56 | 0     | -           | calculated  |
| <b>peak 3</b>  |          |       |             |             |
| center         | 782.08   | 0     | constrained | -           |
| area           | 115 143  | 6264  | free        | -           |
| sigma          | 2.41     | 0     | constrained | -           |
| FWHM           | 5.675 12 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 97 564   | 437   | free        | -           |
| k              | 0.019    | 0.003 | free        | -           |

Table A.35.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample after dosing 50 L of NO<sub>2</sub>, as shown in Figure 6.2. The fit comprises the two peaks of the native network together with an additional Gaussian component; see discussion in the main text. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.



| parameter      | value    | error  | variable    | expression  |
|----------------|----------|--------|-------------|-------------|
| <b>peak 1</b>  |          |        |             |             |
| center         | 778.01   | 0      | constrained | -           |
| area           | 49 082   | 3463   | free        | -           |
| sigma          | 0.6      | 0      | constrained | -           |
| gamma          | 0.2      | 0      | constrained | -           |
| FWHM           | 1.638 84 | 0      | -           | calculated  |
| <b>peak 2</b>  |          |        |             |             |
| center         | 779.99   | 0      | constrained | -           |
| area           | 78 208   | 31 861 | free        | -           |
| sigma          | 0.6      | 0      | constrained | peak1_sigma |
| gamma          | 0.92     | 0      | constrained | -           |
| FWHM           | 2.635 56 | 0      | -           | calculated  |
| <b>peak 3</b>  |          |        |             |             |
| center         | 782.08   | 0      | constrained | -           |
| area           | 68 873   | 24 109 | free        | -           |
| sigma          | 2.41     | 0      | constrained | -           |
| FWHM           | 5.675 12 | 0      | -           | calculated  |
| <b>peak 4</b>  |          |        |             |             |
| center         | 780.6    | 0.4    | free        | -           |
| area           | 81 538   | 47 949 | free        | -           |
| sigma          | 1.1      | 0.6    | free        | -           |
| gamma          | 0.8      | 0.6    | free        | -           |
| FWHM           | 4        | 2      | -           | calculated  |
| <b>Shirley</b> |          |        |             |             |
| constant       | 97 460   | 1054   | free        | -           |
| k              | 0.031    | 0.005  | free        | -           |

Table A.36.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample after dosing 50 L of NO<sub>2</sub>, as shown in Figure 6.1a (middle). In contrast to Figure 6.2, the spectrum was fitted with four instead of three peaks. All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 778.01   | 0     | constrained | -           |
| area           | 35 428   | 628   | free        | -           |
| sigma          | 0.6      | 0     | constrained | -           |
| gamma          | 0.2      | 0     | constrained | -           |
| FWHM           | 1.638 84 | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 779.99   | 0     | constrained | -           |
| area           | 44 311   | 1215  | free        | -           |
| sigma          | 0.6      | 0     | constrained | peak1_sigma |
| gamma          | 0.92     | 0     | constrained | -           |
| FWHM           | 2.635 56 | 0     | -           | calculated  |
| <b>peak 3</b>  |          |       |             |             |
| center         | 782.08   | 0     | constrained | -           |
| area           | 40 446   | 2396  | free        | -           |
| sigma          | 2.41     | 0     | constrained | -           |
| FWHM           | 5.675 12 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 939   | 180   | free        | -           |
| k              | 0.049    | 0.003 | free        | -           |

Table A.37.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample after NO<sub>2</sub> dosing and subsequent annealing to 520 K, as shown in Figure 6.1a (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 778.01   | 0     | constrained | -           |
| area           | 4234     | 226   | free        | -           |
| sigma          | 0.6      | 0     | constrained | -           |
| gamma          | 0.2      | 0     | constrained | -           |
| FWHM           | 1.638 84 | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 779.99   | 0     | constrained | -           |
| area           | 7578     | 449   | free        | -           |
| sigma          | 0.6      | 0     | constrained | peak1_sigma |
| gamma          | 0.92     | 0     | constrained | -           |
| FWHM           | 2.635 56 | 0     | -           | calculated  |
| <b>peak 3</b>  |          |       |             |             |
| center         | 782.08   | 0     | constrained | -           |
| area           | 9326     | 869   | free        | -           |
| sigma          | 2.41     | 0     | constrained | -           |
| FWHM           | 5.675 12 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 100 037  | 71    | free        | -           |
| k              | 0.025    | 0.005 | free        | -           |

