***IN SITU* NANO-
SPECTROSCOPY ON
SURFACE-ANCHORED
METAL-ORGANIC
FRAMEWORKS**

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IN SITU NANO-SPECTROSCOPY ON SURFACE-ANCHORED METAL-ORGANIC FRAMEWORKS

In Situ Nano-Spectroscopie op Oppervlak-Verankerde Metaal-
Organische Raamwerken

(met een samenvatting in het Nederlands)

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1

GENERAL INTRODUCTION

CHAPTER 1

1. GENERAL INTRODUCTION

Ever since the discovery of the first Metal-Organic Framework (MOF) structure, MOF research has primarily been focused on discovering new framework structures.^[1–6] These extremely versatile porous materials possess many discovered and undiscovered topologies and functionalities,^[7] and their unique open structure makes them particularly interesting for applications where interaction with guest molecules plays a central role, such as gas sorption, separation, and conversion.^[2,8,9] However, as for many other functional materials, including zeolites, their discovery is often still based on a process of trial-and-error.^[10,11]

The discovery and optimization of functional MOFs is highly relevant as many chemical and catalytic processes depend on the capture, separation, and conversion of gaseous molecules on functional materials. Such events often preferentially occur on specific defective or undercoordinated sites, which can be introduced by rational design to improve material performance.^[12] To guide all these synthetic efforts, it is of paramount importance to move from a bulk to a nanoscale understanding of structure–performance relationships.^[7] To fill this knowledge gap, new *in situ*, chemical- and highly-sensitive nano-resolution tools are required.^[13]

Previous efforts to study guest–host interactions on the nanoscale, however, have traditionally suffered from limitations known as the pressure and the material gap. For example, in surface science, the use of high spatial resolution tools, such as Scanning Tunneling Microscopy (STM), is often limited to ultra-high vacuum (UHV) conditions. Results acquired at these low pressures are difficult to extrapolate to relevant conditions as increased pressure can drastically change adsorbate interactions and alter sorption and/or conversion mechanisms.^[14] Additionally, these tools are typically applied to (conductive) single-crystal model systems, which are usually insufficient to describe the behavior of complex 3D materials, such as MOFs.

Therefore, in this PhD Thesis, the aim is to take a different approach towards developing functional MOF materials. Specifically, state-of-the-art near-field infrared (IR) spectroscopy on MOF model systems have been applied to 1) obtain fundamental insights in the formation mechanisms and surface chemistry of a MOF material, and 2) obtain *in situ* nanoscale insights into the guest–host interactions of two archetypal MOF materials, namely HKUST-1 and ZIF-8, with various probe molecules. Within this context, the purpose of this introductory PhD Chapter is to familiarize the reader with the most important concepts of (surface anchored) MOF chemistry and the working principles of the near-field IR spectroscopy tools that were used to unravel MOF growth mechanisms and structure–performance relationships.

1.1 METAL-ORGANIC FRAMEWORKS

Metal-Organic Frameworks, or MOFs, are a relatively new class of materials that consists of both metallic and organic moieties.^[1,15–17] The MOF materials class is part of the Porous Coordination Polymer (PCP) family.^[18,19] Per definition, MOFs are composed of repeating coordination entities extending in 1, 2, or 3 dimensions.^[20] Therefore, to compose structures stretching along these dimensions, the organic moieties are required to be polydentate linkers, linking the metal nodes into an extended network often resulting in high crystallinity and large porosity.^[21] However, to properly describe MOF structures, it is insufficient to regard the metal nodes and organic linkers as the sole repeating entities as they do not contain any information to describe the resulting MOF topology.

To better describe, and predict, the structure of MOFs, the concept of secondary building units (SBUs) was introduced.^[22,23] As opposed to the flexible bonds between a single metal and organic linker, SBUs are coordinated clusters of di-, tri-, and tetranuclear metal-organic clusters. These clusters are molecular units with defined structure, shape, and direction which dictate the structure, shape, and direction of MOFs. Not only are they useful in predicting the topology of a MOF, but they are also excellent predictors of MOF robustness.^[24] This becomes especially important when considering (permanent) porosity in MOFs after solvent removal, and thus their functionality.^[25]

A characteristic of MOFs is that they typically exhibit high porosity (in the order of hundreds to thousands of m²/g) since pores with a size proportional to the linker length are created during synthesis.^[26,27] As a result, there are continuing efforts to increase reported porosities by using increasingly long linkers.^[28,29] However, a MOF is only porous when the remaining solvent molecules are evacuated after synthesis. In practice, many MOF structures collapse upon this evacuation step.^[30] The use of rigid SBUs, such as highly connected oxo-clusters, impart higher stability, and lead to permanent porosity.^[31]

This porosity is expressed as pores connecting the MOF surfaces to internal cages, as well as 1, 2, and 3D channel systems.^[27] This large and ordered porosity goes hand-in-hand with a second typical (yet not necessary) characteristic of MOFs: their high crystallinity.^[32] A third characteristic of MOFs is that their functionality is highly tunable as the choices for metals and linkers are virtually infinitely variable.^[33] Specific examples of variable functionality are the incorporation of Coordinatively Unsaturated (metal) Sites (CUS), also characterized as Lewis acid sites, or the incorporation of linkers with Bronsted acid/base sites.^[34,35] The three combined characteristics of MOFs lead to the conclusion that MOFs are very interesting materials in applications depending on their interaction with gaseous guest molecules, such as gas sorption, gas separation, gas sensing, and gas conversion (catalysis).^[36–40] However, other applications for MOFs, such as electronic applications or drug delivery, are also known.

[41,42]

For each of the many potential applications of these materials, a specific MOF could, in theory, be designed. Intensive research effort has focused exactly on this: the discovery of novel MOFs with increased pore sizes/volumes and altered functionalities.^[43] However, in this PhD Thesis, the goal is to better understand the growth and functionality of existing MOFs so that these new fundamental insights can be applied to rational material design strategies as opposed to trial-and-error processes. As a result, this research is limited to well-known and pre-studied MOFs, and not focusing on the synthesis and discovery of new MOFs.

The first MOF used in this PhD Thesis is HKUST-1, for Hong Kong University of Science and Technology (Figure 1.1 a-d).^[44] This MOF was discovered in 1999 by Chui *et al.* and can be created by coordinating Cu^{2+} ions with 1,3,5-benzenetricarboxylic acid (BTC) linkers. HKUST-1 possesses a stable di-nuclear paddlewheel SBU and crystallizes into body-centered cubic crystals in the $Fm-3m$ space group. HKUST-1 possesses two types of pores, namely square and hexagonal pores leading to the formation of a 3D channel pore network. This pore network interconnects three cages of varying size, namely a small octahedral cage of ~ 5 Å, and two larger cuboctahedral cages of ~ 10 Å and 11 Å in diameter. Accordingly, BET specific surface areas of over $1000 \text{ m}^2/\text{g}$ have been reported for this MOF.^[45]

FIGURE 1.1: Building blocks of the metal-organic frameworks HKUST-1 and ZIF-8. HKUST-1 is built-up from copper ions (a) and, b) 1,3,5-benzenetricarboxylic acid (BTC) linkers to form c) a di-nuclear paddlewheel Secondary Building Unit (SBU). The coordination of these SBUs leads to an open crystalline structure (d) with multiple pore and cage sizes. ZIF-8 is built-up from (e) zinc ions and f) 2-methylimidazole linkers to create a metal-linker-metal angle similar to the zeolitic Si-O-Si angle. ZIF-8 possesses g) two types of pores, namely 6-Membered Rings (6 MR) and 4-Membered Rings (4MR) that are characteristic for the sodalite topology (h).

This MOF is particularly interesting for guest-host interaction studies as the metal nodes in the paddlewheel SBU not only coordinate to the bidentate carboxylic acid linkers in its equatorial positions, but can also coordinate to the lone pairs of (solvent) molecules, such as water or DMF, in its axial positions. Upon activation through degassing, these liberated axial positions result in coordinatively unsaturated metal sites that are available for interaction with adsorbates.

However, despite the permanent porosity of HKUST-1, it suffers from a relatively low hydro-thermal stability, which is a general issue limiting the use of MOFs in industrial applications.^[46] Fortunately, there exists a subclass of metal-organic frameworks, namely the class of Zeolitic-Imidazolate Frameworks (ZIFs), that contains MOFs with increased hydrothermal stability.^[47] ZIFs are created by exclusively using imidazolate-type linkers to connect to tetrahedrally-coordinated metals. A characteristic of the imidazolate linkers is that the metal-imidazole-metal angle of the resulting ZIF is highly similar to the Si-O-Si angle in zeolites, thereby making ZIFs isomorphs of zeolites.

Compared to zeolites, ZIFs possess larger pore sizes and volumes, as well as more variable functionality.^[48] When compared to other MOFs, ZIFs tend to possess higher thermal and chemical stabilities due to their structural similarity to zeolites.^[49] For example, whereas many MOFs tend to be unstable in an aqueous medium, ZIFs are hydrophobic materials.^[50] Due to these characteristics, ZIFs are appealing for the same type of applications as MOFs, yet where higher hydrothermal stability is required.

Therefore, the second archetypal MOF used in this PhD Thesis is ZIF-8 (Figure 1.1 e-h).^[49] ZIF-8 is created by coordinating Zn^{2+} ions to 2-methylimidazole (2-mIm) linkers. The ZIF crystallizes into cubic crystals in the $I-43m$ space group and is an isomorph of the sodalite zeolite structure. As such, the ZIF possesses two types of pores, namely a square four-membered ring (4MR, 0.8 Å) and a hexagonal six-membered ring (6MR, 3.4 Å).^[51] These pores create a network connecting sodalite-type cages of 11.6 Å in diameter. In comparison, zeolite sodalite cages have a diameter that is almost a factor of 2 smaller (~6.5 Å). When compared to HKUST-1, ZIF-8 possesses a much higher hydrothermal stability.^[52]

HKUST-1 and ZIF-8, as well as most other MOF materials, are typically synthesized through solvothermal synthesis.^[4] In such a synthesis method, the MOFs precursors are combined in a liquid medium and left to react (at elevated temperatures) over time prior to filtration, drying, and activation. Since MOFs are typically 3D materials, this means that the MOF particles rapidly grow in all directions during synthesis.^[53,54] Since MOFs are grown in liquid media, there is only a very limited number of tools available to study their formation *in situ*, making it difficult to study their self-assembling growth mechanisms in appropriate detail.

1.2 SURFACE-ANCHORED METAL-ORGANIC FRAMEWORKS

Surface-anchored Metal-Organic Frameworks, or SURMOFs, are a type of MOF model system.^[55] In this model system, the MOF is grown (in consecutive steps, *vide infra*) directly on a substrate, rather than deposited, thereby yielding well-defined MOF films.^[56–59] These films have the characteristic properties that they are grown with low roughness and high homogeneity and with variable thickness and orientation.^[60–65] This makes them excellent systems for studying MOF growth, as well as opens these SURMOFs up to novel applications.^[66–68]

The build-up of a SURMOF is shown in Figure 1.2. Depending on its application a MOF can be anchored to several types of substrates. For example, SURMOFs can be grown on a transparent substrate, such as glass, a conductive substrate, such as metal electrodes, or a porous substrate, such as metal oxides or textiles fibers.^[69–72] However, when synthesizing a model system, gold is typically chosen as it presents an almost flat, chemically homogeneous surface that is relatively inert. Yet this mostly inert gold surface can be functionalized for MOF growth by chemisorbing Self-Assembling Monolayers (SAMs) of alkanethiols (Figure 1.2).^[57]

FIGURE 1.2: General structure of a Surface-anchored Metal-Organic Framework (SURMOF). a) A MOF such as HKUST-1 can be anchored on a gold substrate, thereby creating b) a SURMOF. This gold surface is functionalized before MOF growth with c) Self-Assembling Monolayers (SAMs). Self-assembling monolayers are created through the chemisorption of alkanethiol molecules, where the thiol groups anchor to the gold substrate, and the headgroups function as nucleation points for MOF growth.

Thiols are molecules consisting of a thiol anchor group and a headgroup with variable functionality at opposite ends of a hydrocarbon chain.^[73] As a consequence of the strong chemisorption of the thiol groups on gold, and the intermolecular Van der Waals forces between the alkyl groups, ordered monolayers of these molecules form on the surface.^[74,75] After functionalization, a new surface consisting of SAM headgroups is exposed.^[76] These headgroups function as nucleation points and therefore their chemistries are chosen such that

they mimic the chemistry of the MOF linkers/SBUs so that the metal moieties will bind onto them and initiate MOF growth.^[56]

Additionally, the choice of headgroup chemistry will determine the orientation of the SURMOF.^[77,78] This can be explained by considering the paddlewheel SBU of HKUST-1, where the copper ions possess two different binding positions (equatorial and axial).^[44] The SAM headgroups can be tailored to mimic both of these bonding conformations (Figure 1.3). As a result, the SURMOF can grow in different orientations as can be shown using crystallography. When using carboxylic acid headgroups, the HKUST-1 grows in the (111) direction, as observed by XRD, and when using hydroxyl or pyridine headgroups, growth in the (100) direction will be observed.^[77] Additionally, when using a non-polar headgroup, such as a methyl group, SURMOF growth can be suppressed.^[79] Such tunability of the self-assembling monolayers was exploited in **CHAPTER 3** to control SURMOF growth and induce the formation of nano-islands.

There are several possible methods to grow SURMOFs on SAMs, such as solvothermal synthesis, synthesis using an aged mother solution, or a gel layer growth synthesis.^[67,80,81] However, one method supersedes these methods in terms of quality control, namely the Layer-by-Layer (LbL) method.^[69,82,83] In a LbL synthesis, the growth stages are separated into the metal- and linker-growth stages, respectively, thereby allowing the stepwise growth of the SURMOF. This method then provides ultimate control over SURMOF growth stages and thereby the film thickness.

FIGURE 1.3: The orientation-directing properties of Self-Assembling Monolayers (SAMs). a) SAMs with carboxylic headgroups mimic the equatorial bonding positions of the HKUST-1 paddlewheel Secondary Building Unit (SBU), which results in growth in the (111) direction. SAMs with hydroxyl or pyridine headgroups, however, promote growth in the (100) direction. The use of SAMs with non-polar headgroups results in no observable MOF growth. b) Simulated X-Ray Diffraction (XRD) patterns for bulk HKUST-1 (bottom), HKUST-1 grown on hydroxyl/pyridine SAMs (middle), and HKUST-1 grown on carboxylic SAMs (top).^[77]

Figure 1.4 schematically describes the stages of a LbL synthesis using HKUST-1 SURMOF as an example.^[69,84,85] After the functionalization of the gold surface with SAMs (an aliphatic carboxylic acid SAM in this example), the surface is immersed in an ethanolic solution of the Cu^{2+} precursor (step 1). During immersion, the metal ion can both chemisorb on the SAM and physisorb in a multilayer fashion. To remove the physisorbed species, the surface is washed with the ethanol solvent (step 2). Subsequently, the substrate is immersed in the linker-containing solution for growth (step 3) and is then again washed with the solvent (step 4). This cycle constitutes the growth of one layer which theoretically has the thickness of one unit cell. The thickness of the resulting SURMOF is then determined by the number of layers that are grown. **CHAPTER 2** details on investigations of- and findings on the growth mechanisms during LbL synthesis.

These SURMOFs grown through LbL synthesis were first developed as model systems to study SURMOF growth kinetics by Shekhah *et al.*^[55] They were able to do so by directly growing HKUST-1 on gold-coated Quartz Crystal Microbalance (QCM) electrodes. QCM is a technique specifically apt to detect changes in mass.^[86] In this way they were able to measure metal and linker uptake times in solution, resulting in a rationally designed synthesis recipe of automated LbL growth of HKUST-1 SURMOF.

FIGURE 1.4: Schematic showing the growth stages in an HKUST-1 Layer-by-Layer (LbL) synthesis. LbL synthesis starts with a functionalized gold substrate (top) that is alternately immersed in a solution containing the metal precursor (Cu^{2+} , step 1) and a solution with the linker precursor (BTC, step 3). In between growth steps, the substrate is washed with the solvent (ethanol, step 2 and 4) to remove superfluously physisorbed precursors. The thickness of the resulting Surface-anchored Metal-Organic Framework (SURMOF) is dictated by the number of immersion cycles.

1.3 INFRARED NANO-SPECTROSCOPY

In this PhD Thesis, we are specifically interested in the mechanisms of SURMOF growth and guest-host interactions, rather than growth kinetics, for which a different toolbox is necessary. In the case of mechanistic studies, infrared (IR) spectroscopy is typically applied, since this is an excellent technique to monitor (changes in) the bond strengths of materials. However, in the case of IR spectroscopy on SURMOFs, there are limitations, as well as opportunities. For example, since the MOFs are anchored on an (IR-) opaque substrate, typical transmission-based infrared techniques cannot be applied. Additionally, since IR spectroscopy is a technique based on the use of electromagnetic radiation, its use is limited by the Abbe diffraction limit ($\text{resolution}_{\text{max}} = \lambda/2\text{NA}$, NA=numeral aperture of optics). Since we are interested in phenomena occurring on a scale much smaller than this, such as metal-organic bond formation, defect incorporation, sorbent molecule adsorption, etc. the use of such bulk techniques is insufficient. A solution to both these issues was found in the use of a near-field IR technique. This technique couples Atomic Force Microscopy (AFM), suitable for probing relatively flat surfaces such as SURMOFs, with IR spectroscopy, thereby circumventing the diffraction limit.

There are currently two AFM-IR techniques relying on similar, but distinct detection mechanisms: the Photo Thermal AFM-IR (PT-AFM-IR) technique and the Photo-induced Force Microscopy (PiFM).^[87] Both of the techniques were used in the research presented in this PhD Thesis. To explain the working principles of near-field IR spectroscopy techniques, it is relevant to first highlight some fundamental aspects of infrared spectroscopy. In IR spectroscopy, the interaction between molecular bonds and electromagnetic radiation with energy between $4000\text{--}400\text{ cm}^{-1}$ (in the case of mid-IR spectroscopy) is monitored.^[88] The photon energy of the incident light is transferred to a molecular bond in the case that their energy level transition is equal. This transferred energy is then converted into bond translation, rotation, or vibration. For near-field IR spectroscopy, we are specifically interested in the bond vibrations as they give information on the solid host material. These bond vibrations can be subdivided into stretching (symmetric, asymmetric) and bending (in-plane bending: scissoring, rocking, and out-of-plane bending: wagging, twisting) vibrations. For all of these bond vibrations, the selection rule applies that a vibration is only IR active if upon vibration a change in the bond dipole moment occurs.

Since an IR-active molecule will absorb a portion of the incident IR light, the detection of an IR spectroscopy signal typically relies on straightforward $I_0 - I$ (IR beam intensity minus the portion of IR light absorbed) calculations, resulting in a peak (downward for transmission, upward for absorption) in the IR spectrum.^[89] The position of the peak in the spectrum is naturally determined by the energy of the bond under investigation. However, in IR spectroscopy peak broadening often occurs due to inter- and intra-molecular interactions.

As a result of such interactions (e.g., hydrogen bonding) the bond strength varies depending on its position in the material relative to other moieties, carrying important chemical information. However, traditional IR spectroscopy, being diffraction-limited, acquires averaged information in a spot too big to detect distinct environments, changing in the order of nm. As a direct consequence, the use of bulk IR spectroscopy techniques will be insufficient to study, among others, SURMOF growth mechanisms on the nanoscale, whereas near-field IR spectroscopy can.

An example of a near-field IR spectroscopic technique is Atomic Force Microscopy-InfraRed (AFM-IR) spectroscopy (Figure 1.5). Atomic force microscopy is a well-known and developed technique to study the topography and morphology of surfaces of (relatively) flat samples.^[90] It is a type of scanning probe microscopy and has a spatial resolution of less than a nanometer. A short description of the working principle of AFM is as follows: In AFM, a tip mounted on a cantilever is brought in the vicinity of a sample surface and driven to oscillate. Depending on the interaction with the sample surface (e.g., attractive Van der Waals forces, repulsive Coulomb forces) the tip will deviate from its oscillation motion in the x, y, or z-direction. This deviating motion will be translated as topographic or morphological information.

FIGURE 1.5: Schematic showing the coupling of Atomic Force Microscopy (AFM) with infrared (IR) spectroscopy to gain nanoscale chemical information. a) AFM is a technique measuring tip-sample interaction to measure the topography of a material. b) by coupling AFM with an IR laser, the tip-sample interaction detection can be tuned to detect optically induced bond vibrations.

By combining AFM with a spectroscopic element, the AFM tip can be used as an antenna for chemical information collection at the nanoscale. Indeed, when IR light is shone on the material surface under the AFM tip, the IR wavelength, and thus diffraction-limited character will naturally remain unaffected. However, since the detection mechanism is now coupled to an AFM tip whose resolution is limited by (a.o.) the tip diameter, it will only

measure the IR - sample interaction occurring directly below the tip, thereby significantly altering the spatial resolution of the IR technique, as far down as 8 nm. This then allows the user to study material composition on the nanometer scale, while simultaneously detecting the surface topography by AFM.

The exact spatial and temporal resolution of the two different AFM-based near-field IR spectroscopy techniques depends on their respective detection mechanisms (Figure 1.6 a, f). The photothermal technique monitors the thermal expansion of material upon IR light absorption,^[91] while the Photo-induced Force Microscopy (PiFM) technique detects IR light absorption by mirroring the change in the dipole moment of IR active bonds in its gold-coated AFM tip.^[92] Figure 1.5 highlights some similarities and differences between the two techniques.

Both techniques couple AFM with a modulated (or pulsed) mid-IR laser. The required power and pulse repetition rate of the laser, however, are dependent on the phenomenon it aims to probe. In the case of PT-AFM-IR, a pulse of IR light (when absorbed by a bond) will lead to the rapid photothermal expansion of the material due to the induced vibrations.^[93] How much the material expands depends both on the used power (i.e. change in temperature), and on the thermal expansion coefficient according to the relation $\Delta V \sim \alpha \Delta T$, where ΔV is the volume change, α is the thermal expansion coefficient and ΔT is the temperature change.^[94] The thermal expansion coefficient is a material-inherent property, and organic materials typically possess a larger thermal expansion coefficient than inorganic materials. For example, metal oxides often possess a thermal expansion coefficient well below $10 \cdot 10^{-6} \text{K}^{-1}$, whereas the coefficients of polymers are typically 1 or 2 orders of magnitude higher.^[95,96] Since the technique requires a sufficiently large temperature increase to gain a detectable increase in volume, high power levels are typically necessary (max 1 W for PT-AFM-IR, versus max 4 mW for PiFM, which can lead to sample deterioration in the case of AFM-IR).

In the case of the PiFM technique, a pulse of IR light (when absorbed by a bond) will not lead to detectable thermal expansion, because of the lower power.^[97] Instead, a change in the dipole moment of the probed bonds is detected by a gold-coated AFM tip.^[98] The coating layer of gold possesses high polarizability and is, therefore, able to mirror the change in dipole moment occurring directly below the tip. A rapidly photo-induced change in attractive forces between the tip and the sample is then detected and converted IR signal.^[99,100]

Some debate has arisen, however, on the exact origins of the photo-induced force in PiFM. Overall, it was found that the main force giving rise to PiFM signal is due to dipole-dipole interaction mirroring,^[92] yet some literature has suggested that in PiFM, multiple forces can give signal contributions. For example, some reports show that to explain the spectral profile of the photo-induced force, photothermal expansion has to be added as a contributing repulsive force.^[97,100] However, a recent report suggests that this photothermal force has a

negligible effect on the signal, but suggests optomechanical damping of the cantilever oscillation can explain the contrast mechanism of PiFM.^[101] While the exact mechanism is still under debate, literature does agree that PiFM is a highly sensitive tool that can measure infrared nano-spectroscopy with an unparalleled high spatial resolution.

Both techniques only detect IR signals if the measured tip-sample interaction is rapid- and large enough to lead to cantilever resonance, which can be converted to spectral information by applying a Fast Fourier Transform (FFT).^[102,103] Indeed, both the thermal expansion and the change in dipole moment are rapid processes, however, their relaxation times differ quite strongly. Thermal relaxation occurs on the scale of milliseconds, whereas vibrational relaxation processes occur on the scale of 10^{-14} to 10^{-12} seconds.^[104,105] As a result, the repetition rate for the PiFM technique can be increased significantly leading to faster acquisition of IR data.^[106]

The exact spatial resolution of the techniques is also determined by their respective detection mechanisms. In the case of photothermal expansion, it is relevant to highlight that the expansion occurs not just in one direction (in the sample-tip void), but in all directions. Therefore, when an IR laser spot with a size of ~100 microns is shone on the sample, a significant sample volume is optically excited. The spatial resolution is then determined by the signal that is sensed directly under the tip, as well as the signal that is sensed adjacent to this area. This effect leads to sample- dependent (i.e., thermal expansion coefficient dependent) spatial resolution in the range of 20–25 nm, as well as a sensitivity of ~20 nm.^[107,108] This effect also results in a rather large probing depth, up to 1200 nm.^[94]

The PiFM technique does not suffer as much from such proximity effects and therefore boasts a higher spatial resolution of ~8 nm.^[109] The changes in dipole moments are localized effects and therefore most of the signal is measured directly below the tip, where the tip diameter determines the spatial resolution.^[110,111] The gradient force that is measured is a function of tip-sample distance that shows a z^{-4} dependence and therefore can only be measured for tip-sample distances of a few nm.^[98]

However, since the tip is close to the sample surface, tip sides close to the apex will also detect the photo-induced signal. A drawback of PiFM is that the coating of the tip with a material of high polarizability, such as gold, causes the tips to be slightly more blunt than regular AFM tips, thus decreasing the depth profiling resolution.^[112] Since the technique does not require larger sample volumes to detect signal, the sensitivity goes down to monolayer coverings and the probing depth is ~30 nm.^[113]

FIGURE 1.6: Schematic highlighting the similarities between Photo Thermal AFM-IR (PT-AFM-IR) and Photo-induced Force Microscopy (PiFM). a) In PT-AFM-IR, IR absorption is detected via tip displacement due to thermal expansion. b) A high power, modulated laser induces c) strong thermal expansion upon IR absorption resulting in d) tip repulsion and resonance which can be converted to e) a peak in the IR spectrum using a Fast-Fourier Transform (FFT). f) In PiFM attractive forces between tip and sample as a result of IR absorption-induced dipole moment change is measured. Due to the local nature of dipole-moment changes, a lower power (g) and a higher repetition rate (h) can be used to achieve FFT calculated IR spectra (i,j).

Both AFM-IR techniques do possess some general limitations compared to bulk IR spectroscopy techniques, namely, sample limitations, IR light source limitations, and measurement environment limitations.^[114] Specifically, samples are limited to supported and flat samples with a maximum height difference of ~1 micron to accommodate AFM stability. However, by using SURMOF samples rather than MOF powders we could overcome this limitation. Furthermore, AFM-IR requires the use of a tunable laser, such as a Quantum

Cascade Laser (QCL), which at the time of use in this PhD Thesis was only available with a range of 1800-1300 cm^{-1} (high power, PT-AFM-IR) or 1960-780 cm^{-1} (low power, PiFM). Fortunately, peaks of interest for MOFs, such as metal-linker coordination are often present within this range.^[115] Lastly, AFM-IR is an *ex situ* method as the measurement environment is (commercially) limited to ambient conditions (air, room temperature, 1 bar). Since the SURMOF growth can be arrested after each growth step, *ex situ* analysis is sufficient for mechanism elucidation. However, to investigate guest-host interactions of SURMOFs and IR-active probe molecules, this PhD Thesis describes the successful adaptation of the PiFM technique to allow for *in situ* gas sorption experiments.

1.4 SCOPE AND OUTLINE OF THE PHD THESIS

This PhD Thesis describes the use of state-of-the-art infrared nano-spectroscopy on surface-anchored metal-organic frameworks to elucidate growth- and guest-host interaction mechanisms. More specifically, HKUST-1 SURMOFs were analyzed using two near-field AFM-IR techniques to yield insight into the relevance of various Layer-by-Layer (LbL) synthesis parameters. This approach was then expanded to study the self-assembling behavior of Self-Assembling Monolayers (SAMs) acting as nucleation points for the growth of SURMOFs, as well as SURZIFs. These insights led to the development of novel, highly defined model systems. By adapting the PiFM nano-spectroscopic technique to accommodate *in situ* measurements, guest-host interactions between several probe molecules (i.e., D_2O , NO and formaldehyde) and multiple SURMOFs were studied. This led to the deduction of, e.g., (defect) site-specific gas sorption isotherms, visualization of SURMOF transmetalation sites, and observation of structure sensitive gas sorption and conversion on these model systems.

In **CHAPTER 2** a detailed description and analysis of the LbL synthesis of HKUST-1 SURMOF are given. Using a combination of bulk and near-field infrared spectroscopy, the relevant parameters to create high quality, defect-free SURMOFs were identified. Using the highly sensitive AFM-IR techniques, origins of defect creation through the undercoordination of copper acetate precursor molecules were found. This led to the discovery of the growth mechanism of the initial stages of HKUST-1 SURMOF, which in turn resulted in an improved synthesis route in terms of both SURMOF quality and preparation time.

In **CHAPTER 3** a closer look is taken at the self-assembling behavior of the self-assembling monolayers using the PiFM technique. By combining aliphatic and aromatic SAMs, single surfaces with dual headgroup functionalities could be created and used for the growth of nanosized SURMOF, as well as the growth of an amphiphilic bifunctional surface consisting of both SURMOF and SURZIF. These surfaces were subsequently utilized for guest-host interaction investigations using PiFM adapted towards *in situ* measurements. Through

the use of *in situ* PiFM, it shows enhanced D₂O sorption on existing defective HKUST-1 paddlewheel sites, as well as observe D₂O-induced defect formation in real-time. This led to the deduction of site-specific gas sorption isotherms of water on HKUST-1 and a visual representation of defect formation and propagation as a function of water sorption.

