

**Optical properties of Surface-anchored Metal-organic Frameworks
(SURMOFs): Circular Dichroism and Lithographic Patterning**

Zur Erlangung des akademischen Grades eines

DOKTORS DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

von der KIT-Fakultät für Chemie und Biowissenschaften

des Karlsruher Instituts für Technologie (KIT)

genehmigte

DISSERTATION

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Tag der mündlichen Prüfung: 23. April 2026

This work was carried out from May 2022 to December 2025, at the Institute of Functional Interfaces (IFG), Faculty of Chemistry and Biosciences at the Karlsruhe Institute of Technology (KIT) under the supervision of Prof. Dr. Christof Wöll.

Diese Arbeit wurde im Zeitraum von Mai 2022 bis Dezember 2025 am Institut für Funktionelle Grenzflächen (IFG), Fakultät für Chemie und Biowissenschaften, am Karlsruher Institut für Technologie (KIT) unter der Betreuung von Prof. Dr. Christof Wöll durchgeführt.

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ABSTRACT

Surface-anchored metal-organic frameworks (SURMOFs) provide a highly ordered platform for investigating optical phenomena in porous crystalline materials as well as for their integration into solid-state devices. In this work, chiral SURMOFs were systematically investigated with respect to their optical properties, with a particular focus on vibrational circular dichroism (VCD). The experimental results were directly compared with multiscale theoretical simulations, enabling a correlation between molecular structure, crystallographic orientation, and macroscopic optical response.

A central result of this work is the first experimental demonstration of VCD measurements on SURMOF thin films. In contrast to powder-based MOF studies, SURMOFs grown on transparent substrates such as CaF_2 enable transmission-mode VCD measurements without embedding in KBr pellets. This leads to improved signal-to-noise ratios and more reliable spectral interpretation. The measured IR and VCD spectra show good agreement with theoretical predictions and establish SURMOFs as well-defined model systems for chiroptical investigations.

Motivated by theoretical predictions of enhanced optical effects in laterally structured architectures, various lithographic approaches for structuring SURMOF films were investigated. Despite the remaining experimental challenges associated with the realization of chiroptical metamaterials, this work provides important insights into chemical compatibility, achievable resolution, and substrate-related constraints, and demonstrates the feasibility of SURMOF microstructuring.

In a complementary part of this work, azide-functionalized SURMOFs were developed to investigate photoactivated reactivity in an ordered solid-state environment. UV-induced transformations were analyzed using infrared spectroscopy, X-ray photoelectron spectroscopy, and mass spectrometry. Although nitrene intermediates could not be stabilized, the results reveal intermolecular reaction pathways enabled by the periodic arrangement of azide linkers.

Overall, this work highlights SURMOFs as well-structured and chemically tunable systems for optical investigations, lithographic integration, and spatially controlled photochemistry.

ZUSAMMENFASSUNG

Oberflächenverankerte metallorganische Gerüste (SURMOFs) bieten eine hochgradig geordnete Plattform zur Untersuchung optischer Phänomene in porösen kristallinen Materialien sowie für deren Integration in Festkörperbauelemente. In dieser Arbeit wurden chirale SURMOFs systematisch hinsichtlich ihrer optischen Eigenschaften untersucht, mit besonderem Schwerpunkt auf dem vibrationalen Zirkulardichroismus (VCD). Die experimentellen Ergebnisse wurden direkt mit multiskaligen theoretischen Simulationen verglichen, wodurch eine Korrelation zwischen Molekülstruktur, kristallographischer Orientierung und makroskopischer optischer Antwort hergestellt werden konnte.

Ein zentrales Ergebnis dieser Arbeit ist die erste experimentelle Demonstration von VCD-Messungen an SURMOF-Dünnschichten. Im Gegensatz zu pulverbasierten MOF-Studien ermöglichen SURMOFs, die auf transparenten Substraten wie CaF_2 gewachsen sind, VCD-Messungen im Transmissionsmodus ohne Einbettung in KBr-Pellets. Dies führt zu verbesserten Signal-Rausch-Verhältnissen und einer zuverlässigeren spektralen Interpretation. Die gemessenen IR- und VCD-Spektren zeigen eine gute Übereinstimmung mit theoretischen Vorhersagen und etablieren SURMOFs als wohldefinierte Modellsysteme für chiroptische Untersuchungen.

Motiviert durch theoretische Vorhersagen verstärkter optischer Effekte in lateral strukturierten Architekturen wurden verschiedene lithographische Ansätze zur Strukturierung von SURMOF-Filmen untersucht. Trotz der weiterhin bestehenden experimentellen Herausforderungen bei der Realisierung chiroptischer Metamaterialien liefert diese Arbeit wichtige Erkenntnisse zu chemischer Kompatibilität, erreichbarer Auflösung und substratbedingten Einschränkungen und demonstriert die Machbarkeit der Nanostrukturierung.

In einem ergänzenden Teil wurden azidfunktionalisierte SURMOFs zur Untersuchung photoaktivierter Reaktivität entwickelt. UV-induzierte Umwandlungen wurden mittels Infrarotspektroskopie, Röntgenphotoelektronenspektroskopie und massenspektrometrischer Methoden analysiert. Obwohl Nitren-Zwischenstufen nicht stabilisiert werden konnten, zeigen die Ergebnisse intermolekulare Reaktionswege, die durch die periodische Anordnung der Azid-Linker ermöglicht werden. Insgesamt unterstreicht diese Arbeit SURMOFs als gut strukturierte und chemisch abstimmbare Systeme für optische Untersuchungen, lithographische Integration und räumlich kontrollierte Photochemie.

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1 MOTIVATION

Metal–organic frameworks (MOFs) are porous and crystalline materials formed by the link of organic molecules to inorganic clusters or metal ions through strong, directional bonds. This connectivity results in extended two or three-dimensional frameworks¹, as illustrated in the generic structure shown in Figure 1. MOFs have received considerable attention due to their exceptional structural tunability, since even minor modifications to the linker or metal center can result in significant changes in framework topology, pore size, and chemical functionality². In addition to this modularity, their high surface area and chemical versatility make them suitable for a wide range of applications, including gas storage and separation³, heterogeneous catalysis⁴, chemical sensing⁵, and optoelectronic devices⁶. The significance of MOFs was recognized by the 2025 Nobel Prize in Chemistry, awarded to Omar M. Yaghi, Susumu Kitagawa, and Richard Robson for the pioneering works on these framework materials.

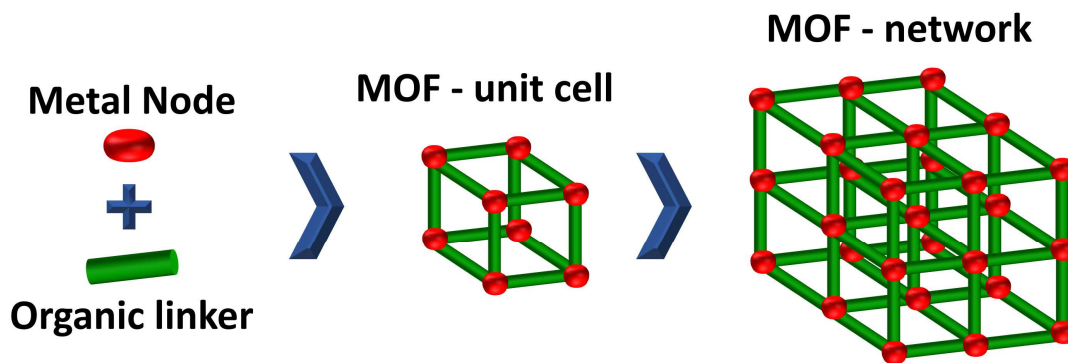


Figure 1: Formation of a generic MOF by Secondary Building Units and organic linkers

Despite their promising properties, the direct integration of MOF powders into solid-state devices remains a significant challenge. For instance, in the fabrication of MOF-based membranes for gas separation, the use of powders often leads to intergranular voids, which compromise both the mechanical integrity and separation performance of the membrane⁷. Beyond membranes, many emerging applications, such as optical coatings, photonic devices, and microelectronic components, require materials with low surface roughness, high film uniformity, and, in some cases, precise crystallographic orientation. These characteristics are difficult to achieve with conventional powder-based processing.

Surface-anchored MOFs (SURMOFs), a class of MOFs grown via a controlled layer-by-layer deposition on functionalized substrates, offer a promising route to overcome these limitations⁸. This growth method enables the formation of homogeneous, continuous, and low-roughness thin films, significantly improving compatibility with microfabricated device architectures⁹. Such uniformity is especially advantageous in applications where the active material must completely and consistently cover the substrate, such as in sensors, where uninterrupted contact between electrodes ensures reliable signal transduction¹⁰, and in membranes, where structural homogeneity is critical for effective separation performance¹¹.

In addition to facilitating integration into devices, the high degree of structural organization achievable in SURMOFs makes them an excellent platform for investigating fundamental MOF properties that are otherwise difficult to assess in powdered form, such as mass transport, diffusion, and surface reactivity⁹. SURMOFs are also advantageous in applications that require transparent thin films, especially when optical measurements in transmission mode are involved. In contrast to MOF powders, which typically require embedding in KBr pellets (often reducing signal-to-noise ratios), SURMOFs can be grown directly on transparent substrates, preserving optical quality and enabling more accurate characterization¹².

Their ordered architecture makes SURMOFs well suited for computational modeling, which can extend beyond planar films to simulate more intricate photonic architectures, such as SURMOF-based metamaterials. In these systems, structural periodicity can give rise to emergent optical or electronic properties, which can expand the applications of the bulk material¹³.

However, achieving such structures requires top-down patterning strategies that offer spatial control without compromising film quality. Existing methods for MOF film patterning often rely on specific reactive functional groups to enable material removal, limiting their general applicability^{14,15}. As a result, the development of more versatile, broadly compatible patterning techniques remains an important challenge. Such methods would benefit a range of applications, including chemical and biosensing, where localized SURMOF regions can be aligned with electrode arrays or microfluidic channels to improve performance; heterogeneous catalysis, where site-specific reactivity is desired; and the design of metamaterials, where precise spatial structuring can enhance properties beyond those of the bulk material¹⁶.

In this work, we collaborated with the Rockstuhl group at the Institute of Theoretical Solid-State Physics in the Karlsruhe Institute of Technology (TFP/KIT) to investigate the optical properties of a chiral SURMOF, both as continuous thin films and as patterned structures designed to function as metamaterials. Theoretical simulations were used to predict the optical response of these materials, while the experimental component focused on validating these predictions and exploring the fabrication feasibility of the proposed geometries. This combined theoretical-experimental approach aimed to advance the fundamental understanding of chiral SURMOF optics but could also contribute to the development of a versatile and generalizable top-down patterning strategy with potential relevance across a wide range of device-oriented applications.

Beyond patterning, another promising direction in SURMOF research lies in the integration of reactive functional groups into the framework backbone to unlock new avenues for post-synthetic modification and reactivity studies. In particular, the incorporation of azide ($-N_3$) functionalities within SURMOF linkers offers a versatile chemical handle for both in situ transformations and externally triggered reactions. Azides are known for their rich photochemistry and their ability to generate highly reactive nitrene intermediates upon exposure to ultraviolet (UV) light^{17,18}. While this reactivity is well explored in solution chemistry, the behavior of azide groups embedded within the ordered, spatially confined environment of a SURMOF remains largely uncharted. By leveraging the structural regularity and solvent-free environment of SURMOF thin films, we sought to explore whether the azide-to-nitrene photoconversion could be stabilized or directed in a solid-state matrix. In collaboration with the Bräse group at the Institute of Organic Chemistry (IOC/KIT), a novel azide-containing linker was synthesized specifically to eliminate side reactions observed in previous attempts, enabling a cleaner and more controllable photochemical response¹⁹. The ultimate goal was to create a photo-activatable SURMOF platform in which reactive nitrenes could be generated and harnessed to trigger secondary reactions, such as covalent binding to guest molecules or polymer chains within the pores, thereby opening the door to applications in stimuli-responsive materials, on-demand crosslinking, and site-selective functionalization. This approach not only deepens our understanding of photochemical reactivity in confined systems, but also introduces new strategies for the design of smart, light-responsive materials based on MOF architectures.

2 INTRODUCTION

This chapter gives an overview of the fundamental concepts for understanding the research presented in this thesis. It introduces the key materials and methodologies that form the basis of the study, beginning with Metal-Organic Frameworks (MOFs) and their structural and functional characteristics and moving further to Surface-Anchored Metal-Organic Frameworks (SURMOFs). The chapter also outlines various synthesis strategies used to prepare these materials. In addition, specific classes of SURMOFs, such as chiral SURMOFs, known for their enantioselective behavior, and azide-functionalized SURMOFs, valued for their chemical reactivity, are defined. This chapter also addresses the patterning of SURMOFs and the approaches used in this work. Together, these topics provide the necessary context for the research questions explored in the following chapters.

2.1 Metal-organic Frameworks (MOFs)

Metal Organic Frameworks are a class of materials whose studies originated from the pioneering work of Yaghi²⁰ and Kitagawa's groups²¹. While the early works from Yaghi included the first MOF with permanent porosity after removal of the solvent (MOF-5)²², Kitagawa's work on Porous Coordination Polymers (PCP) proved the possibility of gas adsorption by MOFs, even before the term MOF was widely used²¹. The scientific impact of MOFs was highlighted by the 2025 Nobel Prize in Chemistry, awarded for the early development of these materials.

MOFs were the foundation for the field of reticular chemistry which formalized the idea of constructing crystalline materials with predictable structures by linking pre-designed building blocks, metal clusters and organic linkers, through strong bonds, forming what is called Secondary Building Unit (SBU)²³. The choice of metal ions influences the geometry, connectivity, and topology of the resulting MOF². The other building block for MOFs is the organic linker. These multidentate ligands have binding sites that can coordinate to the metal nodes due to functional groups present in its structures. These coordinative bonds give rise to the porosity of the MOF structure. Some of the most common functional groups present in the organic linkers are carboxylates, imidazoles, phosphonates and pyridyl groups²⁴. Organic linkers also influence the geometry, pore size and functionality of the resulting MOF, besides offering sites for post-synthetic modification²⁵.

The exceptional porosity of MOFs, make these materials useful in a wide range of applications. Their specific surface area reaches even ultra-large values (up to $\sim 10\,000\text{ m}^2\text{ g}^{-1}$) and often exceeds those of traditional porous solids such as zeolites that are usually in the range of several hundreds of $\text{m}^2\text{ g}^{-1}$ ^{26–29}. Their pore networks allied to a high degree of structural control allows for the rational design of frameworks tailored to specific molecular interactions, enabling selective adsorption, diffusion, and encapsulation of guest species^{30,31}. In gas storage and separation, MOFs can be engineered to exhibit high uptake capacities and precise selectivity for gases such as hydrogen, methane, and carbon dioxide³. Their open frameworks also allow for the integration of catalytic sites, making them effective heterogeneous catalysts for a variety of organic transformations⁴. Beyond traditional applications, MOFs have shown promise in sensing⁵, drug delivery³², water harvesting³³, and ion conduction³⁴, benefiting from their accessible pore environments and structural tunability. As research advances, the combination of high porosity and functional design continues to expand the utility of MOFs across energy, environmental, and biomedical domains³⁵.

One important thing to note is that MOFs have not been assigned a standardized nomenclature, like the one defined by IUPAC; instead, they are typically designated according to the universities or research groups that originally developed them, *i.e.* HKUST-1 (Hong Kong University of Science and Technology - 1), UiO-66/67/68 (University of Oslo - 66/67/68) and MIL-68 (Materials of Institut Lavoisier - 68) or they are part of a series, like MOF-2, MOF-5, etc. and the Zeolitic Imidazolate Frameworks (ZIF).

2.2 Pillar-Layered MOFs

Pillar-layer MOFs is the classification given to MOFs in which 2D sheets are vertically connected by linear ligands acting as pillars, to yield extended 3D frameworks with anisotropic porosity and well-aligned one-dimensional channels³⁶. One example of SBU that is often found in pillar-layer MOFs is the paddlewheel-type SBU ($\text{M}_2(\text{COO})_4$), where M is commonly Cu^{2+} or Zn^{2+} , with ditopic carboxylate linkers such as 1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid (camphoric acid) or 1,4-benzenedicarboxylate (bdc)³⁷. As exemplified in Figure 2, the carboxylate groups, each bearing two oxygen donor atoms, preferentially coordinate to the equatorial positions of the paddlewheel-like SBU, resulting in the formation of two-dimensional (2D) layers. In

contrast, nitrogen-donor ligands favor axial coordination to the paddlewheel nodes, effectively serving as pillars that link the 2D layers into a three-dimensional framework³⁸.

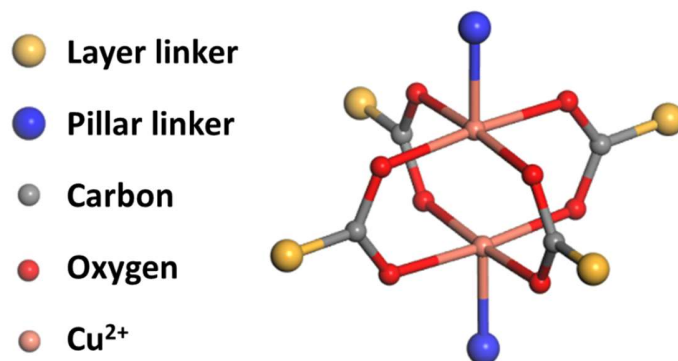


Figure 2: Schematic representation of a Cu–Cu paddlewheel SBU showing equatorial coordination of carboxylate oxygen atoms and axial coordination sites available for pillar ligands.

The pillar-layer design provides precise control over the interlayer spacing, governed by the length and rigidity of the pillar linker, which in turn enables fine-tuning of pore dimensions and diffusion pathways³⁹. This makes pillar-layer MOFs especially suitable for applications where preventing undesired interlayer interactions or reactions is critical, such as the incorporation of reactive functional groups for catalysis or sensing³⁸.

2.3 Surface-anchored MOFs (SURMOFs)

The Surface-anchored Metal-Organic Frameworks, or SURMOFs, are a subclass of MOFs comprising of oriented, crystalline thin films grown directly on functionalized substrates⁴⁰. These films are grown in a layer-by-layer (LbL) process, also known as liquid-phase epitaxy (LPE) by repetitive, alternating immersion of the substrate in solutions of the metal and linker counterparts, with washing steps in between them. The concept was first introduced by Wöll, *et al*, in 2007, showing the growth of HKUST-1 on gold substrates functionalized with a COOH- terminated SAM⁸. The growth of SURMOFs can help overcome the limitations of conventional bulk MOF synthesis, like random crystal orientation, structural heterogeneity and poor processability due to the powder form⁴¹. This method enables the growth of thin films with precise thickness control, by controlling the number of cycles (Figure 3), while also having defined crystallographic orientation, and excellent substrate adhesion, due to the substrate functionalization⁴².

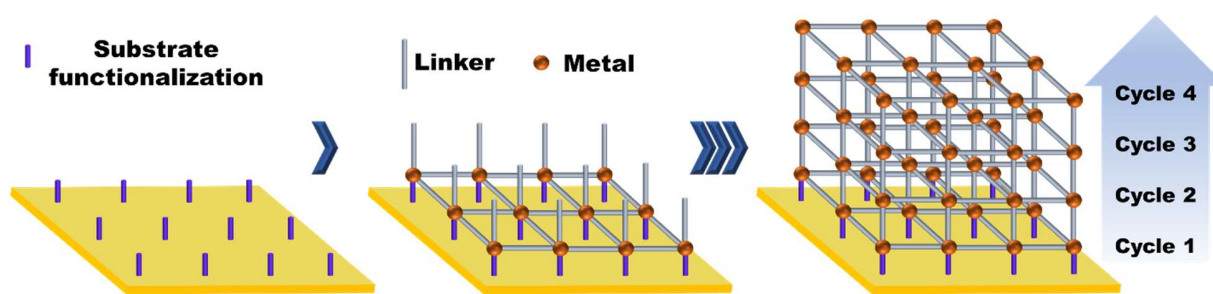


Figure 3: General formation of a SURMOF on a functionalized substrate

The properties of SURMOF have enabled a broad range of applications, including chemical sensing, membrane separations, photocatalysis, and electrochemical devices^{5,43–45}. Besides, the ability to tune film thickness, geometry and interfacial chemistry makes SURMOFs a model system for diffusion experiments, light-matter interactions, and interfacial phenomena⁴¹. The modular nature of MOFs is preserved in the SURMOFs, allowing for the tailored incorporation of functional linkers or metal nodes, and the exploration of new structure/property relationships in thin-film form⁴¹.

2.3.1 Substrate Functionalization for SURMOF growth

One critical step in the controlled growth of SURMOFs is the appropriate functionalization of the substrate surface⁴⁶. This modification must both increase the surface reactivity toward the incoming SBUs and promote the desired crystallographic orientation of the growing SURMOF. Since the way SBUs coordinate to the substrate directly influences important structural features - such as film orientation, crystallinity, and continuity, the surface chemistry must be carefully selected^{47,48}.

A widely used strategy, particularly for gold-coated substrates, is the formation of self-assembled monolayers (SAMs). These are monolayers of molecules composed of three distinct components: an anchor group that binds to the substrate, a backbone that provides structural rigidity, and a terminal group that interacts with the SURMOF precursor (Figure 4a)⁴⁹. The anchor group, typically a thiol in the case of gold substrates or a silyl group in case of silanes for the functionalization of glass and oxides, secures the SAM to the substrate surface, while the terminal group must be chemically compatible with the SBUs to initiate and direct MOF growth. Two

common SAMs used in this context are 16-mercaptohexadecanoic acid (MHDA) and 11-undecanethiol (MUD) (Figure 4b). However, a variety of terminal groups have been employed, such as carboxyl, pyridyl, and amino functionalities, to tailor the surface reactivity⁵⁰. Notably, studies have shown that simply changing the terminal group can switch the preferred orientation of a SURMOF film⁴⁷. Conversely, non-reactive terminations, such as methyl groups, can completely inhibit crystal growth in some cases⁵¹.

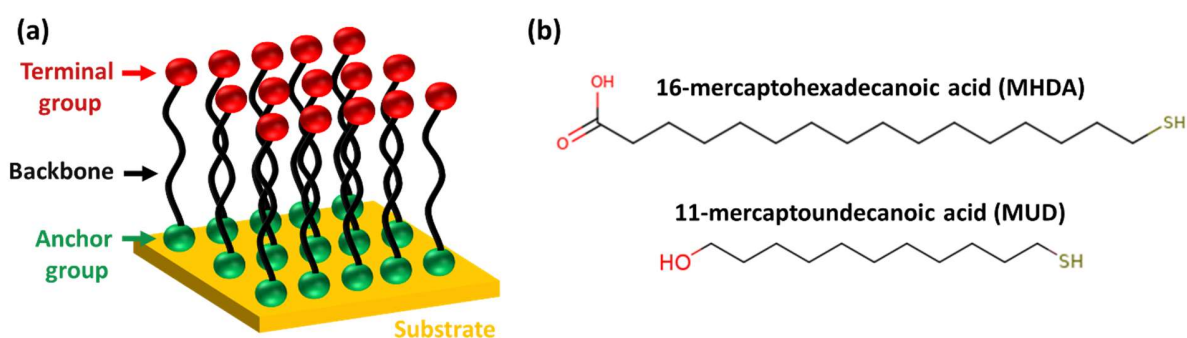


Figure 4: (a) Example of SAM structure and (b) commonly used SAMs for SURMOF growth on gold coated substrates

While SAMs are particularly effective for gold coated substrates, alternative surface treatments are often employed for dielectric or non-metallic substrates such as quartz, glass, or calcium fluoride (CaF_2). Methods such as UV/ozone treatment or oxygen plasma etching are commonly used to increase the density of reactive surface groups (e.g. hydroxyls), or to create surface defects that enhance the substrate's reactivity toward MOF precursors^{52–54}. These treatments serve a similar role to SAMs: they provide a chemically active interface that promotes uniform nucleation and controlled orientation during SURMOF growth. The choice of surface treatment must therefore be matched to both the substrate material and the specific MOF system to achieve high-quality, oriented thin films.