Table A.38.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample after dosing 8000 L of CO, as shown in Figure 6.1b (middle). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 778.01   | 0     | constrained | -           |
| area           | 39 851   | 704   | free        | -           |
| sigma          | 0.6      | 0     | constrained | -           |
| gamma          | 0.2      | 0     | constrained | -           |
| FWHM           | 1.638 84 | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 779.99   | 0     | constrained | -           |
| area           | 49 058   | 1362  | free        | -           |
| sigma          | 0.6      | 0     | constrained | peak1_sigma |
| gamma          | 0.92     | 0     | constrained | -           |
| FWHM           | 2.635 56 | 0     | -           | calculated  |
| <b>peak 3</b>  |          |       |             |             |
| center         | 782.08   | 0     | constrained | -           |
| area           | 46 747   | 2679  | free        | -           |
| sigma          | 2.41     | 0     | constrained | -           |
| FWHM           | 5.675 12 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 435   | 202   | free        | -           |
| k              | 0.044    | 0.003 | free        | -           |

Table A.39.: Fit parameters of the Co  $2p_{3/2}$  core level of the Co–MnTPyP sample after CO dosing and subsequent annealing to 500 K, as shown in Figure 6.1b (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 852.92   | 0     | constrained | -           |
| area           | 19 886   | 1859  | free        | -           |
| sigma          | 0.36     | 0     | constrained | -           |
| gamma          | 0.597    | 0     | constrained | -           |
| FWHM           | 1.6518   | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 855.36   | 0     | constrained | -           |
| area           | 112 453  | 2408  | free        | -           |
| sigma          | 0.36     | 0     | constrained | peak1_sigma |
| gamma          | 1.07     | 0     | constrained | -           |
| FWHM           | 2.451 82 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 108   | 438   | free        | -           |
| k              | 0.133    | 0.004 | free        | -           |

Table A.40.: Fit parameters of the Ni  $2p_{3/2}$  core level after exposure of Ni–MnTPyP to 10 L of NO<sub>2</sub>, as shown in Figure 6.3a (middle). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 852.92   | 0     | constrained | -           |
| area           | 20 339   | 1025  | free        | -           |
| sigma          | 0.36     | 0     | constrained | -           |
| gamma          | 0.597    | 0     | constrained | -           |
| FWHM           | 1.6518   | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 855.36   | 0     | constrained | -           |
| area           | 23 293   | 1297  | free        | -           |
| sigma          | 0.36     | 0     | constrained | peak1_sigma |
| gamma          | 1.07     | 0     | constrained | -           |
| FWHM           | 2.451 82 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 889   | 258   | free        | -           |
| k              | 0.088    | 0.005 | free        | -           |

Table A.41.: Fit parameters of the Ni  $2p_{3/2}$  core level of the Ni–MnTPyP sample after annealing to 510 K following NO<sub>2</sub> dosing, as shown in Figure 6.3a (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 852.92   | 0     | constrained | -           |
| area           | 19 993   | 762   | free        | -           |
| sigma          | 0.36     | 0     | constrained | -           |
| gamma          | 0.597    | 0     | constrained | -           |
| FWHM           | 1.6518   | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 855.36   | 0     | constrained | -           |
| area           | 19 993   | 762   | constrained | peak1_area  |
| sigma          | 0.36     | 0     | constrained | peak1_sigma |
| gamma          | 1.07     | 0     | constrained | -           |
| FWHM           | 2.451 82 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 904   | 233   | free        | -           |
| k              | 0.087    | 0.007 | free        | -           |

Table A.42.: Fit parameters of the Ni  $2p_{3/2}$  core level of Ni–MnTPyP before CO dosing, as shown in Figure 6.3b (bottom). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 852.92   | 0     | constrained | -           |
| area           | 3494     | 882   | free        | -           |
| sigma          | 0.36     | 0     | constrained | -           |
| gamma          | 0.597    | 0     | constrained | -           |
| FWHM           | 1.6518   | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 855.36   | 0     | constrained | -           |
| area           | 30 707   | 1113  | free        | -           |
| sigma          | 0.36     | 0     | constrained | peak1_sigma |
| gamma          | 1.07     | 0     | constrained | -           |
| FWHM           | 2.451 82 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 99 396   | 214   | free        | -           |
| k              | 0.141    | 0.007 | free        | -           |