CHAPTER 4 elaborates on the use of the PiFM technique for *in situ* measurements. In this Chapter, nitric oxide (NO) was used as a probe molecule to further characterize SURMOF heterogeneity on the nanoscale. This methodology was applied to pristine, defective, and (Co-)transmetalated HKUST-1 SURMOFs. It unveiled clustering of defects, pinpointed the locations of paddlewheels with varying oxidation states, and showed exchanged metal centers and their altered adsorption response to the NO guest molecule.

CHAPTER 5 applies *in situ* PiFM with formaldehyde as probe molecule to investigate single-crystal SURZIF-8 materials, which exhibited clearly defined crystal terraces, edges, and corners. It shows the structure-sensitive sorption of formaldehyde and the non-homogeneous sorption behavior within ZIF-8 crystal planes due to the “swing effect” of several surface sites. Furthermore, the necessity of defects for the conversion of formaldehyde was illustrated, and the structure sensitive incorporation of defect sites, as well as the structure sensitive conversion of formaldehyde to formate, di-/poly-oxymethylene, and methoxy species was demonstrated. Lastly, this Chapter shows the use of isotope-labeled formaldehyde feeds, which was used to derive mechanisms for ZIF-8 surface-mediated catalytic conversion of formaldehyde.

CHAPTER 6 summarizes the main findings of this PhD Thesis and presents some concluding remarks as well as an outlook on future research.

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2

MECHANISTIC INSIGHTS INTO GROWTH OF SURFACE- MOUNTED METAL-ORGANIC FRAMEWORK FILMS RESOLVED BY INFRARED (NANO-)SPECTROSCOPY

2. ABSTRACT

Control over assembly, orientation, and defect-free/-rich growth of metal-organic framework (MOF) films is crucial for their future applications. A layer-by-layer approach is considered a suitable method to synthesize highly oriented films of numerous MOF topologies, but the initial stages of the film growth remain poorly understood. In this Chapter, a combination of infrared reflection absorption spectroscopy (IRRAS) and AFM-IR to investigate the assembly and growth of a HKUST-1 SURMOF film is described. IR spectra of the films were measured with monolayer sensitivity and < 10 nm spatial resolution. In contrast to the common knowledge of LbL SURMOF synthesis, we find evidence for the surface-hindered growth and large presence of copper acetate precursor species in the produced MOF thin-films. The growth proceeds via a solution-mediated mechanism where the presence of weakly adsorbed copper acetate species leads to the formation of crystalline agglomerates with a size that largely exceeds theoretical growth limits. In this Chapter, we report the spectroscopic characterization of physisorbed copper acetate surface species and find evidence for the large presence of unexchanged and mixed copper-paddle-wheels. Based on these insights, we were able to optimize and automatize synthesis methods and produce (100) oriented HKUST-1 thin-films with significantly shorter synthesis times, and additionally use copper nitrate as an effective synthesis precursor.

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2.1 INTRODUCTION

Surface-anchored Metal-Organic Frameworks (SURMOFs) can be regarded as promising model systems and were initially created by Shekhah *et al.* to study the synthesis kinetics during the Layer-by-Layer (LbL) synthesis of HKUST-1.^[1] In these initial characterization studies, they have used a Quartz Crystal Microbalance (QCM) to measure mass uptakes of individual SURMOF precursor species (metal, linker) as a function of time.^[2–4] In contrast to using nitrates, which are commonly used for MOF synthesis, they showed the successful separation of CuAc₂ and BTC growth stages, suggesting that this particular metal precursor facilitates the SURMOF formation as its paddle-wheel structure resembles the structure of HKUST-1.^[5]

However, in these and other kinetic studies, growth behavior that was not expected from the LbL model was shown.^[6,7] For example, with QCM, a non-stoichiometric increase in the uptake after each deposition step was found.^[2] Additionally, Surface Plasmon Resonance (SPR) studies found that HKUST-1 SURMOF films could grow significantly faster than one unit cell per layer,^[8,9] whereas the orientation of the obtained films was not always as expected from the termination of Self-Assembling Monolayers (SAMs).^[2,8,9] These observations suggested the presence of a defective growth mechanism during the SURMOF synthesis.

Furthermore, the SPR investigations showed precursor uptake periods of times shorter than typically used reaction times for LbL SURMOF synthesis, indicating shorter reaction time may be feasible for the (relatively) time consuming LbL SURMOF synthesis.^[1,2,5] Already, an approach combining shorter reaction times with LbL growth, Liquid Phase Epitaxy (LPE) spray synthesis, has been developed by Arslan *et al.* for the fast synthesis of highly oriented films.^[10] Films grown in this way, however, also show growth rates far exceeding LbL limits indicating the presence of an additional growth mechanism.

The mechanistic details of the early stages of the [Cu₃(btc)₂] SURMOF growth are still under debate.^[8,11,12] Attempts to unravel LbL growth mechanisms in the initial stages by using spectroscopic tools have been previously performed, for example, by Zhuang *et al.* for the Cu₂(F₄bdc)₂-(dabco) SURMOF (dabco=1,4-diazabicyclo[2.2.2]octane), but so far no conclusive results have been found for HKUST-1.^[13] Therefore, fundamental understanding, and as a result further synthetic improvements, are needed in order to justify advantages of the LbL approach over other synthetic strategies.^[14–18]

In this Chapter, a systematic study of the [Cu₃(btc)₂] SURMOF growth mechanism and synthesis parameters lead to improved synthesis procedures to yield preferentially oriented SURMOF films. In this research we applied two synthetic procedures, namely manual and automated dipping synthesis, for the LbL SURMOF growth of HKUST-1. These two synthetic approaches were purposely chosen to improve our understanding of the growth

mechanism in the initial growth stages (manual synthesis) and based on this understanding, to improve and automatize the synthesis of SURMOFs (automatic synthesis). The latter approach to the synthesis is not new, as it has been previously shown by Wöll *et al.* to produce homogeneous and preferentially oriented SURMOF films.^[19–21] We further provide for the first time spectroscopic fingerprints and clear evidence for the highly hindered SURMOF growth in the presence of CuAc_2 using infrared reflection absorption spectroscopy (IRRAS),^[8,22] and AFM-IR techniques^[23,24] and show that a controlled hetero-epitaxial growth can be unexpectedly achieved by using copper nitrate as a precursor, contrary to the common knowledge in the field.^[5,25]

2.2 RESULTS AND DISCUSSION

In a first set of experiments, Au substrates (Au/Si) were functionalized with 16-mercaptohexadecanoic acid (MHDA) prior to synthesis, a $-\text{COOH}$ terminated SAM intended for growth in the (100) direction.^[12,21] HKUST-1 thin films were manually deposited by alternately immersing the substrates in CuAc_2 and BTC solutions with intermittent rinsing and drying. A consecutive immersion in both CuAc_2 and BTC signifies a full deposition cycle and a half cycle consists of a single immersion in either CuAc_2 or BTC. The immersion times in ethanolic solutions of CuAc_2 and BTC were 10 and 20 min, respectively. IRRAS spectra revealed very interesting details of the initial stages of HKUST-1 growth. If the substrates were subjected to 5 min washing steps in flowing ethanol and subsequent drying each half cycle, a very slow growth of the film was observed (Figure 2.1 a). IRRAS spectra of such thin-films showed very broad bands that are not alike an IR spectrum of $[\text{Cu}_3(\text{BTC})_2]$. Instead, broad bands at 1620 cm^{-1} and 1570 cm^{-1} were present (Figure 2.1 a). Remarkably, if the washing steps consisted of 10 s rinsing in ethanol with drying only after full cycles, the COO^- vibrational modes of $[\text{Cu}_3(\text{BTC})_2]$ at 1650 cm^{-1} and 1380 cm^{-1} appeared much stronger in intensity, indicating significantly faster growth (Figure 2.1 a).

FIGURE 2.1: a) IRRAS spectra of the first three cycles of the LbL synthesis for manual growth with half-cycle (top) and whole cycle (bottom) drying. b) Influence of drying steps on $[\text{Cu}_3(\text{BTC})_2]$ growth. During the first 4 cycles the SURMOF was dried in N_2 flow each half-cycle and hindered growth was observed. The fast growth resumed only after full-cycle drying steps (5th and 6th cycle). c) IRRAS spectra of copper acetate (red), BTC (black), and BTC upon addition of copper acetate (blue).

Additional control experiments showed that the growth rates critically depend on the drying and washing steps (Figure 2.2). The drying step has shown as the most crucial. If substrates were dried after each half-cycle in N_2 flow, almost no SURMOF formation could be consistently observed (Figure 2.1 and 2.2). However, fast growth could again be established on SURMOFs grown in the hindered regime if the drying steps were applied after full deposition cycles (Figure 2.1b). We concluded from this that the SURMOF chemistry does not proceed in an ideal and well-controlled LbL fashion and that the actual growth rates can be strongly altered by the synthesis conditions. We suspect that a half-cycle drying step additionally removes loosely attached $CuAc_2$ species that cannot be completely removed by washing step with ethanol. Importantly, if a large fraction of the weakly adsorbed $CuAc_2$ precursors is removed by rinsing and drying steps, the formation of $[Cu_3(BTC)_2]$ SURMOF occurs through surprisingly hindered, defect-rich growth.

FIGURE 2.2: IRRAS spectra of control experiments performed to verify the effect of drying (a) and washing (b) on SURMOF growth. Samples corresponding to the spectra shown in (a) were washed for 10 s in ethanol and were dried either after each half cycle (top) or each whole cycle (bottom). In the experiments for (b), samples were either washed for a long time (5 min in flowing EtOH) or for a short time (10 s) and were dried after each whole cycle. This Figure shows the detrimental effect of drying each half cycle on SURMOF growth, whereas the length of the washing step was shown to have little influence.

Based on the initial experiments, we hypothesized that the growth proceeds if $CuAc_2$ and BTC species are allowed to form secondary building units (SBUs) in the solution. In order to understand the actual SURMOF growth mechanism, we have further substantiated the chemistry of the formed surface structures. Apart from the characteristic asymmetric and symmetric stretching modes of $[Cu_3(BTC)_2]$ at 1650 and 1380 cm⁻¹,^[26,27] respectively, the presence of the broad band centered around 1570 cm⁻¹ could not be matched with the IR spectrum of the HKUST-1 framework. This band remained present at the surface disregarding the synthesis procedure (drying half/whole cycle, Figure 2.1 a, b). To unambiguously prove

the origin of the IR absorption bands of the films, we have recorded separate IRRAS spectra of CuAc_2 , BTC, and their mixtures of different stoichiometric ratios (Figure 2.1 c and 2.3). Based on this, the broad band at 1575 cm^{-1} could be assigned to the COO^- asymmetric stretching vibration originating from $[\text{Cu}_2\text{Ac}_4]$ paddle-wheels (Figure 2.1 c). Thus, a significant presence of un-exchanged $[\text{Cu}_2\text{Ac}_4]$ species in the $[\text{Cu}_3(\text{BTC})_2]$ films was unexpectedly observed for both samples dried at half- as well as at whole cycles. To the best of our knowledge, this spectroscopically detected presence of precursor CuAc_2 species in the formed SURMOF was not previously shown. The band at 1620 cm^{-1} , which is dominating the IRRAS spectra during the hindered growth, is a signature of mixed $[\text{Cu}_2(\text{BTC})_2\text{Ac}_2]$ building units (*vide infra*) and further supports our observation of the irregularly grown SURMOF film.

FIGURE 2.3: IRRAS spectra of CuAc_2/BTC mixtures with different molar ratios of $\text{Cu}:\text{BTC}$, recorded after evaporation of ethanol, approximately 5 min upon mixing 1 mM solutions of reactants. The disappearance of the paddle-wheel $[\text{Cu}_2\text{Ac}_4]$ species at 1580 cm^{-1} with increasing BTC concentration is visible.

Although the stoichiometric substitution of $[\text{Cu}_2\text{Ac}_4]$ paddle-wheels with BTC linker is critical for regular film growth, no previous studies have reported the IR signature of excess precursor species present in the film.^[1,2] These species are partially exchanged or un-exchanged $[\text{Cu}_2\text{Ac}_4]$ paddle-wheels that remain loosely attached (most likely physisorbed) at the surface of the irregular SURMOF film. Probably, the demanding surface-mediated substitution of acetate $[\text{Cu}_2\text{Ac}_4]$ and BTC linkers required for the true LbL growth is the reason for irregular and defect-rich growth. We exclude the effect of the Au substrate and self-assembly of MHDA as our experiments were performed following reported procedures and across the range of differently prepared substrates. The explanation of the growth mechanism can be found in the solution-mediated chemistry of copper acetate and BTC.

This mechanism is supported by the fact that CuAc_2 and BTC react quickly in the solution when their direct reaction mixtures were inspected by IRRAS (Figure 2.1 c). From this we concluded that $[\text{Cu}_2(\text{BTC})_4]$ precursor SBUs form easily at the solid–liquid interface of a SURMOF where both reactants are present.

FIGURE 2.4: AFM images and PT-AFM-IR spectra recorded on Au/Si and Au/mica HKUST-1 SURMOF thin films. a) AFM image of a thin film on Au/Si measured after 5 deposition cycles using manual synthesis with drying each whole cycle. b) AFM image of a thin film on Au/mica measured after 2 deposition cycles grown in the same way as (a). c) Representative PT-AFM-IR spectra recorded at different positions for the substrates presented in (a,b). Spectrum (#1) is taken on top of a large SURMOF grain (1 black), spectra #2 and #3 are taken at two different positions. An IRRAS spectrum of CuAc_2 (dotted line) is added for comparison. d) Vibrational modes assigned to COO^- originating from the different Cu-paddle-wheel substitutions.

To generalize our findings, we have further used two Au–COOH-terminated substrates, namely Au/Si (surface roughness of 2 nm, same type of substrates used for above-described experiments) and Au/mica (with atomically flat Au (111) terraces). Both substrates were initially used to synthesize HKUST-1 films in the fast growth regime (manual synthesis, full cycle drying, Figure 2.4 a, b). For $[\text{Cu}_3(\text{BTC})_2]$ films prepared on Au/Si, the crystal grains reached 75 nm in height after only five deposition steps (Figure 2.4 a). This growth rate largely exceeds the growth rates predicted from the epitaxial-like LbL synthesis (ca. 1.3 nm per cycle) and agrees well with previous AFM studies.^[8,9] Based on the AFM profile in Figure 2.4 a, we estimate 2.5 times larger amount of material after five cycles than expected from the LbL stoichiometry. By using the AFM-IR technique, it was possible to record point spectra at desired locations on the SURMOF film. IR single-point spectra recorded at one of the large crystals show the expected spectra of SURMOF previously observed with IRRAS, including a significant presence of CuAc_2 (Figure 2.4 c, spectrum (a)). Similar inspection of a film grown after two deposition cycles on Au/mica substrates has revealed 10 nm features

in height (Figure 2.4b). Due to the beam interference from the Au/mica substrates, we have been unable to record IRRAS spectra of thin films deposited on Au/mica. However, single-point spectra could be recorded with photothermal AFM-IR (PT-AFM-IR), regardless of the type of substrate used. Two spectra taken at two different locations on this SURMOF are given in Figure 2.4 c (spectra #2 and #3)).

FIGURE 2.5: Examples of PT-AFM-IR spectra recorded at different locations of differently grown SURMOF films (a)-(c). Note that the band at 1640 cm⁻¹ arises stronger in the fast growth samples. AFM images of 5 layer SURMOF samples on Au/Si (d) and Au/mica (e) grown via manual synthesis with half-cycle drying indicating decreased growth rates as a result of washing and drying steps. f) and g) IR spectra show the formation of HKUST-1 with a characteristic paddlewheel structure.

The spectroscopic potential of (PT-)AFM-IR is highlighted through a clear difference between the two spectra, which indicate different chemical environments at the surface of the film, consisting of varying substitution ratios in [Cu₂Ac_x(BTC)_y]. As IRRAS analysis provides SURMOF averaged information, these location-dependent ratios could not have been detected without AFM-IR. AFM-IR further confirms that apart from the defect-rich SURMOF grains, an amorphous layer of CuAc₂ species is attached to the Au-COOH

surface (Figure 2.4c, spectrum #3). Very strong hindrance in the growth of $[\text{Cu}_3(\text{BTC})_2]$ is noted on Au/mica substrates, as predominantly CuAc_2 species were detected at the surface (Figure 2.5). These results are in line with a previous AFM study that reported both crystalline and amorphous HKUST-1 structures grown on Au-mica.^[9] We further confirmed that different growth rates can result from the sequence of drying steps. AFM topology maps of the samples with the hindered growth prepared with five deposition cycles on Au/Si and Au/mica show MOF grains below 5 nm in height (Figure 2.5). PT-AFM-IR spectra in Figure 2.5 (spectra #1 and #2) indicate the formation of the acetate- related paddle-wheel structures. Examples of AFM-nano-IR spectra, recorded at different locations on various substrates, are shown in Figures 2.5 and 2.6.

FIGURE 2.6: Series of AFM images and their average spectra for different films grown with manual synthesis with drying each whole cycle. The left panel shows AFM images with array positions (blue squares) for IR measurements with their corresponding averaged spectrum displayed on the right. a-c) 1, 2 and 3 cycles of HKUST-1 on Au/Si, respectively and d-f) 2, 3 and 5 cycles of HKUST-1 on Au/mica, respectively. A peak at 1710 cm^{-1} most likely corresponds to COOH vibration of MHDA, which was visible due to signal enhancement between the Au substrate and a gold tip used in AFM-IR contact measurement mode. Note that non-linear near-field enhancements may occur when scanning nm-thick organic layers.

The comparison of IR spectra in Figure 2.4c points toward at least four different Cu-COO^- asymmetric modes that describe varying degrees of substitution of the corresponding copper paddle-wheels. From the positions and intensities of the IR bands for different growth regimes, we infer the following assignments: the band at around 1650 cm^{-1} (mode

ν_1 , Figure 2.4c, d) is a signature of COO^- asymmetric vibration in the fully coordinated $[\text{Cu}_2(\text{BTC})_4]$. This band is present in fully reacted mixtures of Cu-BTC (Figure 2.1c), and also for the films grown with drying each whole cycle (Figure 2.1a); the vibration at 1620 cm^{-1} (mode ν_2) is prominent for the hindered-grown films and belongs to COO^- (from Cu-BTC) in the partially exchanged $[\text{Cu}_2\text{Ac}_2(\text{BTC})_2]$; similarly, the band at 1550 cm^{-1} (mode ν_4) likely belongs to the COO^- (from Cu-Ac) vibrations in the partially exchanged $[\text{Cu}_2(\text{BTC})_2\text{Ac}_2]$, whereas the band at around 1580 cm^{-1} (mode ν_3) is attributed to an asymmetric COO^- mode of $[\text{Cu}_2\text{Ac}_4]$, based on the IRRAS spectra of copper acetate. The arrangement and chemistry of these species could be responsible for the previously observed surface diffusion barriers and defects in $[\text{Cu}_3(\text{BTC})_2]$ films with unclear chemical origin.^[3,28]

Our results indicate that strong CuAc_2 adsorption at the surface may easily facilitate the uptake of precursor species (CuAc_2/BTC) with mass exceeding the equivalent of a monolayer and that ethanol alone may not be sufficient to (homogeneously) wash off these precursor species from the surface. In line with our interpretation, Stavila *et al.* have detected an increasing mass uptake with each step of the LbL synthesis, reaching 50% of additional mass after five cycles.^[2] Ohnsorg *et al.*^[8] were the first to suggest that the linear growth rates observed with QCM^[5] can be interpreted with the growth of large MOF islands via the Volmer-Weber mechanism,^[8,9] rather than a controlled LbL growth. We additionally find that the fast local growth rates are the consequence of the solution-mediated strong interactions between loosely attached (physisorbed) CuAc_2 and BTC, most likely taking place at the solid-liquid interface. Importantly, if the reaction components are carefully separated (e.g., by drying each half-cycle), a very hindered and irregular growth with large presence of CuAc_2 species in the film occurs. Note that this mechanism is particularly strong for HKUST-1 and it may not explain the growth of other MOF frameworks.^[13]

Whereas IRRAS was able to provide only limited and averaged information about growth of the film prepared with the manual synthesis with half-cycle drying steps, we were readily able to apply PiFM-IR to visualize and chemically characterize individual grains after a single LbL SURMOF deposition cycle (Figure 2.7). Two AFM topology images of different size are shown with their corresponding IR maps recorded at 1450 and 1577 cm^{-1} . As such, the excess of CuAc_2 on the surface can accurately be correlated with the topology. The IR maps in Figure 2.7b/e, as well as point spectra taken on the sample surface (Figure 2.7f), support the notion that the CuAc_2 can be heterogeneously distributed over the surface, as well as the fact that extensive washing in combination with drying removes a large amount of physisorbed species resulting in inhomogeneous substrate coverage. However, AFM has shown an increase in SURMOF coverage with layer deposition (Figure 2.10), that is, growth does not occur solely on previously grown SURMOF. The irregular SURMOF crystal shapes observed in AFM for the one layer sample have not been encountered previously and require additional research.

FIGURE 2.7: PiFM AFM images of a 1 layer HKUST-1 SURMOF thin film. The sample was made using manual synthesis, including a drying step each half cycle. a) $5 \times 5 \mu\text{m}^2$ AFM image showing the initial deposition of singular MOF islands. b) PiFM-IR map of the substrate shown in (a) measured at 1450 cm^{-1} , c) Magnification of (b), d) $1 \times 1 \mu\text{m}^2$ AFM image of the same sample and e) PiFM-IR map measured at 1577 cm^{-1} . f) Point IR spectra taken on top of a high feature (red) and on the background (black). Markers 1 and 2 in (b) show the sampling positions. Spectrum #1 clearly shows characteristic HKUST-1 signal whereas the spectrum taken on the background does not. Note that there the intensity in $1600\text{--}1650$ region could be lower due to lower power output of the IR laser in this region.

To improve film quality, a synthesis procedure with washing yet without drying was adopted, as previous results suggest a deteriorating effect on thin film quality by drying. To verify film quality XRD measurements were employed to analyze crystal orientation. XRD samples require a thicker film to ensure sufficient signal, therefore in order to produce films for XRD analysis in a controlled and less labor-intensive manner, an automatic dip-coater was utilized to create SURMOFs of 50–150 deposition cycles.

FIGURE 2.8: Out-of-plane X-ray diffractograms (background corrected) and AFM images of 50 layers thin films synthesized using automatic dip-coating with differentiating Cu-precursor species and deposition/washing times (no drying). The following synthesis steps were used—slow synthesis: CuAc_2 (30 min), BTC (60 min) and ethanol (5 min); fast synthesis: CuAc_2 or $\text{Cu}(\text{NO}_3)_2$ (2 min), BTC (2 min) and ethanol (20 s). a) XRD diffractograms showing bulk film orientation resulting from slow automated synthesis (top) and preferential (100) orientation resulting from fast automated synthesis (middle, bottom). b–d) Corresponding AFM images illustrating resulting SURMOF film quality for slow synthesis with CuAc_2 (b), fast synthesis with CuAc_2 (c), and fast synthesis with $\text{Cu}(\text{NO}_3)_2$ (d). AFM root mean square values are included in AFM images to show improving surface quality through decreasing surface roughness.

Initial attempts to reproduce the highly oriented (100) films, which are expected for $[\text{Cu}_3(\text{BTC})_2]$ framework grown on a carboxylic acid terminated MHDA substrate,^[1] using similar immersion times and washing steps failed (30/60 min for CuAc_2/BTC , respectively, see Experimental Section: slow synthesis procedure 1). The synthesis resulted in films with mixed (100) and (111) preferential orientations (Figure 2.8a, top, CuAc_2 slow synthesis). AFM measurements indicated a highly heterogeneous film with crystal sizes significantly exceeding theoretical limits of the LbL synthesis (Figure 2.8b). This result is in accordance with other reports in literature where authors noticed both (100) and (111) oriented crystallites.^[2,8,9] Remarkably, only reduced immersion times in both reactants and ethanol (2 min for both CuAc_2 and BTC, with a 20 s washing step, see Experimental Section, (fast) synthesis procedure 2) have led to (100) oriented films, (Figure 2.8a, middle, CuAc_2 fast synthesis).^[5] An AFM image shows significantly improved homogeneity of the film (Figure 2.8c). IRRAS spectra for these films are shown in Figure 2.9. We interpret this result in relation to the crystallization rates from the solution. As the growth proceeds due to excess presence of

SBU in the solution, their concentration at the solid–liquid interface is sufficient to produce a (100) oriented film. In contrast, significantly longer synthesis times may lead to higher growth rates that promote crystallization along both (111) and (100) directions.

FIGURE 2.9: IRRAS spectra of three SURMOFs grown by different automated syntheses shown in Figure 2.8. Quantitatively, IRRAS confirms a variation in growth rates which was also shown using AFM (Figure 2.8 b-d). Quality of films grown by CuAc_2 , determined by the degree of Cu-paddlewheel substitution, is increased for fast grown films.

From the results presented above, it is clear that the crystallographic orientation and degree of crystalline defects in a SURMOF film can be dramatically altered solely by synthetic conditions (i.e., the length and sequence of dipping, washing and drying steps) and that the termination of a SAM monolayer may not be overly detrimental for the outcome of the synthesis. To further illustrate this, we have compared two distinct films from manual and automatic synthesis. Even if we do not intend to fully compare (manual, automatic) synthesis procedures for resulting film quality, a comparison does illustrate the differences in underlying growth mechanisms. Using the above-described procedure for manual synthesis with drying each half cycle, a five-layer SURMOF was synthesized (Figure 2.10 a).

FIGURE 2.10: AFM topology images of HKUST-1 SURMOF thin films of 5 layers grown using CuAc_2 by manual synthesis (drying each half cycle) (a) and automated fast (c) LBL synthesis. b) and d) show normalized point spectra taken off and on top of high features in the samples shown in a) and c), respectively. A large difference in shape of spectra taken on/off high features of the manually grown SURMOF indicates a non-uniform sample, whereas the chemical identity both on and off high features for the fast grown sample is homogeneous. Note that due to a dip in laser power between $1620\text{--}1670\text{ cm}^{-1}$, no reliable signal is acquired in this range.

The surface quality improved by applying (fast) automated synthesis, which is visible through increased flatness in the AFM (Figure 2.10c), as similarly shown for the 50-layer XRD sample (Figure 2.8b, c, Figure 2.11). In addition, the chemical (in-)homogeneity was analyzed using PiFM-IR (Figure 2.10b, d). The sample made through manual synthesis (top) showed a non-uniform chemical identity throughout the thin film. On top of larger features, distinctive HKUST-1 peaks were measured (Figure 2.10b, black lines), while no distinctive MOF signal was acquired on the background (Figure 2.10b, red lines). Additionally, a large presence of CuAc_2 , characteristic for hindered growth, was detected. The sample grown using fast automated synthesis, however, was found to be chemically homogeneous and possesses little CuAc_2 , both on top and off of high features. Unfortunately, no statement can be made regarding the local defect concentration as a dip in laser power between $1620\text{--}1670\text{ cm}^{-1}$ prevented the detection of reliable IR signal, however bulk IRRAS experiments have shown fast automated synthesis to promote the full coordination of the $[\text{Cu}_2(\text{BTC})_4]$ paddle-wheel through the solution-mediated growth.

FIGURE 2.11: AFM images of 50 layers HKUST-1 grown by different synthesis (precursor, procedure) and on different substrates. Root mean-square roughness values (rms) are provided as a guideline for the film smoothness. a) Slow synthesis procedure 1 using CuAc_2 on Au/mica, rms= 32.7 nm; b) fast synthesis procedure 2 using CuAc_2 on Au/mica, rms= 8.7 nm; c) fast synthesis procedure 2 using 5 $\text{Cu}(\text{NO}_3)_2$ on Au/mica, rms= 4.0 nm and d) bare Au/mica, rms= 1.4 nm. Clear influence of synthesis parameters can be seen on the growth of large irregular features instead of uniform films. All scale bars are 1 μm .

Despite improvements of film quality by synthesis procedure optimization, the strong surface affinity of CuAc_2 will nonetheless hinder a facile high-quality growth of HKUST-1 SURMOF. This can be overcome by replacing the CuAc_2 precursor with the sterically less demanding copper-nitrate precursor ($\text{Cu}(\text{NO}_3)_2$). Shekhah *et al.* have shown by QCM that the use of $\text{Cu}(\text{NO}_3)_2$ results in a much slower mass uptake than for CuAc_2 .^[5] These results have been explained by a suitable Cu-paddle-wheel structure of CuAc_2 , which is believed to facilitate the SURMOF growth. Strikingly, using $\text{Cu}(\text{NO}_3)_2$ as precursor species resulted in a highly oriented (100) film with a smooth surface and controlled growth that follows the island structure of the Au/Si substrate (Figure 2.8 d and 2.9). By using the highly flat Au/mica substrates we obtained films with surface roughness around 4 nm after 50 cycles (Figure 2.11). An estimation based on IR intensity of Cu-BTC bands suggests roughly 3–5 times higher growth rates for CuAc_2 -based films, as compared to $\text{Cu}(\text{NO}_3)_2$ after 20 immersion cycles (Figure 2.12 a). The big discrepancy in the uptake and growth rates between the two precursors originates from the higher adsorption affinity of CuAc_2 and possibly formation of different SBUs than for $\text{Cu}(\text{NO}_3)_2$.^[6] This result is qualitatively in line with Shekhah *et al.*, although from our results it is clear that $\text{Cu}(\text{NO}_3)_2$ can produce $[\text{Cu}_3(\text{BTC})_2]$ SURMOF, despite much slower surface uptake.^[5] Nevertheless, this uptake is

sufficient to yield an increase of SURMOF growth of approximately one monolayer layer per synthesis cycle. We also note that $\text{Cu}(\text{NO}_3)_2$ has a low affinity for the Au/MHDA surface; when a half-cycle drying step was applied, the amount of formed SURMOF was minimal (not shown here), but the growth of the SURMOF is still possible if the solution-mediated mechanism takes place. This also imposes an important question of what the effect of the SBUs solution concentration is on SURMOF growth. Interestingly, when SURMOF films, grown for 3 immersion cycles according to the manual procedure, are exposed overnight to a direct synthesis solution (i.e., a solution containing both the Cu-precursor and the BTC linker), much faster growth of SURMOF film derived from $\text{Cu}(\text{NO}_3)_2$ is observed (Figure 2.12b, top). This is in sharp contrast to a similar substrate being placed in a direct synthesis solution containing the CuAc_2 precursor (Figure 2.12 b, bottom), which shows only LbL deposition and no delayed SURMOF synthesis from SBUs in the solution over time. This would suggest that (fully) coordinated copper paddle-wheel formation in solution is fast for $\text{Cu}(\text{NO}_3)_2$, but surface deposition is slow due to lower surface affinity. Nevertheless, the crystallization of SURMOF from the direct solution is significantly faster in the case of $\text{Cu}(\text{NO}_3)_2$, which is also the reason why MOF materials are predominantly made with this precursor.