2.3.2 SURMOF preparation Methods

To implement the LbL growth of SURMOFs in a reproducible and scalable manner, several instrumental approaches have been developed to automate the sequential deposition steps⁵⁰. One of the most common methods is the use of dipping robots (Figure 5a), where substrates are alternately immersed in metal precursor and linker solutions with intermediate rinsing steps, under

controlled timing, temperature, and agitation. This approach ensures reproducibility and is widely used in SURMOF fabrication⁴⁰. Pump-based flow systems (Figure 5b) offer another alternative, where solutions are sequentially flowed over the substrate using computer-controlled peristaltic pumps or microfluidic chips^{53,55}. These systems minimize manual handling, and allow for better control over reaction temperature due to the closed system. Spin coating involves depositing a small amount of precursor solution onto a rotating substrate, relying on centrifugal force to spread the film uniformly, like shown on Figure 5c^{56,57}. Spray coating is another fast technique in which the metal and linker solutions are sprayed onto the substrate in sequence, allowing for the rapid deposition of SURMOF layers over large areas or non-planar surfaces, however, the number of SURMOFs that can be obtained by this technique is quite limited^{40,58}. All of these methods are suitable for the LbL growth process, and their differences enable the adaptation of SURMOF fabrication to a variety of experimental and technological requirements⁴⁵.

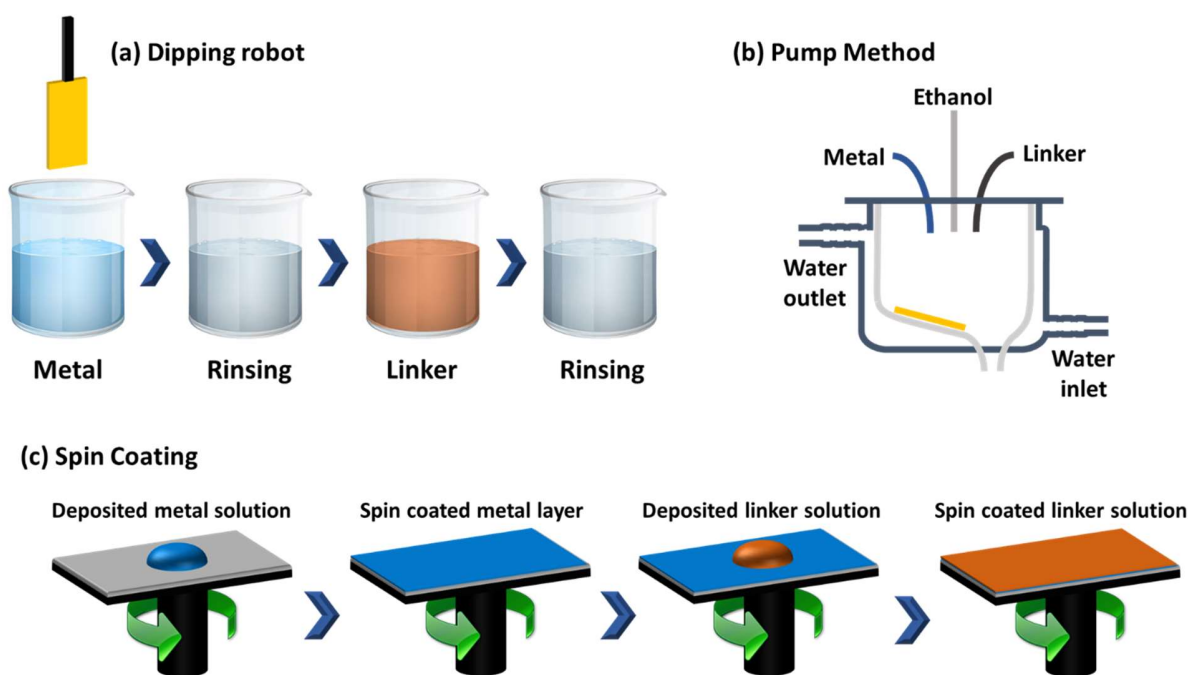


Figure 5: Common LbL methods for SURMOF growth

2.3.3 Chiral SURMOFs

Chirality is a configurational property that describes an object or molecule that cannot be superimposed on its mirror image by any combination of translation and rotation⁵⁹. The term

"chirality" is derived from the Greek word "kheir," meaning "hand", and the left and right hand are the most common example of chirality since they are mirror images but cannot be perfectly overlaid⁶⁰. When addressing molecules and chemical structures, the two non-superimposable mirror images are called enantiomers (Figure 6), and although they share identical composition and connectivity, they often display very different interactions with other chiral systems⁶¹. In nature, this distinction is very commonly found in proteins, enzymes, and nucleic acids, which are inherently chiral, and many biomolecular processes rely on enantioselective recognition⁶². In the pharmaceutical industry the consequences of chirality are equally important, since very often only one enantiomer of a compound is therapeutically active, while its mirror image can be inactive or even harmful⁶³. This duality makes the controlled recognition, separation, and transformation of enantiomers a critical challenge in modern chemistry.

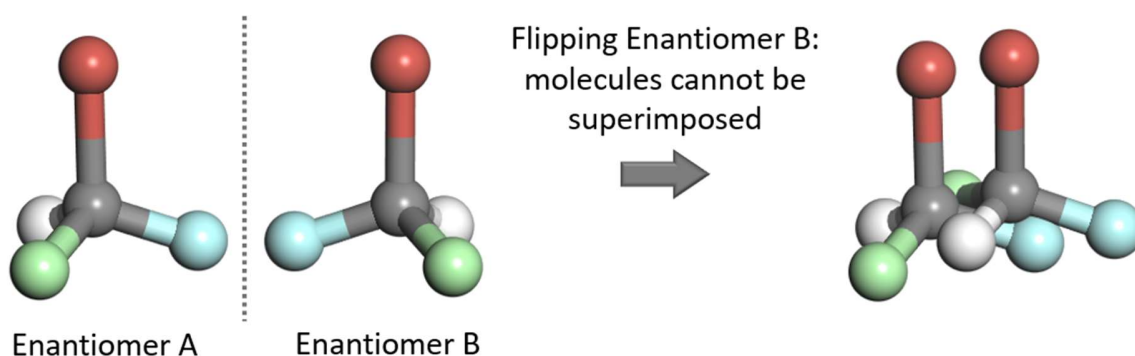


Figure 6: Generic enantiomer representation

The incorporation of chirality into metal-organic frameworks (MOFs) has emerged as a powerful strategy to address this challenge. In MOFs, one of the approaches for the introduction of chirality is the use of chiral organic linkers or metal nodes with chiral coordination environments^{61,63}. When this strategy is applied to SURMOFs, the result is a class of materials that are crystalline, oriented, with highly accessible active sites that combine chirality with the structural precision and processability of thin films^{10,64}. The applications of chiral MOFs are usually based on both their porosity and their stereochemical selectivity⁶⁵. In enantioselective adsorption and separation, chiral MOFs provide ordered pores lined with stereochemically defined binding sites, allowing the preferential uptake of one enantiomer over the other, a capability of great relevance for the purification of pharmaceuticals and fine chemicals^{66,67}. In heterogeneous

asymmetric catalysis, immobilization of chiral moieties within SURMOF pores can create confined catalytic environments that combine the advantages of homogeneous enantioselective catalysis with the stability and recyclability of heterogeneous systems^{10,68}. Chiral SURMOFs have also been explored in sensing technologies, where the selective recognition of chiral analytes is transduced into measurable optical or electronic signals^{10,64,69}.

An essential aspect of understanding and exploiting chiral SURMOFs is the measurement of their optical properties⁶⁶. Because chirality strongly influences the way materials interact with light, optical characterization provides direct insight into the handedness, orientation, and functional performance of the framework. In particular, probing the interaction of chiral MOFs with circularly polarized light is of great importance, as it not only confirms the successful incorporation of chirality into the lattice but also reveals how this chirality manifests in terms of enantioselective recognition and optical activity^{10,65}. Such studies are crucial for applications in enantioselective sensing, optoelectronics, and the design of chiroptical devices where selective response to the handedness of light is a desired functionality. The main spectroscopic tools for probing these properties are electronic circular dichroism (ECD) and vibrational circular dichroism (VCD), which will be discussed further in following sections.

2.3.4 Azide containing SURMOFs

The introduction of azide groups ($-N_3$, Figure 7a) into MOFs opens a versatile pathway toward functional and post-synthetically modifiable porous materials⁷⁰. Azides are highly reactive functional groups that can undergo a wide range of transformations, most notably “click” reactions such as the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)⁷¹. The incorporation of azides into MOF linkers was first explored in the late 2000s as part of efforts to combine the stability and modularity of reticular chemistry with the orthogonality and selectivity of organic click chemistry⁷². This strategy provided a robust route to functionalize frameworks with new chemical groups without compromising their crystallinity or porosity. In SURMOFs, the presence of azide groups directly within the oriented linker network offers the opportunity to perform such transformations under controlled interfacial conditions, where the ordered architecture of the thin film imposes spatial constraints that can influence the outcome of the reaction¹⁹.

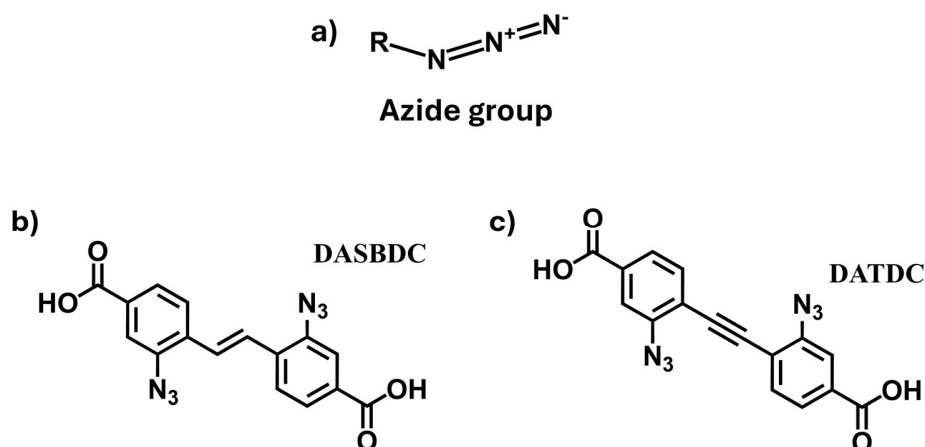


Figure 7: Representation of the chemical structure of the a) Azide group and of azide-containing linkers used for SURMOF growth: b) DASBDC and c) DATDC

A key advantage of embedding azide functionalities within MOF linkers is that it not only allows the study of azide reactivity with a solid-matrix approach, eliminating the need for solvents, but also allows for a well-defined pore environment that can yield products with greater positional control and higher selectivity, since the reactive sites are periodically arranged within the crystal lattice⁷³. In the case of SURMOFs, the thin-film geometry further enhances these benefits: the surface-anchored format allows direct spectroscopic monitoring of azide reactivity, and the absence of competing solvent molecules simplifies mechanistic studies^{19,74}.

A previous study from our group (Song, *et al.*¹⁹) attempted to exploit this advantage by preparing an azide-containing SURMOF with the linker 2,2'-diazido-4,4'-stilbenedicarboxylic acid (DASBDC), shown in Figure 7b. The resulting Cu-DASBDC was exposed to ultraviolet (UV) light under ultra-high vacuum (UHV) conditions. The primary goal of that work was to photo-induce the formation of a nitrene intermediate from the azide group and to stabilize it within the rigid framework, taking advantage of the absence of reactive solvent environments. However, the presence of a double bond in the organic linker led to an intramolecular reaction upon UV irradiation, thus preventing successful stabilization of the nitrene.

To overcome this limitation, a new strategy was developed in collaboration with the group of Prof. Bräse (Karlsruhe Institute of Technology), involving the design and synthesis of a novel linker molecule containing a tolane group, the 2,2'-diazido-4,4'-tolanedicarboxylic acid (DATDC), shown in Figure 7c. The substitution of the double bond with a triple bond was intended to

eliminate intramolecular side reactions and allow for the clean generation of the nitrene upon UV exposure in UHV. This approach aimed to generate sufficiently long-lived nitrenes that could be detected via Infrared Reflection Absorption Spectroscopy (IRRAS), enabling direct observation and characterization of these intermediates.

Beyond fundamental interest, the generation of stabilized nitrenes within the confined and periodic environment of a SURMOF could open new avenues for targeted solid-state reactivity. For instance, light-triggered nitrene formation could be harnessed to crosslink guest polymer chains loaded into the MOF pores, leading to composite materials with enhanced mechanical stability. Additionally, azides can serve as precursors to a variety of other functional groups depending on the reaction conditions; for instance, they can undergo ring expansion reactions or facilitate the insertion of other moieties to yield aryl amines, like shown in Figure 8. The integration of such reactivity within the modular platform of SURMOFs thus offers exciting prospects for the development of light-responsive, multifunctional hybrid materials.

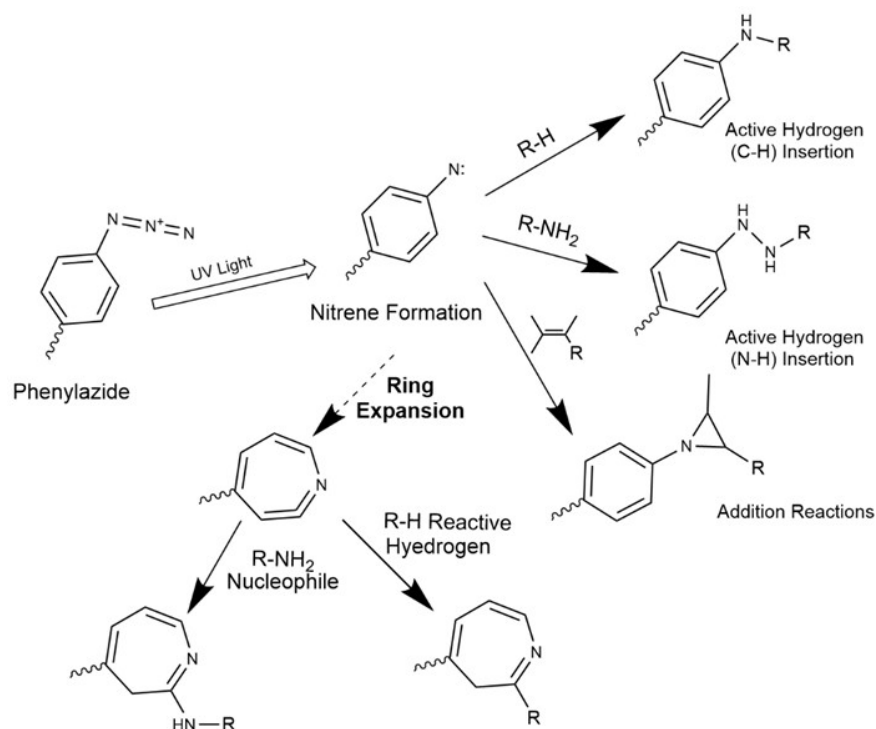


Figure 8: Examples of reactions arising from an azide group under exposure to UV light.

2.4 Patterning of SURMOF-based thin films

The ability to pattern SURMOFs into defined micro- and nanoscale architectures represents a critical step toward their integration into functional devices¹⁴. While SURMOFs offer exceptional porosity and tunability, many applications require spatial control over where the MOF material is deposited, how it interfaces with other components, and how it can be structured at the micron or sub-micron scale¹⁶. The spatially resolved structuring enables the fabrication of MOF-based membranes with selective transport pathways⁷⁵ and microelectronic devices with localized active layers⁷⁶, for example. The development of more general patterning pathways is expected to widen the range of applications of these materials. Beyond these direct applications, patterned SURMOFs also open the door to their use as metamaterials, where periodic structuring at the micro- or nanoscale can, for example, enhance their optical responses when compared to the continuous, unstructured films⁷⁷. In this context, lithographic patterning does not merely serve as a tool for device integration, but as a means of fundamentally altering and enhancing the intrinsic properties of the SURMOF material itself.

From a synthetic perspective, patterning methods can be broadly classified into top-down and bottom-up approaches⁷⁸. In top-down strategies, a continuous SURMOF film is first grown on a substrate and subsequently structured using external techniques such as lithography, etching, or crosslinking. This allows for precise definition of shapes and features with high spatial resolution⁷⁹. In contrast, bottom-up approaches aim to achieve spatial control during the growth itself, for example by using templated substrates, surface functionalization patterns, or directed self-assembly to localize the SURMOF at predefined regions^{42,78}. Both strategies are complementary, and the optimal choice depends on the application requirements. As device architectures grow more complex, particularly in solid-state applications where multiple functional materials are present on the same substrate, the challenge of selectively suppressing SURMOF growth in unwanted regions becomes larger. In such cases, top-down methods provide a practical advantage, since the SURMOF film can first be deposited under standard growth conditions and subsequently patterned to remove regions with high precision⁷⁶. This sequential strategy ensures reliable film formation while still enabling spatial control. However, a general limitation of existing approaches is that SURMOF removal often relies on the presence of specific functional groups, such as halogenated linkers⁸⁰, restricting their applicability to a narrow set of systems.

Developing more universal top-down processes that can be applied to a broader range of SURMOFs, without interfering with their growth chemistry, remains an important challenge that is directly addressed in this work.

2.4.1 Photolithography process

Photolithography is a central technique in micro- and nanofabrication, enabling the creation of spatially defined patterns with resolutions ranging from the micrometer to the nanometer scale⁸¹. Largely developed in the semiconductor industry in the 1970s to define circuit architectures on silicon wafers, photolithography has since evolved into a versatile toolbox with broad applications across materials science, microelectronics, and nanotechnology⁸². Photolithography in the sense of materials science has the goal of transferring a predefined pattern to a surface⁸¹. By combining resist patterning with subsequent steps such as etching or deposition, highly ordered micro- and nanoscale structures can be fabricated with a high degree of spatial control. The use of lithography for SURMOFs can allow them to be incorporated into the same technological frameworks as traditional micro- and nanofabricated devices, creating hybrid platforms where crystalline, porous materials interact directly with semiconductors, dielectrics, or metallic components⁷⁶. The steps of a general process of photolithography are shown on Figure 9 and will be detailed in the following subsections.

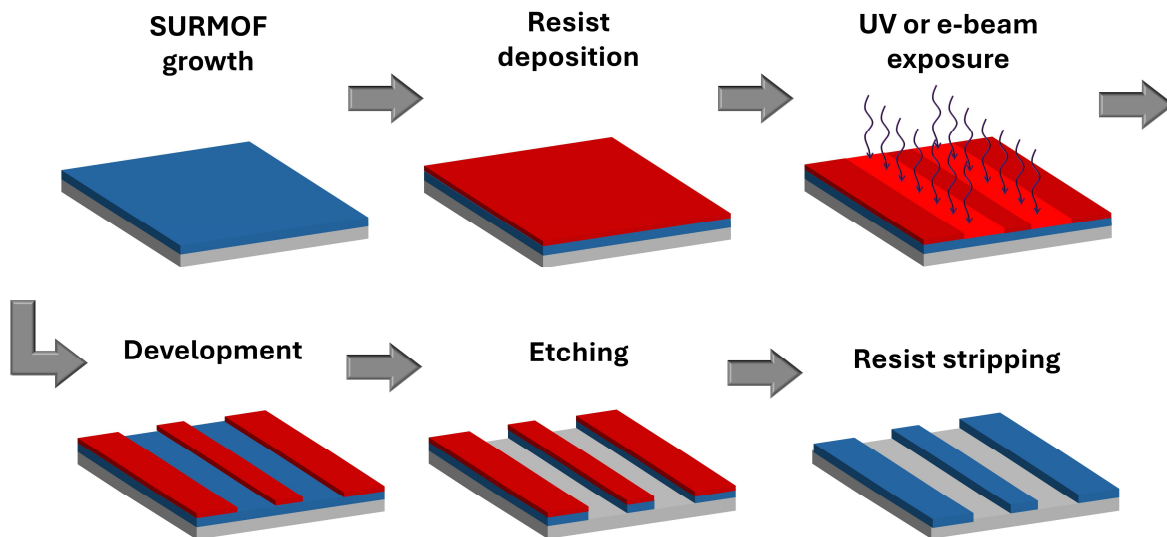


Figure 9: General photolithography procedure for a positive photoresist.

2.4.1.1 Resist Materials and Exposure Mechanisms

The central component of many forms of lithography is the resist, a thin film of organic polymer deposited on the substrate surface to act as a light-, electron-, or heat-sensitive layer⁸³. Resists are typically applied through spin coating, where a liquid solution of the resist is dispensed on the substrate and spread into a uniform thin layer by rapid rotation. After drying, this layer is ready to undergo selective modification by exposure to an energy source⁸⁴.

Resists can be divided into positive and negative types. In positive resists, the exposed regions undergo chemical modification that increases their solubility in a developer solution, leading to selective removal of the irradiated areas. In negative resists, the opposite occurs: exposure induces crosslinking, rendering the irradiated regions insoluble and leaving behind the exposed pattern. The choice between positive and negative resist depends on the required resolution, feature stability, and subsequent processing steps⁸³.

Different lithographic techniques exploit different modes of resist interaction. In photolithography, resists are exposed to ultraviolet (UV) light, either through a photomask (traditional mask aligners) or directly by focused beams (direct laser writing)⁸⁵. These methods provide rapid and scalable patterning over large areas. In electron-beam lithography (EBL), a focused electron beam is scanned across the resist, offering much higher resolution, down to tens of nanometers, but at the expense of slower writing speeds⁸⁶. Thermal scanning probe lithography (t-SPL) employs a nanoscale heated probe to locally remove or chemically modify resist material, enabling sub-20 nm resolution with high precision, but in a relatively slow process⁸⁷. Collectively, these approaches offer a broad range of capabilities, from fast prototyping and large-area patterning to ultra-high-resolution nanostructuring.

2.4.1.2 Pattern Transfer: Development and Etching

After exposure, the resist undergoes a development step, where the soluble portions (depending on positive or negative resist) are removed by immersion in a developer solution, leaving behind a patterned protective layer. This layer defines which regions of the underlying material are to be preserved or etched away⁸³.

Pattern transfer is typically achieved through etching processes, which selectively remove exposed regions of the substrate⁸⁴. Wet etching, using liquid chemicals, is simple and effective but generally isotropic, meaning that etching proceeds in all directions and can underetch areas protected by the resist. In contrast, dry etching techniques rely on plasma discharges to chemically or physically remove material⁸⁵. Among these, reactive ion etching (RIE) is one of the most common methods in advanced microfabrication since it combines chemical reactivity with directional ion bombardment, producing highly anisotropic etching profiles. This directionality is particularly important for SURMOFs, as it allows pattern definition with vertical sidewalls and minimal damage to neighboring regions⁸⁸. Less directional plasma etching can still be effective but might lead to broader feature profiles and reduced resolution.