Table A.43.: Fit parameters of the Ni  $2p_{3/2}$  core level of Ni–MnTPyP after exposure to 1000 L of CO, as shown in Figure 6.3b (middle). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

| parameter      | value    | error | variable    | expression  |
|----------------|----------|-------|-------------|-------------|
| <b>peak 1</b>  |          |       |             |             |
| center         | 852.92   | 0     | constrained | -           |
| area           | 18 956   | 968   | free        | -           |
| sigma          | 0.36     | 0     | constrained | -           |
| gamma          | 0.597    | 0     | constrained | -           |
| FWHM           | 1.6518   | 0     | -           | calculated  |
| <b>peak 2</b>  |          |       |             |             |
| center         | 855.36   | 0     | constrained | -           |
| area           | 23 829   | 1235  | free        | -           |
| sigma          | 0.36     | 0     | constrained | peak1_sigma |
| gamma          | 1.07     | 0     | constrained | -           |
| FWHM           | 2.451 82 | 0     | -           | calculated  |
| <b>Shirley</b> |          |       |             |             |
| constant       | 98 748   | 235   | free        | -           |
| k              | 0.133    | 0.006 | free        | -           |

Table A.44.: Fit parameters of the Ni  $2p_{3/2}$  core level of the Ni–MnTPyP sample after CO dosing and subsequent annealing to 480 K, as shown in Figure 6.3b (top). All parameters are given in eV except for the area and the Shirley parameters. The area and the Shirley constant are given in arb. units. The pass energy was 20 eV.

# Abbreviations

|              |                                             |
|--------------|---------------------------------------------|
| <b>ARPES</b> | angle-resolved photoelectron spectroscopy   |
| $E_b$        | binding energy                              |
| $E_g$        | band gap energy                             |
| <b>CA</b>    | contrast aperture                           |
| <b>DFT</b>   | density functional theory                   |
| <b>DOS</b>   | density of states                           |
| $EA$         | electron affinity                           |
| <b>EDC</b>   | energy distribution curve                   |
| $E_F$        | Fermi level                                 |
| <b>BM</b>    | band map                                    |
| <b>ESCA</b>  | electron spectroscopy for chemical analysis |
| $E_v$        | vacuum level                                |
| <b>EXAFS</b> | extended X-ray absorption fine structure    |
| <b>FA</b>    | field aperture                              |
| <b>FWHM</b>  | full width at half maximum                  |
| <b>FY</b>    | fluorescence yield                          |
| <b>GS</b>    | Gunnarsson–Schönhammer                      |
| <b>HOMO</b>  | highest occupied molecular orbital          |
| <b>HS</b>    | high-spin                                   |
| <b>IMFP</b>  | inelastic mean free path                    |
| $IP$         | ionization potential                        |
| <b>ISC</b>   | inorganic semiconductor                     |
| $E_k$        | kinetic energy                              |
| <b>LEED</b>  | low-energy electron diffraction             |
| <b>LUMO</b>  | lowest unoccupied molecular orbital         |
| <b>LS</b>    | low-spin                                    |
| <b>MCP</b>   | microchannel plate                          |

|                 |                                                          |
|-----------------|----------------------------------------------------------|
| <b>ML</b>       | monolayer                                                |
| <b>MM</b>       | momentum microscopy                                      |
| <b>MO</b>       | molecular orbital                                        |
| <b>MOF</b>      | metal–organic framework                                  |
| <b>MP</b>       | metallated porphyrin                                     |
| <b>NEXAFS</b>   | near-edge X-ray absorption fine structure                |
| <b>OLED</b>     | organic light-emitting diode                             |
| <b>OSC</b>      | organic semiconductor                                    |
| <b>PDOS</b>     | projected density of states                              |
| <b>PES</b>      | photoemission spectroscopy                               |
| <b>PEY</b>      | partial electron yield                                   |
| <b>POT</b>      | photoemission orbital tomography                         |
| <b>QCM</b>      | quartz crystal microbalance                              |
| <b>SAM</b>      | self-assembled molecular layers                          |
| <b>SOMO</b>     | singly occupied molecular orbital                        |
| <b>SPA-LEED</b> | spot profile analysis of low-energy electron diffraction |
| <b>STM</b>      | scanning tunneling microscopy                            |
| <b>STS</b>      | scanning tunneling spectroscopy                          |
| <b>TOF</b>      | time-of-flight                                           |
| <b>TEY</b>      | total electron yield                                     |
| <b>TPyP</b>     | 5,10,15,20-tetra(4-pyridyl)porphyrin                     |
| <b>UHV</b>      | ultra-high vacuum                                        |
| <b>UPS</b>      | ultraviolet photoelectron spectroscopy                   |
| <b>VB</b>       | valence band                                             |
| <b>WKF</b>      | work function                                            |
| <b>XAS</b>      | X-ray absorption spectroscopy                            |
| <b>XLD</b>      | X-ray linear dichroism                                   |
| <b>XPS</b>      | X-ray photoelectron spectroscopy                         |
| <b>XANES</b>    | X-ray absorption near-edge structure                     |
| <b>XMCD</b>     | X-ray magnetic circular dichroism                        |