FIGURE 2.12: a) Comparison of IRRAS spectra of $[\text{Cu}_3(\text{BTC})_2]$ films obtained after 5 (black), 10 (red), and 20 cycles (blue) of manual synthesis, with full cycle drying steps, for copper nitrate (top) and copper acetate (bottom). The estimated peak height ratio between the two reactants results in 3–5 times higher amount of film for copper-acetate-based substrate. b) Comparison of IRRAS spectra of $[\text{Cu}_3(\text{BTC})_2]$ films obtained after 3 cycles of the manual synthesis, with full cycle drying steps (black), and after subsequent addition of the reactant's mixture (i.e., Cu+BTC) overnight (red), copper nitrate (top) and copper acetate (bottom).

Our mechanistic insights enable significantly faster synthesis of the oriented SURMOF films by the LbL method. In our example, we managed to shorten the synthesis time for 100 cycles from almost 7 days to less than 8 h. This places the LbL synthesis of MOF films to a practically reachable time scales as further optimizations are certainly expected. At the same time, the mechanistic details emerging from this work explain the success of other previously reported methods to produce highly oriented MOF films with significantly faster growth rates, such as in the automated spray synthesis.^[10]

2.3 CONCLUSIONS

In this Chapter, a powerful combination of IR spectroscopy-based methods, including AFM-IR spectroscopy, has been used to shed more light on the growth mechanism of $[\text{Cu}_3(\text{BTC})_2]$ films. Through the application of multiple synthesis methods, both initial growth mechanisms can be unraveled and HKUST-1 SURMOF quality can be improved. A manual LbL synthesis, which includes a drying step, provided the careful separation of growing stages, necessary to study the influence of separate precursor (metal/linker) species. As such, for the first time spectroscopic IR signatures for different copper-carboxylate species were reported. Additionally, the extent of drying applied during manual synthesis has been found to largely determine the SURMOF growth rate. We argue that this effect is related to the degree of physisorption of the metal precursor species, CuAc_2 , where a high (non-stoichiometric) amount of adsorbed surface species promotes faster growth.

FIGURE 2.7: Simplified illustrations of the hindered (a) and solution-mediated (b) film growth mechanism of HKUST-1 SURMOF.

From findings supported by bulk IR analysis (IRRAS), we have concluded that HKUST-1 SURMOF does not grow via a pure LbL mechanism, but rather through solution mediated growth (Figure 2.13). As a result, Volmer–Weber type island formation is seen in AFM. These separate MOF grains can be individually characterized chemically by AFM-IR techniques. Chemical (in-)homogeneity can be probed through point specific IR spectrum acquisition as well as IR mapping of precursor- and/or SURMOF species. A second synthesis procedure,

namely an automated dipping synthesis, provided facile means for producing thick LbL films (50–150 layers) suitable for XRD analysis. XRD analysis showed that synthesis procedures comparable to ones reported in literature can produce non-oriented SURMOFs. Therefore, the outcome of the synthesis largely depends on the synthetic procedure and related excess amounts of precursor species.

2.4 EXPERIMENTAL SECTION

The following chemicals were used: 16-Mercaptohexadecanoic acid (99%, Sigma–Aldrich), absolute ethanol (99.5%, Acros), Cu^{II}acetate (98%, Aldrich), Copper(II) nitrate trihydrate (99+%, Sigma–Aldrich), trimesic acid (95%, Aldrich) and acetic acid (99.5%, Acros). Substrates of 60 nm Au on Si, with a 5 nm Ge adhesion layer (provided by AMOLF), and 200 nm Au on mica (Phasis, Switzerland) were functionalized with a self-assembled monolayer (SAM) by immersing in 20 μm 16-mercaptohexadecanoic acid solution (5% acetic acid in ethanol) for 48 h.^[134]

2.4.1 MATERIALS SYNTHESIS

Manual LbL deposition (drying): HKUST-1 thin films were deposited by successively placing Au–MHDA substrates in separate ethanolic 1 mm precursor solutions of CuAc₂ (10 min) and BTC solution (20 min). Each half-cycle, that is, after deposition of Cu-precursor or BTC, was followed by (vigorous) 5 min rinsing with absolute ethanol and immediate drying using flowing nitrogen. All syntheses were performed at room temperature.

Automated solution mediated LbL deposition (no drying): An automatic synthesis procedure (initially developed for successive ionic layer adsorption and reaction (SILAR)) was used to synthesize films in a reproducible fashion. A SILAR coating system with stirrer (HO-TH-03S, Holmarc) was used to program immersion cycles in copper-precursor, BTC and ethanol. No drying step was applied. The stirring speed was kept constant at 150 rpm as well as the precursor solutions concentration (1 mm). All syntheses were performed at room temperature. General synthesis procedures have been derived—(slow) synthesis procedure 1: deposition time of 30 and 60 min in Cu- and BTC solution, respectively, with a washing step including stirring of 5 min in ethanol; (fast) synthesis procedure 2: deposition times of 2 min in Cu- and BTC solution, with a washing step including stirring of 20 s in ethanol.

2.4.2 MATERIALS CHARACTERIZATION

Infrared reflection absorption spectroscopy (IRRAS) spectra were recorded using a PelkinElmer Spectrum 1 infrared spectrometer equipped with grazing angle specular reflectance accessory (Specac) and a mercury cadmium telluride (MCT) detector cooled with

liquid nitrogen. The sample and optics compartments were purged with nitrogen. Incident IR beam was vertically polarized with a grazing incidence angle of 80° . All spectra were recorded with 4 cm^{-1} spectral resolution, $450\text{--}4000\text{ cm}^{-1}$ range, with typically 50 accumulations. For monolayer studies, a gold substrate functionalized with deuterated 1-hexadecane- d_{33} -thiol (C/D/N Isotopes) as SAM was used as a reference. For high-absorbance experiments, clean gold wafers were used as reference.

PT-AFM-IR measurements have been performed using an Anasys nanoIR2 instrument at the facilities of Anasys Instruments (Santa Barbara, CA, USA), as well as at Oak Ridge National Laboratory (ORNL, Oak Ridge, TN, USA). Additionally, photo-induced force microscopy (PiFM) measurements have been performed on a VistaScope instrument from Molecular Vista, using the facilities at Molecular Vista (San Jose, CA, USA). All machines were equipped with a quantum cascade laser (QCL) units and IR spectra were measured in the $1300\text{--}1800\text{ cm}^{-1}$ range. Prior to IR analysis, AFM topology images were made at least two sample positions in either tapping- or contact mode, typical AFM image sizes were $1\times 1\text{ }\mu\text{m}^2$, $3\times 5\text{ }\mu\text{m}^2$ and $5\times 5\text{ }\mu\text{m}^2$. IR point spectra could be collected in dynamic non-contact- (PiFM) and contact mode (nano-IR). AFM-nanoIR spectra acquired using an Anasys nanoIR2 apparatus were analyzed using the Analysis Studio software (version 3.13), AFM-IR (/PiFM) spectra were analyzed using SurfaceWorks software (version 2.3). A Savitsky-Golay filter was applied to the spectra.

AFM topology maps in 3 separate positions on each sample were obtained using a JPK NanoWizard 3 and HA NC Etalon polysilicon tips (force constant $\approx 3.5\text{ N m}^{-1}$, tip curvature radius $< 10\text{ nm}$). The obtained images were post-processed using Gwyddion. After masking larger features using the 'Facet Analysis' function, the images were flattened using a polynomial background subtraction, disregarding the masked features. The calculated volume was obtained by using the 'Facet Analysis' function of Gwyddion, marking the larger grains. Then, the volume value was given using the 'Grain statistics', working with the volume using Laplacian background subtraction.^[30]

X-ray diffraction (XRD) measurements were performed using a Bruker-AXS D2 Phaser equipped with a Co $K\alpha$ radiation ($\lambda=1.78897\text{ \AA}$) source with 2θ from $6\text{--}20^\circ$, using an increment of 0.02° , with a step measurement time of 1 s. Background subtractions were performed using Eva software and diffractograms were normalized to the (2,0,0) peak.

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3

MAPPING DEFECT- ENHANCED ADSORPTION ON SURFACE-ANCHORED METAL-ORGANIC FRAMEWORK NANO- ISLANDS WITH *IN SITU* NANO-SPECTROSCOPY

3. ABSTRACT

Probing gas-solid interfaces at the nanoscale is still a formidable scientific challenge. New nano-spectroscopic methods are needed to understand guest-host interactions of functional materials during gas sorption, separation, and conversion. In this Chapter, we introduce *in situ* Photo-induced Force Microscopy (PiFM) to evidence site-specific interaction between metal-organic frameworks (MOFs) and water. To this end, amphiphilic surface-anchored MOF (SURMOF) model systems have been developed using self-assembly for the side-by-side hetero-growth of nanodomains of hydrophilic HKUST-1 and hydrophobic ZIF-8. PiFM was used to probe local uptake kinetics and to show D₂O sorption isotherms on (defective) HKUST-1 paddlewheels. By monitoring defect vibrations, we visualized in real-time the saturation of existing defects and the creation of D₂O-induced defects.

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3.1 INTRODUCTION

Many chemical and catalytic processes depend on the capture, separation, and conversion of gaseous molecules on functional materials. Such events often preferentially occur on specific defective, undercoordinated sites, which can be introduced by rational design to improve material performance.^[1–3] Prominent examples can be found in the booming field of metal-organic frameworks (MOFs), materials with high porosity, crystallinity, and tunable chemistry which are increasingly finding their way towards applications.^[4,5] To guide synthetic efforts in this field, and in nanomaterials science in general, it is of paramount importance to move from a bulk to a nanoscale understanding of host-guest interactions.

In surface sciences, efforts have been made to gain a nanoscale understanding of the adsorption of gases on material surfaces. However, these efforts have been dominated by several techniques that work under ultra-high-vacuum conditions, far away from real operating conditions, a problem also known as the pressure gap.^[6] In contrast, techniques suitable to study adsorbate interaction at elevated pressures, such as vibrational spectroscopy, lack the required spatial resolution to provide structure-performance relationships of specific (defective) sites.^[7–9] To bridge this gap, new *in situ*, highly-sensitive nano-spectroscopic tools are required.^[8,10,11]

This Chapter introduces *in situ* capability to the emerging field of Photo-induced Force Microscopy (PiFM), a highly sensitive and spatially resolved near-field infrared (IR) technique, to gain new insights into guest-host interactions at working conditions.^[12,13] We showcase that PiFM can be used to study structure-dependent adsorption on defective versus non-defective sites in a MOF by simultaneously uncovering topological and chemical information at the nanoscale with a spatial resolution down to 8 nm.^[13] We selected water (D₂O) as a probe molecule for this proof-of-concept because of its omnipresence in industrial gas streams, but highlight that our approach can be extended to many gases/functional materials.^[14,15]

We have applied *in situ* PiFM to a range of Surface-Anchored Metal-Organic Frameworks (SURMOFs) as is outlined in Figure 3.1. SURMOFs are well-known model systems, based on MOF grown on alkanethiol functionalized gold surfaces.^[16–18] These monolayers of alkanethiols have proven to yield excellent homogeneous SURMOFs^[19,20], yet homogeneous surfaces are not always the most accurate description of actual MOFs. For example, gas sorption and catalysis often thrive on materials with defect-rich surfaces possessing steps, kinks, and edges.

To reproduce such traits, it is vital to either nanosize or pattern the MOF deposits^[21,22]. However, using expensive top-down approaches is unfavorable for the routine screening of SURMOF model systems. Therefore, bottom-up approaches using self-assembly are

an excellent alternative^[23]. Some previous studies reported on creating chemically distinct thiol domains on the Au surface, rather than a homogeneous monolayer, with a mixture of alkanethiols^[24–26]. By applying such an approach, a surface can be created where SURMOF growth is promoted specifically in some domains, and inhibited in others. Here, we nanosized the MOF deposits to stimulate defect formation by manipulating the self-assembly behavior of the thiol molecules promoting/inhibiting MOF growth on the substrates, yielding gapped, and even bifunctional surfaces of HKUST-1 and ZIF-8.^[23,27,28]

HKUST-1, an archetypical MOF, is highly hydrophilic and has low hydrothermal stability as its paddlewheel SBU hydrolyses in the presence of water vapor.^[29,30] On the other hand, Zeolitic-Imidazolate Frameworks (ZIFs), such as ZIF-8, are hydrophobic and show increased hydrothermal and chemical stability. By depositing HKUST-1 and ZIF-8 together on a substrate, one can create a single amphiphilic, bifunctional surface, displaying two highly distinct water-MOF/ZIF guest-host interactions.^[31,32]

FIGURE 3.1: Outline of the used approach. A: various thiol compositions were used for Au substrate functionalization prior to Layer-by-Layer (LbL) synthesis of SURMOF (HKUST-1, green) and SURZIF (ZIF-8, blue) and their mixtures. Carboxylic acids selectively promote HKUST-1 growth, pyridine promotes ZIF-8 growth, while methyl-thiols were used to suppress growth. Aromatic thiols were incorporated to create π -stacked nanodomains leading to either gapped HKUST-1 or ZIF-8; or mixed HKUST-1/ZIF-8. B: *In situ* Photo-induced Force Microscopy (PiFM) was applied to these SURMOFs, SURZIFs, and related mixtures to deduce their interaction with D₂O on the nanoscale.

Subsequently, we studied whether our approach was able to *in situ* detect adsorption of gas molecules on heterogeneous functional surfaces with chemical and nanoscale resolution, and if we could discern site-specific sorption mechanisms and kinetics. This Chapter goes on to report a combination of isotope labeling and *in situ* nano-spectroscopy to ultimately show the enhanced uptake of D₂O on defective HKUST-1 with undercoordinated Cu sites. Furthermore, we provide direct evidence that water dissociatively adsorbs on these defect sites, and that with increasing pressure, molecularly adsorbed water dissociates on the pristine HKUST-1 surface thereby forming new defects. This led to the deduction of site-specific gas sorption isotherms of water on HKUST-1 and a visual representation of defect formation and propagation as a function of water sorption.

3.2 RESULTS AND DISCUSSION

3.2.1 SINGLE-COMPONENT SELF-ASSEMBLED MONOLAYER SURFACES

Literature has reported that alkanethiols with alternate chain lengths or functional groups can co-adsorb on Au^[24,33]. Non-equal thiol solubility is mirrored in the strength of the Van der Waals (VdW) forces exerted between these molecules leading to domain formation^[34]. These domains, in the range of tens of Ångstroms, were visualized using scanning tunneling microscopy (STM) techniques^[24,25]. However, in order to use mixed alkanethiol surfaces for SURMOF preparation, this domain size needs to be increased. Otherwise, the intergrowth of MOF pillars into a single slab will negate the SURMOF nanosizing effects. Therefore, the question is whether we can introduce an alternate stacking effect to create larger thiol domains that are able to promote pillared SURMOF growth in the 10s of nanometers range, thereby making nanosized SURMOF model systems.

To achieve this goal, we used thiols with aromatic backbones instead of aliphatic chains, as we hypothesized that their strong inter-molecular π - π interaction would lead to π -stacking and help to form domains of a substantially larger size. If these larger aromatic thiol domains form, then it is possible to show them using AFM measurements instead of the more demanding STM measurements.^[35,36] However, to verify that the aromaticity is responsible for forming larger domains, chemical identification of the domains is vital.^[37] In earlier studies, far-field infrared spectroscopy was applied to characterize the functionalized gold surfaces, however, this was only able to measure averaged information of mixed compound deposition.^[25,26,38] In this work, we show that recent progress in near-field infrared spectroscopy has made it possible to spectroscopically study the thiol domains beyond the diffraction limit.^[12]

FIGURE 3.2: Analysis of (co-adsorption) of thiol molecules. a) Full GI-ATR-IR spectra of the aliphatic and aromatic thiols show successful chemisorption. Note the presence of a broad peak at 1050 cm^{-1} stemming from a germanium oxide layer on the GI-ATR crystal. b) AFM images of the $-\text{COOH}$ thiols MHDA, MBA, and MMBA show that aliphatic SAMs, such as MHDA, typically display neat Van der Waals-based stacking resulting in a homogeneous self-assembled monolayer displaying low surface roughness. Higher surface roughness was found for aromatic thiol molecules due to π -stacking interactions. Co-adsorption of MMBA and UDT was found with e) bulk GI-ATR-IR, and f) PiFM spectra.

Before combining aliphatic and aromatic thiols, however, it was relevant to know whether the aromatic thiol compounds chemisorb in a similar fashion to alkanethiols.^[39] We used Grazing-Incidence Attenuated Total Reflection Infra-Red (GI-ATR-IR) spectroscopy to show that both aliphatic and aromatic -COOH thiols can chemisorb on an Au surface by measuring their averaged surface (i.e. bulk) IR spectrum (Figure 3.2a). Additionally, AFM measurements were performed to study their stacking behavior (Figure 3.2b-d).

The bulk spectra show the successful adsorption of the various thiols. Although it is very difficult to track any sulfur-based vibrations (S-H, C-S) that may hint towards Au-S bond formation, some film quality estimations of the -COOH thiols could be deduced from the ratio between C=O monomer vibrations (1750 cm^{-1}) and C=O dimer vibrations ($1720\text{--}1706\text{ cm}^{-1}$). These spectra were subsequently used to identify individual species in PiFM analysis.

AFM analysis in Figure 3.2 showed that the long aliphatic chains of MHDA provide an excellent system for stacking in monolayer conformation (low root mean square (rms) value) on the surface through Van der Waals forces. It is known from the literature that aliphatic thiols do not stack perpendicularly on the Au surface, but rather twist their backbone to form a (mono)layer with an angle of 30 degrees relative to the surface normal.^[40] MBA, however, which has the benzene group directly attached to the thiol group, does not possess this flexibility. As a result, the thiol π -stacks either perpendicularly or, as we suspect based on AFM measurements, parallel to the surface (Figure 3.2c).^[41] The heights and rms roughness of the observed features suggest that rather than just bilayer stacking, aggregation of thiols occurred. To achieve the required flexibility, an additional carbon atom was inserted into the backbone between the thiol and benzene, allowing the 4-mercaptomethylbenzoic acid (MMBA) to stack in semi-monolayer conformation. This is reflected in the AFM image in Fig 3.2d, which showed significantly reduced roughness for the MMBA functionalized surface.

To test whether the use of MMBA resulted in accessible SURMOF nucleation points, we performed an HKUST-1 Layer-by-Layer (LbL) synthesis according to our previously reported procedure (Figure 3.3a-c).^[18] An AFM image showed the full coverage of the surface with HKUST-1 SURMOF, therefore we deduced that the MMBA thiol is capable of promoting HKUST-1 SURMOF growth. Additionally, the measured film thickness, and thus growth kinetics, was found to be comparable to previously reported work on HKUST-1 SURMOF on MHDA.^[18] Furthermore, the formation of the preferentially [100] oriented, crystalline HKUST-1 SURMOF was confirmed by its XRD diffractogram.^[18] This showed that the orienting effect observed for aliphatic thiols with a carboxylic headgroup remained present for aromatic MMBA thiols. Lastly, GI-ATR-IR showed the distinct features of Cu-BTC coordination, such as the Cu-coordinated asymmetric and symmetric carboxylate stretching vibrations at 1650 and 1377 cm^{-1} , respectively.^[11,18]

FIGURE 3.3: Synthesis of (gapped) SURMOF and SURZIF films. a) AFM image of 100 layers of HKUST-1 grown on an MMBA surface. It shows a fully covered surface of HKUST-1 as a result of the -COOH headgroups of the SAM. b) oriented (100) crystal growth was observed in the X-Ray diffractogram. c) The bulk IR spectrum displayed peaks typical for HKUST-1. d) AFM image of 100 layers of ZIF-8 grown on a MPyr surface. Full surface coverage and oriented (110) crystal growth was observed,^[69] as well as f) typical IR peaks in the bulk spectrum. g) AFM image showing the deposition of 100 layers of gapped SURZIF-8 on MPyr-UDT. h) Particle height and size analysis shows well-isolated nano-sized SURZIF growth.

3.2.2 MULTIPLE-COMPONENT SELF-ASSEMBLED MONOLAYER SURFACES

Despite the successful implementation of a modified aromatic thiol as SURMOF nucleation layer, the question remains whether domains of growth-promoting aromatic thiol can be formed when mixed with a growth-passivating aliphatic thiol. To study domain formation, an Au surface was functionalized with a MMBA-UDT (11-UnDecaneThiol) mixture. The co-adsorption of both compounds was verified by bulk IR (Figure 3.2e). Interestingly, we observed a diminished dimer IR signal for the MMBA thiols which suggested the successful side-by-side chemisorption of the thiols. Using AFM, we measured a bimodal height distribution (4; 11 nm) on the surface (Figure 3.4a). Even though the UDT thiol has a longer backbone and therefore should be the taller species on the surface, the previously observed stacking behavior of the aromatic thiol groups casts doubt on which average height corresponds to which thiol. To identify the (assumed distinct) chemical identities, we utilized an AFM-based near-field IR spectroscopy tool, namely Photo-induced Force Microscopy (PiFM), which was able to acquire IR information beyond the diffraction limit, down to the nm scale (Figure 3.2f, 3.4c,d).

With PiFM we were able to measure the IR spectrum of 2 different species on the MMBA-UDT surface (Figure 3.4b-d). This showed that the spectrum of the higher feature possessed a band at 1450 cm^{-1} indicating aromatic ring breathing vibrations. So, from these spectra, we deduced that the higher features -which also showed larger domain areas- were the aromatic species. To find out whether this conclusion was valid throughout the surface, we performed a 3D hyperspectral (hyPIR) measurement which consists of a full IR spectrum on each AFM pixel^[167]. Subsequently, we performed Principal Component Analysis (PCA) and clustering on the acquired data set (Figure 3.4c). From this analysis we could not only conclude that the larger grains were indeed the aromatic thiols, but also that the aliphatic thiol coverage was less homogeneous than expected. This may be the result of the disruption of the long-range VdW stacking by the intermittent π -stacking domains.

As a next step, we verified whether it remained possible to grow SURMOF on the aromatic thiol surface without experiencing passivating effects resulting from thiol mixing. On the MMBA-UDT surface, we deposited 100 layers of HKUST-1 (Figure 3.4f). The infrared spectrum in both GI-ATR-IR and PiFM was comparable to HKUST-1 grown on single thiol surfaces (Figure 3.3, 3.4e). From AFM analysis, we found a bimodal distribution of both height (50; 88 nm) and size (28; 53 nm) of the MOF deposits, indicating two growth regimes in the gapped SURMOF. This can be explained by the results of X-Ray Diffraction (XRD) measurements (Figure 3.4g, h): Whereas HKUST-1 grown on a single -COOH thiol surface is preferentially oriented in the [100] direction^[44], the gapped SURMOF displays bulk crystallinity characteristics. This was also visible in the crystal shapes in the AFM images: HKUST-1 crystals growing in the [100] direction tend to display a triangular

FIGURE 3.4: Bottom-up approach for SURMOF nanosizing as probed by *in situ* Photo-induced Force Microscopy (PiFM). A: AFM image of the MMBA-UDT surface showing (B) a bimodal height distribution of nm-sized domains. C: Example of a segmented hyperspectral image (hyPIR) based on PCA and clustering. Pixels in the image are pooled based on spectral similarity, showing the thiol distribution (red: UDT, green: MMBA, blue: Au). D: PiFM point spectra of positions marked in (A). These show aromatic (1450 cm^{-1}) vibrations in the MMBA spectrum (top). E: Point spectra of HKUST-1 grown on MMBA single-thiol SAM (top) and of the markers in (F) (bottom). F: AFM image of 100 layers of HKUST-1 grown on the MMBA-UDT surface showing (G) a gapped SURMOF distribution. F: X-ray diffractogram showing bulk crystallinity of gapped HKUST-1.

shape as opposed to a rectangular shape for the [111] direction.^[45,46] These triangular crystals are larger, indicating faster growth in the [100] direction. Additionally, the size distributions indicate that HKUST-1 mainly grows perpendicular to the substrate surface, thereby creating isolated crystals representing bulk crystal properties, making these systems excellent for guest-host interaction studies.

3.2.3 MIXED METAL-ORGANIC FRAMEWORK SURFACE

By combining two thiols with distinct chemistries, we effectively covered the surface with two chemical functionalities, namely with SURMOF growth-promoting thiols and growth-passivating thiols. Following the same procedure, one could also aim to create a surface where both thiols are growth-promoting, yet for different SURMOF species. If successful this would create a bifunctional SURMOF surface. In order for this to work, a combination of thiols would need to be chosen in such a manner that each thiol promotes the growth of only one SURMOF. Another MOF reported (and shown in Figure 3.3d-h) to be SURMOF compatible is ZIF-8^[42,47]. This MOF is typically grown on -OH terminated thiols, yet this would be an unsuitable combination as HKUST-1 also grows on -OH groups^[44]. However, an inspection of the 2-methylimidazole linker structure suggests that an aromatic pyridine thiol should be highly effective for SURZIF-8 growth.

Therefore, a combination between 4-mercaptopyridine (MPyr) and MHDA was chosen for the synthesis of a mixed SURMOF^[48,49]. PiFM analysis of the MPyr-MHDA covered surface showed distinct chemical identities, as well as similar aromatic thiol domain areas and surface roughness to the MMBA-UDT surface (Figure 3.5a-d). The distribution of species over the surface was visualized using PCA and clustering analysis based on chemical similarities between spectra (Figure 3.5d). Some, but less than for MBA, aggregation of MPyr was observed, which can be ascribed to the varying degree of ring strain experienced by both thiols. These results underline that for the thiol mixes reported in this work, π -stacking, rather than headgroup-based solubility, was the main force creating the larger domains.

After deposition of 10 layers of both MOFs, the resulting surface was analyzed with PiFM (Figure 3.5e-h). AFM images showed MOF/ZIF grains of different morphologies (triangular/hexagonal, respectively) and the IR spectra of these grains were chemically distinct: the triangular grains show IR bands typical for HKUST-1^[18], whereas the octahedral grains show IR bands corresponding to ZIF-8^[50] (Figure 3.5f). As PiFM has a probing depth of approximately 30 nm, the results indicate that the two frameworks grew on individual domains, and not on top of the previously grown SURMOF.^[12,51] Thus, a surface exposing two types of SURMOF, i.e., a bifunctional SURMOF, was synthesized.

FIGURE 3.5: PiFM measurements on (mixed SURMOF grown on) mixed thiol surfaces. A: AFM image of the MPyr-MHDA surface. B: PiFM spectra corresponding to markers shown in (A). C: Domain size distribution of the two thiols shows the creation of domains and some thiol aggregation. D: PCA and clustering analysis showing the distribution of the aromatic (red), aggregated aromatic (orange), and aliphatic (green) species on the surface. E: AFM image of ZIF-8/HKUST-1 grown on MPyr/MHDA. Two grain morphologies suggest the presence of two SURMOFs. F: PiFM spectra corresponding to markers shown in E. The spectra show features typical for HKUST-1 (top) and ZIF-8 (bottom). G: Domain size distribution showing SURMOF areas similar to thiol areas in (C). H: PCA and clustering analysis showing the distribution of SUR-HKUST-1 and SUR-ZIF-8.

Macroscopically, these SURMOFs display a singular bulk characteristic (hydrophilic, hydrophobic) as was shown by rudimentary contact angle measurements (Figure 3.6).^[52] Yet on the nanoscale, to the best of our knowledge, site-specific behavior was unraveled for the first time by the development of real-time *in situ* PiFM nano-spectroscopy. Using this *in situ* PiFM toolbox, we present a nano-spectroscopic case study for the bifunctional SURMOF surface to show the amphiphilic character of the mixed MOF surface.

FIGURE 3.6: Rudimentary contact angle measurements showing hydrophilicity of the HKUST-1 SURMOF (top) and hydrophobicity of the ZIF-8 SURZIF (bottom). Drops of water were deposited on HKUST-1 SURMOF and SURZIF-8. These measurements show the hydrophilic nature of HKUST-1 and the hydrophobic nature of ZIF-8.