Once the etching step is complete, the resist must be stripped, typically by solvents, to leave behind only the patterned material. For SURMOFs, this step is especially critical, since aggressive stripping chemistries can damage the structure. Ensuring compatibility between resist, developer solutions, and etching conditions with the SURMOF is therefore a major challenge in adapting lithography to these materials.

2.4.1.3 Lithography Techniques

Several advanced lithography techniques can be considered for use with SURMOFs. Direct laser writing (DLW), enables flexible prototyping without the need for costly masks, making it ideal for research-scale patterning of SURMOFs. Electron-beam lithography (EBL) provides better resolution and is capable of defining nanoscale features in MOF thin films, though it remains limited by slow writing speeds, high equipment costs and the low electrical conductivity of most SURMOFs, that can lead to degradation. Thermal scanning probe lithography (t-SPL) is an emerging approach that offers nanoscale precision by removing resist material via localized heating with an atomic force microscope (AFM)-type tip⁸⁷. Its compatibility with sensitive materials and absence of high-energy photons or electrons makes it potentially attractive for SURMOF patterning, though its throughput is currently low. These methods illustrate the diversity of lithographic approaches and highlight the need to balance resolution, speed, scalability, and materials compatibility depending on the target application.

2.4.1.4 Compatibility and Challenges for MOFs and SURMOFs

Applying lithography to SURMOFs introduces unique challenges because these materials greatly differ from conventional semiconductors and oxides. MOFs are often chemically sensitive to water, acids, or plasma conditions commonly used in lithographic processes. This raises concerns at nearly every stage: resists and their solvents must not penetrate or degrade the MOF pores; developers must selectively dissolve the resist without attacking the framework; and etching conditions must remove unwanted material while preserving the crystalline order of the remaining SURMOF regions.

Despite these challenges, the successful adaptation of lithographic methods to SURMOFs has immense potential. Precise patterning could enable the fabrication of microarrays for sensing, optically active coatings for photonics and catalytic surfaces with localized reactivity, for example. Moreover, periodic structuring of SURMOFs can impart them with the characteristics of metamaterials, where the deliberate arrangement of features at the micro- or nanoscale gives rise to interesting optical or electronic properties not present in continuous films. In this way, lithography is not only a tool for device integration but also a means to engineer new functionalities into SURMOFs by design.

2.5 Theoretical simulation of SURMOF properties

The vast chemical and structural diversity of metal-organic frameworks (MOFs) offer immense opportunities for tailored functionality, but it also presents a significant challenge in terms of material discovery⁸⁹. Experimental synthesis and characterization of each possible combination of metal nodes, organic linkers, and framework geometries is resource-intensive and time-consuming. In this context, theoretical simulation has become an indispensable tool in guiding the development and optimization of MOFs and SURMOFs⁹⁰. Computational modeling enables the prediction of key properties, such as pore size, mechanical stability, optical behavior, and chemical reactivity, before any experimental effort is made, thereby reducing the screening space and accelerating the design of application-specific materials⁹¹.

For SURMOFs, simulations are particularly powerful due to the ordered, oriented, and highly defined nature of these thin films⁹². Beyond modeling the properties of individual crystalline

domains, simulations can also be extended to study structured films, such as periodic arrays of SURMOF on substrates⁷⁷ or between different materials, like inside of optical cavities⁹³. The architected surfaces are of increasing interest for their potential use as metamaterials, where the macroscopic properties are not only determined by the intrinsic framework but also by the geometry and arrangement of the film⁹⁴. By varying the periodicity, thickness, or morphology of the SURMOF structures, one can computationally assess how these parameters affect properties such as optical activity, circular dichroism, or photonic bandgaps, helping to design functional materials that go beyond the capabilities of homogeneous thin films.

However, the reliability of simulation results critically depends on the validation of the models used. Theoretical predictions must be benchmarked against experimental data to ensure that they capture the relevant physical and chemical phenomena with sufficient accuracy. This is particularly important for complex properties, such as the optical response of chiral SURMOFs, where both molecular-level chirality and thin film ordering contribute to the final signal. In this work, we addressed this challenge by collaborating with the research group of Prof. Carsten Rockstuhl, at the Institute of Theoretical Solid-State Physics (TFP), also at KIT. Their group has developed an advanced multi-scale workflow to describe the optical properties of chiral SURMOF systems. This multi-scale approach ranged from finite-size simulations of an expanded unit-cell to the level of a thin film, including the effects of film thickness, orientation, and structural periodicity.

We applied their simulation framework to our experimentally fabricated chiral SURMOFs, comparing predicted and measured optical responses to evaluate the model's accuracy. This validation step is a critical contribution, reinforcing the usefulness of theoretical tools for designing and understanding functional SURMOF-based metamaterials and is discussed in chapter 5 of this work.

3 METHODS

3.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful, non-destructive technique used to evaluate the crystalline structure, phase composition, and crystalline orientation of materials. Its origins can be traced to the early 20th century, when Max von Laue first demonstrated X-ray diffraction by crystals in 1912, followed shortly by W. H. and W. L. Bragg, who established the fundamental condition for constructive interference in crystalline materials, known as Bragg's law. This work laid the foundation for modern crystallography and materials analysis.

X-rays, with wavelengths on the order of atomic distances ($\sim 1 \text{ \AA}$), interact with the electron clouds of atoms in a solid. When incident on a periodically arranged lattice, these waves are scattered in specific directions, producing constructive interference at angles that satisfy Bragg's law (Equation 1), as depicted in Figure 10.

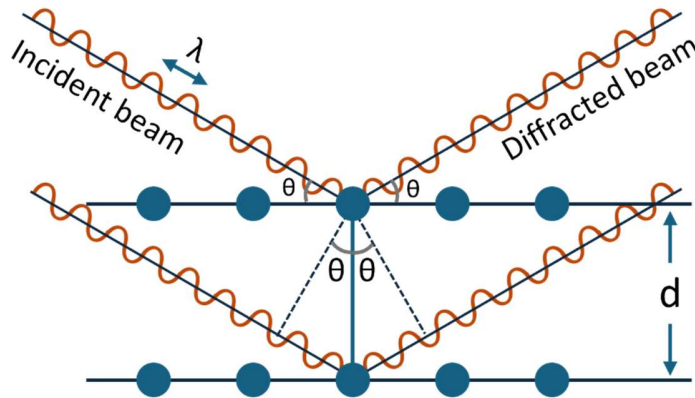


Figure 10: X-rays diffraction on two sequential lattice planes, with blue spheres representing the atoms

$$n\lambda = 2d_{hk} \sin(\theta_{hkl}) \quad (1)$$

Here, n is the diffraction order, λ the X-ray wavelength, d the interplanar spacing, and θ the angle between the incident beam and the lattice planes. The resulting diffraction peaks in an XRD pattern serve as fingerprints of the crystal structure, enabling the identification of lattice constants (usually labeled as a , b and c), crystalline orientation, and long-range order.

To describe which planes are responsible for each reflection, the Miller indices (h, k, l) are used. These are a set of three numbers that indicate how a plane cuts through the unit cell along the x, y, and z directions. Examples of Miller indices for different planes are shown in Figure 11, they are calculated by taking the inverse of the points where the plane intersects the a, b, and c axes, and then converting them into whole numbers, like $(\frac{a}{h}, \frac{b}{k}, \frac{c}{l})$. Each diffraction peak can be matched with a specific set of Miller indices, which helps connect the experimental data to the crystal's structure. By assigning Miller indices to the peaks, we can learn about the size, shape, and symmetry of the crystal, making them a key tool in analyzing XRD results⁹⁵.

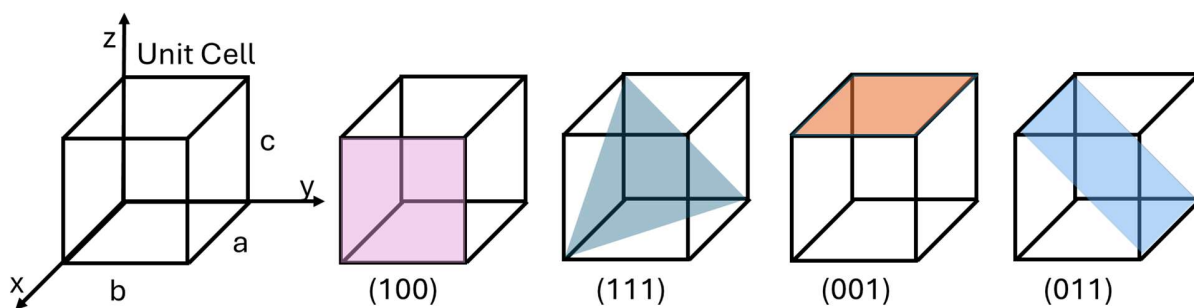


Figure 11: Representation of the Miller indices for different diffraction planes

In this work, two different XRD geometries were used to investigate the structural properties of the SURMOF thin films: out-of-plane and in-plane XRD. These techniques provide complementary information and are essential for characterizing oriented, anisotropic thin films like SURMOFs, a scheme of both techniques is shown on Figure 12.

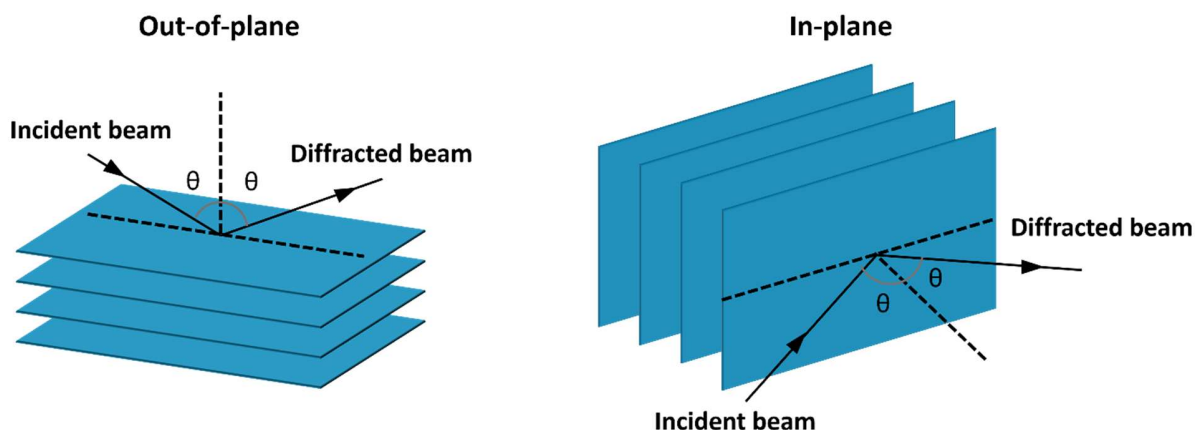


Figure 12: geometry of measuring out-of-plane (left), and in-plane X-ray diffraction (right).

Out-of-plane XRD is more common and closely related to standard powder diffraction. In this configuration, the X-ray beam impinges on the sample at a fixed incident angle θ , and the detector scans the diffracted signal at 2θ . This setup is ideal for identifying planes oriented parallel to the substrate, since it allows to calculate the interplanar spacings perpendicular to the substrate.

In contrast, in-plane XRD involves orienting the incident beam nearly parallel to the film surface, so that diffraction arises from planes oriented perpendicular to the substrate. This geometry is highly sensitive to lateral ordering within the film and is particularly useful for detecting in-plane reflections that are often invisible in out-of-plane scans^{96,97}.

By combining in-plane and out-of-plane geometries, it is possible to build a full picture of the three-dimensional orientation of the SURMOF crystallites, assess their degree of alignment with respect to the substrate, and compare them to powder-diffraction references of the same framework. This comparative approach enables the confirmation of phase purity and provides essential structural insight into the quality and orientation of the thin films grown.

3.2 Circular Dichroism Spectroscopy (CD)

Circular dichroism (CD) is a very common technique to investigate chiral substances and materials. This technique works in two main regimes: electronic and vibrational circular dichroism (ECD and VCD, respectively) and both are based on the differential absorption of left- and right-handed circularly polarized light (CPL) by a chiral medium. CD signals are extremely sensitive to stereochemistry and conformation, and therefore, are used to analyze small molecules, study secondary structure of proteins and even applied in the study of solids like MOFs⁹⁸.

CPL is a type of electromagnetic radiation in which the electric field vector rotates in a circular motion as the wave propagates. This occurs when two linearly polarized waves of equal amplitude, oriented perpendicular to each other, oscillate with a 90° phase difference. The result is a helical movement of the electric field, either clockwise (right-circularly polarized) or counterclockwise (left-circularly polarized), relative to the direction of propagation, like illustrated in Figure 13a.

When CPL interacts with a chiral sample, the asymmetry in the molecular or structural arrangement leads to unequal absorption of the left- and right-handed components, resulting in an ellipsoidal electric field vector, like shown in Figure 13b. The CD signal corresponds to this

difference in absorption and is typically measured either as ellipticity (in millidegrees) or as the differential molar absorption coefficient ($\Delta\epsilon$). The CD spectrum highlights transitions that are sensitive to chirality, allowing the analysis of spatial arrangement and conformational characteristics of chiral systems.

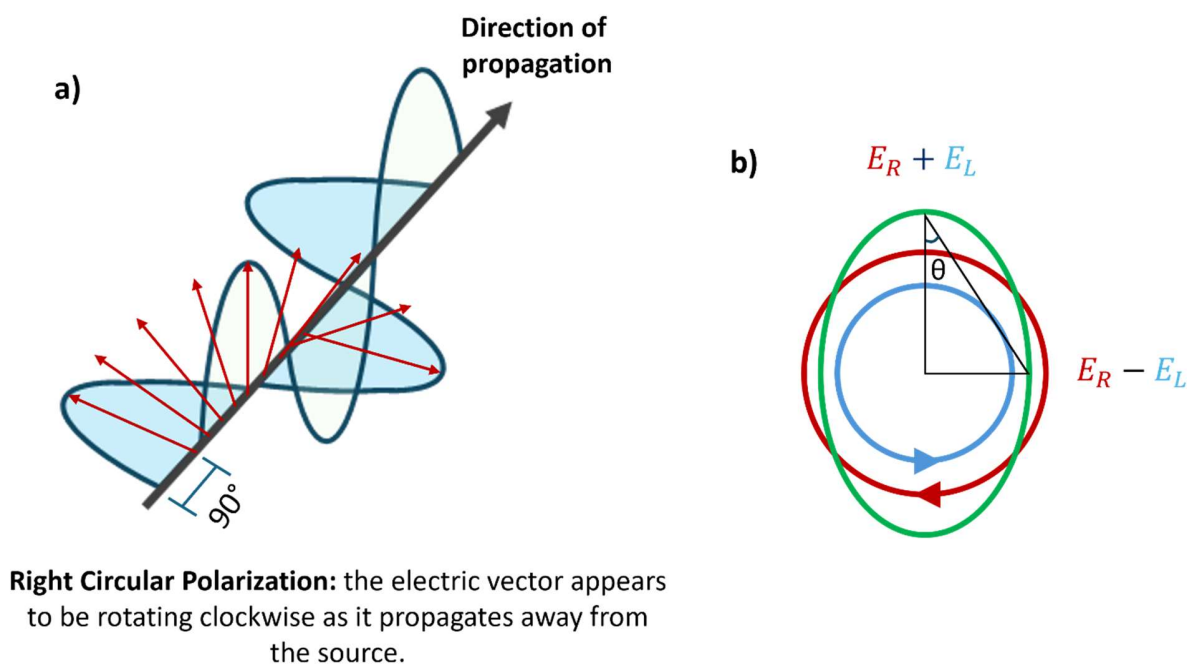


Figure 13: a) Illustration of right-handed CPL and b) different absorption of right- and left-hand CPL resulting in an ellipsoidal electric field

3.3 Scanning Electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a high-resolution imaging technique developed in the 1930s, with the first functional prototype built by Manfred von Ardenne in 1937. SEM enables detailed visualization of surfaces by scanning a focused beam of high-energy electrons over the sample and detecting the resulting signals produced by electron-matter interactions. A typical SEM instrument consists of an electron source (or electron gun), a system of electromagnetic lenses for beam focusing and deflection, a chamber where the sample is placed, various detectors (for different types of measurements), and a vacuum system. The electron beam is usually accelerated at voltages ranging from 0.5 to 30 keV, depending on the resolution required and the nature of the

sample. A high vacuum is typically maintained inside the column and sample chamber to prevent electron scattering by air molecules and to ensure a stable beam.

When the electron beam hits the sample surface, several types of signals are generated, like illustrated in Figure 14. Secondary electrons (SE) are emitted from very close to the surface and are most commonly used to create high-resolution images of surface topography. Backscattered electrons (BSE), on the other hand, originate from deeper interactions and are reflected with an intensity that depends on the atomic number of the material, allowing for contrast between different materials in the sample. In addition, the interaction of the electron beam with atoms in the sample can produce characteristic X-rays, which are detected using Energy-Dispersive X-ray Spectroscopy (EDX) to determine the elemental composition of specific regions.

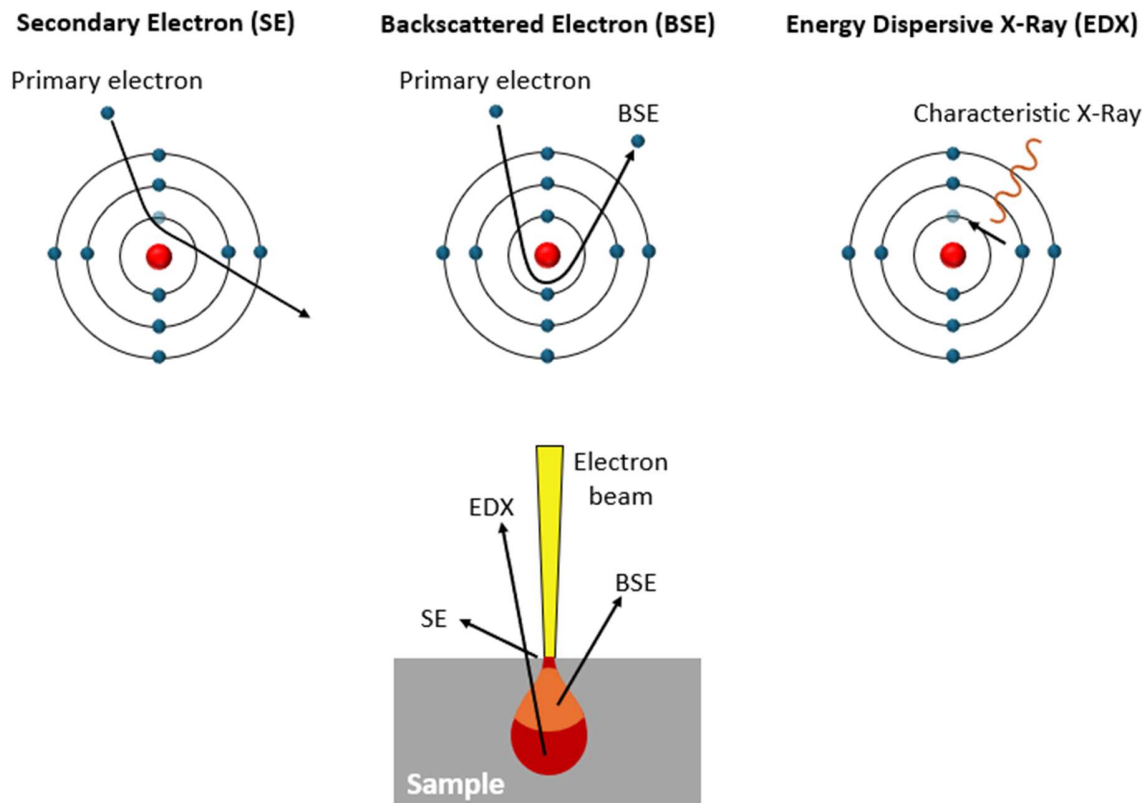


Figure 14: Schematic representation of signal generation mechanisms in SEM and approximate origin and escape depths of SE, BSE, and EDX signals from within the sample when irradiated by the electron beam.

Since most SURMOF samples are non-conductive, direct exposure to the electron beam can lead to charging effects, which distort the image or even degrade the sample. To avoid this, the sample surface is typically coated with a thin layer (approx. 4 nm) of a conductive material such as platinum or gold. Alternatively, Environmental SEM (ESEM) can be used, where a small amount of water vapor is introduced into the chamber to dissipate surface charge without coating. SEM is especially valuable for the characterization of thin films like SURMOFs, not only to observe surface features but also to examine film thickness and internal layering by imaging the cross-section of fractured samples. This makes SEM an essential technique for both morphological and structural analysis^{99,100}.

3.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a high-resolution imaging technique capable of characterizing surface topography and roughness down to the nanometer scale. AFM operates by mechanically probing the sample surface with a sharp tip mounted on a flexible cantilever. As the tip scans across the sample, short-range forces, typically van der Waals interactions, cause deflections in the cantilever, which are detected by a laser beam reflected from the back of the cantilever onto a position-sensitive photodetector. These deflections are translated into height data, generating a precise topographic map of the surface.

The key components of an AFM include the cantilever-tip assembly, laser and photodetector system, a piezoelectric scanner that moves the sample or tip in x, y, and z directions, and a feedback control system that maintains a constant interaction force during scanning, like shown in Figure 15. AFM is typically performed in tapping mode, where the cantilever oscillates near its resonance frequency and intermittently contacts the sample surface. This mode reduces lateral forces and minimizes damage to both the tip and the sample, making AFM a non-destructive technique.

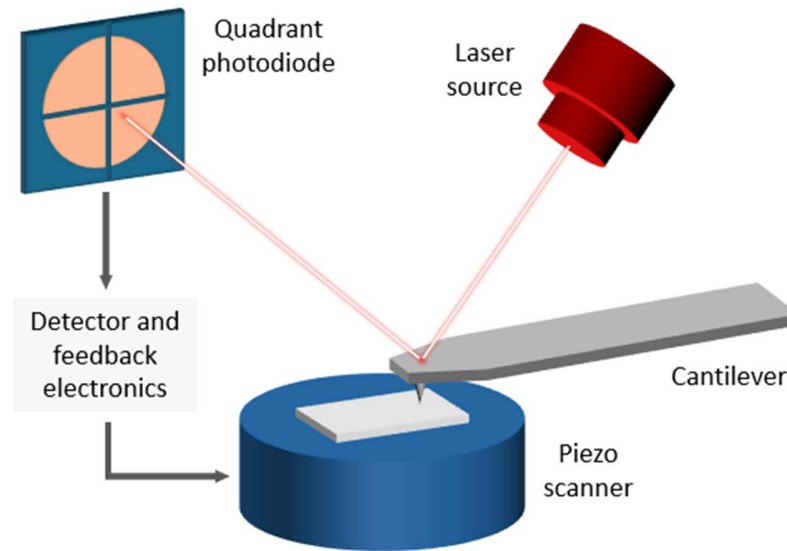


Figure 15: Schematic diagram of the AFM

One of the significant advantages of AFM is that it does not require electrically conductive samples or any conductive coatings. This makes it particularly useful for the analysis of sensitive materials or samples deposited on non-conductive substrates, such as quartz and CaF_2 , where preserving optical transparency is essential for further transmission-based measurements, such as CD¹⁰¹.