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## List of Publications

- V. Mischke, O. Resel, D. Brandstetter, S. Baronio, A. Namar, S. Lueger, G. Koller, P. Puschnig, P. Gargiani, M. Valvidares, M. Sterrer, E. Vesselli, M. Cinchetti, G. Zamborlini, "Stabilizing different cobalt oxidation states in a porphyrin-based metal–organic framework via transmetallation", manuscript in preparation.
- M. Stredansky et al., "Disproportionation of Nitric Oxide at a Surface-Bound Nickel Porphyrinoid," *Angewandte Chemie* **134**, e202201916 (2022)  
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- S. Baronio et al., "Single Atom Coordination in a Manganese–Cobalt Bi-Metallic Framework on Graphene: Geometric and Electronic Structures," *Nanoscale* **17**, 16946 (2025)  
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- K. J. Schiller et al., "Time-Resolved Momentum Microscopy with Fs-XUV Photons at High Repetition Rates with Flexible Energy and Time Resolution," *Scientific Reports* **15**, 3611 (2025)  
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- D. M. Janas et al., "Spin-Selective Interface Engineering in Oxide–Ferromagnetic Junctions via Atomic-Scale Oxygen Control," *Advanced Science* **13**, e23165 (2026)  
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- J. E. Nitschke et al., "Electronic Structure Reorganization in MPS3 via D-Shell-Selective Alkali Metal Doping," *Advanced Science* **13**, e10675 (2026)  
doi: 10.1002/advs.202510675
- A. Yadav et al., "Pressure-Controlled Oxygen Activation at Single Metal Atom Sites in a Manganese-Cobalt Coordination Network on Graphene: From Triplet-Singlet Spin Transition to Superoxo Dissociation," *Nanoscale* (2026)  
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- D. M. Janas, A. Windischbacher, J. E. Nitschke, L. Sternemann, M. S. Arndt, V. Mischke, V. Feyer, I. Cojocariu, D. Baranowski, V. Romankov, J. Dreiser, S. Ponzoni, P. Puschnig, G. Zamborlini, M. Cinchetti, "Charge and Spin Control in Organic Molecular Tunneling Junctions on MgO/Fe", manuscript in preparation.
- L. Dudy, E. Auffray, J.-J. Gallet, F. Bournel, M. Bouaziz, B. S. Mun, S. Jang, Y. Tsujikawa, H. Kondoh, S. Moser, V. Jovic, V. Mischke, P. Keßler, S. Maehl, "Near Ambient Pressure ARPES Setup for Operando Surface Studies", accepted by Review of Scientific Instruments.



# Conference Contributions

- "Pentacene on prototypical antiferromagnets: A photoemission study"  
**Type:** Poster  
**Coauthor:** **Valentin Mischke**, David M. Janas, Jonah E. Nitschke, Vitaly Feyer, Giovanni Zamborlini, Mirko Cinchetti  
**Event:** DPG-Frühjahrstagung 2022  
**Date:** 04-09 September 2022  
**Location:** Regensburg, Germany
- "Exploring the Electronic Structure of  $\text{Fe}_4\text{GeTe}_2$  for Low-Dimensional Spintronic Devices"  
**Type:** Poster  
**Coauthor:** **Valentin Mischke**, Antik Sihi, Declan Nell, A. Halder, Andrea Droghetti, Mirko Cinchetti  
**Event:** 803. WE-Heraus Seminar  
**Date:** 02-05 January 2024  
**Location:** Bad Honnef, Germany
- "The Co-MnTPyP network - A metal-organic framework"  
**Type:** Invited Talk  
**Coauthor:** **Valentin Mischke**  
**Event:** Group Colloquium  
**Date:** 21 February 2025  
**Location:** Würzburg, Germany



# Declaration on the Use of Artificial Intelligence Tools

Artificial intelligence-based tools (e.g. DeepL and ChatGPT) were used exclusively for language editing (clarity, grammar, and style). After using these tools, I have reviewed and edited the content as needed and take full responsibility for the final content of the thesis.



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