Under ambient measurement conditions, the PiFM IR spectra on the HKUST-1 domains show significant interference from water (Figure 3.7a, 3.7b, 1st trace). To remove water, we performed purging cycles in which we fully evacuated the sample compartment and backfilled it with dry N₂ (Figure 3.8). Cycling initially revealed reduced water interference and ultimately exposed the IR spectrum of HKUST-1 without water on its surface (Figure 3.7b, 2nd trace). In contrast, the PiFM spectrum of ZIF-8 domains in air showed little water interference (Figure 3.7b, 3rd trace), and subsequent vacuum/purge cycling experiments did little to change the IR spectrum of ZIF-8 (Figure 3.7b, 4th trace). To further prove the distinct behavior of the two nanosized domains of the bifunctional film, we backfilled the sample compartment with 1000 ppm D₂O (Figure 3.7c). Whereas this change in the environment did not affect the IR spectrum of ZIF-8, the IR spectrum of HKUST-1 presented two new peaks indicating D₂O adsorption (Figure 3.7c,d).

To study the behavior of the hydrophilic SURMOF (HKUST-1) material in D₂O vapor in more detail, we performed *in situ* hyperspectral (hyPIR) measurements which started in N₂ (post vacuum/N₂ purging cycles) and over the course of 5 hours ended with 9000 ppm D₂O in the sample chamber by flowing 3 vol.% D₂O/N₂ at 25 mL/min (Figure 3.8). During this hyPIR measurement, continually acquired point spectra with a 1 sec time resolution followed gas sorption events on the SURMOF. The resulting D₂O concentration-dependent spectra are plotted in Figure 3.8a.

FIGURE 3.7: Amphiphilic nature of the bifunctional mixed SURMOF (HKUST-1) /SURZIF (ZIF-8) as evaluated with *in situ* Photo-induced Force Microscopy (PiFM). A: AFM image of 10 layers of ZIF-8/HKUST-1 grown on MPyr/MHDA. Markers indicate the location of point spectra taken for HKUST-1 (yellow) and ZIF-8 (red) before and after vacuum/N₂ purge cycles. B: IR spectra show the removal of ad-/physisorbed water on the ambient HKUST-1 and the water-independent IR spectrum of ZIF-8. C: IR spectra of both species after the introduction of 1000 ppm D₂O, and D: Zoom-in IR spectra of the two areas marked in (C) showing the appearance of new peaks in the HKUST-1 spectrum.

The *in situ* spectra show the appearance and intensity increase of two IR bands over time at 890 and 1725 cm⁻¹ (gray boxes), corresponding to molecularly adsorbed D₂O and deuterated carboxylic acid, respectively, indicating clear guest-host interactions.^[53,54] These findings correspond to previous reports that have shown that HKUST-1 provides two types of sites for water sorption, namely the paddlewheel's axial coordinatively unsaturated sites for the molecular sorption of water, and the paddlewheel's equatorial sites for dissociative sorption of water leading to the breaking of the metal-carboxylate bond and the formation of a paddlewheel defect.^[29,54,55] To characterize this guest-host interaction further, we have determined the ratios of several IR bands over time (Figure 3.8b-d).

FIGURE 3.8: *In situ* Photo-induced Force Microscopy (PiFM) of D_2O sorption on SURMOF HKUST-1. **A:** *In situ* PiFM spectra during D_2O sorption with increasing D_2O concentration. Clear changes in the IR absorptions were observed in the regions indicated by colored boxes. Peak ratios of spectra in (A) show (B): Creation of free deuterated carboxylic acid, as well as (C): Framework desaturation, and (D): D_2O sorption isotherms for (bottom) averaged HKUST-1 and (top) defective paddlewheel sites. **E:** Proposed mechanism of defect formation upon D_2O adsorption on HKUST-1, **F:** Spatiotemporal visualization of defect formation (indicated by red, 1 sec/pixel) using principal component analysis (PCA) and clustering of time-based sections of hyPIR images upon D_2O sorption.

The ratio plotted in Figure 3.8d (dark blue) represents the average gas sorption isotherm of D₂O on the SURMOF surface. However, since adsorption on defects is expected to be favored, PCA and clustering was performed on the *in situ* hyPIR data to cluster spectra by spectral similarity, that is, chemical variation of the host (Figure 3.9). Therefore, pixels grouped together in a cluster show similar behavior during D₂O flow. The PCA image of the *in situ* hyPIR measurement in Figure 3.10 a shows a gradient over time, signaling a change in the spectrum over time. This change is initiated by D₂O flow. We studied the averaged spectrum of the clusters used in PCA (Figure 3.9b). In this analysis, cluster 1 (sand-colored) described the initial HKUST-1 in N₂, and cluster 6 (green) described HKUST-1 post-sorption. The clusters in between (2-5) describe the response to D₂O, where the lower the cluster number, the faster the response (e.g. pink). Of the spectra of these clusters, we calculated the ratio between a known defect vibration (1625 cm⁻¹) and the pristine paddlewheel vibration (1640 cm⁻¹, Figure 3.9c). This revealed that surface regions exhibiting a higher concentration of defects show a faster response to D₂O.

To further study D₂O sorption on defects and to allow for the comparison of site-specific behavior as a function of D₂O concentration, we divided the hyPIR measurement into time-based sections of 18 x 128 pixels and clustered these sections. We used both the average spectrum of each section as well as PCA and clustering result of each of the sections to compare the surface-averaged and defect-specific isotherms. In each section, the 890/1372 cm⁻¹ ratio was calculated for the clusters showing the highest defect concentration. As a result, Figure 3.8d shows the site-specific gas isotherms displaying the difference in uptake kinetics between the average HKUST-1 surface and the nanoscale regions of defect-rich HKUST-1.

FIGURE 3.9: Principal Component Analysis (PCA) and clustering analysis of the hyperspectral (hyPIR) measurement of the HKUST-1 surface in D_2O flow. PCA and clustering was performed on the full hyPIR image to analyze sorption kinetics, as well as on concentration-dependent sections of the image, to analyze site-specific gas sorption isotherms. Spectra of clusters used for analysis are shown, colors correspond to clusters in images.

TABLE 3.1: Table showing the increase in approximate defect site density of the HKUST-1 surface as a result of D₂O sorption. Percentages were calculated by taking the ratio between pixels of defect clusters and pixels of pristine clusters of the sectioned hyPIR image.

Section / D ₂ O pressure	Defect cluster coverage percentage
1 / 1500 ppm	2%
2 / 3000 ppm	9%
3 / 4500 ppm	7%
4 / 6000 ppm	18%
5 / 7500 ppm	21%
6 / 9000 ppm	23%
7 / 9000 ppm	25%

Additionally, we studied the effect of D₂O adsorption on the integrity of the HKUST-1 framework. We observed the creation of free deuterated carboxylic acid over time (Figure 3.8c), which suggested the hydrolysis of HKUST-1 paddlewheels made up of coordinated acids (Figure 3.8e). This is in line with mechanisms previously proposed in literature.^[29,54] However, using our novel *in situ* PiFM approach in combination with isotope labelling we were able to provide direct (nanoscale) evidence for this mechanism. To further study paddlewheel hydrolysis, we calculated the ratio between the aromatic breathing vibration and the coordinated acid vibration, which showed a clear trend of framework destruction upon D₂O sorption (Figure 3.8c). As we hypothesized that this framework destruction led to the formation of new defects, we have used PCA and clustering to map the location of defect-rich areas over the SURMOF surface, resulting in visual confirmation of the creation of faulty paddlewheels as a result of (heavy) water adsorption (Figure 3.9f). Furthermore, quantification of this analysis showed an approximate increase in defect density from 2% to 25% (Table 3.1), whereas inspection of the sections additionally indicated the non-random formation of propagated defects.^[56] Notably, this disintegration of the HKUST-1 paddlewheels did not lead to extended morphological change, underlining the importance of (nano-)spectroscopy in guest-host interaction studies (Figure 3.10).

FIGURE 3.10: AFM images of the area used for the in-situ PiFM measurement before- and after D_2O flow. Note that the spent image is taken in lower resolution (128x128 px instead of 256x256 px). In the AFM images, no structural changes are visible, yet PiFM showed strong chemical changes due to D_2O flow. This underlines the relevance of in-situ nano-spectroscopic tools for the analysis of SURMOFs during gas-sorption.

3.3 CONCLUSIONS

We have demonstrated in this Chapter the use of *in situ* nanoscale IR spectroscopy to investigate guest-host interactions within MOF and ZIF thin-films. We highlighted the sensitivity of the developed method by mapping mixed thiols SAMs, which were used as templates for SURMOF and SURZIF growth through the layer-by-layer synthesis. The resulting amphiphilic HKUST-1/ZIF-8 surface was analyzed to reveal individual nanometer-sized hydrophilic and hydrophobic domains. Furthermore, the hydrophilic HKUST-1 material was studied to show enhanced D_2O sorption on existing defective paddlewheel sites, as well as D_2O induced defect formation in real-time. Future research will focus on expanding the number of probe gases applied to *in situ* PiFM, such as NO and CO, for gas sorption, and ultimately reactive gases for catalysis research on the nanoscale.

3.4 EXPERIMENTAL SECTION

3.4.1 MATERIALS SYNTHESIS

Chemicals: The following chemicals were used: 16-mercaptopentadecanoic acid (MHDA, 99%, Sigma-Aldrich), 4-mercaptopentanoic acid (MBA, 99%, Sigma-Aldrich), 11-undecanethiol (UDT, 98%, Sigma-Aldrich), 4-(mercaptomethyl)benzoic acid (MMBA, 98+%, Sigma-Aldrich), 4-mercaptopyridine (MPyr, 95%, Sigma-Aldrich), ethanol (99.5%, Acros), copper(II) nitrate trihydrate (99+%, Sigma-Aldrich), trimesic acid (95%, Aldrich), zinc(II) nitrate hexahydrate (98%, Sigma-Aldrich), 2-methylimidazole (99%, Sigma-Aldrich), methanol (99.9%, Sigma-Aldrich). Substrates of 60 nm Au on Si, with a 5 nm Ge adhesion layer were provided by AMOLF.

Substrate preparation: Gold wafers were cleaned in three successive steps. They were rinsed with ethanol, dried in flowing N_2 (4 bar), and cleaned using UV-ozone for 20 min. The clean substrates were immersed in a 1 mM ethanolic SAM solution for 48 h. When 1:1 mixtures of SAMs were used in solution, the total concentration was kept at 1 mM. After functionalization, substrates were rinsed in flowing ethanol before drying with N_2 (4 bar).

MOF deposition: HKUST-1 SURMOF was synthesized according to our previously described protocol^[18]. ZIF-8 Layer-by-Layer (LbL) parameters for the Successive Ionic Layer Adsorption and Reaction (SILAR) setup were: a dipping time of 2 min in both the methanolic metal- (10 mM) and linker (20 mM) solution, respectively. After dipping, the substrate was stirred in methanol for 3 s at 150 rpm.

3.4.2 MATERIALS CHARACTERIZATION

X-Ray Diffraction (XRD) measurements were performed on a Bruker D8 in grazing incidence diffraction geometry. Diffractograms were recorded in a 2θ range of 4-20 degrees, the incident angle was 0.3 degrees. A copper source was used.

Grazing-Incidence Attenuated Total Reflection (GI-ATR) measurements were performed using a grazing angle ATR VeeMAX 2 accessory (Pike technologies) in a PerkinElmer Spectrum 1 spectrometer with an MCT detector. The Ge crystal had a set angle of 65 degrees. Spectra were acquired by averaging 50 spectra in the range 4000-650 cm^{-1} with a resolution of 4 cm^{-1} . The infrared beam was vertically polarized, the incident angle was 80 degrees, the spectrometer (optics and sample compartment) was purged with nitrogen prior to measurements. Clean gold wafers were used as a background.

Photo-induced Force Microscopy (PiFM) measurements were performed using a VistaScope from Molecular Vista, Inc. NCHAu25-W AFM tips (Force constant 10-130 N/m, Resonance frequency > 320 kHz) coated with 25-70 nm of gold by Molecular Vista were used in dynamic non-contact mode. A driving amplitude of 2 nm was used, and a frequency sweep of the cantilever was performed prior to measurements to determine cantilever resonance frequencies. After this sweep, detection of topography was set to the second mechanical eigenmode resonance (f_1), and photo-induced signal detection was set to the first mechanical eigenmode resonance (f_0). Determination of the first mechanical mode was repeated after approaching the tip to the surface. By using independent eigenmodes, topography and PiFM signal could be detected simultaneously. Using a cantilever setpoint between 80-85%, 256x256 pixel topography images of varying sizes were collected. The midIR source was a Block Engineering tunable quantum cascade laser (QCL) providing a working range of 1965-785 cm^{-1} . Averaged IR spectra were taken in sideband mode (pulse modulation: $f_m = f_1 - f_0$) with a pulse duration of 32 ns, and with a spectral resolution of 1 cm^{-1} . Power levels (iris set between 55-90°, <1 mV of most intense peak during engaged first

eigenmode frequency sweep) and acquisition times (between 0.1-1 sec) were varied between measurements in such a way that with minimal power, sufficient signal was collected ($>300\ \mu\text{V}$ of most intense peak in engaged first eigenmode frequency sweep). The approximate lateral resolution of IR spectra was $<10\ \text{nm}$. PiFM data was analyzed using SurfaceWorks software.

Hyperspectral Photo-induced Infrared (hyPIR) images of 128×128 pixels were measured *ex situ* and *in situ*. Scanning speeds were adapted for spectrum acquisition times. For the *in situ* measurements, a vacuum cell was placed over the AFM head and sample stage. A vacuum pump and a three-way valve with lines to dry N_2 , and N_2 flowing through a D_2O saturator were connected. Prior to *in situ* measurements, the vacuum cell was evacuated and backfilled with dry N_2 three times. *In situ* hyPIR measurements were set for 5 h. The measurement started in N_2 and gradually D_2O was introduced. We flowed 3 vol.% $\text{D}_2\text{O}/\text{N}_2$ at 25 mL/min, reaching 9000 ppm in the sample chamber.

Principal Component Analysis (PCA) and k-means clustering was used to analyze the hyPIR images. Prior to PCA and clustering, the data was normalized by sum image division. In the TXM-XANES-Wizard^[57], the data was mean-centered prior to PCA and k-means clustering. The appropriate number N of principal components (PCs) was selected upon inspection of scree plot, eigenspectra, and eigenimages. K-means clustering was then performed in N -dimensional PC space using twice the number of clusters ($2 \times N$). The result of k-means clustering was subsequently refined gaussian mixture modeling (GMM) using expectation maximization (EM). This provided a class membership value (between 0 and 1) of each pixel to each cluster. The spectrum of each cluster was then determined as the weighted average of all pixels using this class membership. This method thus efficiently pools pixels based on spectral similarity (and not on spatial correlation) and provides excellent estimates for the most different spectra present in the data. The *in situ* hyPIR images were divided into 7 time-based domains. Of each of these sections, the averaged IR spectrum was used to describe average D_2O sorption over time/ D_2O concentration. These spectra were used to construct Figure 3.4a-d. Each of these sections was clustered using PCA to study the D_2O sorption behavior on defect sites at known D_2O concentrations. These clustered sections were used to construct Figure 3.4b, f.

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4

VISUALIZING STRUCTURE SENSITIVITY IN GAS SORPTION AND CONVERSION ON METAL- ORGANIC FRAMEWORKS WITH *IN SITU* NANO- INFRARED SPECTROSCOPY

4. ABSTRACT

Many catalytic processes depend on the sorption and conversion of gaseous molecules on the surface of (porous) functional materials. These events often preferentially occur on specific, undercoordinated surface sites. The fraction of active versus non-active surface sites, and thereby material functionality, can vary due to material geometry, a phenomenon known as structure sensitivity. However, so far, the deduction of site-specific gas sorption/conversion behavior for porous functional materials has been limited due to a lack of nanoscale *in situ* characterization techniques. Here we show the combination of *in situ* Photo-induced Force Microscopy (PiFM) with Density Functional Theory (DFT) calculations to study the sorption and conversion of formaldehyde on ZIF-8 with nanoscale resolution. With this methodology, we observed structure sensitive formaldehyde sorption on crystal corners, edges, and facets in unprecedented detail. Furthermore, we found that due to complexation, strongly adsorbed formaldehyde was not converted on pristine ZIF-8. However, after the incorporation of defective linkers, structure sensitive conversion of formaldehyde through a methoxy- and a formate mechanism was found. Additionally, *in situ* PiFM allowed us to visualize non-homogenous intra-crystal plane sorption and conversion behavior on the nanoscale. With this research, we showcase the high potential of *in situ* PiFM for structure sensitivity studies on porous functional materials.

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4.1 INTRODUCTION

The performance of a functional material is often determined by only a small percentage of its surface sites and their atomic configuration. This phenomenon, known as structure sensitivity, describes the relationship between exposed crystal surfaces and rate of conversion and is well known in the field of heterogeneous catalysis.^[1–3] This phenomenon occurs when distinct surface sites possess a different reactivity.^[4] Changes in dispersion between surface sites thus result in a change in overall activity.^[5]

Structure sensitivity is often described for supported metal nanoparticle catalysts, where the variation of metal nanoparticle size results in the exposure of a different fraction of active surface sites, leading to size-dependent performance (Figure 4.1a).^[6] Different types of structure sensitivity apply to specific chemical reactions. For example, in type II structure sensitivity, the conversion is limited by the rate of π -bond activation, which specifically occurs over highly active step-edge or kink sites.^[7] These sites require ensembles of atoms, and their fraction increases with NP size, up to a material-dependent maximum. Similarly, type I structure sensitivity describes the decrease in intrinsic rate with NP diameter due to a loss of isolated unsaturated sites for σ -bond activation.^[4] Furthermore, for other chemical reactions, this size-dependency is absent, leading to the concept of structure insensitivity (type III).^[8]

FIGURE 4.1: Schematic describing structure sensitivity in a) supported nanoparticles (NPs), and b) in porous functional materials. a) Three general types of structure sensitivity are recognized for supported NPs, where a relationship between intrinsic conversion rate and NP size is found based on which type of bond (sigma/pi) needs to be activated during the rate-determining step. Adapted from ^[1] b) Structure sensitivity in, e.g., ZIF-8 describes the crystal plane-dependent sorption and conversion energies of adsorbates.

While for dense, non-porous metal nanoparticles, it is relatively easy to distinguish between bulk atoms and the wide variety of distinct surface atoms, this distinction is more difficult for porous functional materials, such as zeolites and metal-organic frameworks (MOFs), due to their inner porosity (Figure 4.1b).^[9,10] However, analogous to metal nanoparticles, it

is often observed for porous functional materials that their functionality is concentrated on their outer surface and not in their inner porosity.^[11] As a result, some evidence of similar structure sensitivity behavior for porous functional materials can be found in literature.^[12–14] For example, Pang and coworkers showed with *ex situ* Scanning Electron Microscopy (SEM) analysis that for ZIF-8 crystals that were exposed to acidic SO₂ gas, the external surface of the (100) facet showed higher stability than the (110) facet.^[15] However, this *ex situ* technique was unable to describe the interaction between the (often highly reactive) high-energy planes, such as edges and corners during gas exposure, to pinpoint highly active sites during gas sorption and reaction.^[16]

Additionally, in a study performed by Chen *et al.*, structure-directing agents were used for the design of ZIF-8 crystals preferentially expressing (110) or (100) facets.^[17] In this manner, the superior performance of the ZIF-8 (100) plane over the (110) plane in a catalytic Knoevenagel condensation reaction was shown. Using X-ray Photoelectron Spectroscopy (XPS) analyses, they linked the superior performance of the (100) facet to the higher density of Zn²⁺ moieties on the surface. However, limited in their approach due to the spatial resolution of the used spectroscopic techniques, this study was unable to investigate the potentially large influence of not just the crystal facets but also the edges and corners.

Specifically, these high-energy edge and corner crystal planes often present highly important sorption and/or conversion sites within functional materials.^[18] The undercoordinated nature of these planes is often mimicked in defect engineering approaches.^[19,20] For example, through the incorporation of defective linkers, undercoordination of metal sites can be achieved. As a result, these metal sites can behave as Lewis acid sites with potentially increased activity towards gas sorption and/or conversion.^[21,22] The localized integration of these defects can be characterized by highly sensitive techniques such as High-Resolution Transmission Electron Microscopy (HRTEM), Scanning Electron Diffraction (SED), or Atom Probe Tomography (APT).^[23–26] However, to study the nanoscale guest-host interaction between (defective) surface sites of functional porous materials, novel surface sensitive *in situ* techniques are required.^[27–32]

Traditionally, structure sensitivity studies have been limited to surface science techniques, such as Scanning Tunneling Microscopy (STM) or Low-Energy Electron Diffraction (LEED), as it can be applied to (low index) single crystal samples of metals.^[33,34] However, STM operates under strict sample and condition limitations, known as the materials- and pressure gap, respectively. For example, the materials gap restricts measurements to conductive single crystal model systems only, thereby hindering the extrapolation of its results to complex 3D materials and preventing analysis of porous functional materials with low conductivity altogether.^[35,36] Additionally, the pressure gap limits STM operation to vacuum conditions, several orders of magnitude below industrial conditions, thereby often failing to describe

guest-host interaction at relevant conditions.^[37] Bridging of these gaps was achieved for metal NPs in, for example, the Fischer-Tropsch and Sabatier reaction by performing bulk (IR) studies on metal NPs with a highly defined size distribution at industrial conditions.^[6,16,38,39]

However, when applying bulk spectroscopic techniques, such as infrared spectroscopy, dispersion in bulk/surface atoms will result in a loss of information on porous functional material performance. One of the first efforts made to bridge this gap has been performed by Roeffaers *et al.*, who showed with *in situ* Single-Molecule Fluorescence (SMF) microscopy that a single edge on an otherwise pristine crystal facet could largely influence the performance of a layered double hydroxide.^[40] During the catalytic conversion of individual organic molecules, they found that while transesterification occurred all over the large (0001) terrace, the hydrolysis of the same molecule only occurred on a (1010) edge present within the (0001) terrace. Using conventional bulk techniques, this edge plane would have been overlooked, thereby leading to an incorrect interpretation of the performance of the (0001) facet. Whereas this SMF technique is an excellent approach, it does need fluorescent molecules, which limits its application towards the understanding of small molecules' sorption and activation.^[41]

FIGURE 4.2: Experimental approach. To study nanoscale guest-host interaction, we a) synthesized (defect-engineered) surface-anchored ZIF-8 crystals. b) To these crystals, we applied *in situ* Photo-induced Force Microscopy (PiFM), a nano-infrared technique with a spatial resolution down to 8 nm, in the presence of formaldehyde vapor. With this approach, we identified preferential sorption and conversion sites on ZIF-8 crystals.

Therefore, in this Chapter, we describe the use of *in situ* Photo-induced Force Microscopy (PiFM), in combination with Density Functional Theory (DFT) calculations, to unravel structure sensitivity in gas sorption and conversion on the surface of a MOF material in unprecedented detail (Figure 4.2b).^[42] We used surface-anchored ZIF-8 crystals with well-defined crystal plane termination for nanoscale guest-host investigations with formaldehyde, a Volatile Organic Compound (VOC) indoor pollutant (Figure 4.2a).^[43–46] Using this approach, we found that gas sorption preferentially occurred on high index crystal planes, such as corners and edges, via chemisorption on surface ZIF-8 ligands. Additionally, we found that the incorporation of defects (i.e., pyrrole ligands) resulted in defect clusters on the

ZIF-8 surface, which led to the structure sensitive conversion of formaldehyde via two distinct mechanisms evidenced by the *in situ* PiFM technique. Overall, we found the sorption and conversion performance of the ZIF-8 crystals to be heavily dependent on structure sensitivity phenomena, and we expect the gathered insights and approach to be highly relevant for a wide range of micro- and nano-structured functional materials.

4.2 RESULTS AND DISCUSSION

Surface anchored ZIF-8 microcrystals with well-defined facets were synthesized through a Layer-by-Layer (LbL) synthesis.^[42,47] Both pristine and defective ZIF-8 crystals were synthesized (Figure 4.3a, c-i). Pristine crystals were synthesized using zinc nitrate and 2-methylimidazole linkers, and defect-engineered ZIF-8 crystals were produced through the addition of 10% defect linker (pyrrole) in the reaction mixture (Figure 4.2a). Both types of crystals express six crystal plane terminations, namely (100) and (110) facets, (210) and (211) edges, and (111) and (310) corners (Figure 4.3d).^[48] While the incorporation of defect linkers did not affect the geometry of the ZIF-8 crystals, it did alter the plane expression ratios (Figure 4.3d-i). AFM images of several pristine and defective crystals show the increase in (100):(110) facet aspect ratio with defect linker incorporation. This result indicates that the incorporation of defects changes the plane-energies in a non-equal manner. This change in plane energies may, for example, be due to strain relaxation of the surface terminations (*vide infra*).^[49]

The synthesized pristine and defect-engineered ZIF-8 crystals were used for nanoscale guest-host interaction studies using *in situ* Photo-induced Force Microscopy. With this technique, we were able to record hyperspectral (4D) images of the crystals composed of a full infrared spectrum (1D) on every pixel (3D: x, y plane, and z height) during stepped gas sorption from 0-40 mbar of formaldehyde (16 vol.% in H₂O). The crystal-averaged *in situ* IR spectra show the sorption of formaldehyde on the ZIF-8 surface. This adsorption is observed through the increase of IR bands at 1280, 1200, and 895 cm⁻¹, corresponding to $\delta_{\text{CH}_2, \text{rock}}$, $\delta_{\text{CH}_2, \text{wag}}$, and $\nu_{\text{C-O}}$, respectively.^[50,51] The $\nu_{\text{C=O}}$ vibration of physisorbed formaldehyde was not observed as the C=O double bond was broken due to strong chemisorption of the formaldehyde carbon atom to ZIF-8 surface nitrogen atoms (*vide infra*).

FIGURE 4.3: Highly symmetrical ZIF-8 crystals express well-defined crystal planes for both (a) pristine and (c) defective crystals. b) Six crystal planes are visible, namely (100) and (110) facets, (210) and (211) edges, and (111) and (310) corners. Aspect ratios were calculated for d-f) pristine ZIF-8 crystals and g-i) defective ZIF-8 crystals. With defect linker incorporation, the aspect ratio changed in favor of (100) facet expression.

To study the sorption behavior as a function of crystal planes, we masked areas of the hyperspectral image based on morphology data. Subsequently, for each crystal plane, we created contour plots displaying their *in situ* nano-IR spectra (4.5a-f). This showed the distinct behavior of the crystal planes with increasing formaldehyde pressure. Each crystal plane showed IR bands describing ZIF-8 characteristics, such as bands at ~ 1590 , 1480 , 1140 , and 990 cm^{-1} corresponding to $\nu_{\text{C=N}}$, $\delta_{\text{arom.}}$, $\nu_{\text{C-N}}$, and δ_{NH} vibrations, respectively. With pressure, each of the planes shows the appearance $\delta_{\text{CH}_2, \text{rock}}$, $\delta_{\text{CH}_2, \text{wag}}$, and $\nu_{\text{C-O}}$ vibrations of formaldehyde at 1280 , 1200 , and 895 cm^{-1} , respectively. However, the pressure at which these formaldehyde bands appeared differed for the different crystal planes. For example, these contour plots showed that the (310) corner demonstrated a markedly faster response to formaldehyde than the (211) edge, as well as the (110) facet, which demonstrated that the sorption of formaldehyde is, in fact, structure sensitive. The response pressures for the δ_{CH_2} ,

$\delta_{\text{CH}_2, \text{wag}}$ vibrations were plotted as a function of the crystal plane in Figure 4.5g. From this plot we observed the trend that sorption occurs first on corners, then edges, and then facets in the following order: (310) > (111) > (210) > (211) > (110) ~ (100).

FIGURE 4.4: a) Surface-averaged PiFM spectra over increasing formaldehyde pressure showed the increase of three infrared bands indicating gas sorption. b) Gas sorption occurs by breaking the C=O bond and by forming a covalent C-N bond between the carbon atom of formaldehyde and a nitrogen atom of the linker molecule. Due to this chemisorption, $\nu_{\text{C-O}}$ and δ_{CH_2} vibrations were observed, as well as an absence of $\nu_{\text{C=O}}$ vibrations.

To be able to link gas sorption behavior to specific (undercoordinated) surface sites, an accurate description of the surface termination of ZIF-8 planes is required. Using DFT calculations, we have modeled three of the crystal surfaces, namely the (100) and (110) facet planes and the high index (310) corner plane (Figure 4.6a-c). These facet planes were chosen to study geometry effects between two large surface area, low-energy facets. Additionally, we chose these facets to study why defect linker incorporation resulted in a change in (100):(111) aspect ratio. Lastly, the corner plane was selected to compare sorption behavior differences between low energy planes (facets) and high energy planes (corner).

As ZIF-8 is a highly symmetrical crystal, surface termination options are limited, and surfaces can approximately be described by the expressed metal-linker ratio. Nonetheless, DFT calculations resulted in three planes with distinctly individual surface chemistry. For example, DFT predicted the presence of partial charges on the (110) and (310) planes (Figure 4.6b, c). Thermodynamic calculations computed the surface energies of the planes to be 10.11, 12.3, and 13.17 meV/Å² for the (110), (100), and (310) plane, respectively, confirming the more reactive nature of higher index planes.^[52]

FIGURE 4.5: Experimental observations of structure sensitive gas sorption. Contour plots show the change in the IR spectrum for a, b) facets c, d) edges and e, f) corner planes. g) From the contour plots, response pressures of these crystal planes were found, highlighting the structure sensitive sorption of formaldehyde. These response pressures were explained via the use of DFT calculations, showing crystal plane-dependent binding conformations and energies for formaldehyde.