AFM plays a crucial role in evaluating surface roughness and topography of thin films like SURMOFs. It is especially valuable in the characterization of patterned or etched surfaces, providing precise measurements of step heights and etched features, which is essential for assessing the effectiveness of lithography or surface structuring processes. Although AFM is limited to relatively small scanning areas and is more time-consuming than other surface imaging methods, its nanoscale resolution, non-invasiveness, and high sensitivity to vertical features make it a powerful tool in the analysis of functional thin films and device-relevant surfaces.

3.5 Confocal Laser Scanning Microscopy (CLSM)

Confocal Laser Scanning Microscopy (CLSM) is an optical imaging technique that provides high-contrast, three-dimensional surface profiles by selectively detecting light from a single focal plane within the sample. This is achieved by scanning a focused laser beam across the sample and

collecting the reflected or emitted light through a pinhole aperture placed in front of the detector. The pinhole blocks out-of-focus light, enabling optical sectioning and significantly improving depth resolution compared to conventional widefield microscopy.

A typical CLSM setup consists of a laser source, scanning mirrors to raster the beam across the sample, a high-numerical-aperture objective lens for focusing, a dichroic mirror to separate excitation and emission paths, the pinhole aperture, and a photodetector (usually a photomultiplier tube or avalanche photodiode), like shown in Figure 16. For surface profiling applications, especially those requiring quantitative height data, the system can be equipped with a white light interferometer or confocal profilometer module, allowing precise, non-contact topographical measurements.

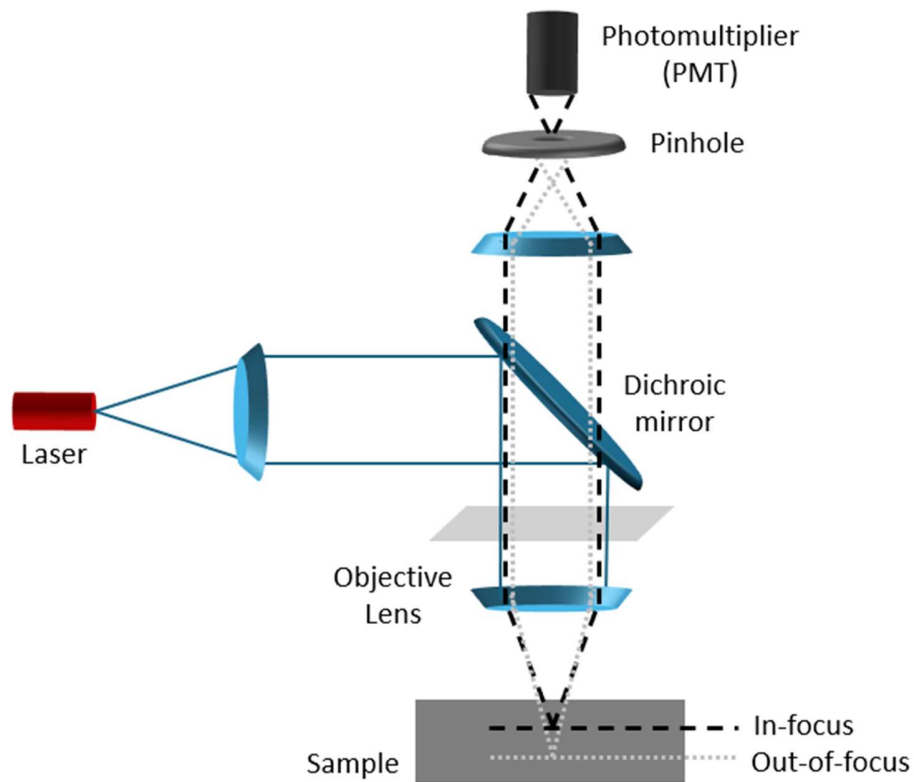


Figure 16: Schematic of a CLSM

CLSM is particularly useful for measuring step heights and surface roughness over relatively larger areas and at much faster acquisition rates than AFM. This makes it ideal for surveying a larger area of a sample in a short amount of time, especially after lithographic patterning, where

feedback on etching quality or film uniformity is needed. However, one limitation of CLSM is its lower vertical and lateral resolution compared to AFM, which may not capture very fine surface features or nanoscale variations accurately^{102,103}.

Because of this, CLSM and AFM can be used in a complementary manner: CLSM enables rapid screening and coarse quantification of topographical features across multiple regions, while AFM provides high-resolution validation on selected areas of interest. This combined approach ensures both throughput and accuracy in surface characterization, making it particularly effective in thin film and patterning studies on SURMOFs.

3.6 Infrared Spectroscopy (IR)

Infrared (IR) spectroscopy is a powerful analytical technique widely used to investigate the vibrational modes of molecules. By measuring the absorption of IR radiation across a range of wavelengths, this method enables the identification of functional groups and provides insights into structural changes following chemical treatments or physical processing. IR spectroscopy is particularly well suited for studying organic compounds, as their characteristic bond vibrations typically fall within the mid-infrared (MIR) range, spanning approximately 4000 to 400 cm⁻¹. Within this window, absorption bands correspond to stretching, bending, and other vibrational motions of molecular bonds.

The physical principle behind IR spectroscopy is based on the interaction between electromagnetic radiation and molecular vibrations. This interaction can be understood by using mechanical analogies. In the simplest model, a chemical bond behaves like a harmonic oscillator, where two atoms are connected by a spring. This model follows Hooke's Law, which states that the restoring force of a spring is proportional to its displacement. The vibrational frequency (ν) of a bond in this system is given by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$

where κ is the force constant (stiffness of the bond), and μ is the reduced mass of the two atoms involved. The energy levels in this model are equally spaced, and transitions between levels are governed by quantum mechanical rules.

However, real molecular bonds do not behave perfectly like springs. At higher vibrational energies, bonds begin to stretch non-linearly. This deviation from ideal behavior is better described by the Morse potential, which accounts for bond dissociation and results in an anharmonic oscillator model. In this more accurate model, the energy levels are not equally spaced, the spacing between them becomes progressively smaller as the energy increases, like shown in Figure 17.

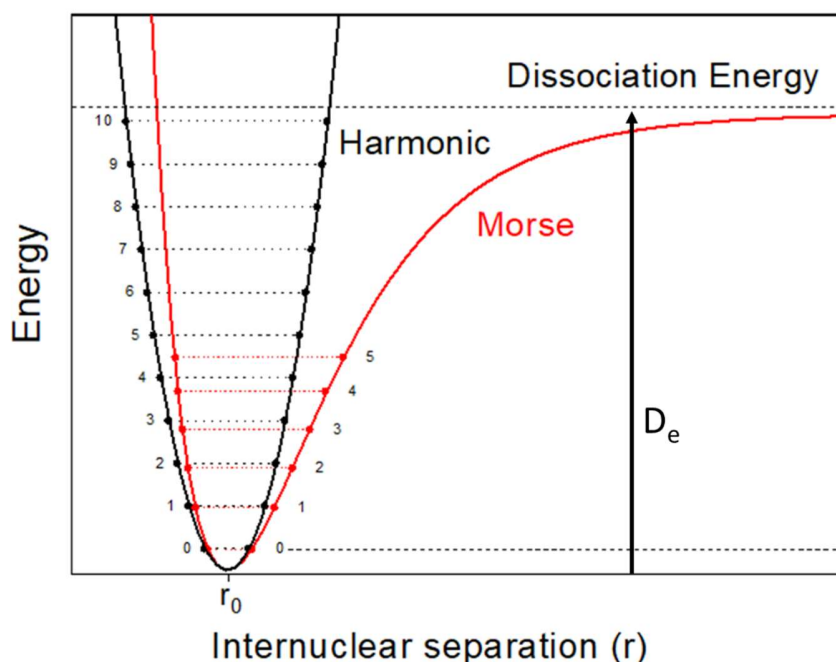


Figure 17: The harmonic oscillator potential (black) with equally spaced energy levels and Morse potential (red) where energy level spacing decreases as the energy approaches the dissociation energy

This anharmonicity has important consequences: it allows transitions to overtone and combination bands (not just the fundamental mode) to exist and it predicts more accurately the absorption behavior seen in experimental IR spectra.

For a molecule to absorb IR light and undergo a vibrational transition, there must be a change in its dipole moment during the vibration. When the energy of an incoming IR photon matches the energy gap between two vibrational levels (typically between the ground state $v = 0$ and the first

excited state $v = 1$), absorption occurs. This results in a peak in the IR spectrum, and the frequency at which this happens is characteristic of the specific bond and its environment. For instance, the carbonyl group ($\text{C}=\text{O}$) typically absorbs strongly around 1700 cm^{-1} , due to the double bond's high bond strength (force constant) and the relatively light mass of oxygen. In contrast, a $\text{C}-\text{O}$ single bond, such as in alcohols or ethers, absorbs at much lower frequencies, typically around $1000\text{--}1300\text{ cm}^{-1}$, because single bonds are weaker and stretch more easily under the influence of infrared light¹⁰⁴.

3.6.1 Infrared Reflection-Absorption Spectroscopy (IRRAS)

IRRAS is a surface-sensitive technique ideal for analyzing thin films on metallic substrates, such as gold-coated surfaces. In this method, IR light is reflected off the substrate at a grazing angle, enhancing the interaction with the film as it passes through the sample twice, once before and once after reflection. The sensitivity of IRRAS arises from the reflection geometry and the surface selection rule, which dictates that only vibrational modes with dipole moment changes perpendicular to the surface are IR-active. This makes IRRAS particularly useful for probing the orientation of molecules in self-assembled monolayers or SURMOFs grown on metal substrates. The measurements are typically done within the MID-IR range, spanning from 4000 cm^{-1} to 200 cm^{-1} .

3.6.2 Transmission IR

For samples on non-metallic, transparent substrates such as CaF_2 , transmission mode is more appropriate. In this configuration, IR light passes directly through the sample and the substrate, and the transmitted beam is analyzed. The light typically passes once through the film, and the substrate's low reflectivity does not interfere significantly with the signal. Transmission IR detects both parallel and perpendicular vibrational modes, though the relative intensity can vary depending on the angle of incidence and polarization. This method is especially advantageous for SURMOFs grown on IR-transparent crystals, allowing characterization without sample transfer or complex preparation steps.

4 EXPERIMENTAL METHODS

4.1 CHEMICALS USED

Name	Abbreviation	Source
16-Mercaptohexadecanoic acid	MHDA	Sigma Aldrich
11-Mercapto-1-undecanol	MUD	Sigma Aldrich
(1R,3S)-(+)-camphoric acid	D-cam	Sigma Aldrich
(1S,3R)-(-)-camphoric acid	L-cam	Sigma Aldrich
Ethanol	EtOH	VWR
Acetone	-	VWR
Nitrogen	N ₂	Air Liquide
Copper (II) acetate monohydrate	CuOAc	Alfa Aesar
Zinc acetate dihydrate	ZnOAc	Alfa Aesar
Benzene-1,4-dicarboxylic acid	BDC	Alfa Aesar
Benzene-1,3,5-tricarboxylic acid	BTC	Alfa Aesar
1,4-Diazabicyclo[2.2.2]octane	DABCO	Alfa Aesar
4,4'-(Ethyne-1,2-diyl)bis(3-azidobenzoic acid)	DATDC	*

*Material is not commercially available and was synthesized by Dr. Julian Brückel, part of the group of Prof. Dr. Stefan Bräse in the Institute of Organic Chemistry, KIT.

All chemicals were used as received without further purification.

The substrates used were:

- “Gold substrates” are composed of silicon single crystal wafer with a coating of 100 nm gold [100] with an adhesion layer of 5 nm titanium. The substrates are purchased from Georg Albert PVD-Beschichtungen, Germany.
- Silicon single crystal wafers were purchased from Active Business Company GmbH.
- Quartz windows, optically polished, 20 mm Ø x 1 mm thickness, were purchased from GVB GmbH - Solutions in Glass.
- CaF₂ IR-windows, optically polished, 20 mm Ø x 1 mm thickness, were purchased from Korth Kristalle GmbH.

4.2 SUBSTRATE FUNCTIONALIZATION

Substrate preparation is a critical first step in achieving homogeneous SURMOF growth. Proper surface functionalization creates nucleation sites across the entire substrate, like exemplified in Figure 18, promotes strong film adhesion, and significantly influences the orientation of the resulting MOF crystals.

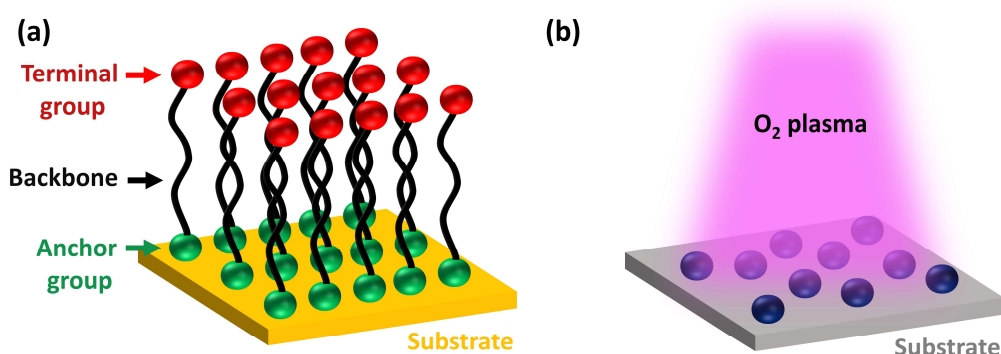


Figure 18: Example of a) SAM and b) O₂ plasma functionalized substrates.

4.2.1 Functionalization of gold-coated Si substrates with MHDA SAM

The gold-coated substrate was washed with ethanol and then immersed in a 20 μM ethanolic solution of 16-mercaptohexadecanoic acid (MHDA), supplemented with 10% by volume of glacial acetic acid to inhibit dimerization and maintain the protonated form of MHDA on the surface. The treatment was carried out at room temperature, in the dark, for 48 hours. After this period, the substrate was carefully rinsed with pure ethanol and dried using a nitrogen stream just prior to the MOF synthesis. The resulting functionalized surface is uniformly covered with carboxyl ($-\text{COOH}$) groups.

4.2.2 Functionalization of gold-coated Si substrates with MUD SAM

The gold substrate was washed with ethanol and then immersed in a 1 mM ethanolic solution of 1-mercapto-1-decanol (MUD). The treatment was carried out at room temperature, in the dark, for 24 hours. After this period, the substrate was carefully rinsed with pure ethanol and dried using a nitrogen stream just prior to the MOF synthesis. The resulting functionalized surface is uniformly covered with hydroxyl ($-\text{OH}$) groups.

4.2.3 Plasma functionalization for quartz and CaF₂

The procedure began with a thorough cleaning of the substrates using acetone followed by ethanol, with drying under a nitrogen stream between each step. After cleaning, the substrates were treated in an oxygen plasma cleaner (Nano low-pressure plasma system, Diener Electronics, Ebhausen, Germany) at 0.5 mbar pressure and 50 SCCM oxygen flow for 30 minutes. This plasma treatment not only increases the surface hydrophilicity but also removes any remaining organic contaminants. Immediately after the treatment, the substrates were immersed in the ethanolic solution of the metal ions and the process was started. As an alternative, one additional step was included where the metal solution was heated (50-70 °C) and kept under heating for 30 min before initiating the synthesis, to ensure a better distribution on the surface, ensuring a uniform start to the layer-by-layer growth. This process was applied to silicon wafers, quartz and CaF₂ substrates.

4.2.4 UV/Ozone functionalization for quartz and CaF₂

This method was used as a simpler alternative to the plasma treatment. The substrates were washed with acetone, followed by ethanol rinse and then dried using a nitrogen stream and promptly transferred to a UV/ozone cleaner (UV Ozone Cleaner, Ossila, Sheffield, United Kingdom) for 15 minutes to remove any residual organic contaminants and enhance surface activation. Immediately after this treatment, the substrates were immersed in the ethanolic solution containing the metal ions and the process was started. As an alternative, one additional step was included where the metal solution was heated (50-70 °C) and kept under heating for 30 min before initiating the synthesis, to ensure a better distribution on the surface, ensuring a uniform start to the layer-by-layer growth. This process was applied to silicon wafers, quartz and CaF₂ substrates.

4.3 SYNTHESIS TECHNIQUES

SURMOFs are grown on appropriately functionalized substrates via a quasi-epitaxial, step-by-step liquid-phase deposition process. At each step, one of the framework's building blocks, either the metal node or the organic linker, chemisorbs onto reactive sites created during the previous step. The duration of each deposition step was optimized experimentally to ensure uniform growth. To maintain film quality and avoid unwanted surface defects, each deposition step is followed by

thorough rinsing with a suitable solvent to remove any physisorbed species, which could otherwise desorb later and compromise the homogeneity of the film.

Different layer-by-layer growth techniques can be employed depending on the desired framework structure and substrate compatibility. In this work, the specific methods selected for the synthesis of each SURMOF system are described below.

4.3.1 Pump Method

The main advantage of the pump method lies in its ability to precisely control the synthesis temperature, which can be set up to 70 °C. In this setup, the functionalized substrate is placed flat inside a custom-made glass reaction cell, which features a tilted base and a surrounding jacket for temperature control via an external thermostatic circulator, like shown in Figure 5b (Chapter 2). A four-channel peristaltic pump was used to automate the flow of solutions, with each channel independently delivering the metal precursor, the organic linker, and the rinsing solvent, while the fourth channel handled waste removal. All channels were synchronized and controlled via a PC interface, ensuring accurate timing, volume delivery, and smooth operation throughout the synthesis cycles. The synthesis temperature, which ranged from 50 °C to 70 °C, was optimized for each MOF system and is discussed in detail in the corresponding results sections. Immersion times were also adjusted case by case based on experimental optimization. The group's standard protocol, which served as a starting point for optimization, involved 15 minutes of immersion in the metal solution and 25 minutes in the linker solution, with rinsing steps in between. The results of these optimizations and any deviations from the standard parameters are discussed in the subsequent sections.

In the standard condition, both $\text{Cu}_2(\text{DCam})_2(\text{DABCO})$ and $\text{Zn}_2(\text{DCam})_2(\text{DABCO})$ SURMOFs were synthesized from ethanolic solutions of 1 mM $[\text{M}(\text{OAc})_2 \cdot x\text{H}_2\text{O}]$ ($\text{M} = \text{Cu}^{2+}$ or Zn^{2+}) and 0.2 mM D-Cam with DABCO as pillar-linker. The substrates used were MUD-functionalized gold, quartz, and CaF_2 . Specific adjustments to immersion times or reagent concentrations, particularly for roughness optimization, are detailed in the results and discussion chapter.

4.3.2 Dip-Coating

In the dip-coating approach, the functionalized substrate is sequentially immersed in a set of reservoirs containing the synthesis solutions, like shown in Figure 5a (Chapter 2). Each growth cycle typically begins with immersion in the metal node solution, followed by two rinsing steps in ethanol, then immersion in the organic linker solution, and finally another two rinsing steps in ethanol. The double rinsing minimizes cross-contamination between solutions, as the rinsing is based on passive convection.

To improve the quality and uniformity of the SURMOF films, certain synthesis parameters were adapted depending on the system. For example, pillar-layer SURMOF systems required elevated temperatures during the initial growth cycles (typically the first ten) to promote nucleation; these syntheses were conducted at 55 °C. Ultrasonic agitation was also applied in some processes to enhance surface interaction and remove weakly bound species.

The standard immersion times used were 10 minutes for the metal precursor solution and 15 minutes for the linker solution, with 2×1 minute rinses in ethanol between each step. In some syntheses, a dual-linker strategy was implemented, requiring an adjusted sequence: metal > rinse > rinse > linker 1 > linker 2 > rinse. In these cases, the entire sequence was treated as one complete growth cycle. Immersion times were also varied in selected experiments to optimize the resulting film, and any deviations from the standard procedure are discussed in the relevant sections of the text.

HKUST-1:

HKUST-1 films were synthesized using 1 mM $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$ in ethanol as the metal precursor and 0.2 mM trimesic acid (BTC) in ethanol with 10% water as the organic linker solution. MHDA-functionalized gold substrates were employed.

Cu-DATDC-DABCO:

For the Cu-DATDC-DABCO system, multiple synthesis conditions were screened, including variations in concentration and immersion time. The optimized conditions are discussed in the results and discussion chapter.

4.3.3 Spin Coating

The spin-coating method offers a rapid and reproducible means of producing uniform SURMOF films over large surface areas. In this approach, precursor solutions are manually dispensed onto a functionalized substrate, which is rotated at high speed to ensure even spreading and to remove excess material via centrifugal force, like shown in Figure 5c (Chapter 2). This method is especially advantageous when rapid deposition and minimal reagent consumption are desired.

This method was used in the synthesis of HKUST-1 SURMOFs on plasma treated Si wafers. In a typical cycle, the 2x2 cm substrate was first covered with 800 μL of the 1 mM $\text{Cu}(\text{OAc})_2$ solution for 10 min before the process began. The spin coater was set to constantly spin at 2000 rpm (dynamic mode) and another 800 μL of $\text{Cu}(\text{OAc})_2$ were dropped onto it. Two rinsing steps with ethanol (1000 μL each) were performed and then 800 μL of 0.2 mM BTC were dropped on the substrate. Two other rinsing steps were performed to remove any loosely bound species.

The number of deposition cycles was selected based on the desired film thickness. Typically, 40 deposition cycles yielded films with a thickness of approximately 80–100 nm.

4.4 ANALYTICAL INSTRUMENTS

4.4.1 X-Ray Diffraction (XRD)

X-ray diffraction measurements were performed using a Bruker D8 Advance diffractometer equipped with a Cu $K\alpha$ radiation source ($\lambda = 0.154 \text{ nm}$) and configured in a θ – 2θ geometry. A position-sensitive detector was employed to capture the diffracted intensities. Data acquisition was carried out with a step size between 0.01° and 0.02° , over a 2θ range typically spanning 4° to 20° , depending on the sample type. Each scan was collected with an integration time of 0.5 s per step.

For measurements involving gold-coated substrates, vertical displacement (sample height) errors were corrected by referencing the (111) reflection of gold, standardized at $2\theta = 38.196^\circ$. Powder samples were recorded under continuous rotation to ensure optimal averaging of crystallite orientations. Post-processing, including background subtraction and peak analysis, was conducted using Bruker EVA version 3 software.

4.4.2 Electronic Circular Dichroism Spectroscopy (ECD)

Circular dichroism spectra in the solid state were obtained using a Jasco J-810 CD spectropolarimeter, operating at room temperature across the spectral range of 163 to 900 nm. Measurements for SURMOF samples deposited on quartz substrates were typically collected between 600 and 180 nm, with bare quartz plates serving as the background reference. Spectra were acquired with a step interval of 0.5 nm, a scan speed of 20 nm min⁻¹, a response time of 4 s, and a fixed spectral bandwidth of 1 nm. To account for anisotropic optical contributions and surface birefringence, measurements were recorded at eight angular orientations of the sample relative to the incident beam axis (0°, 45°, 90°, 135°, 180°, 225°, 270°, and 315°), and subsequently averaged to obtain the final spectrum.

4.4.3 Scanning Electron Microscopy (SEM)

Surface morphology was characterized using a PHILIPS XL30 scanning electron microscope equipped with a field emission cathode. Imaging parameters, including acceleration voltage, working distance, and magnification, were optimized individually for each sample to ensure optimal resolution and contrast.

To prevent surface charging during imaging, most samples were coated with a conductive platinum layer approximately 4 nm thick. The coating was applied using a high-vacuum sputter coater (Leica EM ACE600) immediately prior to measurement. For transparent samples that couldn't be covered, the environmental mode was used.

4.4.4 Atomic Force Microscopy (AFM)

Atomic force microscopy was carried out using a Bruker Dimension Icon system operating in standard tapping mode under ambient laboratory conditions. Topographical images were acquired to assess surface morphology, roughness, and nanostructural uniformity of the SURMOF films.

High-quality HQ:NSC18/Al BS cantilevers (μ Masch) were employed for all measurements. These probes have a nominal force constant of 2.8 N m⁻¹ and a resonance frequency of approximately 75 kHz, offering reliable sensitivity for soft and moderately rough surfaces. Scan

parameters, including scan rate, area, and resolution, were optimized as needed for each sample to ensure accurate surface profiling.

4.4.5 Confocal Laser Scanning Microscopy (CLSM)

Topographical imaging and surface roughness measurements were performed using a Keyence VHX-7000N digital confocal microscope operating in automatic mode. In this configuration, the system autonomously selected the appropriate vertical scanning range based on the surface features of each sample, ensuring optimal focus and height resolution across the measurement area.

Roughness analysis was conducted using a 50 $\times$ objective lens, which provided a balance between lateral resolution and field of view. This magnification allowed for sufficient sensitivity to surface features while enabling the characterization of larger areas compared to higher-magnification lenses such as the 150 $\times$ objective. In addition to roughness quantification, this technique was employed to evaluate the topography and step height of microstructured films, offering complementary morphological information to that obtained from SEM and AFM measurements.

4.4.6 Infrared Reflection–Absorption Spectroscopy (IRRAS)

Infrared spectra were acquired using a Bruker Vertex 80 Fourier-transform infrared spectrometer operating in reflection–absorption mode (FT-IRRAS). Measurements were performed under grazing incidence conditions, with the angle of incidence set to 80° relative to the surface normal to maximize surface sensitivity. The spectral resolution was set to 2 cm⁻¹.

All spectra were referenced against a perdeuterated C₁₆-thiol self-assembled monolayer (SAM), which served as the background. To minimize contributions from C–C vibrational modes and enhance signal-to-noise ratio, both sample and reference spectra were collected with 1024 co-added scans.

To eliminate atmospheric interference from water vapor, the sample chamber was continuously purged with dry synthetic air, and scans were repeated until no detectable water bands remained. Subsequent baseline correction and data processing were carried out using Bruker OPUS software.

4.4.7 Transmission Infrared Spectroscopy

Transmission measurements were performed using the same equipment for IRRAS, a Bruker Vertex 80, but with a different setup where radiation passed through the transparent samples, straight to the detector.

All spectra were referenced against a clean CaF_2 window, which served as the background. The setup was the same as for IRRAS.

5 VALIDATION OF A SIMULATION MODEL FOR SURMOFS AND THEIR USE AS METAMATERIALS

5.1 Introduction

Surface-anchored metal-organic frameworks (SURMOFs) represent a significant advancement in the integration of MOFs into solid-state devices. Their ability to form uniform, crystalline thin films on functionalized substrates makes them ideal candidates for both applied technologies and fundamental studies. Among the many directions currently explored, the optical properties of chiral SURMOFs have garnered growing interest due to their unique interaction with circularly polarized light, enabling potential applications in chiroptical devices, enantioselective sensing, and photonic metamaterials^{10,64,69}.

In particular, vibrational circular dichroism (VCD) has remained relatively underexplored in the context of MOFs, largely due to the practical challenges of performing such measurements on powdered materials. Typically, MOF powders must be embedded in KBr pellets for VCD analysis, a process that introduces significant scattering and reduces the signal-to-noise ratio¹⁰⁵. To address this limitation, we focused on using SURMOFs, which can be grown directly on transparent substrates such as calcium fluoride (CaF_2), allowing for direct transmission-mode VCD measurements without the need for additional preparation steps. This approach not only improves the reliability and resolution of the measurements, but also enables orientation-dependent studies of vibrational activity, something not feasible with powders.

This chapter presents our collaborative work with the Rockstuhl group, at the Institute of theoretical Solid-State Physics also at the Karlsruhe Institute of Technology (TFP/KIT), who developed a multiscale simulation model that combines quantum chemical calculations with electromagnetic scattering theory. The model predicts chiroptical responses, such as electronic and vibrational circular dichroism and other infrared optical properties, starting from atomistic molecular structures and extending to larger-scale film geometries. Our role was to validate the model experimentally by comparing its predictions with optical measurements from actual SURMOF thin films. The successful validation of this model for thin films has been published in collaboration with Prof. Rockstuhl¹⁰⁶.

The simulation framework can be extended beyond planar films to more complex metastructures, including periodic arrays and other patterned architectures. These designs offer pathways to engineer the optical response of the SURMOF beyond the capabilities of bulk materials, effectively enabling their use as metamaterials. In this context, the model becomes a powerful tool not only for interpreting existing structures, but also for guiding the design of future ones.

To experimentally realize these metamaterial structures, we explored different lithographic techniques to spatially structure the SURMOF thin films. A range of methods was employed, including Direct Laser Writing (DLW) and Thermal Scanning Probe Lithography (t-SPL), in an effort to fabricate both micro- and nanostructured patterns. These approaches aimed to replicate the geometries modeled in the simulations and assess the practical feasibility of translating theoretical designs into real devices. The resulting structures were evaluated in terms of pattern fidelity and film integrity.

In the sections that follow, we detail the growth of the chiral SURMOFs, the methods used to characterize their optical properties, and the experimental efforts to replicate simulated metastructures. Through this combined theoretical-experimental approach, we demonstrate the potential of SURMOFs as tunable, functional platforms for advanced photonic applications and lay the groundwork for their further development in metamaterials engineering.

5.1.1 SURMOF growth

Two chiral SURMOF systems were synthesized and analyzed in this study, based on either Cu^{2+} or Zn^{2+} as metal centers. Copper is widely used in SURMOF fabrication due to its established coordination chemistry and robust film-forming properties, whereas zinc offers advantages for optical and computational studies due to its completely filled d-shell. Notably, Zn^{2+} avoids the quenching of electronic excitations typically associated with Cu^{2+} dimers, making it more suitable for detailed photophysical analyses and for validating the predictive accuracy of the simulation model⁵⁷.

Both frameworks were constructed using enantiomerically pure camphoric acid and diazabicyclooctane (DABCO) as organic linkers to form pillar-layer architectures. As a standard

nomenclature, the resulting frameworks are named as $[M_2(X\text{-Cam})_2(\text{DABCO})]$, where $M = \text{Cu}$ or Zn , and $X = \text{D}$ or L depending on the camphoric acid enantiomer. The SURMOF components and a schematic of the resulting structure are shown in Figure 19.

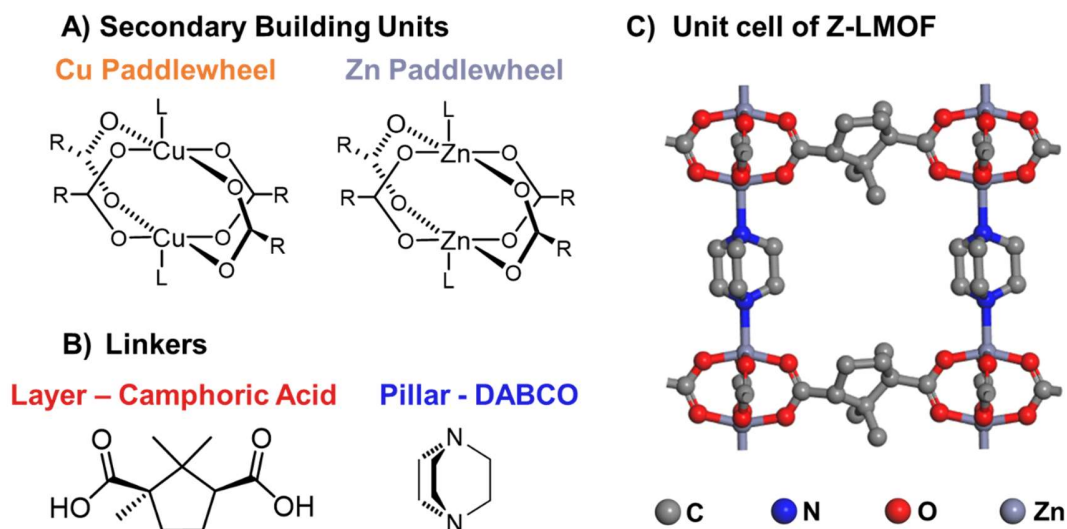


Figure 19: SURMOF a) SBUs, b) linkers and c) basic structure.

The two linkers play distinct structural roles in the SURMOF, camphoric acid, containing two carboxyl groups, coordinates to the equatorial positions of paddlewheel-type SBUs, thereby forming extended two-dimensional sheets. DABCO, a nitrogen-containing bidentate ligand, coordinates along the axial sites, acting as a vertical pillar to bridge adjacent layers³⁸. This arrangement leads to the formation of anisotropic frameworks with well-defined directional porosity.

Camphoric acid was selected due to its intrinsic chirality arising from two stereogenic centers, which exist in either the 1R,3S (D-Cam) or 1S,3R (L-Cam) configurations. Incorporation of this chiral linker into the MOF framework endows the resulting material with enantioselective properties, making it attractive for applications such as chiral recognition, asymmetric catalysis, and enantiomeric separation^{62,107,108}. Additionally, the optical activity imparted by the chiral environment is observable by electronic circular dichroism (ECD), and further extended into the mid-infrared region through VCD, which probes a larger set of transition modes and provides enhanced structural insight.

SURMOF growth was carried out via layer-by-layer deposition on appropriately functionalized substrates, using identical synthesis parameters for both metal systems, as described under the standard conditions in Section 4.3.1. Depending on the intended characterization method, the films were grown on gold, CaF_2 , or quartz substrates. Gold was primarily used for IRRAS and microscopy studies due to its conductivity and suitability for surface-sensitive techniques, while CaF_2 and quartz were selected for transmission-mode optical measurements requiring substrates that were transparent in different wavelengths. Initial syntheses were performed using the D-Cam enantiomer, due to its greater commercial availability. When optical characterization required enantiomeric comparison, the same deposition conditions were applied to the L-Cam analogue, yielding films with comparable morphology and quality.

However, notable differences in film adhesion and nucleation behavior were observed between the copper- and zinc-based systems, as evidenced by SEM imaging (Figure 20). The copper-based SURMOFs demonstrated more consistent nucleation and greater film continuity, particularly on CaF_2 substrates. In contrast, the zinc-based SURMOFs exhibited localized growth but failed to form a continuous film across the entire substrate surface. It is also important to note that, due to the non-conductive nature of CaF_2 , significant surface charging occurred during SEM imaging. This effect occasionally led to artifacts such as apparent cracking or partial delamination of the film, as shown in Figure 20b.

To enhance the deposition of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ and promote uniform film formation, a thin seeding layer of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ was introduced immediately following substrate functionalization. A few growth cycles of the copper-based SURMOF were applied to establish a continuous initial framework onto which Zn^{2+} ions could subsequently coordinate. This strategy facilitated the nucleation and growth of the zinc-based SURMOF across the entire substrate area previously coated with the Cu-based layer. The results can be seen in the AFM images in Figure 21. The SURMOF crystallites exhibit a characteristic platelet morphology. In the initial Cu-based SURMOF layer, both flat-lying and upright-standing platelets are observed, forming a partially oriented base layer across the substrate. In contrast, the Zn-based SURMOF displays significantly larger crystallites, but these also lack uniform orientation, with many of the surface crystallites deviating from ideal alignment.

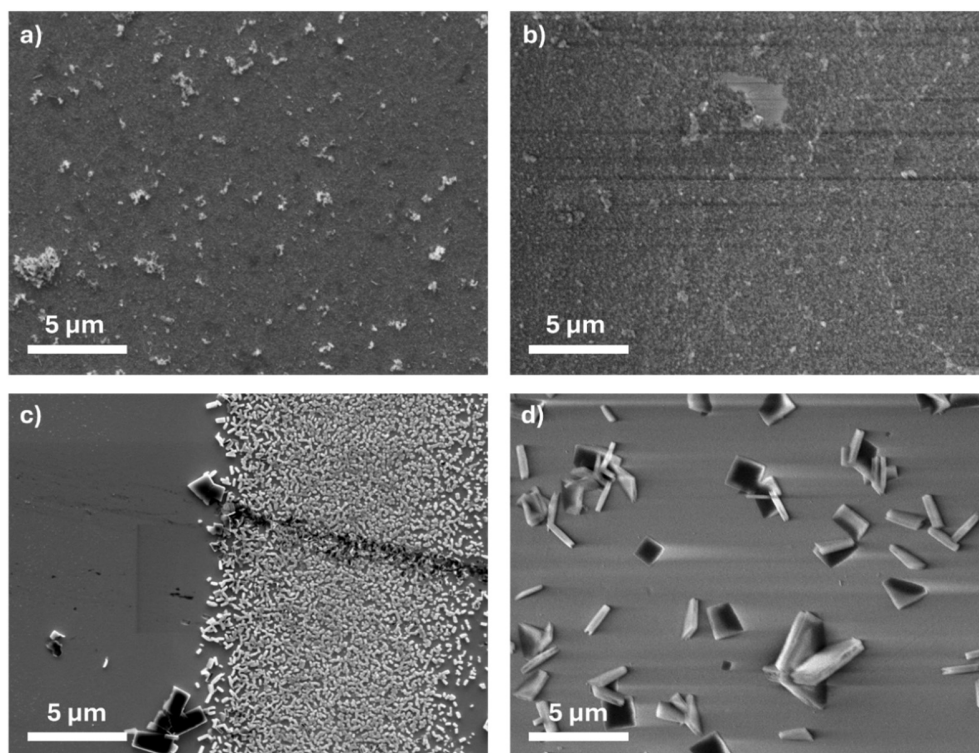


Figure 20: SEM images of Cu₂(D-Cam)₂(DABCO) on **a)** Au, **b)** CaF₂ and Zn₂(D-Cam)₂(DABCO) on **c)** Au and **d)** CaF₂.

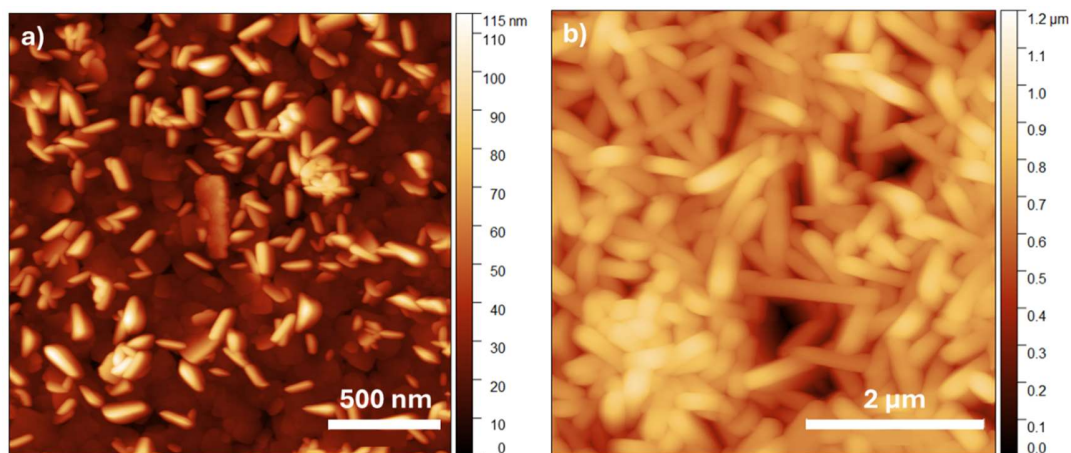


Figure 21: AFM images of **a)** a seeding layer consisting of 20 cycles of Cu₂(D-Cam)₂(DABCO), and **a b)** Zn₂(D-Cam)₂(DABCO) film grown in 80 additional cycles on top of the seeding layer, both deposited on CaF₂.

To confirm the formation of the target SURMOF structure, XRD patterns were compared with literature powder diffraction data for Zn₂(D-Cam)₂(DABCO). In addition to structural verification, this technique provides information on the crystallinity and preferential orientation of the resulting thin films. The XRD results obtained from SURMOFs grown on different substrates are presented

in Figure 22 along with the simulated powder diffraction for $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ found in literature¹⁰⁹.

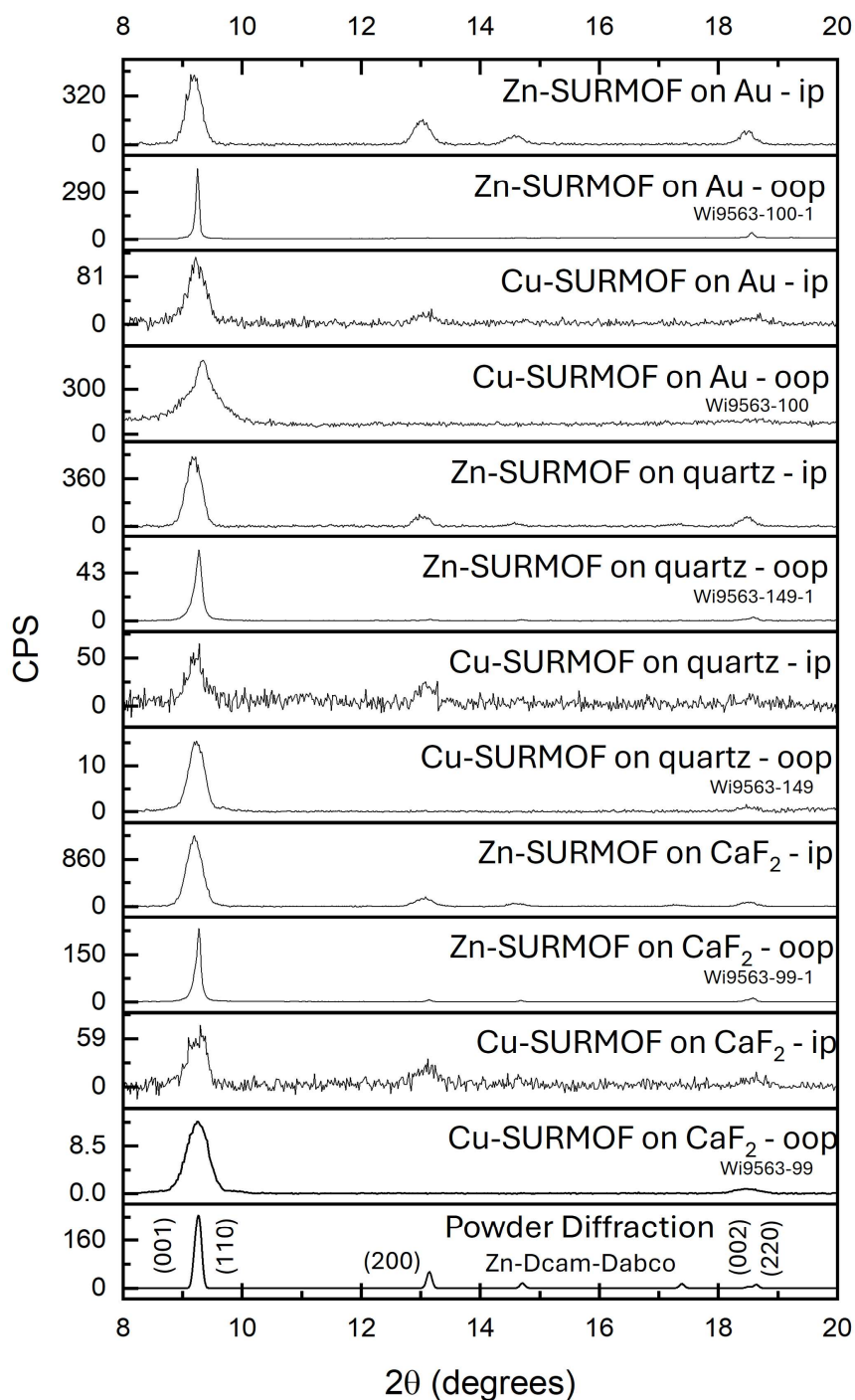


Figure 22: XRD diffractograms in-plane (ip) and out-of-plane (oop) of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ and $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ SURMOFs grown on gold-coated Si wafers, quartz and CaF_2 compared to the simulated powder diffraction for $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ obtained from literature¹⁰⁹.

These SURMOFs structure adopt a tetragonal pillar-layer architecture (space group $P4_212$). In X-ray diffraction, the primary contribution to scattering arises from heavier atoms, such as Zn^{2+} , meaning that the observed reflections primarily correspond to the spatial periodicity imposed by the organic linkers between the metal centers. For this structure, the (100) reflection reflects the periodicity along the camphoric acid linker axis, while the (001) reflection corresponds to the direction defined by the pillar linker, DABCO. Due to crystallographic symmetry, the (100) reflection is forbidden, and the (001) and (110) reflections could not be fully resolved under the available instrumental resolution. This constraint limited the ability to quantitatively determine the relative distribution of crystallite orientations within the film.

In out-of-plane XRD geometry, only lattice planes that are parallel to the substrate surface contribute to the detected reflections. Consequently, the presence and intensity of reflections such as (001) and (200) provide insight into the predominant orientation of the MOF crystallites. For example, a strong (001) reflection indicates that DABCO linkers are aligned perpendicular to the substrate, whereas a significant (200) reflection would correspond to camphoric acid linkers lying in that direction. In in-plane geometry, the opposite behavior would be expected.

In the present case, reflections corresponding to both the (001) and (200) planes were observed in the out-of-plane diffractograms. The comparatively lower intensity of the (200) reflection, relative to literature powder patterns and in-plane results, suggests that the (001) orientation is dominant in the film.

The film thickness of $Zn_2(D-Cam)_2(DABCO)$ grown on gold and CaF_2 substrates was estimated from cross-sectional SEM images, as seen in Figure 23. These samples were prepared with different numbers of deposition cycles, tailored to the sensitivity requirements of the respective optical characterization techniques. In all cases, a seeding layer of 20 cycles of $Cu_2(D-Cam)_2(DABCO)$ was first deposited to facilitate uniform growth of the Zn-based SURMOF. On gold substrates, used primarily for IRRAS measurements, an additional 80 Zn-MOF cycles yielded films approximately 400 nm thick. In contrast, films grown on CaF_2 substrates, used for transmission and VCD spectroscopy, underwent 150 growth cycles, resulting in a thickness of approximately 900 nm. The larger thickness on CaF_2 was essential to have a measurable signal in the VCD measurements.