By introducing formaldehyde into the DFT calculations, we were able to predict binding energies between formaldehyde and the individual crystal planes and thereby rationalize experimental findings (Figure 4.6d-f). Via this method, we found that upon adsorption, the formaldehyde forms a complex with the ZIF-8 surface sites. These complexes are highly stable, as was evidenced through their calculated binding energies ($E_{\text{ads}} = -99, -143, \text{ and } -177 \text{ kJ/mol}$ for the (100), (110), and (310) plane, respectively). The formaldehyde molecules chemisorb by forming a carbon adduct with a nitrogen atom from the linker.^[11,53] Furthermore, the geometry of the (110) and (310) planes allows for an additional bond between the oxygen atom of formaldehyde and the zinc metal center of ZIF-8, thereby stabilizing the complex further. These calculations thereby explain the absence of molecularly adsorbed formaldehyde in the infrared spectra, as well as preferential inter-facet sorption behavior.

FIGURE 4.6: Density Functional Theory (DFT) models of the a) (100), b) (110), and c) (310) crystal planes show the plane-dependent surface terminations of ZIF-8. The calculated energy of the (310) plane showed the higher-intensity nature of the corner plane. d-f) shows that calculated adsorption energy of formaldehyde on the (100), (110), and (310) planes. This shows the predicted chemisorption of formaldehyde by the formation of a $\text{C}_{\text{FA}}\text{-N}_{\text{ZIF}}$ adduct. Additional stabilization of formaldehyde through an $\text{O}_{\text{FA}}\text{-Zn}_{\text{ZIF}}$ adduct was found for (110) and (310) planes.

So far, it has been assumed that the (structure sensitive) sorption of sorbates occurred on uniform and defect-free crystal planes. However, even in crystallographically pristine crystals, non-homogeneous behavior can be present.^[54] Therefore, we studied intra-plane heterogeneities in gas sorption behavior (Figure 4.7a). To this end, we recorded a 500x500 nm² image of a crystal in formaldehyde, in which we mapped the infrared intensity of the 1200 cm⁻¹ band, corresponding to chemisorbed formaldehyde. A formaldehyde pressure of 25 mbar was used. Previous plane-averaged *in situ* analysis showed that this pressure was sufficient for formaldehyde sorption on corners and edges but insufficient for sorption on facets (Figure 4.5g). As a result, the infrared map revealed a strong visual response to formaldehyde on the edges and corners. However, more strikingly, it revealed that the crystal facets displayed clear non-homogeneous behavior towards gas sorption: nano-islands within the (100) and (110) planes showed sorption of formaldehyde.

These nano-islands observed in pristine ZIF-8 microcrystals are indicative of underlying intra-facet defect structures or alternative plane terminations. Size analysis of these domains gave average areas of $118 \pm 95 \text{ nm}^2$ within the (110) facet and $240 \pm 216 \text{ nm}^2$ within the

(100) facet, thereby showing the clustered nature of these extended domains. IR mapping of the same area, but with the laser tuned to an aromatic vibration ($\nu_{\text{C=N}}$, 1590 cm^{-1}) of the ZIF-8 framework, showed an inverted image. This highlighted the unresponsive nature of the predominant surface area of the facets as a result of shielding by formaldehyde adsorbates while simultaneously negating topography-induced instrumental effects (Figure 4.7b). This was confirmed further by IR point spectra taken on-, and in between, these nano-islands (Figure 4.7d). These spectra showed reproducible ZIF-8 features for both types of locations but only showed adsorbed formaldehyde signal ($1280, 1200 \text{ cm}^{-1}$) in spectra taken on the nano-domains.

FIGURE 4.7: Nanoscale visualization of non-homogeneous crystal plane chemistry. a) An infrared map tuned to an adsorbed formaldehyde band showed the presence of nanoislands within the facets. b) An infrared map tuned to a ZIF-8 framework vibration showed an inverted image. c) These nanoislands were found to correspond to high energy surface terminations found through DFT calculations. d) Point spectra taken on/off these nanoislands (markers in (a) and (b)) show non-homogenous sorption behavior.

To understand the reason for such localized signals, we performed further DFT calculations, looking deeper into the surface structure of the ZIF-8 facets. These calculations revealed that both the (110) and (100) facets possessed two possible surface terminations, a high- and a low energy termination. For example, the (100) facet can present a surface that possesses

characteristics similar to the high energy (310) plane, as well as similar surface energy ($13.6 \text{ meV}/\text{\AA}^2$, Figure 4.7c). Thermodynamics dictate the preferential expression of the low energy termination. However, in the larger crystal facets, some areas of high energy termination can successfully be stabilized. As a result, these high-energy domains show stronger formaldehyde binding energies (-169 versus -99 kJ/mol for the (100) facet) and, therefore, a faster response to VOC vapor.

To further explore the site-specific formaldehyde adsorption, we purposefully incorporated 10% of the pyrrole defect linker in the ZIF-8 crystals (Figure 4.2a, Figure 4.8a). This defect linker was expected to promote the expression of undercoordinated metal centers and thereby yield Lewis acidic sites. Isotope-labeled deuterated pyrrole was used to unambiguously pinpoint the distribution of these defects and correlate their performance, using their spectral fingerprint. To verify defect linker incorporation, we acquired a $200 \times 200 \text{ nm}^2$ hyperspectral image of a defective ZIF-8 crystal in N_2 (Figure 4.8a). Crystal-averaged IR spectra showed the vibrational fingerprint of pyrrole- d_5 by two IR bands at 960 and 885 cm^{-1} , corresponding to the δ_{CD} and $\nu_{\text{C=C}}$, respectively.^[55] By then monitoring these bands as a function of location, we could locate their preferential sites of defect expression and their degree of clustering (Figure 4.8b). Furthermore, by linking these bands to formaldehyde sorption behavior, we could establish site-specific guest-host interactions (*vide infra*).

To visualize defect distribution at the nanoscale, we used Principal Component Analysis (PCA) and clustering of hyperspectral images of defective crystals to group pixels based on spectral similarities (Figure 4.8b). The spectra of the clusters revealed that clustering mainly occurred based on defect concentration, as all spectra showed a largely unchanged ZIF-8 spectrum, yet showed variation in relative δ_{CD} and $\nu_{\text{C=C}}$ band intensities (Figure 4.8c). Therefore, of each of the 7 clusters, we calculated the peak ratio between pristine and defective ZIF-8 vibrations to describe their relative defect concentration (e.g., $1590/885 \text{ cm}^{-1}$). Subsequently, we overlaid the clustered image on the morphology of the ZIF-8 crystal. This resulted in the sectioning of the clustered image into a (100), (110), and (110) facet (Figure 4.8b). From the clustered image, it became clear that all three facets required at least three clusters to accurately describe their surface chemistry. Furthermore, we observed that these clusters showed domain formation similar to the previously shown nano-islands of the pristine crystals. Size analysis of these domains ($116 \pm 76 \text{ nm}^2$, and $240 \pm 215 \text{ nm}^2$ for (100) and (110) facets, respectively) showed area sizes decidedly comparable to the domain areas found in the pristine crystal. Since the clustering occurred based on defect concentration, it can therefore be expected that these domains will express a different defect concentration than the parent facets.

FIGURE 4.8: Defect linker distribution studies of a defective ZIF-8 crystal shown in (a). The box marks the location of the clustered hyperspectral image in b). Using Principal Components Analysis (PCA) and clustering, our hyperspectral dataset was clustered into regions with similar spectral features. These clusters show a variable relative defect concentration calculated through spectral peak ratios (c). Size analysis of the nanoislands in (b) and Figure 4.7a show comparable domain sizes. e) A bubble plot of defect peak ratio as a function of facet where the size of the bubble is proportional to the pixel fraction of that cluster. Facet-averaged defect concentrations are marked with a star. f) For each of the crystal planes, the peak ratios describing their relative defect and Zn-OH concentration were calculated, showing higher defect concentrations for higher energy planes.

We then plotted the relative coverage of the facets with each cluster, together with their spectrally derived relative defect linker concentration, to describe the non-homogeneous character of the facets (Figure 4.8e). This was plotted together with the weighted average of the clusters to give the averaged defect content of each section. In this way, we were able to deconvolute plane-averaged defect concentrations into domains of high/low defect concentration. This indicated that the domains of high energy surface termination were more susceptible to defect incorporation than their low energy counterparts, possibly as a form of strain relaxation.^[49]

Since the intra-plane high energy domains showed a larger affinity for defects, it was of interest to study if this plane energy-based defect incorporation trend also held for the inter-plane surface energies. To this end, we measured a $1 \times 1 \mu\text{m}^2$ hyperspectral image of a defective

crystal in N_2 and calculated the $1590/885\text{ cm}^{-1}$ peak ratios of the individual planes, as well as for the crystal-averaged infrared spectrum (Figure 4.8f). These ratios showed the structure sensitive expression of defect sites, where the (310), (210), (211) planes show an above-average concentration of defects. Further inspection of the hyperspectral data revealed the presence of infrared bands at 840 and 790 cm^{-1} , corresponding to two δ_{OH} vibrations of $Zn-OH_2$ sites (Figure 4.8f).^[56] These bands, that scale with defect concentration (with an exception for the (110) plane), indicate the enrichment of the surface chemistry with strong Lewis acid (Zn^{2+}) and weak base ($Zn-OH$) sites.

FIGURE 4.9: Structure sensitive conversion of formaldehyde over defect-engineered ZIF-8. a) A contour plot of the *in situ*, surface-averaged infrared spectra of defective ZIF-8 shows the presence of formate, di-/poly-oxymethylene (DOM/POM), and methoxy surface species. For the conversion of formaldehyde, a (b) methoxy and (c) a formate mechanism were spectrally derived.

To discern between the effects of facets and defects on the structure sensitive adsorption of formaldehyde (0-40 mbar), we repeated the *in situ* PiFM experiments on the defective crystals (Figure 4.9a). Comparable to the pristine crystals, the rising intensity of 1280 , 1200 , and 895 cm^{-1} bands indicated the sorption of formaldehyde. However, in addition to these, bands arising at 1580 , 1380 , 1320 , 1150 , and 1060 cm^{-1} were found. These bands suggest the presence of different surface adsorbates, such as formates, dioxymethylene (DOM) and polyoxymethylene (POM), and methoxy species, respectively (Figure 4.9a, b).^[51,57] The systematic occurrence of these adsorbates thus showed that defect-mediated conversion of formaldehyde was taking place on the ZIF-8 surface.^[57,58]

We used our spectroscopic findings to propose formaldehyde conversion mechanisms (Figure 4.9b). It was found that two mechanisms operate in parallel on the defective ZIF-8 surface: the methoxy and the formate mechanism.^[59,60] In the methoxy mechanism, the chemisorbed formaldehyde undergoes a Cannizzaro-type reaction to form methoxy, a precursor for methanol and formic acid. In the formate mechanism, the formaldehyde is chemisorbed on the surface in the form of polymers such as dioxymethylene (DOM) and polyoxymethylene (POM), which can undergo an oxidation reaction to form monodentate formates, a precursor to formic acid. Highly relevant for these mechanisms is the hydrolysis of the open zinc sites, which provides an additional source of oxygen that is continuously replenished after conversion by the present water vapor. These findings are in line with bulk IR studies on oxide-supported metal nanoparticles where support oxygen is instrumental to the conversion of formaldehyde.^[61,62]

FIGURE 4.10: a-c) DFT calculations show the lowered adsorption energy of formaldehyde on defective surfaces, thereby lowering the activation energy barrier for conversion. d) A plot comparing the crystal-averaged response pressures of sites with high/low defect concentrations shows that a higher defect concentration does not necessarily equal faster formaldehyde sorption/conversion. e) A plot comparing inter-plane response pressures of surface species shows the structure sensitive conversion of formaldehyde. e) When comparing the (100) facet intra-plane response pressures, the defect sites were shown to exhibit a faster response than the pristine sites.

To rationalize these findings, we compared DFT models of the pristine and defective (100), (110), and (310) surfaces Figure 4.6, Figure 4.10a-c). Due to the undercoordinated metal sites in defective ZIF-8, formaldehyde readily coordinates to the zinc atom via an oxygen adduct. However, when pyrrole is incorporated into the ZIF-8 framework instead of 2-methyl imidazole, its only nitrogen atom is used to form the framework bond. As a result, formaldehyde that coordinates to the undercoordinated zinc atom is no longer stabilized further by an additional $C_{FA}-N_{ZIF}$ adduct due to steric constraints. This leads to lower adsorption energies on the defective planes (-67, -77, and -101 kJ/mol for the (100), (110), and (310) plane, respectively) and thereby expected lower activation energy for conversion.

Consequently, it was found that a higher average concentration of defects did not necessarily equal a faster response to formaldehyde (Figure 4.10d). Using PCA and clustering, we identified defect-rich and defect-poor areas spanning the crystal surface and compared their *in situ* spectra. Both areas displayed guest-host interaction showing the conversion to DOM/POM, formate, and methoxy species, thereby showing defect linker incorporation over the whole crystal surface. Their response pressures were found to be similar, thus highlighting that defects are required for formaldehyde conversion yet do not guarantee faster formaldehyde sorption/conversion.

4 Comparison of the inter-plane response pressures for intermediate surface species confirmed that the formaldehyde conversion, as well as the sorption, remained structure sensitive as a function of crystal plane chemistry with the following order: (310) > (210) > (211) > (110) > (100) (Figure 4.10e, the change in (100):(110) aspect ratio prevented the analysis of the (111) plane). Furthermore, a comparison of the response pressures of the various intermediate species showed that DOM/POM and methoxy species typically form at lower pressures than formate species, suggesting that at lower pressures, the methoxy mechanism is the predominant conversion route. An exception to this trend is found for the (110) facet. While this facet mainly showed surface-averaged behavior, its methoxy species response pressure dips to 25 mbar (compared to 30 mbar for crystal-averaged ZIF-8).

Lastly, we describe the synergy between structure sensitivity and defects (Figure 4.10f). Both in the pristine and the defective crystal, the (100) facet showed the poorest performance. With PCA and clustering, we identified the defective sites within a single (100) plane and compared their sorption behavior to the pristine sites on the same plane plus the facet average *in situ*. This showed that defect sites outperformed their pristine counterparts yet still underperformed in comparison to defect sites in high energy planes. This finding conclusively showed that not all defect sites are equal, which adds a layer to structure sensitivity of formaldehyde sorption and its subsequent conversion on ZIF-8.

4.3 CONCLUSIONS

By using a combination of nanoscale *in situ* PiFM measurements and DFT calculations, we have shown the existence and importance of structure sensitivity in gas sorption and conversion over metal-organic frameworks (MOFs). We have shown that for (defect-engineered) ZIF-8, not only formaldehyde gas sorption preferentially occurs on high energy planes, such as edges and corners ((310) > (210) > (211) > (110) > (100)), but also on localized high-energy domains within low energy facets. These domains display the nanoscale, intra-facet heterogenous functionality within porous crystalline solids. Furthermore, we were able to pinpoint deuterated pyrrole defect clustering and preferential incorporation in high energy planes. Using DFT calculations, we linked these defects to formaldehyde conversion. Structure sensitivity was found to be the predominant factor determining formaldehyde conversion activity, rather than overall defect concentration. We showcased the use of *in situ* PiFM for direct observation of site-specific guest-host interactions, and we expect this approach to be a highly applicable analytical toolbox for establishing structure-performance relationships for (porous) functional materials to guide their rational synthesis.

4.4 EXPERIMENTAL SECTION

4.4.1 MATERIALS SYNTHESIS

Chemicals: The following chemicals were used: 4-mercaptopyridine (MPyr, 95%, Sigma-Aldrich), ethanol (99.5%, Acros), zinc(II) nitrate hexahydrate (98%, Sigma-Aldrich), 2-methylimidazole (99%, Sigma-Aldrich), pyrrole (98%, Sigma-Aldrich), pyrrole-d₅ (98 atom% D, Sigma-Aldrich), methanol (99.9%, Sigma-Aldrich), formaldehyde (16% w/v in H₂O, Thermo Scientific). Substrates of 60 nm Au on Si, with a 5 nm Ge adhesion layer were provided by AMOLF.

Substrate preparation: Gold wafers were cleaned in three successive steps. 1) A photo-resist layer was removed by rinsing the substrate first in acetone, then in deionized water, and lastly in ethanol. 2) The substrates were dried with flowing N₂ (4 bar), and 3) cleaned using UV-ozone for 20 min. These clean substrates were immersed in 2mL of 1 mM ethanolic 4-mercaptopyridine solution for 48 h to functionalize the gold surface with nucleation points for ZIF-8 growth. After functionalization, substrates were rinsed in flowing ethanol before drying with N₂ (4 bar).

MOF deposition: Surface-anchored ZIF-8 (SURZIF-8) crystals were grown on the gold substrate using a Layer-by-Layer (LbL) synthesis.^[63] Automated LbL synthesis was performed using a Holmarc Successive Ionic Layer Adsorption and Reaction (SILAR) setup. Parameters used were: 100 layers of SURZIF-8 were deposited on the substrate by

consecutively dipping the substrate for 2 min in 1 mM methanolic Zn solution and 2 min 2 mM methanolic linker solution. After these deposition steps, the substrate was rinsed in methanol for 3 sec while stirring at 50 rpm. The substrate was not dried in between cycles and was left to dry in air after deposition of 100 layers. During synthesis, solvent was replenished every 30 min. For the defective SURZIF-8 samples, a molar ratio of 10:90 pyrrole(-d₃):2-methylimidazole was used while the overall linker solution concentration was kept constant.

4.4.2 MATERIALS CHARACTERIZATION

X-Ray Diffraction (XRD) was performed on a Bruker D8 in grazing incidence diffraction geometry. XRD patterns were recorded in a 2θ range of 4-20 degrees; the incident angle was 0.3 degrees. A Cu source was used.

Photo-induced Force Microscopy (PiFM) measurements were performed using a VistaScope from Molecular Vista, Inc. NCHAu25-W AFM tips (Force constant 10-130 N/m, Resonance frequency > 320 kHz) coated with 25-70 nm of gold by Molecular Vista were used in dynamic non-contact mode. A driving amplitude of 2 nm was used, and a frequency sweep of the cantilever was performed prior to measurements to determine cantilever resonance frequencies. After this sweep, detection of topography was set to the second mechanical eigenmode resonance (f_1), and photo-induced signal detection was set to the first mechanical eigenmode resonance (f_0). Determination of the first mechanical mode was repeated after approaching the tip to the surface. By using independent eigenmodes, topography and PiFM signal could be detected simultaneously. Using a cantilever setpoint between 80-85%, 256x256 pixel topography images of varying sizes were collected. The midIR source was a Block Engineering tunable quantum cascade laser (QCL) providing a working range of 1965-785 cm⁻¹. Averaged IR spectra were taken in sideband mode (pulse modulation: $f_m = f_1 - f_0$) with a pulse duration of 32 ns, and with a spectral resolution of 1 cm⁻¹. Power levels (iris set between 55-90°, <1 mV of most intense peak during engaged first eigenmode frequency sweep) and acquisition times (between 0.1-1 sec) were varied between measurements in such a way that with minimal power, sufficient signal was collected (>300 μV of most intense peak in engaged first eigenmode frequency sweep). The approximate lateral resolution of IR spectra was <10 nm. PiFM data was analyzed using SurfaceWorks software.

***In situ* PiFM measurements** The procedure for *in situ* PiFM measurements was as follows. Samples were placed on the PiFM sample stage and were covered by the vacuum cover to create the gas cell. The topography of the crystals was investigated in air, and system quality checks (such as cantilever quality, laser alignment, etc) were run. Subsequently, the gas cell was purged of air by performing three vacuum/N₂ purge cycles. In these cycles the cell was put under vacuum for 10/5/3 minutes, refilled with N₂, and left to purge for 10/5/3 minutes for

cycle 1-3, respectively. The pressure was then decreased to 0.8 bar N_2 to increase sensitivity through an increase in Q factor, while simultaneously preventing air contamination of the gas environment. The absence of water in the gas cell was verified by taking an infrared spectrum in direct drive mode. Due to a change in gas environment/cantilever dampening, a new frequency sweep was performed prior to approaching the surface. Additionally, the IR laser alignment was checked before *in situ* measurements, and then kept (when possible) unchanged throughout the measurement series to prevent alignment artefacts. Using 256x256 pixel topography data, a ZIF-8 crystal was selected for *in situ* analysis. To verify ZIF-8 chemistry, IR point spectra were taken (0.3 sec per spectrum, 200 averages). These spectra were then used to optimize the spectrum acquisition time (between 0.1-0.4 sec per spectrum), as well as laser power levels (PiF intensity for the most intense IR band <1 mV) for the hyperspectral measurements. The image resolution was set to 64x64 pixels for the hyPIR measurements to ensure fast data collection and tip quality preservation. All hyPIR images were recorded at set pressures, not during flow to prevent flow-induced noise. Set pressures of 0, 5, 10, 15, 20, 25, 30, 35, and 40 mbar of formaldehyde were used. Formaldehyde pressure was increased by flowing a stream of nitrogen through a bubbler with 16% w/v formaldehyde in water, thereby also introducing water to the gas environment, with the cantilever retracted 300 micrometers from the surface. During *in situ* measurements, quality checks were performed by ensuring low amplitude signals, and avoiding topography-induced PiF signal, by adapting feedback parameter- and setpoint values. In between, or after hyPIR measurements, more IR spectra and IR maps at relevant wavenumbers were taken.

Hyperspectral data analysis was performed using a combination of SurfaceWorks (Molecular Vista), Gwyddion, and TXM-Wizard software. Masking of hyperspectral images was performed manually for (defective) ZIF-8 crystals at increasing formaldehyde pressure to construct plots shown in Figure 4.5, 4.8f, and 4.10d-f. The masking procedure was as follows: for each hyperspectral measurement, the morphology data was inspected for crystal plane localization (Figure 4.11a, b). A map detailing crystal plane locations was drawn up (Figure 4.11c). Individual masks for all individual planes were drawn within the morphology data using a tailor-made Matlab script. Examples for a (110) facet mask, a (210) edge map, and a (111) corner map are given in Figure 4.11d-f. These maps were overlaid on the hyperspectral image (Figure 4.11b). Resulting mask-averaged spectra were inspected for outlier behavior. After discarding of outlier data, mask-averaged IR spectra were then further averaged per crystal plane to increase the S/N ratio. These formaldehyde pressure-dependent, plane-averaged IR spectra were subsequently used for contour plot construction and peak ratio calculations.

FIGURE 4.11: Experimental approach for crystal-plane specific analysis. a) Highly defined ZIF-8 crystals provide facile identification of crystal planes in b) hyperspectral images at varying formaldehyde pressure. c) Measurement-specific crystal plane maps were drawn for the construction of masks. d, e, and f) gives examples of a mask used for a facet, edge, and corner, respectively. Spectra of individual masks were analyzed for outlier behavior before averaging plane-dependent masked spectra to improve the S/N ratio.

Principal Component Analysis (PCA) and k-means clustering was used to analyze the hyPIR images. Prior to PCA and clustering, the data was normalized by sum image division. In the TXM-XANES-Wizard^[64], the data was mean-centered prior to PCA and k-means clustering. The appropriate number N of principal components (PCs) was selected upon inspection of scree plot, eigenspectra, and eigenimages. K-means clustering was then performed in N -dimensional PC space using twice the number of clusters ($2 \times N$). The result of k-means clustering was subsequently refined gaussian mixture modeling (GMM) using expectation maximization (EM). This provided a class membership value (between 0 and 1) of each pixel to each cluster. The spectrum of each cluster was then determined as the weighted average of all pixels using this class membership. This method thus efficiently pools pixels based on spectral similarity (and not on spatial correlation) and provides excellent estimates for the most different spectra present in the data.

4.4.3 DENSITY FUNCTIONAL THEORY CALCULATIONS

Surface models. Using density functional theory (DFT) we studied nature of surface terminations of three ZIF-8 orientations, namely {100}, {110} and {310} facets. It is crucial to realize that for each of {100}, {110} and {310} ZIF-8 planes, different surfaces can be constructed by varying the slicing height as illustrated in Figure 4.12. For both {001} and {100}, and the {310} surface, two and three surface terminations are possible, respectively, which differ in the density of Zn atoms per surface area as well as in the number of Zn-N bonds cleaved, giving rise to various under-coordinated sites. In our model, we assumed that surface terminations were always neutral as was done in the work of Weng *et al.*, i.e., charged surface terminations are not considered as they require diffusive double layer of ions from solution to maintain overall charge neutrality of the system.^[65] It has been shown that surface Zn-sites can be unsaturated or capped by various terminating groups, such as hydroxyl, carbonate, and monodentate 2-methylimidazole (Mim), depending on the system conditions, the modelling of which exceeds the scope of this work.^[11,65] Instead, we assume zero coverage of surfaces with the aim to elucidate general structural characteristics of various ZIF-8 facets with the emphasis on identifying important differences between them, independently of system conditions.

FIGURE 4.12: Different heights of cleavage along the {100} {110} and {310} planes visualized by a green, yellow, and red line, respectively.

In the next step, adsorption of formaldehyde was studied by adsorbing one furfuryl alcohol molecule on each side of the clean surface. To model a presence of defective linkers only the most stable termination of each facet was considered, on which a methyl-imidazole (Mim)

molecule was replaced by a pyrrole molecule and the surface was subsequently re-optimized. The adsorption of formaldehyde was then modelled in the same manner as for pristine surfaces.

Computational details. DFT calculations were conducted using version 6.1. of CP2K software, within Gaussian and plane wave (GPW) approach.^[66] GTH pseudopotentials combined with TZVP-MOLOPT basis set and plane-wave density cutoff 700 Ry were employed. The target convergence of SCF cycle was set to 10^{-6} . All geometries were optimized using PBE exchange-correlation functional with a semi-empirical Grimme D3 correction.^[67,68] Initially, the bulk structure together with the unit cell was optimized and after that unit cell dimensions were kept fixed. The optimized unit cell dimensions were 17.069 Å in each direction, i.e., a cubic representation of the bulk ZIF-8 was used. Subsequently, all possible {100}, {110} and {310} surface terminations were constructed, and the structure was re-optimized. Each of the surfaces was approximated by a symmetric two-dimensional periodic slab models separated from each other in a perpendicular direction by a layer of vacuum at least 15 Å thick. To avoid the interaction of the two surfaces within the same slab, the convergence of the slab thickness with respect to surface energy was tested. Based on the results, the slab depth of at least five Zn layers was chosen for each of the models. During the optimization, the middle Zn layers were fixed, while at least the top two Zn layers were allowed to relax. The thermodynamically most stable surface was the one with minimal surface energy, which was computed as:

$$\text{Equation 4.1} \quad \gamma = \frac{1}{2A}(E_{\text{slab}} - NE_{\text{Zn(Mim)}_2})$$

where E_{slab} is the energy of the symmetric slab with a total surface area of $2A$ and N and are the number of the elementary building blocks in the slab and corresponding energy computed from the bulk structure, respectively. Within our model, we have used Eq. 4.1 to determine preferred termination of pristine {100}, {110} and {310} facets. The surface energy of defective surfaces was calculated in a similar fashion:

$$\text{Equation 4.2} \quad \gamma = \frac{1}{2A}(E_{\text{slab}} - NE_{\text{Zn(Mim)}_2} - N_{\text{pyrrole}}E_{\text{pyrrole}} + N_{\text{pyrrole}}E_{\text{Hmim}})$$

with being the amount of defective linkers present on the surface (two) and and are the gas phase energies of pyrrole and neutral methyl-imidazole in the gas-phase.

The adsorption energy of formaldehyde is given by:

$$\text{Equation 4.3} \quad E_{\text{ads}} = E_{\text{slab-FA}} - E_{\text{slab}} - 2E_{\text{FA}}$$

where $E_{\text{slab-FA}}$ is the energy of the clean surface and is the energy of formaldehyde in the gas-phase. The factor two in Eq. 4.2 originates from the symmetry of the slab.

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5

MAPPING OF LOCATION- AND COORDINATION- DEPENDENT REDOX PROPERTIES OF METAL NODES IN A BIMETALLIC METAL-ORGANIC FRAMEWORK

5. ABSTRACT

The nature, concentration, and spatial arrangement of metal sites in porous functional materials, such as Metal-Organic Frameworks (MOFs), affect their physicochemical material properties and functionality. For example, research on bimetallic MOFs has shown that the distribution of introduced metal nodes can affect MOF gas separation, catalysis, and luminescence performance. However, this distribution is strongly dependent on the synthesis method used to incorporate multivariate sites. As a result, it is highly relevant to gain a nanoscale understanding of site location and coordination to correlate arrangement to function. However, with bulk methods, such as Infrared-/Raman- spectroscopy and X-ray Photoemission Spectroscopy (XPS), the spatial resolution is insufficient to study intra-crystal metal distributions. In this Chapter, we show that by coupling *in situ* Photo-induced Force Microscopy with nitric oxide as a probe molecule, it is possible to probe metal node distribution and local coordination environment of bimetallic Co:Cu-HKUST-1 samples. With this method, we were able to visualize $\text{Cu}^{2+}/\text{Cu}^{+}$ -node expression on HKUST-1 surfaces. Furthermore, by monitoring peak shifts of NO vibrations, it was even possible to detect Co-sites of a singular 2+ oxidation state, yet with varying coordination environments (framework vs. defective). Visual detection of these metal nodes allowed for direct comparison of synthesis methods on resulting electronic properties of bimetallic HKUST-1. Moreover, monitoring of the reductive disproportionation activity over the MOF surface led to the deduction of site-specific redox properties of (defective) Co/Cu-sites. This Chapter details the proof-of-concept for nanoscale metal distribution investigations applicable to a wide range of porous functional materials, such as MOFs and ion-exchanged zeolites.

This PhD Thesis Chapter is based on the following publication:

“Mapping of Location- and Coordination-Dependent Redox Properties of Metal Nodes in a Bimetallic Metal-Organic Framework”, Guusje Delen, Matteo Monai, Ramon Oord, Florian Meirer, and Bert M. Weckhuysen, *in preparation*.