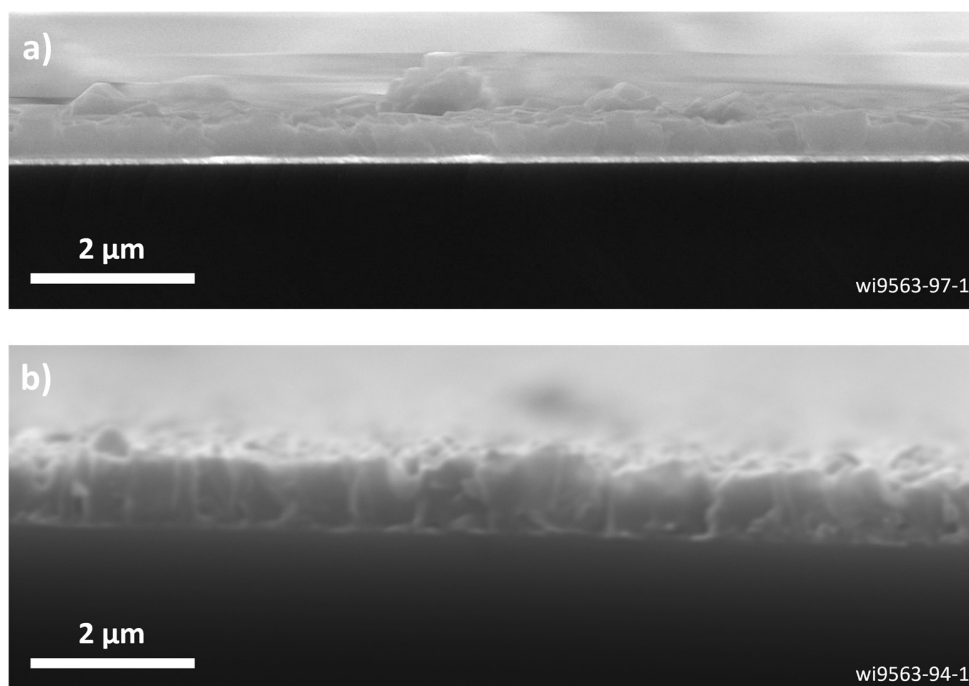


Figure 23: Cross-section SEM images of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films on a) Au and b) CaF_2 substrates.

With the thin films' topography and crystallinity thoroughly characterized, the samples were subsequently employed for spectroscopic analysis, enabling direct comparison with the theoretical predictions.

5.1.2 Comparison of Experimental and Theoretical Optical Characterization

An overview of the multiscale simulation workflow developed by our collaborators to simulate the optical properties of SURMOF thin films is presented in Figure 24, and a more detailed description of the model can be found in Fingolo, *et al*¹⁰⁶.

The workflow began with the construction and full optimization of periodic unit cell models for both Cu- and Zn-based SURMOFs, incorporating the L-enantiomer of camphoric acid. These optimizations were performed using periodic density functional theory (DFT), taking into account the paddlewheel-type metal nodes and the directional connectivity imposed by the camphorate and DABCO linkers.

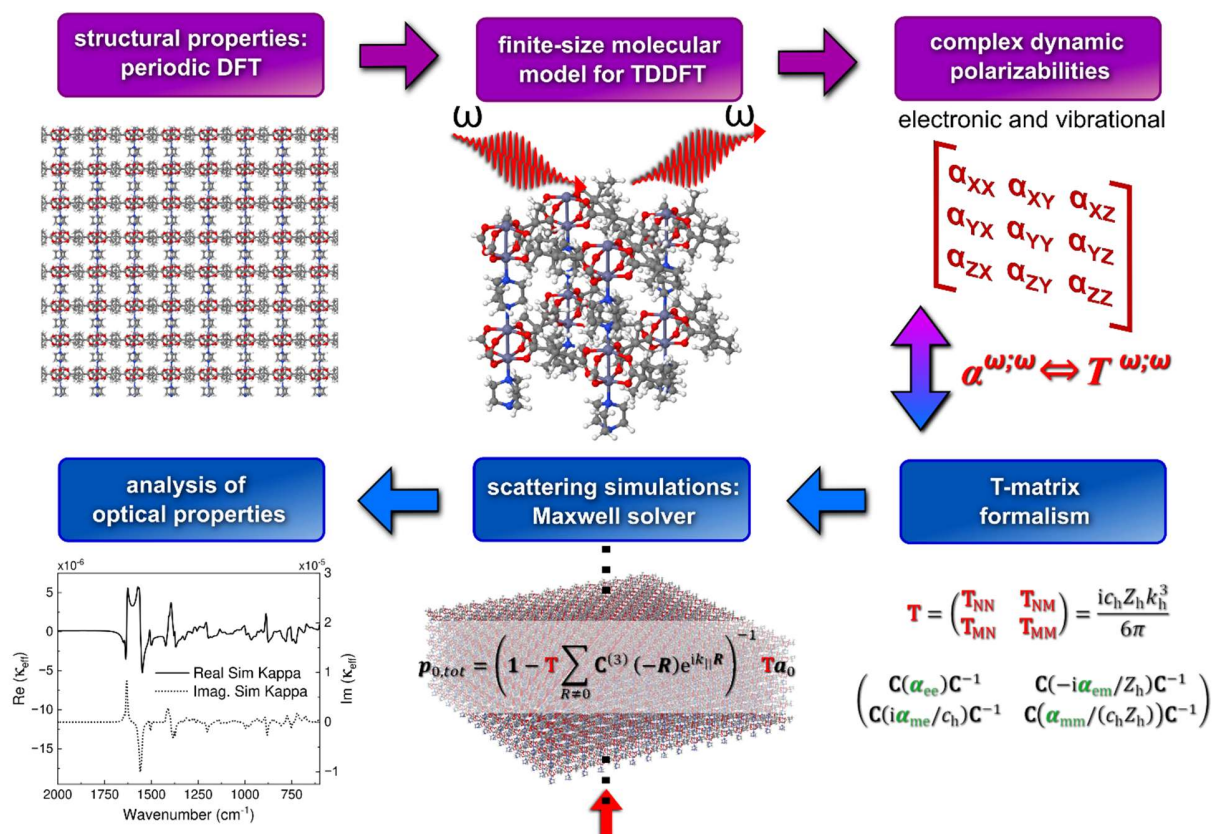


Figure 24: Scheme representing all the steps in the multiscale workflow

From the optimized unit cells, finite-size molecular models were constructed by stacking two unit-cells along each crystallographic axis. To chemically stabilize these supercells, hydrogen atoms with “infinite” mass were added to cap broken coordination sites, enabling accurate quantum chemical calculations on isolated clusters. This approach allowed for the determination of complex dynamic polarizability tensors essential for simulating the material’s optical behavior.

With the finite-size model, the infrared absorption spectrum was simulated and compared with the experimental data, as shown in Figure 25a to ensure the model was suitable for subsequent simulation steps. The calculated spectra successfully reproduced the position of the most intense vibrational bands, located around 1630 cm⁻¹ and 1415 cm⁻¹, which correspond to asymmetric and symmetric vibrations involving the carboxylate groups, respectively.

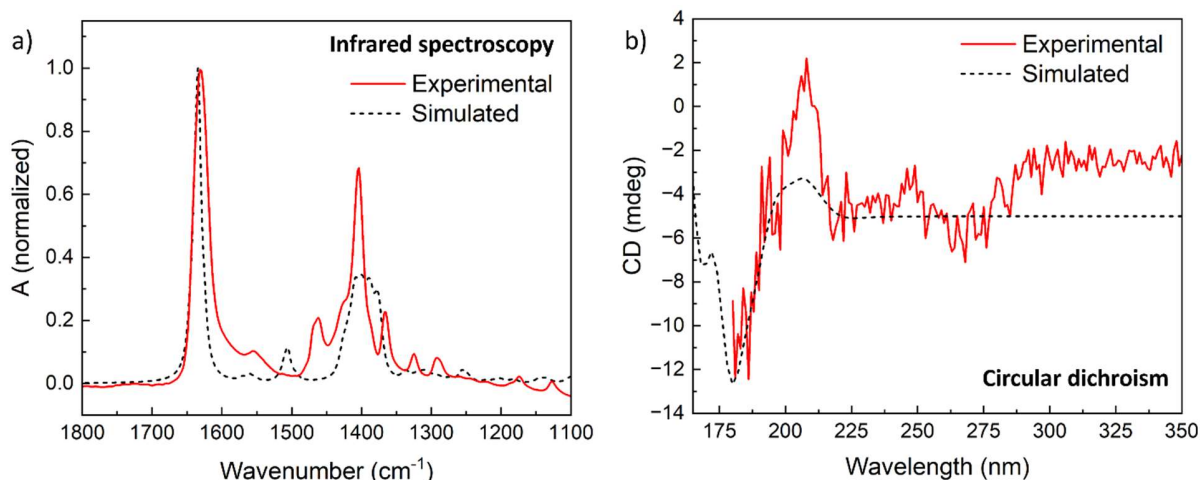


Figure 25: Comparison between experimental and simulated results for a) IR spectroscopy and b) CD spectroscopy of $\text{Zn}_2(\text{L-Cam})_2(\text{DABCO})$ SURMOF.

The CD spectrum shown in Figure 25b exhibited a similar overall shape to the simulated data, with a dominant band centered around 180 nm, indicating good agreement and further supporting the validity of the molecular model. However, the experimental spectrum suffered from a low signal-to-noise ratio, which clearly required further optimization. Besides, due to instrumental limitations, measurements could not be extended below 180 nm, restricting the spectral range available for direct comparison with the theoretical predictions.

The validated finite-size model was subsequently used to calculate the complex polarizability tensors, which served as the basis for constructing transition matrices (T-matrices). These matrices were then employed in Maxwell scattering simulations to predict the full optical response of the SURMOF films, thereby bridging the atomistic structure and macroscopic light-matter interactions.

Since the experimental data indicated a mixed orientation of the crystallites in the SURMOF films, the simulation model employed an orientationally averaged approach. This was done by averaging the T-matrix over all possible orientations, resulting in isotropic effective material parameters. This strategy was necessary because the exact proportion of crystal orientations could not be reliably quantified from the XRD data. Additionally, the typical crystallite size in the films was significantly smaller than the wavelength of light used in the spectroscopic experiments,

justifying the use of this homogenization method for comparison with far-field optical measurements.

The resulting model was used to simulate optical quantities like: the squared power reflectance (R^2), power transmittance (T), and vibrational circular dichroism (ΔA), and these were directly compared to experimental data to assess the predictive capability of the multiscale framework. In this context, vibrational circular dichroism was defined as the differential absorbance:

$$\Delta A = A_+ - A_-$$

Where:

$$A_{\pm} = -\log_{10}(T_{\pm})$$

$A_{\pm}$ is the absorbance of left (+) and right (-) hand circularly polarized light and $T_{\pm}$ denotes the respective power transmittance. For experimental comparison, the simulated ΔA spectrum of $\text{Zn}_2(\text{L-Cam})_2(\text{DABCO})$ was multiplied by -1 to yield the mirror-image response of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$, assuming ideal chiral symmetry. The SURMOF films used in transmission and VCD measurements had seeding layers of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$, however, the simulations were performed using pure Zn SURMOF models, which is reasonable given the strong structural and spectral similarity between the two metal systems. The films were grown on CaF_2 substrates and illuminated from the air side using circularly polarized light.

Importantly, the simulations take into account the experimental geometry and optical path length through the film. For example, in transmission measurements, the light passes through the sample once, while in reflectance experiments, such as IRRAS, it effectively passes through the film twice due to reflection from the underlying substrate. The film thickness on gold substrates was around 400 nm while for CaF_2 substrates it was approximately 900 nm, as estimated before from Figure 23. The increased thickness on CaF_2 was necessary to enhance the weak VCD signal. These parameters, including the different optical paths and film thicknesses, were incorporated into the simulation model to improve the accuracy of the predicted spectral responses.

In the reflectance and transmittance spectra ($1800\text{-}900\text{ cm}^{-1}$), shown in Figure 26a and b, there was very good agreement between the simulated and experimental results, particularly in the positions of the most intense vibrational bands at around 1630 cm^{-1} and 1415 cm^{-1} that refer to the asymmetric and symmetric vibrations of the $-\text{COO}$ group, respectively. This close alignment in band positions confirms the reliability of the simulation model in capturing the key optical features

of the SURMOF films. Although some discrepancies were observed in the relative band intensities, most notably, a slight overestimation of the absorption near 1625 cm^{-1} , these are likely due to experimental factors such as film roughness or minor variations in local orientation, rather than to compositional differences such as the presence of the copper-based seeding layer. Given that copper and zinc are neighbors in the periodic table, both materials are expected to have very similar optical responses, especially in the IR part of the electromagnetic spectrum.

The simulated and experimental VCD spectra (Figure 26c and d), on the other hand, showed excellent correspondence in both band positions and relative intensities. Minor baseline offsets (negative for Zn-LMOF, positive for Zn-DMOF) are frequently encountered in solid-state VCD and likely arise from residual birefringence, baseline correction artifacts, or polarization leakage. Importantly, all key spectral features, particularly bands at 1636 , 1556 , 1417 , and 1404 cm^{-1} , were accurately reproduced, and the anticipated mirror-image relationship between enantiomers was clearly observed. The ability to perform these measurements directly on SURMOFs deposited on transparent substrates, without KBr embedding, provided a major advantage by preserving film morphology and improving the signal-to-noise ratio.

The simulation model also proved effective in predicting the spectroscopic activity of specific vibrational modes across different techniques. For instance, the band at approximately 1558 cm^{-1} appears only weakly in the IR spectrum but is among the most intense features in the VCD spectra, a distinction that was successfully captured in the theoretical predictions. These results prove the robustness of the multiscale simulation approach in connecting atomistic-level structural details with the macroscopic chiroptical properties of SURMOF thin films.

Having validated the model with the optical behavior of uniform films, we next extended its application to simulate patterned SURMOF structures, aiming to explore their potential as metamaterials. If successful, this transition would allow us to investigate how spatial structuring and periodicity could modulate the chiroptical response, offering a design framework for tailoring optical functionalities beyond those achievable with homogeneous films.

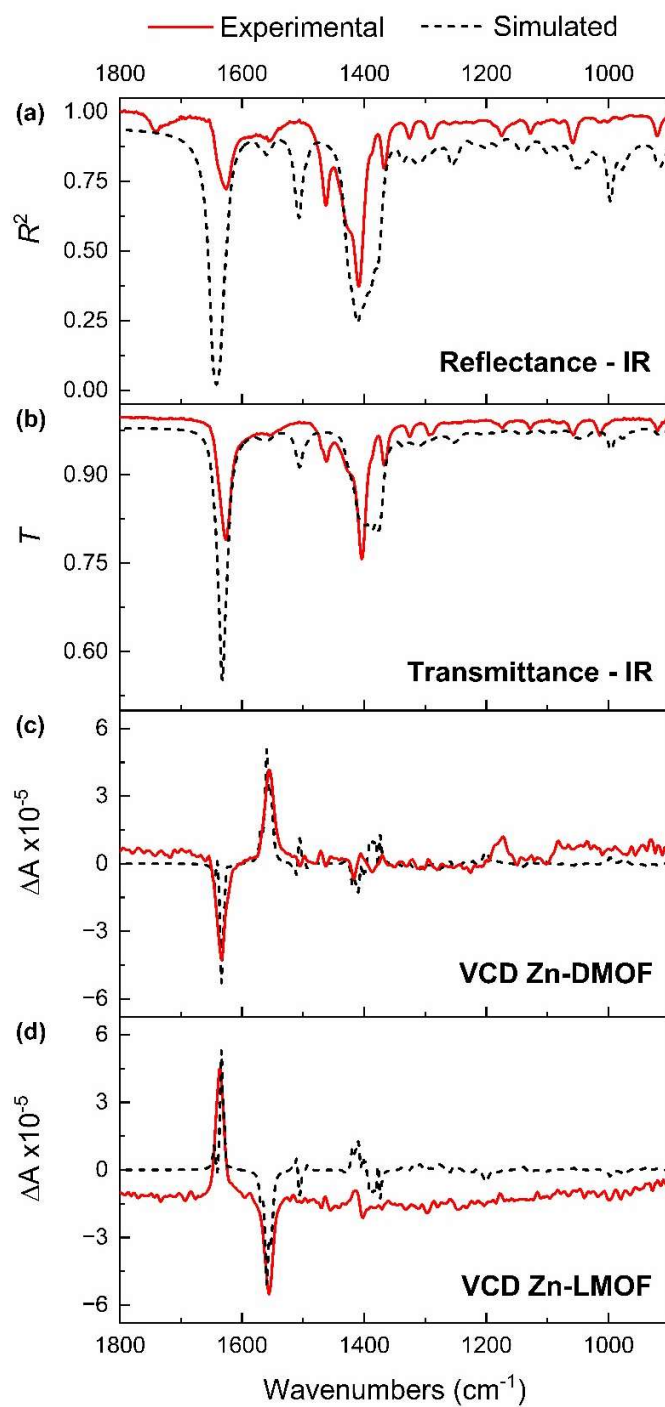


Figure 26: Comparison between experimental and simulated spectra for Zn-based SURMOFs: a) IRRAS, b) transmission-mode IR, c) VCD of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$, and d) VCD of $\text{Zn}_2(\text{L-Cam})_2(\text{DABCO})$.

5.2 Extension of the Model for Patterned Structures and Geometry Optimization

Building upon the successful validation of the multiscale model for uniform SURMOF thin films, the simulation framework was subsequently applied to predict the optical response of patterned architectures. Specifically, the model was used to simulate the ECD and VCD of periodic arrays of SURMOF cylinders, like shown in Figure 27, enabling direct comparison with planar films of equivalent thickness. Through systematic variation of the structural geometry, an optimal enhancement in ECD was predicted for an array of cylinders with diameter of 144.48 nm and spacing of 162 nm, while VCD amplification was calculated for structures with diameter of 3.1 μm and spacing of 7.2 μm . These results showed the potential of geometrical confinement to modulate and enhance chiroptical signals.

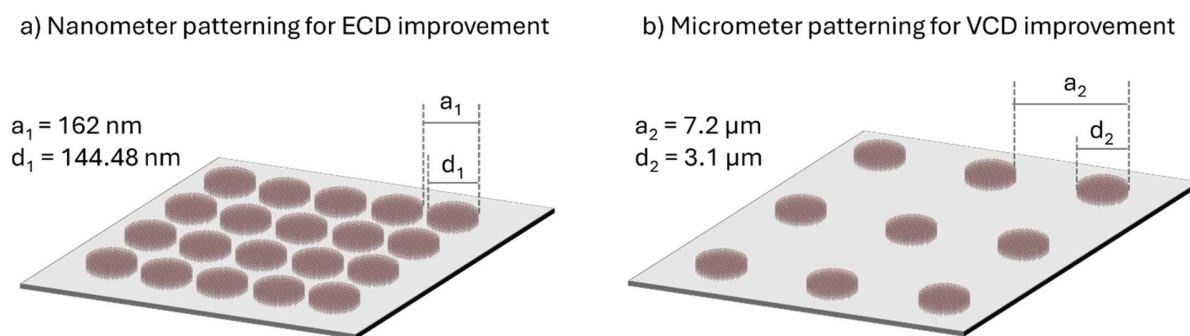


Figure 27: Representation of the optimized structures for enhancement of CD signals in different wavelengths

As these theoretical data were generated by collaborators in the Rockstuhl group and are not yet published, more details on the simulations will not be disclosed in this thesis. Nonetheless, motivated by the promising predictions, we proceeded with the attempt to experimentally realize such patterned SURMOF structures using a range of lithographic techniques, which are discussed in the following sections.

5.3 Fabrication of Patterned Thin Films

Different lithographic techniques were employed to fabricate these structured films with defined lateral patterns. These patterning strategies aimed to replicate the cylindrical arrays, while preserving the integrity and crystallinity of the chiral MOF layers.

5.3.1 Direct Laser Writing (DLW)

To fabricate microstructured SURMOF films targeting enhanced VCD signals, DLW was employed using the Heidelberg Instruments DWL 66+ system at the Institute of Microstructure Technology (IMT) in KIT with the help of Stefan Hengsbach and Dr. Klaus Bade. This high-precision lithography technique enables patterning at the micrometer scale with full design flexibility, making it compatible with our goal of creating structured SURMOFs.

SURMOF films of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ were grown on functionalized CaF_2 substrates under the standard layer-by-layer conditions (as described in Section 4.3.1), ensuring good crystallinity, surface homogeneity, and reproducibility. Following the MOF growth, a $1\ \mu\text{m}$ thick layer of AZ1505 photoresist (positive-tone resist) was spin-coated onto the SURMOF surface. In this system, the areas exposed to the laser become soluble in a basic developer solution, while the unexposed regions remain protected by the resist. Before proceeding with the full lithographic protocol, it was necessary to verify that the photoresist and its removal process would not compromise the structural integrity of the underlying SURMOF. Therefore, a preliminary compatibility test was performed in which the photoresist was spin-coated onto the SURMOF and subsequently stripped using acetone, the standard solvent for AZ1505 removal.

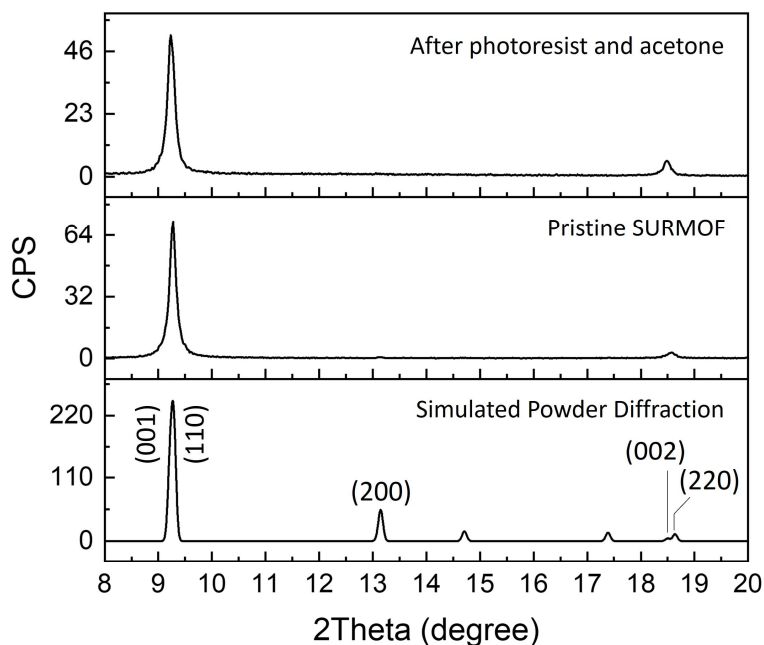


Figure 28: Comparison between the simulated powder diffractogram of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ ¹⁰⁹ and diffractograms before and after spin-coating of AZ1505 resist and subsequent removal with acetone.

As evidenced by the XRD patterns shown in Figure 28, the SURMOF preserved its crystallinity throughout this treatment, confirming that the resist-coating and stripping steps are benign and establishing a reliable foundation for the subsequent development and etching processes.

The developer used was AZ400K, a commercial solution based on potassium hydroxide (KOH), which requires dilution in deionized water prior to use. This composition posed a challenge: both KOH and water are known to chemically degrade SURMOFs. As such, our objective was to carefully optimize the development time, seeking a window where the exposed resist could be removed cleanly without initiating chemical degradation of the underlying MOF film.

Despite efforts to fine-tune the development time, no condition was found that adequately balanced resist removal and SURMOF preservation. The developer solution consistently permeated beneath the resist structures, leading to significant degradation of the underlying MOF at the edges of the protected areas. This undesired undercutting effect was visible even in structures with relatively large dimensions: circular patterns with diameters of 250 μm exhibited substantial border damage, while smaller features, such as 10 μm microstructures, were entirely destroyed during development.

These effects are clearly illustrated in Figure 29. The entire 250 μm -diameter circular feature is shown in Figure 29a; although the central region appears preserved, the perimeter shows a completely different topography and appears to be thinner. To clarify this process, Figure 29b presents a schematic cross section of the underetching process hypothesized to occur during development. The developer solution, which is harmful to the SURMOF, penetrates the porous film beneath the resist, partially degrading the borders of the protected area. Figure 29c provides a magnified view of the interface between the protected center and the deteriorated border, where developer penetration led to localized SURMOF degradation beneath the photoresist. Figure 29d shows a close-up of the outer edge of the pattern, comparing the damaged perimeter with the fully exposed region beyond the structure, where both the resist and SURMOF were completely removed by the development and subsequent etching steps.

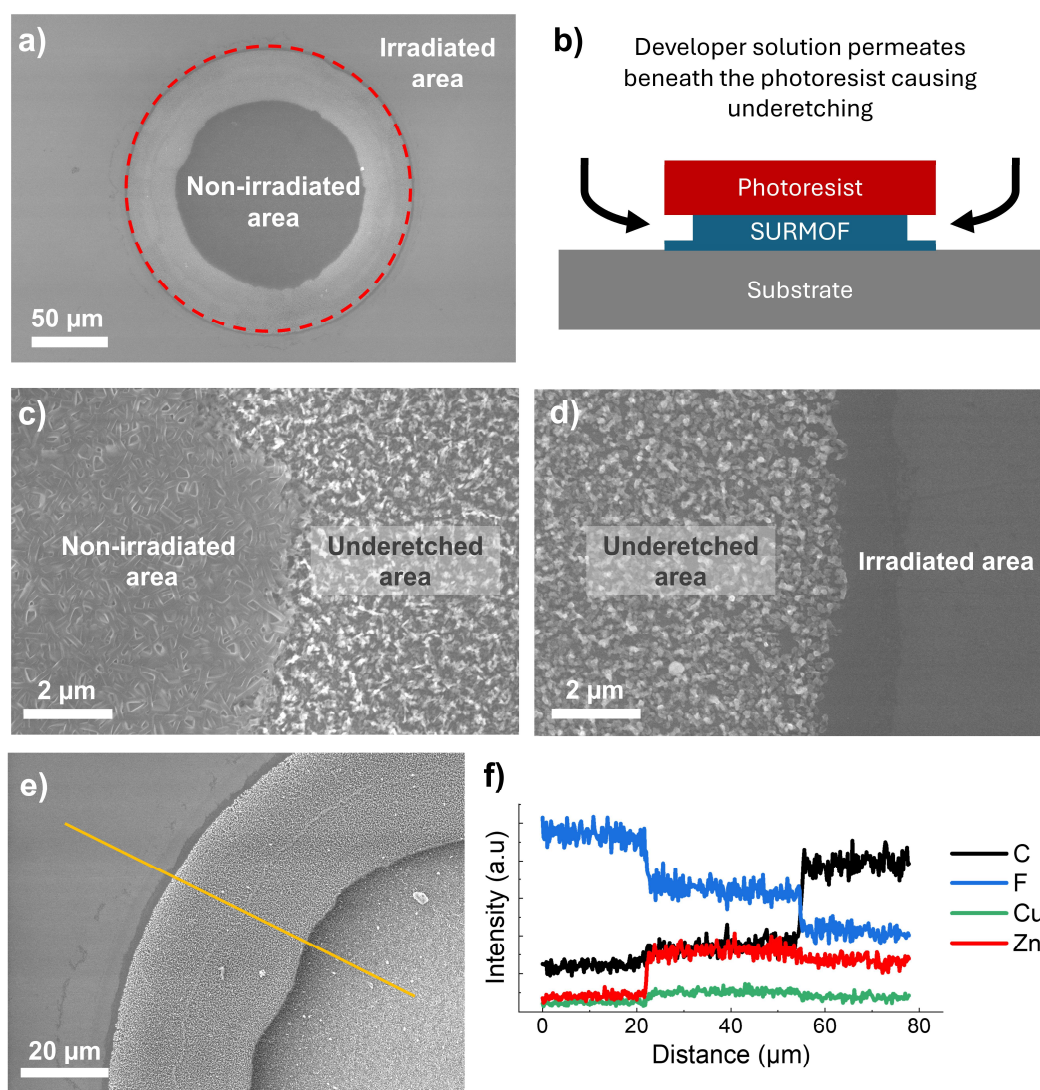


Figure 29: a) SEM image of a 250 μm diameter circle of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ after photolithography, b) Scheme showing the cross section of the material during under etching, c) Higher magnification image of the interface between the protected central region and the underetched border, and d) outer edge of the structure, comparing the underetched perimeter with the surrounding exposed region where both photoresist and SURMOF were completely removed. e) SEM image of the same patterned region, with the line used for EDX analysis indicated. f) Elemental distribution along the marked line obtained via EDX line scan, confirming partial degradation of the SURMOF at the edges due to developer infiltration.

To further assess the chemical composition and degradation profile of the patterned structures, EDX was performed along the line shown in Figure 29e. The line scan began in the exposed region outside the circle, traversed the damaged perimeter, and extended into the center of the protected area. The resulting elemental distribution, shown on Figure 29f, provides insight into the extent

and nature of SURMOF degradation. Fluorine, originating from the CaF_2 substrate, exhibited three distinct intensity plateaus: highest outside the circle (where the SURMOF was fully removed), moderately reduced at the damaged perimeter, and lowest in the central protected region. This trend indicates increasing coverage by residual film material toward the center. Carbon showed a slight increase at the perimeter and a marked rise in the center, further confirming the presence of intact SURMOF material only in the central zone. Interestingly, the zinc signal was lower in the area outside the circle, but remained relatively constant between the damaged perimeter and the central region, suggesting that while the organic linker components were chemically degraded on these borders during development, the metal nodes persisted at the surface, possibly as residual metal oxides. This hypothesis is consistent with the altered visual appearance and reduced thickness of the border regions. Copper intensity remained low across the damaged and central areas, as expected from its presence only in the thin seeding layer beneath the Zn-based SURMOF.

These findings made it clear that even large-scale features could not be patterned with sufficient fidelity, as the resist coverage proved inadequate to fully shield the SURMOF from chemical attack during development. The lateral permeation of the KOH-based developer led to extensive degradation at the edges of the structures, preventing the reliable fabrication of the micron-scale patterns required to experimentally verify the predicted enhancement in VCD signals. In light of this limitation, a modified approach was pursued: a protective intermediate layer of PMMA was introduced between the SURMOF and the photoresist, like shown in Figure 30a. This additional layer was spin coated to act as a physical barrier, preventing direct contact between the developer and the MOF film. The subsequent removal of the PMMA was planned via extended O_2 plasma etching, which would just extend the etching step a bit longer.

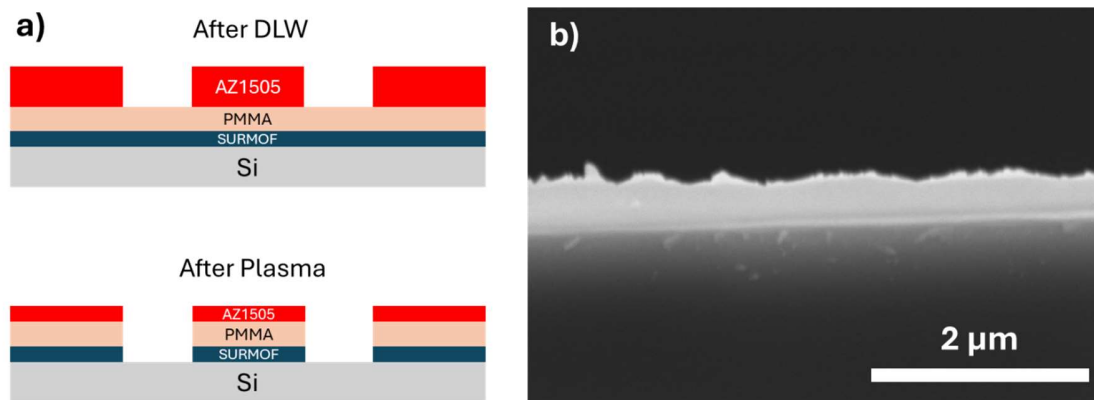


Figure 30: a) expected process after the addition of a PMMA layer for protection of the SURMOF and b) 400 nm PMMA layer formed by spin coating of 2.5% wt. PMMA in toluene.

Based on prior experience within our group, PMMA could be spin coated over SURMOFs when dissolved in toluene. To ensure that this layer would effectively prevent contact between the KOH-based developer and the underlying MOF during lithographic processing, several spin-coating conditions were systematically tested. The goal was to achieve the thinnest possible PMMA coating while ensuring full surface coverage without defects such as pinholes, which would compromise its protective function.

Through these tests, the optimal condition (2.5% wt. in Toluene) yielded a continuous PMMA film approximately 400 nm thick, like shown in Figure 30b. Thinner coatings would be desirable for minimizing total stack height, however, they exhibited surface defects and incomplete coverage, making them unsuitable. This optimized PMMA layer was then adopted for subsequent sample preparation and lithography.

As the presence of PMMA beneath the photoresist could influence the exposure characteristics during DLW, an additional set of exposure tests was conducted. Various conditions of laser power were evaluated, from 40 to 250 mW, to identify parameters that would ensure precise pattern definition through the modified resist-PMMA-SURMOF stack. These adjustments were essential for maintaining lithographic fidelity while preserving the SURMOF beneath the protective PMMA layer.

These initial exposure tests were conducted using spin-coated HKUST-1 films on silicon wafers, chosen due to the rapid and reproducible synthesis. Figure 31 displays the results for three selected laser powers: 90, 140, and 250 mW, which were chosen based on preliminary screening. Lower powers, such as 40 mW, produced no observable change on the surface, whereas 70 mW was the lowest power at which the pattern began to develop with discernible definition.

Each power condition is presented under two stages: after development and after oxygen plasma etching. The virtual mask used for writing included a variety of structures with different shapes and dimensions, allowing for a comprehensive assessment of how the lithographic performance varied across geometries.

After development, the 250 mW exposure resulted in significant pinhole formation throughout the resist-PMMA-SURMOF stack, compromising the integrity of the protective PMMA layer. The 140 mW condition also exhibited some localized pinholes, though it was not initially clear whether

these fully penetrated the PMMA and exposed the underlying SURMOF. In contrast, the 90 mW condition produced patterns that appeared free of pinholes, suggesting it was the most promising option at this stage in terms of maintaining PMMA coverage and thus protecting the MOF.

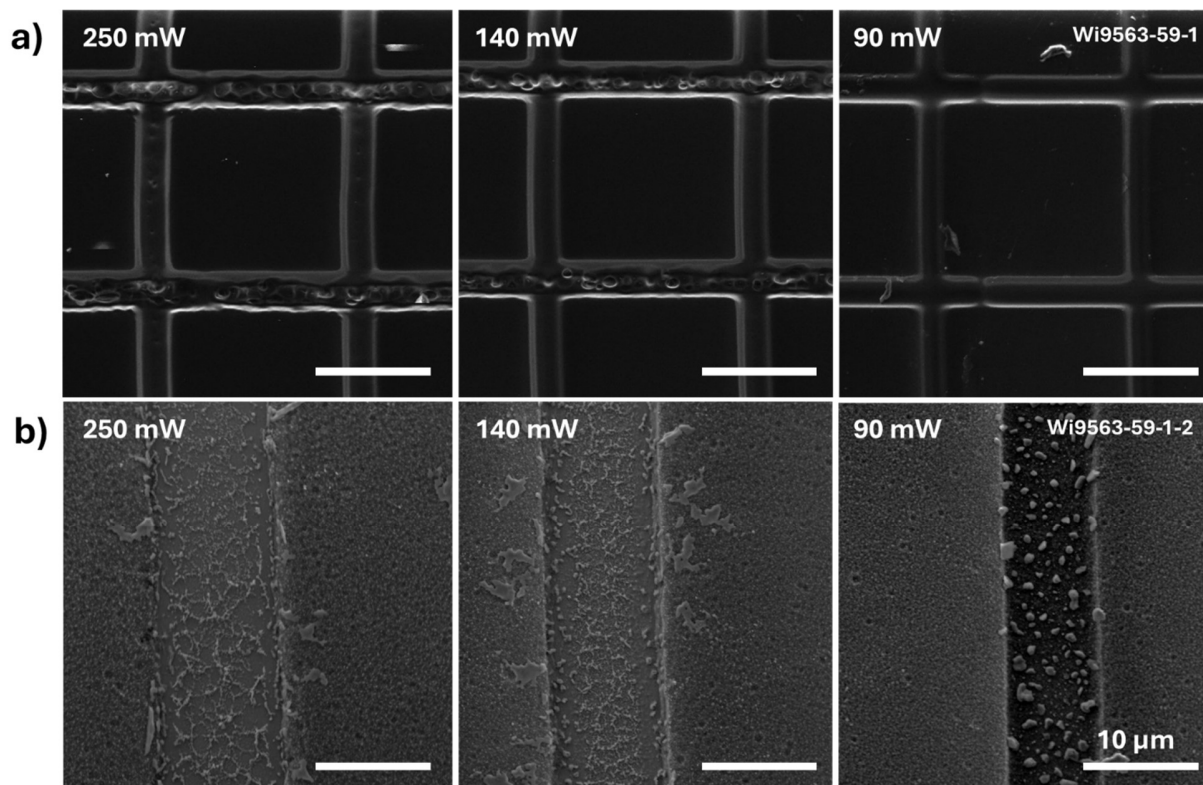


Figure 31: SEM images of HKUST-1 thin films coated with PMMA and patterned via DLW. The channels represent the irradiated areas, where photoresist was removed: a) after development and b) after plasma etching. Stages a) and b) show different parts of the structure, with channels of different sizes. Scale bar: 10 μm .

However, post-etching analysis revealed important trade-offs between pattern fidelity and etching efficiency. While the 90 mW condition maintained well-defined pattern edges and consistent channel width, significant residues were observed in the exposed (etched) areas. These residuals proved difficult to remove, even with extended plasma exposure times, and exhibited high resistance to further etching, suggesting partial cross-linking or redeposition effects. On the other hand, higher power conditions (140 and 250 mW) enabled more effective removal of SURMOF material in the exposed regions, leaving behind cleaner channels. This came at the expense of structural precision, as some degree of overetching was observed, leading to lateral widening of the patterned features beyond the intended mask dimensions.

Following the plasma etching step, the PMMA layer was stripped to evaluate the final quality of the patterned structures. SEM analysis, shown on Figure 32, revealed that at higher exposure powers (250 mW), pinhole formation had indeed occurred, since the edges of the patterned features were slightly different, indicating that the developer had permeated through the protective layers and locally degraded the underlying SURMOF. Although the etching was more effective at these conditions, the loss of structural integrity at the borders rendered them unsuitable for precise patterning.

The 90 mW condition initially appeared promising after the etching step, with seemingly well-preserved pattern edges. However, once the PMMA was removed, the exposed SURMOF structures exhibited highly irregular borders, indicating poor lateral resolution. This was attributed to the persistent residues formed during etching, which likely shielded sections of the SURMOF unevenly. As a result, some areas remained partially protected, leading to incomplete material removal and distorted feature geometry. Besides that, substantial residual debris was left in the open channels, possibly due to plasma-resistant byproducts from the polymer stack.

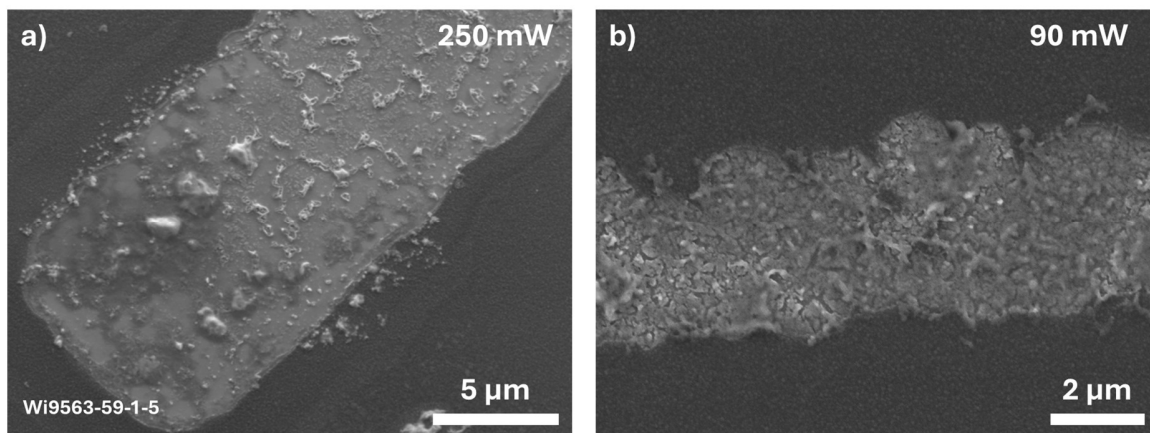


Figure 32: SEM images of HKUST-1 thin films coated with PMMA and patterned via DLW with laser power of a) 250 mW and b) 90 mW after PMMA stripping.

It is important to note that the test structures fabricated here were larger than the target feature sizes required for VCD enhancement. Given the inability to produce clean, uniform patterns even at these larger scales, it became clear that this approach was unsuitable for fabricating high-resolution SURMOF microstructures.

However, this outcome does not reflect limitations of the DLW system itself, which is a common tool for high-resolution patterning. Since the instrument is part of the KNMFi user

facility, it has a high demand and introducing new resist and process would require extensive optimization and posed a major bottleneck. As such, alternative lithographic strategies with better material compatibility and process flexibility were pursued in collaboration with another institute in the subsequent stages of this work.

5.3.2 Thermal Scanning Probe Lithography (t-SPL)

To explore the fabrication of nanoscale patterns for enhancing the ECD response, thermal scanning probe lithography (t-SPL) was employed using the NanoFrazor system from Heidelberg Instruments. This technique offers some advantages over conventional photolithography, particularly in the context of sensitive materials like SURMOFs. Unlike traditional methods that rely on light exposure and chemical developers, t-SPL utilizes a thermal resist, poly(phthalaldehyde) (PPA), which undergoes localized decomposition when heated by a nanoscale tip. The degraded resist sublimates directly during patterning, eliminating the need for a wet development step. This solvent-free process is particularly advantageous for SURMOFs, which are known to degrade upon exposure to basic or aqueous developers.

However, a critical requirement of the NanoFrazor system is that the substrate surface must exhibit very low roughness, ideally below 10 nm, to enable precise tip control and uniform resist thickness. Initial measurements revealed that $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ SURMOFs grown on quartz substrates exhibited root-mean-square (RMS) surface roughness values around 70 nm and average roughness of 139 nm, significantly above the system's operational threshold. This required further optimization of the growth procedure before these samples could be used in t-SPL. An AFM image of such a sample is shown in Figure 33a.

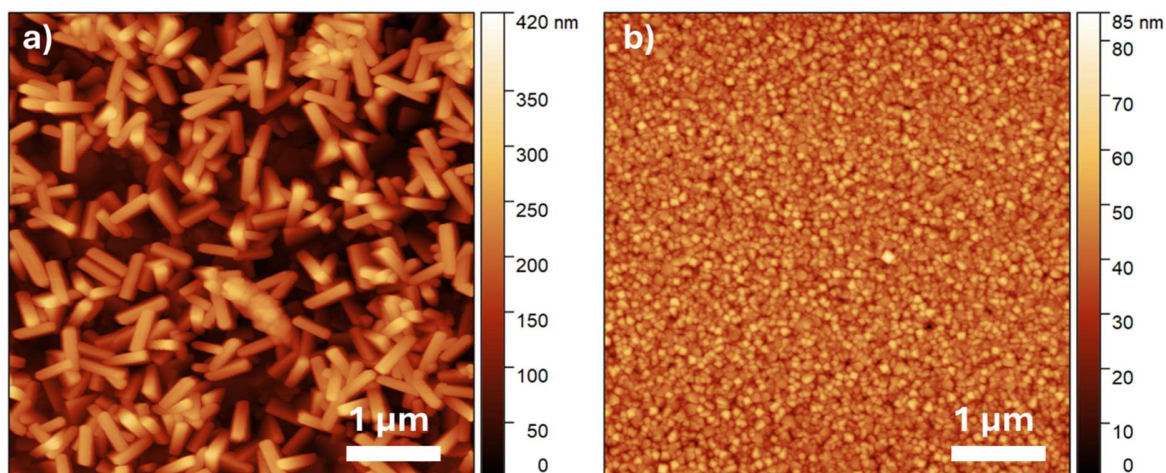


Figure 33: AFM images of a) $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ on quartz grown with the standard process and b) HKUST-1 on Si wafer

In contrast, films of HKUST-1 synthesized on silicon wafers already met the surface roughness requirement, with RMS around 7 nm and average roughness around 40 nm, offering a viable model system for initial process development (Figure 33b). These samples were used in preliminary t-SPL tests to establish exposure conditions, assess pattern transfer fidelity, and evaluate the general compatibility of the resist-MOF stack with the lithographic process. Insights from these tests were intended to inform future application of t-SPL to chiral SURMOFs once surface roughness could be sufficiently reduced.

5.3.2.1 High resolution patterning of HKUST-1

To evaluate the feasibility of nanostructuring SURMOFs using t-SPL, a multistep patterning strategy was developed and applied to HKUST-1 grown on silicon wafers. The workflow, illustrated in Figure 34, was devised in collaboration with Dr. Matthias Barczewski and Dr. Stefan Walheim from INT/KIT and aimed to combine the advantages of t-SPL with materials and processes compatible with SURMOF chemistry. The process consisted of the following steps: (1) SURMOF growth, (2) spin-coating of a poly(methyl methacrylate)/ methyl acrylate (PMMA/MA) lift-off layer, (3) spin-coating of the thermal resist poly(phthalaldehyde) (PPA), (4) patterning of PPA using the Nanofrazor system, (5) development of the PMMA/MA using a mild isopropanol-

based solvent, (6) chromium deposition, (7) lift-off of the remaining PMMA/MA, and (8) reactive ion etching (RIE) with O₂ to transfer the pattern into the MOF layer.

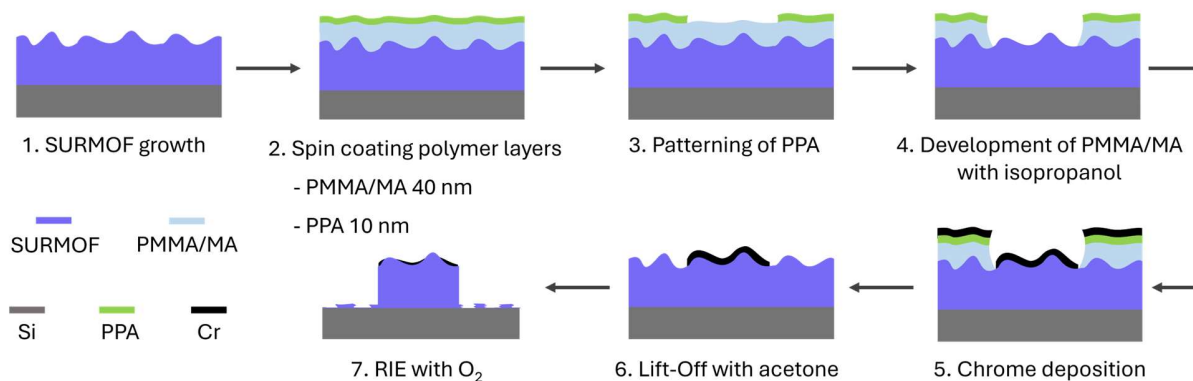


Figure 34: Schematic representation of the t-SPL process

Each step was thought of to account for both the physical limitations of the patterning tool and the chemical sensitivity of the MOF substrate. The PPA layer, required for thermal lithography, was applied at a thickness of only 12 nm. However, such a thin film is insufficient to serve as a robust etch mask during RIE. Therefore, a ~40 nm thick PMMA-based layer was first deposited onto the SURMOF by spin-coating, serving as an intermediate protective scaffold. This intermediate layer served multiple purposes: it smoothed the film surface to reduce local roughness and mechanical strain on the thermal tip during patterning, and it provided a removable scaffold that could later be replaced by a more etch-resistant material. Unlike the PMMA used in the DLW experiments, which was prepared in-house, the formulation used here was a commercially available PMMA/MA copolymer. This mixture incorporates methyl acrylate monomers, which are known to enhance the adhesion, flexibility, and overall processability of the polymer. These properties resulted in improved surface coverage and film uniformity, even at reduced thicknesses, making this version of PMMA more suitable for integration with the thermal scanning probe lithography process.