5.1 INTRODUCTION

Metal-Organic Frameworks (MOFs) are often made with transition metals as the metal nodes in their structures.^[1–3] The use of transition metals is common as they are able to form complexes with organic linkers. As a result of using these transition metals, MOFs possess specific electronic properties and functionalities.^[4] For example, MOFs tend to be colored substances because of the optical properties of the used metal.^[5] Furthermore, MOFs are often highly active towards gas sorption (and conversion) since transition metals can change their oxidation states and bind adsorbates to their surface.^[6]

Coordination of the metal site to organic linkers modulates the electronic structure of the metal nodes.^[7,8] But, as was previously described in Chapters 1–4, MOF scaffolds often contain coordination defects.^[9–11] This then results in multiple electronic structures per metal element. Therefore, a single metal node can exist in multiple oxidation states within a single MOF structure, where each oxidation state will possess alternate redox properties.^[12,13] Furthermore, by introducing additional multivariate metal nodes to the scaffold, thus creating a bimetallic MOF, one can change the electronic structure of the MOF further.^[7,14] This incorporation of multivariate nodes is an increasingly common technique to engineer the performance of a MOF, e.g., towards enhanced gas sorption and/or conversion.^[15–17] Yet, as a result, a MOFs' localized electronic properties become highly dependent on its local environment.^[18]

It then follows that the overall, and local, electronic structure of a MOF will also rely on the synthesis method used to incorporate and coordinate (bi-)metallic nodes. Typically, two general types of synthesis are used to create bimetallic MOFs, namely direct *de novo* synthesis and post-synthetic modification (PSM) of an existing MOF.^[17,19] Both synthesis routes have their advantages and disadvantages. For example, while a direct synthesis is typically good at incorporating metal nodes within a framework, the synthesis can lead to an undesired framework structure or topology.^[20,21] In contrast, the PSM method will retain the original framework, but can face difficulty in displacing the original metal node.^[22–24]

To then describe and understand the changed electronic structure of bimetallic MOFs, bulk techniques, such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES), or surface-sensitive techniques, such as X-ray photoelectron spectroscopy (XPS), are routinely applied.^[25–28] Such techniques will give an averaged concentration ratio of metal species within a MOF structure or in its surface. However, such techniques are typically unable to probe whether a metal species is incorporated into the framework (versus adsorbed precursor species, in the case of PSM) or whether there are framework changes (in the case of direct synthesis). Furthermore, the micrometer-scale spatial resolution of XPS prevents its applicability to study the local environment of the metal nodes and their spatial arrangement. More recently, techniques with higher spatial resolution, such as transmission electron

microscopy (TEM) and atom probe tomography (APT), have also been applied to study metal distributions in multivariate MOFs on the atomic scale.^[29,30] However, electron beam damage often hinders TEM investigations of MOFs, and the APT technique suffers from strict sample preparation limitations requiring a bulk volume of materials. Furthermore, neither technique is extendable to *in situ* investigations of site-specific redox properties.

However, the location of metal node expression can significantly influence the performance of a (metal) site.^[31,32] For example, outer surface atoms are typically found to be more active towards gas sorption/conversion than bulk sites.^[33] Furthermore, Chapter 4 highlighted the intimate relationship between location and performance in the sorption and conversion of formaldehyde adsorbates. Additionally, in bifunctional materials where a spatial arrangement of sites is required for symbiotic functionality, clustering of multivariate nodes can result in diminished performance.^[34]

While PiFM possesses the required spatial resolution to investigate local electronic structures within bimetallic MOFs, it does not possess the required chemical sensitivity to identify metal-organic bonds with varying oxidation states. Fortunately, from bulk IR studies, it is known that using NO as a probe molecule gives detailed insights into metal sites and their oxidation states and redox properties.^[35–39] This can be done by monitoring the position of the $\nu_{\text{N=O}}$ vibration of NO molecules coordinated to a transition metal site.^[40] This gives indirect information on the electron density of the metal d-orbitals since a cation able to induce an increased amount of back-donation to the π^* orbital of the NO molecule (thereby weakening the N=O bond) will shift the vibration to lower wavenumbers.^[41–43] Furthermore, sites with redox activity will be able to reductively disproportionate the NO molecule to form NO_2 and N_2O . Detection of these species will then give insight into the redox activity of specific metal sites.^[44]

In this Chapter, we have adapted the *in situ* PiFM methodology to accommodate the NO molecule to probe the local electronic structure of bimetallic HKUST-1. We applied this methodology to HKUST-1 with various amounts of cobalt multivariate nodes that were incorporated through both a transmetalation synthesis and a direct synthesis as a proof-of-concept. We then used these samples to evaluate the effect of the synthesis method on MOF composition, metal node distribution, framework variation, and site-specific redox properties. Using this approach, we found that a transmetalation synthesis resulted in cobalt preferentially exchanging defective copper sites, while a direct synthesis resulted in a higher ratio of cobalt nodes incorporated into the framework. However, for the direct synthesis sample, this led to the disruption of oriented Surface-anchored MOF growth, which in turn led to a morphology-dependent NO disproportionation activity. We expect the present approach to be a game-changer in the probing of bimetallic MOFs, with potential for gas sorption, catalytic and photocatalytic applications, where transmetalation or other synthetic strategies may be used to introduce active sites in specific positions.

5.2 RESULTS AND DISCUSSION

5.2.1 MONOMETALLIC CU-HKUST-1

We used *in situ* Photo-induced Force Microscopy (PiFM) to assess the surface electronic properties of monometallic Cu-HKUST-1 Surface-Anchored Metal-Organic Framework (SURMOF). To this end, we have adapted our previously described PiFM methodology to accommodate nitric oxide (NO) in the sample chamber as a probe molecule. We analyzed the sorption of NO gas on SURMOF copper sites in NO pressures from 0-70 mbar. We did this through hyperspectral (hyPIR) mapping of the surface at variable pressure where a hyPIR image corresponds to a full (1965-775 cm⁻¹) infrared (IR) spectrum at each Atomic Force Microscopy (AFM) pixel. Figure 5.1a shows the resulting surface-averaged *in situ* spectra as a function of pressure. These spectra indicate the sorption of NO nitrosyls on various sites (Cu⁺/Cu²⁺) and in various conformations (NO, NO₂).

The *in situ* spectra show the appearance of several new IR bands. These bands were divided into two ranges: the NO-coordination range (1900-1700 cm⁻¹) and the nitro range (1650-1050 cm⁻¹).^[43] Within the NO-coordination range, we could distinguish between IR bands corresponding to NO···Cu²⁺ and NO···Cu⁺ sites at 1880 and 1787 cm⁻¹, respectively. These bands correspond to mono-nitrosyl species on Cu²⁺ sites and di-nitrosyl or *cis*-dimer species on Cu⁺ sites, formed through nitrogen-adducts on the axial positions of the HKUST-1 paddlewheel (Figure 5.1b).^[35]

Additionally, the *in situ* PiFM spectra showed that Cu-HKUST-1 formed NO₂ species on its metal sites (Figure 5.1c). This NO₂ was potentially formed through reductive NO disproportionation according to equation 5.1, which would result in NO₂ and N₂O surface species (N₂O vibrations were not observed due to our limited spectral range).^[45-47]

We found IR bands of three distinct NO₂ binding conformations, namely 1) bidentate chelating-, 2) monodentate, and 3) bidentate bridged NO₂ at 1190, 1345, and 1620 cm⁻¹, respectively (Figure 5.1d).^[12,48] Literature states that reductive disproportionation can occur on Cu⁺ sites where the bidentate chelating NO₂ is an intermediate species in the formation of monodentate NO₂ from nitric oxide.^[49,50] However, the bidentate bridged species can only be formed on two adjacent Cu⁺ sites, indicating that this type of NO₂ was not formed on sites of the structured HKUST-1 framework but on non-framework clusters of Cu⁺ sites.^[51] Therefore, the bidentate bridged NO₂ does not describe the redox properties of HKUST-1, while the bidentate chelating- and monodentate nitro species do.

FIGURE 5.1: *In situ* PiFM investigations of electronic properties of monometallic HKUST-1 sites. a) *In situ* PiFM spectra of Cu-HKUST-1 at increasing NO pressure. Inset shows NO coordination to $\text{Cu}^{2+}/\text{Cu}^+$ sites at $1880/1787\text{ cm}^{-1}$. Highlighted areas show the aromatic vibration of the MOF linker used for peak ratio calculation (1450 cm^{-1}) and rising bands in the NO_2 region ($1350\text{--}1180\text{ cm}^{-1}$). b) Schematic displaying coordination conformations of NO to the (defective) HKUST-1 paddlewheel. c) Zoom-in of the NO_2 region of the *in situ* spectra. The rise of two IR bands shows the presence of monodentate- and bidentate chelating NO_2 species. d) Schematic showing the molecular structure of present surface species. e) Bar plot showing peak ratios calculated for *in situ* spectra at increasing NO pressure. These peak ratios show increasing NO sorption and conversion with pressure. Inset data points show the $1787/1880\text{ cm}^{-1}$ peak ratio over pressure. This ratio showed the preferential sorption of NO on Cu^{2+} sites at lower pressures.

To compare the reductive coordination of NO on the $\text{Cu}^{2+}/\text{Cu}^+$ sites, we calculated peak ratios describing NO sorption on these sites as a function of pressure (Figure 5.1e). We calculated NO bands' ratios relative to the aromatic breathing vibration of the BTC linker of HKUST-1 at 1450 cm^{-1} .^[9] We chose this $\delta_{\text{arom.}}$ band as it is independent of metal-linker coordination, thus potential framework destruction upon NO sorption would not influence its intensity. The peak ratios show an increasing amount of NO coordinated with the Cu^{2+} and Cu^+ sites with increasing pressure.

To compare the redox reactivity of the $\text{Cu}^{2+}/\text{Cu}^+$ sites, we then calculated the ratio between coordinated $\text{NO}\cdots\text{Cu}^+$ and $\text{NO}\cdots\text{Cu}^{2+}$ ($1787/1880\text{ cm}^{-1}$). Notably, this ratio changed with pressure: at lower pressures, there is a relatively smaller amount of $\text{NO}\cdots\text{Cu}^+$ present, which

indicated that NO preferentially coordinated to the Cu^{2+} sites, which is in line with findings in the literature. With increasing NO pressure, the amount of monodentate NO_2 also increases, according to the reaction equilibrium between NO and NO_2 (Equation 5.1).

To visualize sorption/conversion sites and deduce site-specific structure-performance relationships, we acquired infrared maps with a sample-specific spatial resolution of less than 5 nm by scanning the surface while locking in the frequency of the infrared bands of interest (Figure 5.2a). We determined this estimation of spatial resolution by taking a line trace of a high-resolution IR map and assessing the line trace slopes (Figure 5.2b). We used steep slopes within the line that used multiple pixels to establish this slope. Of this slope, we then determined the x-axis width to calculate the sample-specific IR mapping spatial resolution.

[52]

With this IR mapping methodology, we found extended Cu^{2+} and highly localized Cu^+ domains on the HKUST-1 SURMOF (Figure 5.2c). We gained this insight by scanning two 1×1 micron² IR maps tuned to the 1880 cm^{-1} vibration of $\text{NO} \cdots \text{Cu}^{2+}$, and the 1787 cm^{-1} vibration of $\text{NO} \cdots \text{Cu}^+$ and overlaying this intensity map with the AFMHead-Z image (showing grain morphology). Size analysis shown in Figure 5.2g of these domains showed extended areas ($1043 \pm 46 \text{ nm}^2$) of pristine HKUST-1 and the presence of defective HKUST-1 domains of substantial sizes ($119 \pm 76 \text{ nm}^2$). This result indicated that the defect species in HKUST-1 have clustered in a non-random fashion, with Cu^+ -rich domains concentrated on the MOF crystals' interfaces, such as inter-MOF grain boundaries.^[29]

Further zooming in on the $\text{NO} \cdots \text{Cu}^+$ map of a 200 nm pyramidal-shaped crystallite revealed that the paddlewheel defects within crystals were mainly expressed on the unsaturated crystal planes, i.e., edges and corners (Figure 5.2d). Furthermore, an IR map using the $\text{NO} \cdots \text{Cu}^{2+}$ vibration showed that the Cu^{2+} species predominantly form on the lower-energy facets (Figure 5.2e). To support this claim, we took PiFM point spectra on areas of interest (grain boundary, crystal facet, crystal edge) and compared them to the bulk spectrum in N_2 (Figure 5.2f). These spectra showed the structure sensitive $\text{NO} \cdots \text{Cu}^+$ coordination on boundaries > edges > facets, thereby proving the *in situ* PiFM technique's sensitivity and chemical specificity and the chemically distinct character within the SURMOF. Together these images showed a plane-dependent defect concentration of monometallic HKUST-1 SURMOF.

FIGURE 5.2: Infrared mapping of Cu-defect sites with <5 nm spatial resolution. a) 250x250 nm² IR map of the 1787 cm⁻¹ band intensity as a function of location shows the presence of localized domains of Cu⁺ sites. b) PiFM intensity profile of the line trace shown in (a). By analyzing steep slope regions, the spatial resolution of the IR mapping feature was estimated to be <5 nm. c) 1x1 μm² IR map of the 1787 cm⁻¹ band intensity overlaid on an HKUST-1 SURMOF morphology image. Together with zoom-ins of the map shown in d) and e), the IR map showed the concentration of defective Cu-sites on inter-grain boundaries and on the high energy planes of HKUST-1 crystallites. f) Point spectra taken within the IR map shown in (c) on a crystal boundary, crystal edge, and crystal facet, compared to the HKUST-1 spectrum in N₂. Spectra showed the enhanced coordination of NO on grain boundaries and interfaces.

5.2.2 TRANSMETALATED CU/CO-HKUST-1

To showcase the sensitivity of the *in situ* PiFM method to surface redox properties, cobalt nodes were introduced in the HKUST-1 sample through transmetalation syntheses, a commonly employed post-modification procedure for MOFs engineering. Since we performed the LbL synthesis of Cu-HKUST-1 in ethanol, we also chose to perform the transmetalation by immersing the SURMOF sample in concentrated ethanolic cobalt (II) nitrate solution for 48 h. The degree of transmetalation was then influenced by changing the temperature between RT and 70°C.^[27] These transmetalated samples were subsequently used for *in situ* PiFM measurements.

The PiFM images (Figure 5.3f,h) and grazing incidence XRD (Figure 5.4g) showed that the structure of the film was not significantly modified by transmetalation, consistent with previous research showing that transmetalation could occur without loss of crystallinity, even at higher cobalt concentrations (up to 50% in ethanol at 70°C).^[27] Transmetalation thus allowed us to decouple structural and compositional effects and show the sole effect of Co on gas sorption and surface redox chemistry in HKUST-1.

The *in situ* PiFM measurements of transmetalated HKUST-1 at 50 mbar of NO pressure showed changes in the IR spectrum when compared to the pristine samples, as shown in the difference spectra (Figure 5.3a). One can observe the rise of a broad, convoluted band at 1740 cm⁻¹ in Figure 5.3b associated with NO sorption on the newly introduced cobalt sites. Additionally, after transmetalation, a decrease in 1787 cm⁻¹ band (NO···Cu⁺) intensity was observed, coupled with an increase in 1880 cm⁻¹ band (NO···Cu²⁺) intensity. Furthermore, a shift in HKUST-1 framework vibrations from 1370 to 1380 cm⁻¹ was observed (Figure 5.3c). Moreover, we found NO₂ bands rising at 1465 and 1300 cm⁻¹ suggesting the ability of cobalt sites to reductively disproportionate NO (Figure 5.3d).^[53,54] Lastly, we found bands that indicated the presence of NO₃ species on the sample surface (950 cm⁻¹). These nitrate species were expected to be a direct consequence of the synthesis method, where some cobalt precursor remained on the surface after ion exchange.

The assignments of the band were done by considering the potential sites of metal nodes exchange, namely the framework and the defective sites. Therefore, the *in situ* spectra must show the interaction between NO and two types of cobalt sites (framework, defective). The rise of the convoluted band at 1730/1755 cm⁻¹ indicated small differences in electronic properties between the two sorption sites. Therefore, these bands were assigned to NO coordinated to cobalt sites of different binding conformations but of a single valency (Co²⁺).^[45] As a result, we assigned the bands at 1730 and 1755 cm⁻¹ to nitrosyl vibrations of NO···Co_{defect} and NO···Co_{framework}, respectively (Figure 5.3d).

To further analyze the incorporation of cobalt into the HKUST-1 framework, we inspected the framework vibrations of the transmetalated SURMOF. It is known that in HKUST-1, the metal sites coordinate to the linkers by forming bidentate carboxylate bonds with symmetric and asymmetric COO⁻ stretching vibrations at 1650 and 1370 cm⁻¹, respectively.^[9] However, the transmetalated HKUST-1 shows broadening of the 1370 cm⁻¹ band (Figure 5.3c). With increasing transmetalation temperature, and thus suspected increasing Co-content, the band blueshifts to 1380 cm⁻¹. In the difference spectra, we observed the same effect for the 1650 cm⁻¹ band. This shift confirmed the incorporation of cobalt into the SURMOF skeleton. From literature, it is known that such cobalt framework sites are able of reductive disproportionation of NO.^[45] Therefore, we have assigned the vibrations at 1465 and 1300 cm⁻¹ to the symmetric and asymmetric ν_{N-O} vibrations of monodentate NO₂ on coordinated Co²⁺ (Figure 5.3d).

FIGURE 5.3: *In situ* PiFM investigations of the (local) electronic structure of Co-transmetalated HKUST-1 SURMOF. a) Difference spectra constructed by subtracting the spectrum of Cu-HKUST-1 at 50 mbar NO from the *in situ* spectra of the transmetalated samples. Spectral changes were observed in the NO and NO₂ region and of the framework vibrations, indicating the incorporation of cobalt into the HKUST-1 framework. Additionally, NO₃ species of remaining cobalt precursors were found on the SURMOF surface. b) Zoom-in of the NO region of the *in situ* spectra shows the appearance of a convoluted band at 1755/1730 cm⁻¹, indicating NO coordination to the framework- and defective Co-sites. c) Zoom-in of the ν_{COO} vibration of the HKUST-1 paddlewheel shows a shift in peak position with increasing transmetalation temperature. d) Schematic showing the IR band positions of NO/NO₂ species coordinated to (defective) cobalt sites. e) Peak ratios of vibrations shown in (d) relative to the $\nu_{\text{N=O}}$ vibration of NO coordinated to Cu²⁺ at 1880 cm⁻¹ show the increased incorporation of cobalt with increasing transmetalation temperature. Additionally, it showed the preferential exchange of Cu⁺ sites and the resulting morphology-dependent exchange behavior of cobalt. f) A 250x250 nm² AFM image of the highly defective valleys area of HKUST-1 SURMOF. g) The clustered hyperspectral image of the area shown in (f) where highlighted pixels possess a similar spectral identity corresponding to defective cobalt-(green) and copper (blue) sites. The distribution of pristine Co/Cu-sites was found to be relatively homogeneous. h) and (g) show the analog analysis of a pyramidal crystallite. The distribution maps show the preferential exchange of cobalt on grain boundaries and high energy planes, as well as the presence of large non-framework Cu⁺ clusters insensitive to transmetalation.

Additionally, it is worth reiterating that since PiFM is not a quantitative technique, only relative intensities rather than absolute intensities can be compared. Therefore, the observed rise in 1880 cm^{-1} did not necessarily equal an increase in Cu^{2+} concentration. Therefore, we have calculated the surface-averaged spectra peak ratios to compare redox character between (transmetalated) samples (Figure 5.3e). The calculated $1787/1880\text{ cm}^{-1}$ ratio indicated a decrease in the number of $\text{NO}\cdots\text{Cu}^+$ sites relative to the number of $\text{NO}\cdots\text{Cu}^{2+}$ sites, which in turn indicated a preferential exchange of Cu^+ sites with cobalt nodes. This finding was in line with previous findings that suggested that transmetalation preferably occurs at under-coordinated metal sites.

To then describe the change in the relative concentration of (defective) cobalt sites of the transmetalated samples, we calculated the peak ratios of their surface-average spectra (Figure 5.3e). Of the sample transmetalated at 70°C , we segmented the hyperspectral image into two areas: one area describing a pyramidal crystallite and one area describing the valleys found between these crystallites. We opted for this segmentation since monometallic HKUST-1 showed a discrepancy in defect site concentration between these two areas. Based on this discrepancy, we expected a difference in transmetalation behavior. We then deconvoluted the $1755/1730\text{ cm}^{-1}$ band and used these values to calculate the $1755/1450$ and $1730/1450\text{ cm}^{-1}$ peak ratios to describe the relative concentration of framework and defective cobalt sites. These ratios showed that with increasing transmetalation temperature, the concentration of both pristine and defective cobalt sites increased, at the expense of Cu^+ . Furthermore, it showed that the valleys showed a higher degree of transmetalation than the pyramidal HKUST-1 crystallites due to their higher initial concentration of defective copper sites.

To visualize this preferential transmetalation, we zoomed in on a “valleys” area of the SURMOF, showing small HKUST-1 grains with many inter-crystallite boundaries and an area showing a single pyramidal HKUST-1 crystallite (Figure 5.3f, h). We segmented these $250 \times 250\text{ nm}^2$ area’s hyperspectral images through Principal Component Analysis (PCA) and clustering.^[55] This resulted in several clusters, with each cluster linking pixels to a similar spectral identity (Figure 5.3g, i). We calculated these clusters’ peak ratios, describing their relative concentration of (defective) copper and cobalt sites. We selected the clusters best describing defective copper and defective cobalt to construct cation site distribution images. We do not show the distribution of framework copper and cobalt sites as PCA and clustering showed that their distribution was relatively homogeneous. In contrast, the defective sites clustered into specific domains.

The distribution map of the valley area showed the concentration of defective cobalt species on the inter-grain boundaries. Comparison between the transmetalated distribution map and the mono-metallic IR map gave visual confirmation that the Cu^+ boundary sites had been exchanged, thereby forming defective cobalt sites. Similarly, the pyramidal crystallite

showed a preferential exchange of copper sites with cobalt on the crystals' corner and edges. Nonetheless, the distribution map also showed that some domains of Cu^+ sites remained. However, these domains were not found on the grain boundaries but on top of the grains' surface. These domains were indistinguishable in the area's topography data and appeared to be non-framework defective Cu^+ sites. As a result, we hypothesized that these sites are non-porous and thus not available for transmetalation. We therefore also suspect that these sites were the non-framework Cu^+ sites responsible for the formation of bidentate bridged NO_2^- .

5.2.3 DIRECT SYNTHESIS OF CU/CO-HKUST-1

To assess the synthesis method's effect on the incorporation of cobalt sites, we also performed "direct" Layer-by-Layer syntheses of bimetallic HKUST-1 SURMOFs using solutions of copper- and cobalt nitrate in ethanol, with molar ratios of $\text{Cu}:\text{Co} = 25:75, 50:50, 75:25$, and $100:0$. AFM images of the as-synthesized SURMOFs showed a change in sample morphology with increasing cobalt nitrate concentration (Figure 5.4a-f). Whereas the 25:75 sample still resembled a surface covering film with similar morphology to the monometallic HKUST-1, the samples with higher concentrations of cobalt form individual crystallites of different shapes: pyramidal and triangular prism. These correspond to HKUST-1 grown in the (100) direction and in the (111) direction, respectively, as was also supported by grazing incidence XRD evidence (Figure 5.4g, *vide infra*).^[36,56]

FIGURE 5.4: Change in sample morphology and orientation in direct synthesis with increasing cobalt nitrate concentration. a-c) AFM images of Co/Cu-HKUST-1 SURMOF grown through direct LbL synthesis, with insets

showing the used ratio of Co-/Cu-nitrate precursor. With increasing cobalt nitrate concentration, individual crystallites were formed. d-f) Zoom-ins of individual grains showing a (d) pyramidal, (e) triangular prism, and (f) rod morphologies. g) Grazing-incidence XRD diffractograms showing the cobalt-induced change in HKUST-1 crystal orientation.

The 75:25 sample yielded some other rod-like grains, which were not recognized as a crystal morphology of HKUST-1 (Figure 5.4f). Therefore, we expected these grains to be some high-Co content structures. The 100:0 sample did not yield any SURMOF material, strongly suggesting that the growth of Co-SURMOF necessitates pre-nucleated Cu-SURMOF crystallites.

XRD patterns of the samples showed that crystallinity was preserved and confirmed the presence of both the (100) and (111) orientations of the samples made through direct synthesis (Figure 5.4g). Since we performed the direct synthesis on carboxylic acid self-assembled monolayers, the SURMOF was expected to grow in the (100) direction. To explain the presence of (111) oriented crystals, we hypothesized that early layer disorder caused by the cobalt moieties resulted in mixed-orientation SURMOF. As a result, we expected the triangular prism grains to possess a higher overall defect concentration.

For example, for the 75:25 sample, it was clear that the high concentration of cobalt nitrate resulted in a relatively large fraction of HKUST-1 crystals grown in the (111) direction. Interestingly, however, the degree of orientation disruption appears to be larger for the 25:75 sample than for the 50:50 sample. We hypothesized that the 50:50 sample had a large enough concentration of cobalt precursor to fully disrupt the film-wise deposition of SURMOF, leading to the growth of individual crystallites. These individual crystallites then grew in either the (100) or the (111) orientation in a relatively unperturbed fashion. In contrast, in the 25-75 sample, the cobalt nitrate introduced disorder in the entire SURMOF film, leading to a disordered and presumably defect-rich sample.

We have assessed the electronic properties of the bimetallic HKUST-1 grown through direct synthesis with *in situ* NO PiFM. However, previous research has shown that different crystals exposing different crystal facets may also present different gas sorption behavior.^[57–59] Therefore, where possible, we compared the *in situ* spectra of crystallites of both crystal orientations. We calculated these spectra's relevant peak ratios to compare NO sorption on Cu⁺, Cu²⁺, and (defective) Co²⁺ between samples, relative to the monometallic HKUST-1 (Figure 5.5a). These relative peak ratios showed a steady decrease in NO coordination to copper sites and a steady increase in NO coordination to cobalt sites, with increasing expected cobalt nitrate concentration. Additionally, it showed that for samples grown through direct synthesis, the cobalt nodes also preferentially incorporated in the location of Cu⁺ sites, as evidenced by the more substantial decrease of Cu⁺ sites concentration relative to the Cu²⁺ site concentration.

FIGURE 5.5: Peak ratios of direct synthesis samples showing cobalt-induced changes in HKUST-1 electronic structure. a) Peak ratios between NO coordination bands and the aromatic breathing vibration of the linker (1450 cm⁻¹) show the (morphology-dependent) increase in cobalt content with increasing cobalt nitrate concentration. b) Peak ratios showing the (morphology-dependent) change in redox properties with increasing Co-content. Dashed and solid lines show the Co-content of the sample transmetalated at 70 °C.

The 25:75 sample is an exception to this trend. While this sample did show a decrease in relative Cu²⁺ concentration, it simultaneously showed an increase in relative Cu⁺ concentration. To explain this, we refer back to the XRD diffractogram of the sample. There we observed strong disorienting effects of the cobalt precursor on the SURMOF film, which we expected to lead to an increased defect concentration. NO coordination to an increased concentration of Cu⁺ sites thus supported our hypothesis.

Furthermore, we observed the morphology-dependent incorporation of cobalt sites. For both the 50:50 and the 75:25 samples, the peak ratios showed a relatively higher concentration of

defective cobalt (and copper) sites in the triangular prism-shaped crystallites. This finding confirmed the hypothesis that bimetallic HKUST-1 grown in the (100) direction experienced less perturbation by the added cobalt nodes and were more similar in framework structure to the monometallic SURMOF. Lastly, we observed that the 50:50 samples contained a low overall amount of framework sites. This result suggested that to achieve a high relative concentration of cobalt framework sites, either a low amount of cobalt precursor, leading to a highly copper-defective film, or a high amount of cobalt precursor, leading to individual Co-rich crystallites, is required. The cobalt content of these Co-rich crystallites of the 75:25 sample even surpassed the cobalt content of the transmetalated samples.

We then scrutinized the NO_2 region of the *in situ* spectra of the direct synthesis samples and the transmetalated samples (Figure 5.5b). We calculated the peak ratios describing monodentate nitro-groups on defective copper sites ($1345/1450\text{ cm}^{-1}$) and framework cobalt sites ($1465/1450\text{ cm}^{-1}$). Comparing these ratios for the direct synthesis samples showed a decrease in NO_2 formed on copper and an increase in NO_2 formed on cobalt, with increasing cobalt precursor concentration. The pyramid morphology grains, which were known to possess a higher relative concentration of cobalt framework sites relative to defective cobalt sites, outperformed their triangular prism-shaped counterparts in terms of NO_2 formation. This result confirmed that cobalt framework sites were responsible for reductive disproportionation of NO. Similarly, of the sample transmetalated in warm ethanol, the pyramidal crystallite showed remarkably higher potential for NO disproportionation than the less defined valley grains. This finding was rationalized by the knowledge that this area had a high relative concentration of Cu^+ sites that preferentially exchanged to form defective cobalt sites, thereby significantly reducing the concentration of sites with disproportionation activity. In contrast, the pyramidal crystallite's more pristine structure resulted in a higher relative concentration of cobalt framework sites on which NO_2 formation subsequently occurred.

Whereas in transmetalated samples, the cobalt mainly replaced the readily available Cu^+ sites, there is, in theory, more freedom of incorporation location in the direct synthesis. To evidence Co distribution in the LbL bimetallic samples and to identify possible preferential cobalt expression within the pyramidal and prism-shaped crystallites, we used PCA and clustering on the hyperspectral images of the 50:50 sample (Figure 5.6a-d). Of these clustered images, we again identified clusters describing the behavior of (defective) copper and cobalt sites based on their NO coordination and NO_2 formation behavior, as well as their framework vibrations (Figure 5.6e-h).

FIGURE 5.6: Direct synthesis node distribution. a), c) AFM image images of hyperspectral measurements of a pyramidal and a triangular prism grain. b), d) clustered distribution maps of defective Co/Cu-nodes showing preferential expression sites. e) Averaged spectral identities of clustered pixels shown in (b). f)–h) Zoom-ins of the (f) NO region, (g) framework vibration, and (h) NO₂ region.

This analysis unveiled that the cobalt framework sites were incorporated in a reasonably homogeneous fashion over the extended crystal surfaces, while defect sites were preferentially expressed on the pyramids' high energy crystal planes, such as edges and corners (Figure 5.6b). The highly undersaturated and flexible corner planes appear to facilitate the flexible incorporation of non-native framework species, comparable to what was observed for

transmetalation in the monometallic HKUST-1, which has the same (100) crystal orientation.^[60] A different case was observed for the triangular prism crystallites, which showed a multivariate core-shell structure, with a Co-defect rich outer shell (50 nm) encapsulating a Cu⁺-rich core (Figure 5.6d).^[61] This is in accordance with the fact that no nucleation and growth was observed for monometallic Co-HKUST-1, suggesting nucleation of a Cu-rich crystallite is first necessary for Co-SURMOF growth.

To get more insights into the effect of morphology on the electronic and redox properties of bimetallic HKUST-1, we measured pressure dependent *in situ* spectra for both crystallite shapes (Figure 5.7a). These spectra show increasing NO coordination with increasing pressure on the copper and cobalt sites for both crystal orientations. However, we observed a discrepancy in NO coordination performance. While both orientations showed infrared bands corresponding NO $\cdots$ Cu²⁺ at 25 mbar, only the triangular prism grains showed NO $\cdots$ Cu⁺ vibrations at that pressure. Furthermore, at 25 mbar, both morphologies show NO $\cdots$ Co²⁺-framework vibrations, but only the triangular prism grains showed NO $\cdots$ Co²⁺-defect vibrations. Overall, this showed that NO coordinated to Co-framework sites prior to Co-defect sites. Moreover, it showed that the triangular prism morphology exhibited more NO sorption on its defective sites at lower NO pressures. Two possible explanations for these observations can be given. 1) Previous analyses showed that the triangular prism crystallites have a higher overall relative concentration of defect sites, thus providing more sites for NO coordination, and 2) the change in crystal orientation makes the exposed crystal plane of the triangular prism crystallites more susceptible to NO sorption at lower pressures. However, since bulk analysis showed that both morphologies showed the presence of a large number of defective sites, the sorption of NO appeared to be structure sensitive.

The pressure-dependent *in situ* spectra of the NO₂ region of the two morphologies also showed increasing NO₂ formation with increasing NO pressure. However, due to the overlap of IR bands in this region, morphology-specific formation behavior was more challenging to distinguish after visual inspection of the spectra. Therefore, we have deconvoluted the bands to pinpoint relative intensities of the 1300/1345 cm⁻¹ bands describing monodentate coordination to Co and Cu, respectively. At both pressures, the triangular prism crystallites possessed a lower band ratio, confirming that these grains have a larger relative Cu⁺ concentration. However, we also observed for both morphologies that this ratio dropped with increasing pressure. This signaled that, in general, NO₂ formed on Co-framework sites before NO₂ formed on Cu-defect sites.

FIGURE 5.7: Pressure-dependent *in situ* IR spectra showing morphology-dependent NO sorption and conversion performance. a) NO coordination region showing preferential NO sorption on triangular prism crystallites, and b) preferential NO conversion on pyramidal crystallites.

To study the preferential sites of NO₂ formation in more detail, we isolated the *in situ* PiFM spectra of areas of interest identified in the Co-Cu-distribution maps (Figure 5.6b,d), namely the corner, edge, and facet of the pyramidal crystallite and the core, and shell of the triangular prism crystallite. We realized this by masking these areas in the hyperspectral images at 50 mbar NO of the crystallites. Of these area-averaged PiFM spectra, we subsequently calculated peak ratios describing 1) monodentate NO₂, 2) bidentate chelating NO₂, and 3) bidentate bridging NO₂. We plotted these ratios in a radar plot to comprehensively compare the environment-dependent redox behavior (Figure 5.8).

This radar plot showed the ratio between monodentate NO₂ on Co and Cu-sites (1465/1425 cm⁻¹) to gain an understanding of relative distributions within crystallites. This ratio indicated the overall lower production of monodentate NO₂ on the triangular prism grain. Furthermore, within this grain, we observed the presence of more NO₂@Cu⁺ in its core. Despite the uniform distribution of Co-framework species, the high Cu⁺ content of its core shifted the ratio between areas, leading to location-specific surface species. In contrast, we found the structure insensitive formation of monodentate NO₂ on the pyramidal crystallite surface. We rationalized this finding by the previous observation of a homogeneous distribution of Co-framework species over its surface and its low overall Cu⁺ concentration.

FIGURE 5.8: Radar plot showing structure sensitive NO_2 formation on bimetallic Co/Cu-HKUST-1. Peak ratios of masked areas of both grain morphologies at 50 mbar of NO show the overall lower amount of NO_2 formed on the surface of triangular prism grains. Furthermore, the ratios show the structure sensitive formation of NO_2 intermediate species.

Nevertheless, the corners (and edges) of the pyramidal grains gave a higher concentration of intermediate bidentate chelating NO_2 species formed over these Cu^+ sites. Therefore, we hypothesized that these high energy crystal planes could not stabilize the transition towards monodentate NO_2 as well as the lower energy crystal facets. Similarly, for the triangular prism grains, we observed that the defective cobalt-rich shell showed a high concentration of bidentate chelating NO_2 species. Since this area is low in Cu^+ concentration but high in cobalt concentration, we hypothesized that a higher cobalt concentration in the local environment of the Cu^+ sites perturbed the interaction with NO_2 , thereby limiting conversion to the intermediate species.

Lastly, we found the structure sensitive formation of bidentate bridged NO_2 species on the pyramidal structure, where high energy planes produced more of this non-framework mediated adsorbate. On the triangular prism grains concentration of these species was low and structure insensitive. We linked these bidentate bridged species to the Cu^+ clusters found in the distribution maps of the transmetalated samples (Figure 5.3g, i). This observation highlights the high-energy planes' tendencies for restructuring to minimize surface energy. Overall, these structure (in)sensitive insights provide a scaffold for the rational synthesis of bimetallic HKUST-1 with specific redox properties.

5.3 CONCLUSIONS

We have demonstrated the use of *in situ* nano-scale IR spectroscopy with nitric oxide as probe molecule to investigate both electronic and redox properties within a (bi-)metallic HKUST-1 SURMOF. With this method we visualized the nanoscale distribution of multivariate metal ions. This distribution of metals strongly influenced the HKUST-1 electronic properties and, therefore,

its functionality. Specifically, *in situ* PiFM showed that it was able to locate cobalt nodes of a singular oxidation state, yet with differences in coordination, within the SURMOF. Identification of these distinct coordination states would not have been possible using bulk IR spectroscopy due to band broadening or with XPS/APT due to the singular oxidation state. Furthermore, with *in situ* PiFM, we found that the redox properties of Co-HKUST-1 are largely dependent on this coordination, as only cobalt nodes incorporated into the HKUST-1 framework showed NO disproportionation activity. Therefore, with *in situ* PiFM, we could conclude that the redox properties were distribution-dependent rather than concentration-dependent. As a result, we highlighted the relevance of the synthesis method on the incorporation of the multivariate cobalt node and the resulting (redox) properties of Co/Cu-HKUST-1. Figure 5.9 shows an overview of the nano-scale detection of defective and pristine cobalt and copper sites and their redox properties.

FIGURE 5.9: Overview of electronic and redox properties of bimetallic Co/Cu-HKUST-1 made through transmetalation (top) and direct synthesis (bottom). Schematic representations of surface species indicate preferential expression sites of metals and preferential conversion sites of NO_2 .

For the transmetalated samples, it shows that the Cu⁺ sites present at inter-grain boundaries and at crystal interfaces were preferentially exchanged with cobalt nodes to form undercoordinated Co-sites. Furthermore, it showed the presence of non-framework Cu⁺-domains insensitive to transmetalation on high-energy planes of HKUST-1 crystallites. Moreover, it showed the ability of the transmetalation synthesis to exchange Cu-framework sites with Co-sites, to create coordinated Co-paddlewheel sites. However, we also showed the relatively low potential of the transmetalated samples for NO disproportionation.

For the samples made through direct synthesis, we observed the growth of individual crystallites with distinct (100)/(111) orientation due to cobalt-precursor-induced early layer disorder. Bimetallic HKUST-1 grown in the (111) direction showed a relatively high Co/Cu-defect concentration. As a result, it showed a high potential for NO sorption. Furthermore, these defect sites segregated to form a core-shell structure with a Cu⁺-rich core encapsulated with a Co-rich shell. This showed the need for nucleation and growth of a Cu-rich framework prior to Co-incorporation.

Bimetallic HKUST-1 grown in the (100) direction showed a relatively low Cu/Co-defect concentration. It more closely resembled the framework structure of monometallic HKUST-1 while incorporating a relatively high concentration of cobalt sites into its framework. It showed a higher aptitude to NO conversion than the (111) grains. Furthermore, it showed structure sensitive redox behavior, where NO intermediate conversion species were found more on its high energy planes.

These insights are highly relevant in the development of functional bimetallic MOFs for gas sorption and conversion application. Our methodology will pave the way for investigations for rational synthesis routes for the introduction of active sites into specific positions (of MOFs). Future research will focus on the incorporation of other multivariate nodes (through alternative synthesis routes) and the detection of their local electronic structure.

5.4 EXPERIMENTAL SECTION

5.4.1 MATERIALS SYNTHESIS

Chemicals: The following chemicals were used: 16-mercaptohexadecanoic acid (MHDA, 99%, Sigma-Aldrich), ethanol (99.5%, Acros), copper(II) nitrate trihydrate (99+%, Sigma-Aldrich), trimesic acid (95%, Aldrich), cobalt(II) nitrate hexahydrate (98%, Sigma-Aldrich). Substrates of 60 nm Au on Si, with a 5 nm Ge adhesion layer were provided by AMOLF.

Substrate preparation: Gold wafers were cleaned in three successive steps. They were rinsed with ethanol, dried in flowing N₂ (4 bar), and cleaned using UV-ozone for 20 min.

The clean substrates were immersed in a 1 mM ethanolic SAM solution for 48 h. After functionalization, substrates were rinsed in flowing ethanol before drying with N_2 (4 bar).

MOF deposition: (Bi-metallic) HKUST-1 SURMOF was synthesized according to our previously described protocol^[9]. In short: A SILAR coating system with stirrer (HO-TH-03S, Holmarc)) was used to program immersion cycles in copper-precursor, BTC and ethanol. Overall concentrations of copper(-cobalt) and BTC solutions were 1mM. Dipping steps of 20 sec were alternated by rinsing steps in EtOH (20 sec, 150 rpm). 100 Layers of (bi-metallic) HKUST-1 was deposited per sample.

Transmetalation: A monometallic Cu-HKUST-1 was transmetalated with a cobalt(II) nitrate solution at room temperature and at 70°C according to protocol described in ^[27]. Ethanolic cobalt nitrate solutions were used (2.54 mmol/10 mL). Both transmetalation syntheses were performed by submersing the sample in cobalt-solution for 48 hours. The sample was washed with ethanol and dried in low pressure N_2 flow before GI-XRD and *in situ* PiFM analysis.

5.4.2 MATERIALS CHARACTERIZATION

Grazing incidence X-Ray Diffraction (GI-XRD) was performed on a Bruker D8 Advance setup. A scanning range of 4 - 20°, with an increment of 0.03° and a step time of 7 seconds was used. It operated using a Eiger2 R 500K detector in 0D mode. The incident angle was 0.2°, a Goebel mirror with 0.1 mm Divergence Slit, and 0.3° Equatorial Soller secondary optics were used.

Photo-induced Force Microscopy (PiFM) measurements were performed using a VistaScope from Molecular Vista, Inc. NCHAu25-W AFM tips (Force constant 10-130 N/m, Resonance frequency > 320 kHz) coated with 25-70 nm of gold by Molecular Vista were used in dynamic non-contact mode. A driving amplitude of 2 nm was used, and a frequency sweep of the cantilever was performed prior to measurements to determine cantilever resonance frequencies. After this sweep, detection of topography was set to the second mechanical eigenmode resonance (f_1), and photo-induced signal detection was set to the first mechanical eigenmode resonance (f_0). Determination of the first mechanical mode was repeated after approaching the tip to the surface. By using independent eigenmodes, topography and PiFM signal could be detected simultaneously. Using a cantilever setpoint between 80-85%, 256x256 pixel topography images of varying sizes were collected. The midIR source was a Block Engineering tunable quantum cascade laser (QCL) providing a working range of 1965-785 cm^{-1} . Averaged IR spectra were taken in sideband mode (pulse modulation: $f_m = f_1 - f_0$) with a pulse duration of 32 ns, and with a spectral resolution of 1 cm^{-1} . Power levels (iris set between 55-90°, <1 mV of most intense peak during engaged first eigenmode frequency sweep) and acquisition times (between 0.1-1 sec) were varied between

measurements in such a way that with minimal power, sufficient signal was collected (>300 μV of most intense peak in engaged first eigenmode frequency sweep). The approximate lateral resolution of IR spectra was <10 nm. PiFM data was analyzed using SurfaceWorks software.

Hyperspectral Photo-induced Infrared (hyPIR) images of 128x128 pixels were measured *ex situ* and *in situ*. Scanning speeds were adapted for spectrum acquisition times. For the *in situ* measurements, a vacuum cell was placed over the AFM head and sample stage. A vacuum pump and a three-way valve with lines to dry N_2 , a bottle of 10% NO in N_2 were connected. Prior to *in situ* measurements, the vacuum cell was evacuated and backfilled with dry N_2 three times. *In situ* hyPIR measurements were set for 5 h. NO pressure was increased stepwise.

Principal Component Analysis (PCA) and k-means clustering was used to analyze the hyPIR images. Prior to PCA and clustering, the data was normalized by sum image division. In the TXM-XANES-Wizard^[178], the data was mean-centered prior to PCA and k-means clustering. The appropriate number N of principal components (PCs) was selected upon inspection of scree plot, eigenspectra, and eigenimages. K-means clustering was then performed in N-dimensional PC space using twice the number of clusters (2 x N). The result of k-means clustering was subsequently refined gaussian mixture modeling (GMM) using expectation maximization (EM). This provided a class membership value (between 0 and 1) of each pixel to each cluster. The spectrum of each cluster was then determined as the weighted average of all pixels using this class membership. This method thus efficiently pools pixels based on spectral similarity (and not on spatial correlation) and provides excellent estimates for the most different spectra present in the data.

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6

SUMMARY, CONCLUDING REMARKS, AND FUTURE PERSPECTIVES

6. SUMMARY, CONCLUDING REMARKS, AND FUTURE PERSPECTIVES

This PhD Thesis describes the use of nano-infrared spectroscopy to study the growth and functionality of Surface-anchored Metal-Organic Frameworks (SURMOFs). Furthermore, it details the development of *in situ* Photo-induced Force Microscopy (PiFM) to describe site-specific properties and functionalities within SURMOFs. This technique was applied to the model systems of two archetypal MOFs, namely HKUST-1 and ZIF-8.

Within this framework, this PhD Thesis contains six Chapters. **CHAPTER 1** gives a general introduction into the field of (SUR)MOFs and nano-infrared spectroscopy. **CHAPTER 2** details the use of two types of *ex situ* nano-IR spectroscopy to study the growth mechanism of HKUST-1 SURMOF. **CHAPTER 3** describes the development of *in situ* PiFM with D₂O as a probe molecule to describe site-specific guest-host interaction within a mixed MOF-ZIF film. **CHAPTER 4** elaborates on the development of *in situ* PiFM on ZIF-8 to uncover the structure-sensitive sorption and conversion of formaldehyde as probe molecule. **CHAPTER 5** discusses the use of NO as probe molecule in *in situ* PiFM to distinguish between metal nodes within bimetallic HKUST-1 SURMOF.

In this Chapter, a summary of the research performed in the experimental Chapters and details the main findings of these Chapters. Furthermore, some perspectives on future research venues within the scope of this PhD Thesis are given.

6.1 SUMMARY

In **CHAPTER 2**, the growth mechanism of HKUST-1 SURMOF in a Layer-by-Layer (LbL) synthesis was studied using a combination of IR spectroscopy technologies. For example, IRRAS studies of the precursor solutions, as well as HKUST-1 films, allowed us to spectroscopically assign all vibrations of HKUST-1, including its precursors. By monitoring these vibrations, it was possible to evaluate the effect of synthesis parameters (i.e., manual vs. automated synthesis, dipping time, washing, drying, precursor solution concentration) on the resulting quality of the SURMOF materials.

FIGURE 6.1: Schematic depicting a) the growth mechanism of hindered SURMOF when using drying steps, and b) the solution-mediated growth mechanism of HKUST-1 SURMOF.

Subsequently, some SURMOFs prepared with varying synthesis parameters were analyzed with nano-IR spectroscopy. Due to a lack in bulk band-broadening in near-field IR spectroscopy, we were able to assign IR bands to the fully, partially, and non-coordinated paddlewheels of HKUST-1. As a result, we could identify local defect concentrations of HKUST-1 SURMOF. In this manner, the detrimental effect of drying was found, as well as the beneficial effect of a short deposition step using copper nitrate (instead of copper acetate) on the HKUST-1 SURMOF quality. As a result, a solution-mediated growth mechanism was established, which in turn resulted in an improved synthesis route in terms of both SURMOF quality and preparation time (Figure 6.1).

CHAPTER 3 describes the initial development of *in situ* PiFM and its application to uncover site-specific guest-host interaction between (heavy) water and mixed HKUST-1/ZIF-8 films. By using a mixture of carboxylic acid alkanethiol and pyridine-thiol for substrate functionalization, we have created a bifunctional surface for HKUST-1/ZIF-8 nucleation and growth within a single SURMOF film. Point spectra on HKUST-1 grains in air showed strongly water-modulated IR signal, whereas the ZIF-8 grains did not. Subsequent removal of air from the sample chamber and backfilling with N₂ showed desorption of water from the hydrophilic HKUST-1 surface and a largely unchanged spectrum of the ZIF-8 surface. As a result, we could show the successful synthesis of an amphiphilic film using self-assembly methods.

Using the *in situ* PiFM methodology, the Chapter then zoomed-in on (defective) HKUST-1 sites at increasing D₂O pressure. This analysis showed enhanced D₂O sorption on existing defective HKUST-1 paddlewheel sites versus pristine sites. Furthermore, we have observed D₂O-induced defect formation in real-time. This led to the deduction of site-specific gas sorption isotherms of water on HKUST-1 and a visual representation of defect formation and propagation as a function of water sorption.

In **CHAPTER 4**, the newly developed *in situ* PiFM technique was applied to (defect-engineered) SURZIF-8. Together with DFT calculations, this methodology was used to study the structure sensitive sorption and conversion of formaldehyde. It showed that formaldehyde exhibited preferential sorption on high energy planes (i.e., corners and edges). DFT explained this behavior by describing the stronger chemisorption of formaldehyde on these planes. However, IR mapping in formaldehyde vapor showed the non-homogeneous sorption behavior of crystal planes: domains of alternate surface termination were found with DFT to provide alternate binding sites.

The properties of ZIF-8 were modulated by incorporating isotope-labeled defect linkers leading to enhanced Lewis acidity. Defect linker incorporation was found to be structure sensitive, thus suggesting plane energy relaxation upon defect expression. The defect-engineered ZIF-8 was found to be able to convert formaldehyde in a structure-sensitive manner, with the crystal corners and edges outperforming the crystal facets in terms of conversion. Additionally, two conversion mechanisms were found through the detection of intermediate species on the ZIF-8 surface.

In **CHAPTER 5**, *in situ* PiFM was used to uncover the local electronic properties of bimetallic Co:Cu-HKUST-1 by monitoring the shift of the $\nu_{\text{N-O}}$ vibration of the nitric oxide probe molecule. We were able to distinguish between Cu²⁺ of the coordinated HKUST-1 paddlewheels and the defective Cu⁺ sites, as well as coordinated and defective cobalt sites of single oxidation state. We found that cobalt site expression location was strongly dependent on the synthesis method. When transmetalating a monometallic Cu-HKUST-1 SURMOF, the cobalt nodes preferentially exchanged with readily accessible Cu⁺ sites, while keeping the morphology of the parent sample intact. In contrast, when using a direct synthesis with a mixed Co:Cu precursor solution, we observed the growth of individual crystallites with different crystal orientations and (defective) cobalt site concentrations.

With the *in situ* PiFM technique, we compared the redox properties of metal sites in these bimetallic HKUST-1 samples by evaluating their reductive NO disproportionation abilities. Since *in situ* PiFM was able to map the nanoscale distribution of metal ion (coordination), the redox behavior could be directly linked to specific ion properties. In this manner, different synthesis methods could be coupled to (bulk) functionality. As a result, we found that the transmetalation resulted in a sample with poor disproportionation performance as

it possessed a low concentration of redox active Co and Cu sites. The direct synthesis led to mixed redox behavior between crystallites grown in the (100) and (111) direction. HKUST-1 grown in the (100) direction showed the structure sensitive disproportionation of NO₂ disproportionation. HKUST-1 grown in the (111) direction showed little, and moreover very local, disproportionation properties. This proof-of-concept is expected to be highly applicable for other porous functional materials and their rational synthesis.

6.2 CONCLUDING REMARKS

This PhD Thesis has shown the applicability of (*in situ*) nano-infrared spectroscopy for the study of model systems of Metal-Organic Frameworks. This technique has shown great value in uncovering MOF growth, MOF material properties, and MOF functionality. In this section, some concluding remarks are made on these topics, as well as on *in situ* PiFM development, spanning the Chapters of this thesis.

6.2.1 DEVELOPMENT OF *IN SITU* PHOTO-INDUCED FORCE MICROSCOPY

This thesis details the development of *in situ* PiFM. This *in situ* functionality is highly desired as it gives the possibility to study guest-host interactions between MOFs and adsorbates to determine their functionality, but it also allows for the use of probe molecules to determine local material properties. For example, in **CHAPTER 3**, we used D₂O as a guest molecule in the PiFM technique (Figure 6.2). This molecule was chosen to study the site-specific interaction between SURMOF and (heavy) water. This interaction is highly relevant for future applications of HKUST-1, or other MOFs, in industry, as water has a ubiquitous presence in industrial gas streams. Therefore, linking the local chemistry to a site-specific gas sorption isotherm will allow for the rational synthesis of more robust materials.

Additionally, in **CHAPTER 4**, we have used formaldehyde as a probe molecule. This probe molecule is a Volatile-Organic Compound (VOC) and is a model probe representing various undesired aldehydes and ketones that require capture and/or conversion for neutralization. Since only the outer surface of ZIF-8 was found to be responsive to interaction with guest molecules, sorption of formaldehyde on ZIF-8 using bulk IR spectroscopy was not observed due to the unfavorable dispersion of bulk and surface sites. Therefore, to study the sorption and conversion of formaldehyde on ZIF-8, the surface-sensitive PiFM technique was required. Furthermore, previous *ex situ* studies have found a disparity in crystal facet performance, i.e., structure sensitivity in gas sorption/conversion.^[1,2] However, limited by either their spatial resolution (e.g., IR and Raman), by their *in situ* capabilities (e.g., SEM, TEM, XPS and APT), or their sample limitations (e.g., STM), it was previously impossible gather direct evidence for crystal plane-dependent gas sorption/conversion performance on the nanoscale.

FIGURE 6.2: Schematic outlining the applicability of *in situ* PiFM for site-specific material property/functionality detection. *In situ* PiFM is able to detect sorption behavior of a probe molecule, such as D_2O . This sorption behavior gives information on nanoscale hydrophilicity and can link local chemistry to gas sorption behavior.

CHAPTER 5 further shows the relevance of *in situ* PiFM. While PiFM possesses the required spatial resolution to study local environments within SURMOFs, it is currently only able to probe IR active vibrations in the $1965\text{--}775\text{ cm}^{-1}$ range. As a result, it cannot provide information on, for example, metal-metal bonds, nor is it apt to study metal sites of varying oxidation states. However, by coupling PiFM with NO as a probe molecule, electronic properties of metal sites (of varying oxidation state) within SURMOF films could be studied. With this methodology, a spatial resolution of $<5\text{ nm}$ for the IR mapping ability was shown. This proof-of-concept study is highly applicable to other research within the field of material science to uncover nanoscale metal distributions.

6.2.2 SYNTHESIS OF MOF AND ZIF MODEL SYSTEMS

This thesis has provided several insights on (the relevance of) different syntheses of HKUST-1 and ZIF-8 model systems. First, **CHAPTER 2** describes a systematic study of Layer-by-Layer synthesis parameters. This analysis found that in order to quickly grow defect-free SURMOFs, one should fit synthesis parameters to match the solvent-mediated growth mechanism of HKUST-1 SURMOF. However, dependent on the envisioned application, a smooth, defect-free may not be desired. For example, when synthesizing membranes for gas separation, the presence of framework defects is typically highly undesired, as those allow for the diffusion of gas outside the MOF-native pore channels and cages.^[3] However, literature has shown that for several applications, such as gas sorption and conversion, the presence of defects can be highly beneficial for the material performance.^[4–6]

FIGURE 6.3: Schematic describing the influence of synthesis method on metal node distributions in bimetallic Co:Cu-HKUST-1. For example, transmetalation with cobalt nitrate leads to the scavenging of Cu^+ -sites and thus a low Cu^+ concentration. Direct synthesis disrupts oriented SURMOF growth leading to a high Cu^+ concentration. Dependent on the HKUST-1 orientation ((111)/(100)), cobalt is incorporated as defect, or as framework site, respectively. These distributions will strongly affect material (redox) properties.

Therefore, in **CHAPTER 3**, the growth of defect-free HKUST-1 was disrupted to provide MOF grains with an increased concentration of defective sites. This was not done by tweaking the synthesis parameters of the LbL synthesis but rather by introducing disorder in the self-assembled monolayer of thiol molecules responsible for nucleation and growth of HKUST-1 and ZIF-8. This provided insight into the function of the thiol molecules. With this approach, we found that the growth-orientation function is only present when an unperturbed monolayer of thiols is chemisorbed on the gold surface. However, even when disrupted, the thiol molecules provided effective nucleation and growth sites, and since the orientation-directing effect was absent for these samples, model systems of bulk orientation

were made. This provided the opportunity to compare HKUST-1 sites of alternate orientation, morphology, and functionality within one sample, thus better describing powder samples of MOFs.

Furthermore, the use of a bifunctional growth-promoting self-assembling monolayer allowed for the deposition of HKUST-1 and ZIF-8 within a single film. PiFM analysis of these films ruled out longitudinal hetero-growth of frameworks. Additionally, domain radius comparison between SAM films and SURMOF films showed that the LbL growth resulted in minimal lateral growth of the grains, thus preventing MOF/ZIF intergrowth.

In **CHAPTER 5**, we showed the strong influence of the synthesis method on the incorporation of multivariate metal nodes (Figure 6.3). Bimetallic Co:Cu HKUST-1 was synthesized by either performing a post-synthetic transmetalation or a direct LbL synthesis with mixed Co:Cu metal precursor solutions. When using a transmetalation synthesis, the morphology of the sample did not change, and we found that the cobalt nodes preferentially exchanged the readily available defect sites. As a result, the transmetalated sample possessed a high amount of undercoordinated cobalt sites. In contrast, when using a direct synthesis, the morphology of the sample did change into a mixed-orientation sample of HKUST-1 crystallites. Both these morphologies incorporated the cobalt nodes in an alternate manner, where (111) grains showed a high concentration of defective cobalt sites and the (100) grains showed a high concentration of coordinated cobalt sites. This showed the relevance of sample preparation on resulting metal distribution and thus material properties.

Sample morphology was also found to be of significant importance in the performance of ZIF-8 crystals in **CHAPTER 4**. The sorption and conversion of formaldehyde were found to be largely dependent on the exposure of specific crystal planes, as well as the presence of defects. The incorporation of defects was found to alter the aspect ratio of the ZIF-8 crystals. The defect linker induced relaxation in higher energy facets, resulting in a larger relative exposure of these facets. Additionally, by incorporating defects, open metal sites were produced that were able of formaldehyde conversion, while its pristine counterpart was not. Defect engineering of MOF/ZIF crystals was thus found to be able to provide new functionalities within a material. These insights can benefit the rational synthesis of MOF/ZIF crystals for a specific application, for example, by forcing the exposure of specific crystal planes by the use of growth modulators, by nanosizing, or by defect engineering.

6.2.3 SURMOF MATERIAL PROPERTIES AND FUNCTIONALITY

By using (*in situ*) PiFM, it was possible to establish site-specific structure-property/performance relationships for (multivariate) HKUST-1 and (defect-engineered) ZIF-8. For example, in **CHAPTERS 2** and **3**, we found location-specific conformations of the HKUST-1 paddlewheel for SURMOFs that showed pristine bulk characteristics in AFM,

XRD, and in bulk IR spectroscopy. By linking the local defective nature of HKUST-1 sites, we were able to establish the site-specific D_2O sorption isotherm of undercoordinated HKUST-1 paddlewheels. Furthermore, in **CHAPTER 4**, we were able to link defect sites to the conversion to formaldehyde as opposed to adsorption on the pristine sites of ZIF-8. Moreover, in **CHAPTER 5**, we found that, unlike coordinated Cu^{2+} -sites, defective Cu-sites were able to disproportionate NO adsorbates. In contrast, for cobalt, we found that cobalt incorporated into the HKUST-1 framework was able to form NO_2 , yet defective Co-sites were not. This shows the ability of *in situ* PiFM to acquire direct evidence for the performance of defect-engineered sites.

FIGURE 6.4: Graph showing the formaldehyde pressure that was required to induce formaldehyde conversion via the methoxy mechanism and the formate (DOM/POM) mechanism. Comparison between ZIF-8 bulk characteristics (dashed line) and (small) crystal planes shows the structure sensitive conversion of formaldehyde over high-energy planes such as corners and edges.

Moreover, **CHAPTER 4** describes the detection of structure sensitive sorption and conversion of formaldehyde. Overall, defective sites were found to be necessary for formaldehyde conversion, but the required formaldehyde pressure for conversion was found to be crystal plane-dependent. Due to the high spatial resolution of the PiFM technique, it was even possible to analyze the small corner planes of the ZIF-8 crystals. These corners (and edges) were found to require lower formaldehyde pressures for conversion than the crystal facets (Figure 6.4). While these facets showed lower overall formaldehyde conversion performance, with *in situ* PiFM, we found intra-facet domains showing better conversion performance. According to DFT analysis, these domains corresponded to alternate surface terminations of the same crystal plane. Thus, by using *in situ* PiFM, we found surface termination-specific gas sorption and conversion behavior.

Finally, with *in situ* PiFM, we found the synthesis-dependent distribution of metal sites in bimetallic HKUST-1 in **CHAPTER 5**. This distribution of metals strongly influences its electronic properties and, therefore, its functionality. Specifically, it showed that it was able to locate cobalt nodes of a singular oxidation state, yet with differences in coordination, within the SURMOF. Identification of these distinct coordination states would not have been possible using bulk IR spectroscopy due to band broadening or with XPS/APT due to the singular oxidation state. Furthermore, with *in situ* PiFM, we found that the redox properties of Co-HKUST-1 are largely dependent on this coordination, as only cobalt nodes incorporated into the HKUST-1 framework show NO disproportionation activity. Therefore, with *in situ* PiFM, we could conclude that the redox properties were distribution-dependent rather than concentration-dependent.

6.3 FUTURE PERSPECTIVES

The development of the *in situ* PiFM technique has paved the way for many future research avenues to study the properties of functional materials, including their synthesis. Therefore, in this section, some perspectives for future research are outlined.

6.3.1 ISOTOPIC LABELING FOR CATALYSIS INVESTIGATIONS

This thesis has shown the use of D₂O, NO, and formaldehyde probe molecules to uncover MOF/ZIF material properties. The NO and formaldehyde probe molecules not only showed adsorption, they additionally showed conversion on certain MOF sites. However, conversion of adsorbates does not necessarily equal catalytic conversion, since it may be stoichiometric, followed by irreversible adsorption of the product. Alternate feeding of isotope-labeled probe molecules can provide evidence for catalytic conversion, based on reversible shifts in IR frequency, similarly to Steady-State Isotopic Transient Kinetic Analysis (SSITKA) studies. This approach will provide insights into site-specific activity, conversion mechanisms, and relative kinetics between conversion sites.

6.3.2 USE OF ALTERNATE PROBE MOLECULES

This thesis has used probe molecules to show MOF/ZIF stability (D₂O), functional material performance (formaldehyde), and metal distributions and electronic properties (NO). From bulk IR studies, more probe molecules are known to provide useful insights in surface properties of functional materials. For example, pyridine is an excellent probe for Lewis- and Brønsted acidity, CO can unveil metal oxidation state and coordination, pyrrole can probe surface basicity, methanol can probe both acidity and basicity, etc.

To use such alternate probe gases two main limitations should be overcome. First, the currently used laser allows for the acquisition of IR spectra in the fingerprint range only, specifically from 1965–775 cm^{-1} . This range is insufficient to show relevant vibrations of, e.g., linearly adsorbed carbon monoxide on metals and metal ions (2150–2000 cm^{-1}). To extend the IR working range to 4000 cm^{-1} , an additional Optical Parametric Oscillator (OPO) laser can be installed.

The second limitation is the *in situ* gas cell. The current system uses a large volume (20 L) vacuum cell as a gas cell. This cell brings the full system (including all optics components) in contact with the guest molecules introduced during *in situ* measurements. This limits the use of contaminating probe molecules such as pyridine. Additionally, the use of carbon monoxide is potentially dangerous when in contact with a large number of system components since it readily forms toxic carbonyl compounds when in contact with nickel contained in e.g., stainless steel. A solution for these issues would be the construction of gas-tight, probe-specific small volume gas cells with suitable materials.

6.3.3 MEASURING *IN SITU* PIFM AT ELEVATED TEMPERATURES

Several industrially-relevant catalytic reactions are thermally activated (e.g., hydrogenation and reforming reactions). Therefore, to expand the capabilities of *in situ* PiFM, control over the chamber temperature is desired. However, increasing the temperature of an AFM-based technique brings challenges. The system temperature influences the properties of piezo ceramics, cantilever resonance frequency, and the photodiode detector. Therefore, to limit temperature-induced measurement artifacts, it is highly relevant to use a setup producing local heating. Such a heating stage for the PiFM setup is in development. This stage provides local heating of the bottom of the sample, thereby heating the whole sample. By combining this stage with active cooling of the AFM components, high-temperature measurements may be achieved. Additionally, if the loading of samples is high enough, it would be possible to couple the gas cell to a gas chromatograph (GC) or a mass spectrometer (MS) to introduce *operando* possibilities to the setup.

6.3.4 EXPANDING THE RANGE OF FUNCTIONAL MATERIALS

At the start of this PhD research, the only known AFM-IR technique was the photo-thermal technique. Since this technique required materials with a large thermal expansion coefficient, metal-organic frameworks were thought of as specifically apt materials for nano-IR investigations. However, since the PiFM technique does not rely on photo-thermal expansion phenomena, inorganic materials can also be studied. Examples of functional inorganic materials of interest are zeolites, metal oxides, and supported metal nanoparticles.

This thesis has shown the applicability of *in situ* PiFM in the investigation of formaldehyde conversion on the surface of ZIF-8. Similarly, supported platinum nanoparticles are able to oxidize formaldehyde at room temperature.^[4,5] By investigating these metal nanoparticles in formaldehyde vapor on various metal oxide support after reduction treatment, *in situ* PiFM can be used to study interfacial effects in metal/metal oxide systems, such as spillover phenomena, bifunctional M/MO_x sites chemistry, and Strong Metal-Support Interaction (SMSI) effects. However, one prerequisite for such studies is a relatively large size in nanoparticles, due to the nm-scale resolution of the PiFM method.

Furthermore, it has already been shown that *ex situ* PiFM can be used to study the coking behavior of zeolites used in the Methanol-To-Hydrocarbons (MTH) reaction.^[6] After modification of the *in situ* PiFM setup to ensure high chemical resistance of the gas cell, as well as local heating, it may be possible to study this phenomenon *in situ*. Similarly, it would be possible to monitor DeNO_x reactions over ion-exchanged zeolites.

6.3.5 COUPLING FURTHER AFM-BASED TECHNIQUES

It is fair to state that AFM-IR is not the first technique to use an AFM tip as an antenna for vibrational spectroscopy signal. Tip-Enhanced Raman Spectroscopy (TERS) is a technique that uses an extremely sharp AFM tip to concentrate Raman scattering in the small volume just below the tip, thereby breaking the diffraction limit for Raman spectroscopy. Therefore, it should also be possible to combine multiple tip-based techniques within one setup. Such a setup could combine PiFM with TERS, as well as Kelvin Probe Force Microscopy (KPFM) and Photoluminescence. Such a setup would provide full the nanoscale spectroscopic characterization of functional materials (under reaction conditions).

6.4 REFERENCES

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APPENDICES

APPENDIX A: LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
APT	Atomic Probe Tomography
BTC	1, 3, 5-benzenetricarboxylic acid
CuAc ₂	Copper acetate
CUS	Coordinatively Undersaturated Site
Dabco	1,4-diazabicyclo[2.2.2]octane
DFT	Density Functional Theory
DOM	Dioxymethylene
EM	Expectation Maximization
FA	Formaldehyde
FFT	Fast Fourier Transform
GC	Gas Chromatography
GI-ATR-IR	Grazing Incidence Attenuated Total Reflection Infrared
GMM	Gaussian Mixture Modeling
GPW	Gaussian Plane Wave
GTH	Goedecker-Teter-Hutter
HKUST-1	Hong Kong University of Science and Technology 1
HRTEM	High Resolution Transmission Electron Microscopy
hyPIR	Hyperspectral
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IR	Infrared
IRRAS	Infrared Reflection Absorption Spectroscopy
KPFM	Kelvin Probe Force Microscopy
LbL	Layer-by-Layer
LEED	Low Energy Electron Diffraction
LPE	Liquid Phase Epitaxy
MBA	4-mercaptobenzoic Acid
MHDA	16-mercaptohexadecanoic Acid
Mim	2-methyl Imidazole
MMBA	4-(mercaptomethyl)benzoic Acid
MOF	Metal-Organic Framework

MPyr	4-mercaptopyridine
MR	Membered Ring
MS	Mass Spectrometry
NP	Nanoparticle
OPO	Optical Parametric Oscillator
PBE	Perdew-Burke-Ernzerhof
PC	Principal Component
PCA	Principal Component Analysis
PCP	Porous Coordination Polymer
PiFM	Photo-induced Force Microscopy
POM	Polyoxymethylene
PSM	Post-synthetic Modification
PT-AFM-IR	Photothermal Atomic Force Microscopy
QCL	Quantum Cascade Laser
QCM	Quartz Crystal Microbalance
RMS	Root Mean Square
SAM	Self-Assembling Monolayer
SBU	Secondary Building Unit
SED	Scanning Electron Diffraction
SEM	Scanning Electron Microscopy
SILAR	Successive Ionic Layer Adsorption and Reaction
SMF	Single Molecule Fluorescence
SMSI	Strong Metal-Support Interaction
SPR	Surface Plasmon Resonance
SSITKA	Steady-State Isotopic Transient Kinetic Analysis
STM	Scanning Tunneling Microscopy
SURMOF	Surface-anchored Metal-Organic Framework
TEM	Transmission Electron Microscopy
TERS	Tip-Enhanced Raman Spectroscopy
TXM	Transmission X-ray Microscopy
TZVP	Triple-Zeta Valence polarization
UDT	11-undecanethiol
UHV	Ultra-High Vacuum
UV	Ultraviolet
VdW	Van der Waals
VOC	Volatile Organic Compound
XPS	X-Ray Photoemission Spectroscopy
XRD	X-Ray Diffraction
ZIF	Zeolitic Imidazolate Framework

APPENDIX B: NEDERLANDSE SAMENVATTING

Dit proefschrift beschrijft het gebruik van nano-infrarood spectroscopie om de groei en reactiviteit van oppervlak-verankerde metaal-organische raamwerken (SURMOFs in dit Proefschrift) te bestuderen. Verder beschrijft het de ontwikkeling van *in situ* Foto-geïnduceerde Kracht Microscopie (Photo-induced Force Microscopy, of PiFM in dit Proefschrift) om plaats-specifieke eigenschappen en functionaliteiten binnen SURMOFs te beschrijven. Deze techniek werd toegepast op modelsystemen van twee archetypische MOFs, namelijk HKUST-1 en ZIF-8.

Binnen dit kader bevat dit proefschrift zes hoofdstukken. **HOOFDSTUK 1** geeft een algemene inleiding op het gebied van (SUR)MOFs en nano-infrarood (nano-IR) spectroscopie. **HOOFDSTUK 2** beschrijft het gebruik van twee soorten *ex situ* nano-IR spectroscopie om het vormingsmechanisme van HKUST-1 OPPMOR te bestuderen. **HOOFDSTUK 3** beschrijft de ontwikkeling van *in situ* PiFM met D₂O als gast molecuul om de plaats-specifieke gast-MOF interactie te bestuderen in een gemengd HKUST-ZIF membraan. **HOOFDSTUK 4** gaat verder in op de ontwikkeling van *in situ* PiFM op ZIF-8 om de structuurgevoelige sorptie en conversie van formaldehyde bloot te leggen. **HOOFDSTUK 5** bespreekt het gebruik van NO als gast molecuul in *in situ* PiFM om onderscheid te maken tussen metaalionen binnen bi-metallisch HKUST-1. Ten slotte geeft **HOOFDSTUK 6** een samenvatting van het onderzoek dat in de experimentele hoofdstukken is uitgevoerd en geeft het de belangrijkste bevindingen van deze hoofdstukken weer. Verder worden enkele perspectieven gegeven voor toekomstige onderzoeksrichtingen binnen het onderwerp van dit proefschrift.

In **HOOFDSTUK 2** werd het vormingsmechanisme van HKUST-1 SURMOF in een Laag-voor-Laat (Layer-by-Layer of LbL in dit Proefschrift) synthese bestudeerd met behulp van een combinatie van infrarood (IR) spectroscopie technologieën. Door gebruik te maken van de IR technieken konden IR vibraties van zowel de reactanten als van de gemaakte HKUST-1 membranen worden onderzocht. Met behulp van deze onderzoeken konden we alle IR vibraties van de HKUST-1 (reactanten) in het IR spectrum toewijzen. Door vervolgens deze vibraties gedurende de LbL synthese te volgen, konden we het effect van syntheseparameters, zoals handmatige vs. geautomatiseerde synthese, onderdompelingstijd, wassen en drogen, en reactant concentraties, op de kwaliteit van het HKUST-1 membraan bestuderen.

Vervolgens werden enkele SURMOFs met verschillende syntheseparameters bereid en daarna geanalyseerd met nano-IR spectroscopie. Vanwege de afwezigheid van bandverbreding bij nano-IR spectroscopie konden we specifieke IR vibraties toewijzen aan de volledig-, gedeeltelijk- en niet-gecoördineerde waterrad-structuur van HKUST-1. Daardoor konden we lokale defectconcentraties van HKUST-1 SURMOF identificeren. Op deze manier werd

het nadelige effect van drogen gevonden, evenals het gunstige effect van een korte depositietijd met kopernitrat (in plaats van koperacetaat) op de HKUST-1 SURMOF-kwaliteit. Verdere analyse van deze resultaten leidde tot het opstellen van een HKUST-1 vormingsmechanisme gebaseerd op groei in de vloeistoffase. Dit inzicht resulteerde vervolgens in een verbeterde syntheseroute, zowel wat betreft SURMOF-kwaliteit als bereidingstijd (Fig. 7.1).

FIGUUR 7.1: Diagram over de relevantie van LbL synthese parameters op HKUST-1 membraan kwaliteit. a) Bij het gebruik van droogstappen vindt verhinderde, defectieve MOF groei plaats. b) Bij de afwezigheid van droogstappen, worden gefysisorptie reactanten op het oppervlak efficiënt omgezet tot defect-vrije SURMOF.

HOOFDSTUK 3 beschrijft de ontwikkeling van in situ PiFM en zijn toepassing op het blootleggen van plaats-afhankelijke gast-gastheer interactie tussen (zwaar) water en gemengde HKUST-1/ZIF-8 membranen (Fig. 7.2). Door een mengsel van carbonzuur alkaanthiol en pyridine-thiol te gebruiken voor het functionaliseren van het goud substraat, creëerden we een zelf-assemblage bi-functioneel oppervlak voor HKUST-1/ZIF-8 nucleatie en groei op één enkel SURMOF-oppervlak. Puntspectra op HKUST-1 materiaal aan de lucht vertoonden een IR signaal dat sterk werd beïnvloed door de aanwezigheid van water op het HKUST-1 oppervlak. Het ZIF-8 materiaal vertoonde dit gedrag niet. De daaropvolgende verwijdering van de lucht uit de monsterkamer en hervulling met N_2 toonde desorptie van water van het hydrofiele HKUST-1 oppervlak en een grotendeels onveranderd spectrum van het hydrofobe ZIF-8-oppervlak. Daarmee werd de succesvolle synthese van een amphifiel membraan met behulp van zelfassemblagemethoden aangetoond.

Met behulp van in situ PiFM zoomt het hoofdstuk vervolgens in op HKUST-1 (defecten) bij toenemende D_2O -druk. Deze analyse toonde aan dat meer D_2O -sorptie plaatsvond op reeds defecte HKUST-1 locaties versus volledig gecoördineerde locaties. Bovendien namen we D_2O -geïnduceerde defectvorming over tijd waar. Dit leidde tot de deductie van locatie-specifieke gassorptie-isothermen van water op HKUST-1 en een visuele weergave van de vorming en propagatie van defecten als functie van waterabsorptie.

FIGUUR 7.2: De ontwikkeling van in situ PiFM om SURMOF/ZIF stabiliteit in waterdamp te onderzoeken. Met behulp van zelfassemblage methoden vond de gemengde depositie van MOF en ZIF eilanden op een enkel substraat plaats. Adsorptie van zwaar water (D_2O) vond enkel plaats op de HKUST-1 eilanden en niet op ZIF-8. Reeds bestaande defecten faciliteerden snellere adsorptie van D_2O , en adsorptie veroorzaakte tevens de inductie van verdere defecten.

In **HOOFDSTUK 4** werd de nieuwe in situ PiFM techniek toegepast op (bewust defecte) SURZIF-8. Samen met “Density Functional Theory” (DFT) berekeningen werd deze methode gebruikt om de structuurgevoelige sorptie en omzetting van formaldehyde te bestuderen (Fig. 7.3). Het toonde aan dat formaldehyde bij voorkeur adsorbeert op hoogenergetische vlakken (met name hoeken en randen) van de ZIF-8 kristallen. DFT verklaarde dit gedrag door de sterkere chemisorptie van formaldehyde op deze vlakken te beschrijven. Door het in kaart brengen van het IR signaal van formaldehyde op ZIF-8 kristallen tijdens adsorptie toonden we echter aan dat de kristalvlakken niet-homogeen sorptiegedrag vertoonden. We vonden nano-domeinen die bij lagere formaldehyde druk al adsorptie vertoonden. Met behulp van DFT herleidde we dit gedrag tot de aanwezigheid van alternatieve oppervlakte-terminaties, en dus alternatieve bindingsplaatsen.

De eigenschappen van ZIF-8 werden aangepast door isotoop-gelabelde defect linkers in de ZIF in te bouwen, wat leidde tot de verhoogde Lewis-zuurgraad van het materiaal. De incorporatie van deze defect linker bleek structuurgevoelig te zijn. Als gevolg werd de kristalvlak energie verlaagd en veranderde de verhouding tussen verschillende kristalvlakken op het oppervlak van het ZIF-8 kristal. De defecte ZIF-8 bleek in staat om formaldehyde op een structuurgevoelige manier om te zetten, waarbij hoeken en randen al bij een lagere formaldehyde druk omzetting vertoonden. Bovendien vonden we twee conversiemechanismen voor het omzetten van formaldehyde. Dit werd gedaan door de detectie van intermediaire moleculen op het ZIF-8-oppervlak. Deze resultaten toonden de relevantie van nano-spectroscopie studies op materialen waar kristalvlakken met een klein oppervlak een groot effect op het bulk functioneren van een materiaal kunnen hebben.

FIGUUR 7.3: Plot van de structuur gevoelige omzetting van formaldehyde over kristalvlakken van ZIF-8. De omzetting van formaldehyde kan gebeuren via een formaat-, dan wel methoxy-, mechanisme. Het formaat mechanisme gebruikt DOM/POM intermediairen om formaat op het ZIF oppervlak te vormen. De onverzadigde vlakken van het ZIF-8 kristal, zoals hoeken en randen, kunnen bij lagere druk formaldehyde omzetten dan de verzadigde facetten.

In **HOOFDSTUK 5** werd in situ PiFM gebruikt om de lokale elektronische eigenschappen van een bi-metallisch Co:Cu-HKUST-1 materiaal bloot te leggen. Dit deden we door de verschuiving van de $\nu_{\text{N=O}}$ vibratie van het stikstofmonoxide gast-molecuul te volgen. Hierdoor waren we in staat om onderscheid te maken tussen Cu^{2+} en Cu^+ ionen van de gecoördineerde en de defecte locaties binnen de HKUST-1 waterrad structuur. Op dezelfde manier konden we gecoördineerde en defecte kobaltionen met eenzelfde oxidatietoestand ($2+$) vinden. We ontdekten dat de locatie van de kobaltionen sterk afhankelijk was van de synthesemethode. Bij een ionenuitwisseling synthese van een mono-metallisch Cu-HKUST-1 monster wisselden de kobalt ionen bij voorkeur uit met de gemakkelijk bereikbare Cu^+ plaatsen, terwijl de morfologie van het originele materiaal intact bleef. Bij gebruik van een directe synthese met behulp van een gemengde Co:Cu reactantoplossing daarentegen, observeerden we de groei van individuele kristallen met verschillende kristaloriëntaties en lokaal wisselende concentraties van kobalt coördinatie defecten.

FIGUUR 7.4: Schematische representaties van koper en kobalt ion distributies in bi-metallisch HKUST-1. Bi-metallisch HKUST-1 werd gesynthetiseerd via een transmetallatie (boven) en een directe synthese (onder). Tijdens transmetallatie werden bij voorkeur Cu^+ sites vervangen door kobalt ionen. Bij een directe synthese leidde een hoge concentratie kobalt tot de creatie van HKUST-1 in verschillende oriëntatie en morfologie. Afhankelijk van deze oriëntatie en morfologie veranderde de lokale structuur van de kobalt ionen. Bovendien, afhankelijk van de synthese methode, en de bijbehorende ionendistributie, werden de redox eigenschappen van het bulk materiaal beïnvloed.

Vervolgens vergeleken we met *in situ* PiFM de redox-eigenschappen van al de verschillende metaalionen in deze bi-metallische HKUST-1 monsters door hun vermogen tot reductieve NO disproportionering te evalueren. Aangezien *in situ* PiFM de nanoschaal distributie van de verschillende ion (coördinaties) kon vinden, kon het redox gedrag worden gekoppeld aan specifieke ion conformaties. Daardoor konden de verschillende synthese methoden aan (bulk) functionaliteit worden gekoppeld. Op deze manier vonden we dat de ion uitwisselingssynthese resulteerde in een membraan met een laag disproportionerings-vermogen aangezien het een lage concentratie aan Co- en Cu ionen met redox activiteit bezat. De directe synthese

leidde tot gemengd redoxgedrag tussen kristallen gegroeid in de (100) en de (111) richting. HKUST-1 gegroeid in de (100)-richting vertoonde de structuurgevoelige disproportioneer- ing van NO. De HKUST-1 gegroeid in de (111)-richting vertoonde weinig, en bovendien zeer lokaal disproportioneeringsvermogen. Deze bevindingen zijn samengevat in Fig. 7.4. We voorspellen dat deze analyse kan worden toegepast op vele andere materialen en daardoor is in situ PiFM een zeer relevante tool voor materiaalkundig onderzoek naar ionen distributie en coördinatie en hun invloed op bulk gas sorptie en conversie.

APPENDIX C: LIST OF PUBLICATIONS AND PRESENTATIONS

C.1. THIS PHD THESIS IS BASED ON THE FOLLOWING PUBLICATIONS

Guusje Delen^{*}, Zoran Ristanović^{*}, Laurens D. B. Mandemaker, Bert M. Weckhuysen, “Mechanistic Insights into Growth of Surface-Mounted Metal-Organic Framework Films Resolved by Infrared (Nano-) Spectroscopy”, *Chem. Eur. J.* 2018, 24, 187–195. ^{*}Both authors contributed equally to this publication.

Guusje Delen, Matteo Monai, Florian Meirer, Bert M. Weckhuysen, “*In situ* Nanoscale Infrared Spectroscopy of Water Adsorption on Nanoislands of Surface-Anchored Metal-Organic Frameworks”, *Angew. Chem. Int. Ed.* 2020, 60, 1620-1624.

Guusje Delen, Matteo Monai, Katarina Stančíaková, Florian Meirer, and Bert M. Weckhuysen, “Structure Sensitivity in Gas Sorption and Conversion on Metal-Organic Frameworks”, *in preparation*.

Guusje Delen, Matteo Monai, Ramon Oord, Florian Meirer, and Bert M. Weckhuysen, “Mapping of Location- and Coordination-Dependent Redox Properties of Metal Nodes in a Bimetallic Metal-Organic Framework”, *in preparation*.

C.2. OTHER PUBLICATIONS BY THE AUTHOR

Jingbo Nan, Helen E. King, Guusje Delen, Florian Meirer, Bert M. Weckhuysen, Zixiao Guo, Xiaotong Peng, Oliver Plümper, “The Nanogeochemistry of Abiotic Carbonaceous Matter in Serpentinites from the Yap Trench, Western Pacific Ocean”, *Geology*, 2020, 49, 330-334.

Miguel Rivera-Torrente, Laurens D. B. Mandemaker, Matthias Filez, Guusje Delen, Beatriz Seoane, Florian Meirer, Bert M. Weckhuysen, “Spectroscopy, microscopy, diffraction and scattering of archetypal MOFs: formation, metal sites in catalysis and thin films”, *Chem. Soc. Rev.* 2020, 49, 6694-6732.

Laurens D. B. Mandemaker, Miguel Rivera-Torrente, Guusje Delen, Jan P. Hofmann, Matthias Lorenz, Alex Belianinov, Bert M. Weckhuysen, “Nanoweb Surface-Mounted Metal-Organic Framework Films with Tunable Amounts of Acid Sites as Tailored Catalysts”, *Chem. Eur. J.* 2020, 26, 691-698.

Mohammad Amirilargani, Giovana N. Yokota, Gijs H. Vermeij, Renaud B. Merlet, Guusje Delen, Laurens D. B. Mandemaker, Bert M. Weckhuysen, Louis Winnubst, Arian Nijmeijer, Louis C. P. M. de Smet, Ernst J. R. Sudhölter, “Melamine-Based Microporous Organic Framework Thin Films on an Alumina Membrane for High-Flux Organic Solvent Nanofiltration”, *ChemSusChem*, 2020, 13, 136-140.

Rogier P. Brand, Laurens D. B. Mandemaker, Guusje Delen, Niek Rijnveld, Bert M. Weckhuysen, “Behavior of a Metal-Organic Framework Thin-Film at Elevated Temperature and Pressure as Studied with an Autoclave-Inserted Atomic Force Microscope”, *ChemPhysChem*, 2018, 19, 2397-2404.

Laurens D. B. Mandemaker, Matthias Filez, Guusje Delen, Huanshu Tan, Xuehua Zhang, Detlef Lohse, Bert M. Weckhuysen, “Time-Resolved In Situ Liquid-Phase Atomic Force Microscopy and Infrared Nanospectroscopy during the Formation of Metal-Organic Framework Thin Films”, *J. Phys. Chem. Lett.* 2018, 9, 1838-1844.

Donglong Fu, Katie Park, Guusje Delen, Özgün Attila, Florian Meirer, Derek Nowak, Sung Park, Joel E. Schmidt, Bert M. Weckhuysen, “Nanoscale infrared imaging of zeolites using photoinduced force microscopy”, *Chem. Comm.* 2017, 53, 13012-13014.

C.3. ORAL PRESENTATIONS

“Creating Heterogeneous SURMOF Surfaces via Self-Assembly”. 20th Netherlands’ Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands, March 2019.

“Creating Heterogeneous SURMOF Surfaces via Self-Assembly”, 6th International Conference on Metal-Organic Frameworks & Open Framework Compounds (MOF), Auckland, New Zealand, December 2018. Awarded ‘Best Lecture’ prize.

“Microscopy and Spectroscopy on Thin-Films for (Electro-)Catalysis.” Invited presentation at the 233rd The Electrochemical Society (ECS) conference, Seattle, United States of America, May 2018.

“Infrared Nano-spectroscopy of Surface-anchored Metal-Organic Frameworks.”, Invited lecture at Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, January 2018.

C.4. POSTER PRESENTATIONS

“Near-Field Nano-Spectroscopy of Porphyrin-based Surface-Anchored Metal-Organic Frameworks”. 21st Netherlands’ Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, the Netherlands, March 2020.

“Near-Field Nano-Spectroscopy of a Porphyrin-based Surface-Anchored Metal-Organic Framework”, 7th CHemistry as an INnovating Science (CHAINS) Conference, Veldhoven, The Netherlands, December 2019.

“Tailoring Metal-Organic Framework Thin Films via Mechanistic Insights obtained with Atomic Force Microscopy”, 19th Netherlands’ Catalysis and Chemistry Conference (NCCC), Noordwijkerhout, The Netherlands, March 2018.

“Revealing Details of the Growth of HKUST-1 SurMOF Materials using Advanced Atom Force Microscopy”, 2nd European Conference on Metal-Organic Frameworks and Porous Polymers (EuroMOF), Delft, The Netherlands, October 2017.

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ABOUT THE AUTHOR

Guusje Delen was born on the 20th of September, 1991 in Zutphen (the Netherlands). She grew up in the small city called Lochem, where she decided at the age of fourteen that she wanted to pursue a PhD in Chemistry. After finishing school in 2009, she started an Undergraduate degree in Chemistry at the University of Birmingham (United Kingdom). In 2010 she transferred to Utrecht University to finish her Undergraduate degree there, including a Bsc. project under supervision of prof. dr. Petra De Jongh. After gaining her Bsc. Degree, she took a gap year to travel the world and teach Chemistry to high school students. In 2014 she started her 'Nanomaterials: Chemistry and Physics' degree at Utrecht University, where she performed her Msc. Project under supervision of prof. dr. ir. Krijn P. de Jong. Additionally, she worked as a teaching assistant at Utrecht University, and as an R&D intern for Philips Lighting (now Signify) for 6 months. In 2016 she began her PhD project on Nano-Spectroscopy in the group of prof. dr. ir. Bert M. Weckhuysen. The results of this research project are described in this Thesis.