Following t-SPL, the pattern defined in the PPA layer was transferred into the underlying PMMA through development in isopropanol containing 2% water. This solvent mixture was selected for its compatibility with SURMOFs, avoiding damage from harsher developers while maintaining sufficient PMMA solubility and wettability. After pattern transfer, a 10 nm layer of chromium was deposited by thermal evaporation. Chromium was selected due to its higher

resistance to oxygen plasma comparing to the polymers used as resist. In this way, chromium can act as a temporary hard mask during RIE, however, due to its low thickness this metal was also removed alongside the exposed SURMOF during the RIE etching step. Ideally, an optimal time could be found where all the Cr could be removed without damaging the SURMOF layer protected by it.

Initially, alternative process variants without the chromium layer were considered, relying on thickened PMMA alone to protect the MOF film. However, these approaches posed challenges due to the limited etch resistance of polymeric materials under O₂ plasma and the difficulty in achieving complete residue-free pattern transfer.

For a first experiment a structure of around 30 μm was chosen, so we could work on a faster mode of the Nanofrazor. Details in the range of less than 200 nm require the high-resolution mode, which is considerably slower. The KIT logo was chosen for these first experiments and the results in some of the stages can be found in Figure 35.

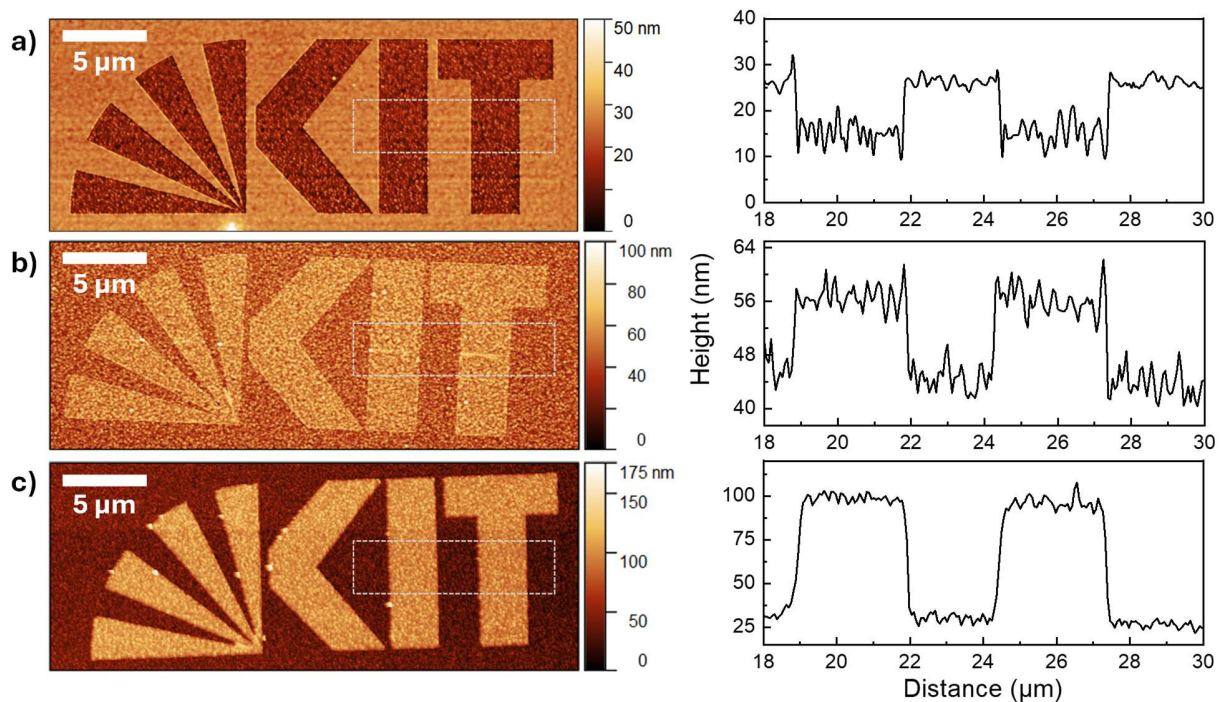


Figure 35: AFM images and topography profiles of HKUST-1 sample processed in the Nanofrazor after: a) PPA patterning, b) chromium deposition and PMMA lift-off and c) RIE etching.

As shown in Figure 35a, following the PPA patterning step (Stage 3 in Figure 34), the intended nanostructure was successfully defined on the SURMOF surface. The height profile reveals a step of approximately 12 nm, indicating that the PPA layer was fully removed in the exposed regions. This enabled uniform deposition of the chromium masking layer, followed by lift-off of the underlying PMMA, resulting in the patterned Cr mask shown in Figure 35b (Stage 6, Figure 34). The measured Cr thickness was close to the targeted 10 nm, although some variation arises due to surface roughness. Subsequent oxygen RIE etching (Figure 35c, Stage 7 in Figure 34) yielded sharply defined features, with high-resolution vertical edges resulting from the directional nature of the etching process. The measured step height was approximately 75 nm, slightly below the initial film thickness of 80 nm, suggesting nearly complete etching of the SURMOF in the exposed regions. SEM imaging was used to further assess the surface morphology and remaining material post-etching and the result is shown in Figure 36.

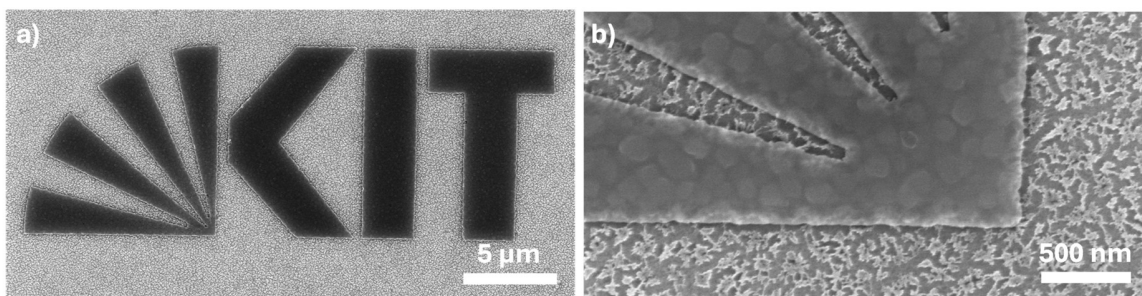


Figure 36: SEM images of the KIT logo patterned on HKUST-1.

As with the AFM analysis, SEM imaging shows the excellent lateral resolution of the patterned features. At higher magnification (Figure 36b), the grain boundaries of the original HKUST-1 film can be seen, indicating that the underlying crystal morphology was largely preserved during processing. Additionally, residual material left behind by the RIE process could be observed in the etched regions. The fact that the flat substrate was not fully exposed suggests that the plasma etching did not completely remove the material, likely due to the formation of thin, more resistant oxide residues during the process. However, given the limited extent of this residual layer, the process was deemed sufficiently successful, and the workflow was carried forward to investigate the feasibility of high-resolution patterning with smaller feature sizes.

The next step involved high-resolution patterning of a grid composed of 30×20 squares, each 200 nm in side length and separated by 150 nm gaps. AFM images acquired at various stages of

the process are shown in Figure 37. After the thermal removal of the PPA layer (stage 3, Figure 34), the patterned structures were clearly visible (Figure 37a). Despite the reduced feature size being comparable to the dimensions of individual HKUST-1 crystallites, making precise depth measurement from the AFM profile challenging, the patterning of the resist appeared successful, with complete removal of the PPA in the exposed regions.

The subsequent PMMA lift-off step proved more problematic. The narrow spacing between the squares hindered the efficient penetration of the solvent, and the standard protocol was insufficient to remove the PMMA entirely. Figure 37b highlights the presence of residual PMMA, likely resulting from inadequate solvent access and poor detachment from the MOF surface. Additional time or ultrasonic agitation may be required to fully remove PMMA in such high-resolution structures. Nonetheless, the RIE etching was performed, and the Cr-masked regions successfully preserved the patterned squares. Although AFM-based height measurements were difficult due to tip convolution effects at these aspect ratios, the measured heights were generally consistent with the expected values based on the original film thickness.

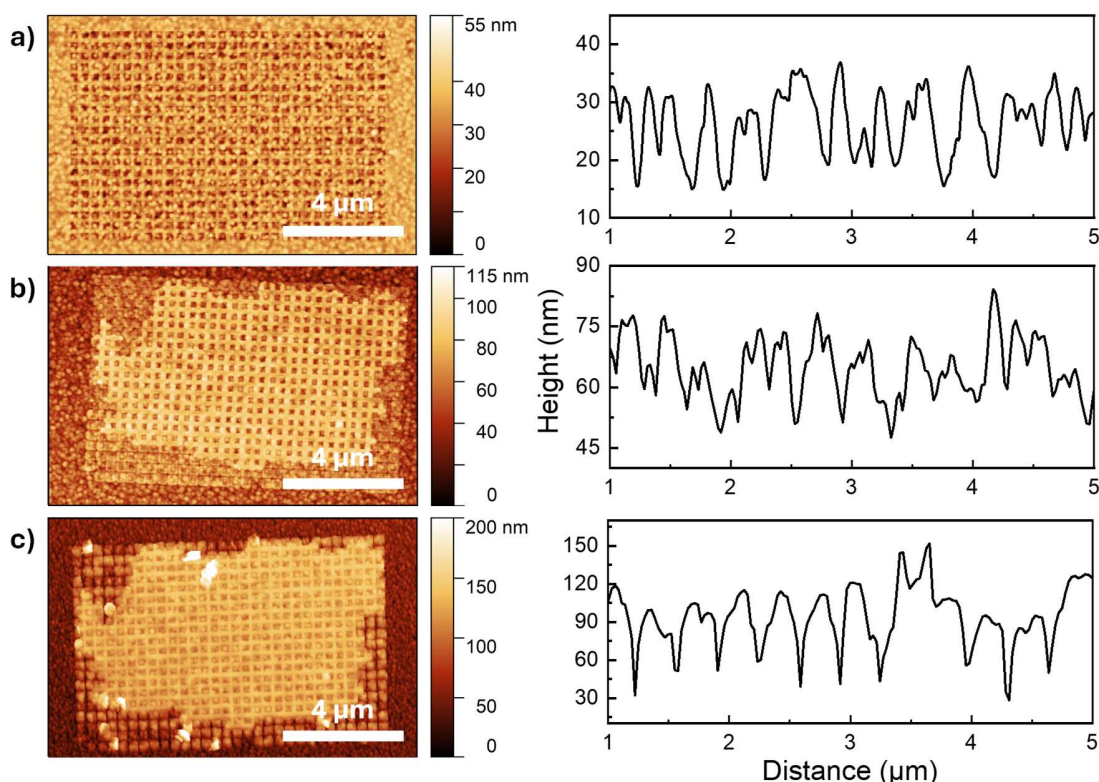


Figure 37: AFM images and topography profiles of a grid of 30x20 squares on HKUST-1 patterned with the Nanofrazor after: a) PPA patterning, b) chromium deposition and PMMA lift-off and c) RIE etching.

SEM imaging of the final structures (Figure 38) revealed that some of the squares were dislodged from the substrate, possibly due to beam-induced charging or damage during imaging. However, the preserved features exhibited well-defined square geometry, validating the overall resolution and pattern fidelity of the process.

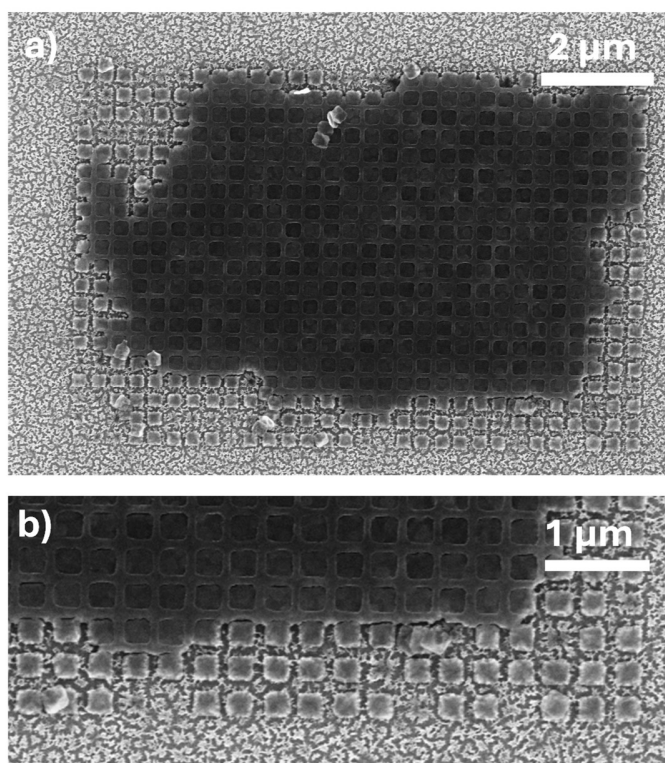


Figure 38: SEM images of a grid of 30x20 squares patterned on HKUST-1.

While some adjustments are still required to improve reproducibility and reliability at this scale, this experiment served as a successful proof of concept. Based on these encouraging results, the process was further developed for the high-resolution patterning of the target SURMOF $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$, as discussed in the following chapter.

5.4 Summary

In this chapter, the $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ SURMOF was used as a model system for validating theoretical predictions of chiroptical responses in MOF thin films and for exploring their potential use as optical metamaterials. The SURMOF was successfully grown on a variety of

substrates tailored for different optical techniques, enabling systematic IR, ECD, and VCD measurements. Direct comparison with multiscale theoretical simulations developed by the Rockstuhl group (TFP/KIT) showed very good agreement in spectral features and chiroptical signatures, thereby validating the simulation framework for SURMOF thin-film systems.

A particularly important outcome of this work was the first experimental demonstration of VCD measurements on SURMOFs. By growing chiral SURMOFs directly on transparent substrates, such as CaF_2 , transmission-mode VCD measurements could be performed without embedding the material in KBr pellets. This approach enabled non-destructive characterization, improved signal-to-noise ratios, and can allow the orientation dependence of the chiroptical response to be systematically investigated, which is not accessible in powder-based MOF studies.

Motivated by theoretical predictions of enhanced CD signals in laterally structured architectures, different lithographic approaches were explored to pattern $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ SURMOFs. DLW proved challenging due to the chemical sensitivity of SURMOFs to common developers, which caused pronounced underetching and degradation at feature edges. The introduction of an in-house spin-coated PMMA protective layer partially mitigated this issue but led to significant residues after development and etching, limiting its practical applicability.

For higher-resolution patterning, thermal scanning probe lithography (t-SPL) was investigated. Since $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films prepared under standard conditions exhibited surface roughness exceeding the limits required for t-SPL, HKUST-1 thin films were employed as a proof-of-concept system. Using this approach, micrometer-scale structures were successfully fabricated, and RIE proved effective in achieving well-defined, directional material removal. Patterning at sub-200 nm length scales revealed limitations in the PMMA lift-off process, indicating the need for more vigorous removal strategies. Nevertheless, the partial success of these experiments demonstrated the feasibility of nanostructuring MOF thin films and provided a solid foundation for transferring the approach to $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$.

Overall, this chapter demonstrates the successful validation of theoretical models for chiral SURMOF thin films, establishes VCD as a powerful and non-destructive characterization technique for SURMOFs, and provides critical insights into the opportunities and limitations of lithographic patterning strategies. The surface roughness constraints identified here directly

motivated the targeted optimization of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$, which is addressed in the subsequent chapter.

6 MACHINE-LEARNING-ASSISTED OPTIMIZATION OF SURMOF THIN FILMS

6.1 Introduction

The growth of SURMOFs is governed by a complex, high-dimensional parameter space in which multiple experimental variables simultaneously influence film morphology, crystallinity, orientation, and overall functional performance. Parameters such as synthesis temperature, precursor concentration, exposure time, and deposition protocol are known to strongly affect nucleation density, growth kinetics, defect formation, and crystal ordering^{110,111}. While this high degree of tunability enables SURMOFs to be tailored for specific applications, it also renders their optimization non-trivial, particularly when multiple target properties must be achieved simultaneously.

In application-driven materials development, optimization is rarely univariate. In the present work, SURMOFs were developed for subsequent nanostructuring using lithographic techniques, which imposes strict and partly competing requirements. On the one hand, the surface roughness must be minimized to enable high-resolution patterning; on the other hand, high crystallinity must be preserved, a defining characteristic of MOFs that reflects the integrity of their long-range ordered framework and is essential for maintaining its optical features. A smooth but amorphous film is therefore unsuitable. This multi-objective nature of the optimization problem makes traditional one-factor-at-a-time approaches inefficient, slow, and prone to misleading conclusions due to unaccounted parameter interactions.

Machine-learning-based optimization strategies provide a powerful alternative by enabling the systematic exploration of large experimental spaces while explicitly accounting for multivariate correlations. In recent years, such approaches have gained increasing relevance in materials science and industrial R&D, driven by their ability to reduce experimental effort, accelerate process development, and improve reproducibility. By mathematically defining the experimental space and using algorithm-guided decision-making, machine learning allows resources to be focused on the most informative experiments rather than on exhaustive or heuristic trial-and-error approaches.

These developments are closely aligned with the emerging concept of self-driving laboratories, in which synthesis, characterization, data analysis, and experimental planning are increasingly

automated. In fully autonomous systems, human intervention is largely limited to defining objectives and evaluating results, thereby minimizing operator-dependent variability and human-induced bias. While the present work does not constitute a fully autonomous laboratory, it represents a significant step toward this paradigm by combining automated synthesis with algorithm-based experimental planning and evaluation.

In this chapter, a machine-learning-assisted optimization strategy is presented for the controlled growth of SURMOF thin films with low roughness and high crystallinity. Using the Synthesis Condition Finder (SyCoFinder), synthesis parameters were systematically explored within a multi-dimensional experimental space, enabling simultaneous optimization of surface roughness and crystallinity, two critical characteristics for lithographic compatibility and structural integrity. Automated pump-based synthesis ensured reproducibility, while quantitative fitness metrics translated experimental outcomes into data suitable for algorithmic evaluation and iterative refinement. The workflow was first applied to the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer, whose quality critically determines the morphology of subsequent $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films, and was then extended to optimize the chiral SURMOF itself. This data-driven approach significantly reduced roughness while preserving crystallinity and demonstrates how machine-learning-guided experimentation can accelerate SURMOF development, improve reproducibility, and support more autonomous materials optimization workflows.

6.2 Optimization of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$

To systematically explore the multi-dimensional parameter space and identify optimal fabrication conditions, the Synthesis Condition Finder (SyCoFinder) tool was employed. This optimization algorithm allows users to define a set of synthesis parameters, specify upper and lower boundaries for each, and then it generates a series of randomized yet statistically meaningful synthesis conditions.

For this study, five experimental parameters were selected for variation:

1. Synthesis temperature
2. Metal solution concentration
3. Linker solution concentration

4. Metal solution immersion time
5. Linker solution immersion time

These parameters were chosen based on prior experience and an understanding of SURMOF growth kinetics, especially when using the pump-based layer-by-layer synthesis protocol. For instance, it is well known that pillar-layer MOFs exhibit hindered growth at low temperatures, and that both solution concentration and exposure duration can significantly influence nucleation density, growth rate, and resulting film morphology¹¹². In particular, shortening the residence time could lead to faster synthesis without compromising quality, whereas altering concentration may influence not just growth speed but also crystal size distribution and ordering.

The experiments began by testing the growth of the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer on quartz substrates pre-treated with O_2 plasma. Each synthesis condition was used to grow 30 cycles of the Cu SURMOF to ensure comparability across samples. The focus on optimizing the roughness of this initial layer was strategic: starting from a smoother and more homogeneous base is essential, as any surface irregularities in the seed layer would inevitably propagate into the $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ top layer, compromising the final film quality. Table 1 summarizes the standard synthesis parameters and the range of values explored during optimization.

Table 1: Parameters chosen for the roughness optimization of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$

Variable	Standard condition	Optimization limits
Temperature [°C]	60	70 - 50
Metal Concentration [mM]	1	0.5 - 5
Linker Concentration [mM]	0.2	0.1 - 1
Metal immersion time [s]	600	600 - 1800
Linker immersion time [s]	900	900 - 2700

The parameter ranges from Table 1 were then input into the SyCoFinder tool, which generated a set of randomized synthesis conditions, and this was called the 1st Generation of the optimization. For each of the 10 suggested conditions, three samples were prepared in parallel using three different pump systems. While all pumps operated under the same principle and had comparable dimensions, they were independent devices. This parallel approach not only enabled a broader

evaluation of the parameter space but also allowed us to assess the robustness and reproducibility of each synthesis condition across different equipment setups.

6.3 Crystallinity Evaluation

To evaluate the performance of each synthesis condition, we quantified the crystallinity of the resulting films using XRD. For each sample, the diffraction pattern was analyzed using the DIFFRAC.EVA software (Bruker), which calculates two key parameters: the *global area*, corresponding to the total integrated intensity under the entire curve, and the *reduced area*, which excludes the amorphous background and is therefore proportional to the degree of crystallinity. As each synthesis condition was tested in triplicate, three reduced area (Re) values were obtained and averaged to determine the mean crystallinity and its standard deviation.

To facilitate comparison and ranking of the conditions, the crystallinity values were normalized to generate a fitness score. A target value of 100 was defined for optimal crystallinity, and the fitness score for each condition was calculated using the equation:

$$fitness (crystallinity) = \frac{Re}{100}$$

This normalized score ranges from 0 (completely amorphous) to 1 (target crystallinity), enabling straightforward assessment of the relative success of each synthesis condition.

6.4 Roughness evaluation

Surface roughness was assessed using a 3D laser scanning confocal microscope (Keyence) equipped with a 50× magnification lens. This magnification provided a suitable compromise between lateral resolution and field of view ($290 \times 220 \mu\text{m}^2$), allowing the analysis of an area representative of the overall film morphology. While AFM offers higher precision, its limited scan area may not accurately reflect sample-wide surface features. For each sample, three confocal images were acquired, and roughness was calculated individually for each image using the Sa (arithmetical mean height) parameter provided by the Keyence analysis software. This metric is an extension of the Ra parameter used for line profiles, and expresses the absolute mean deviation

of the surface height from the arithmetical mean plane and is widely used for surface roughness evaluation.

Given that each synthesis condition was tested in triplicate, this resulted in nine roughness values per condition. The average roughness for each condition was then used to calculate a corresponding fitness score. Since lower surface roughness is desirable, the fitness value was defined using the equation:

$$fitness(roughness) = \frac{1}{roughness_x / roughness_{best}}$$

where $roughness_x$ is the roughness of each synthesis condition and $roughness_{best}$ is the lowest roughness observed among all conditions of each generation. This formulation ensures that the roughness fitness values remain in the 0-1 range, with higher values corresponding to smoother surfaces. For example, the value of 1 is only achievable by the condition with the lowest roughness, whose equation will be:

$$fitness(roughness) = \frac{1}{roughness_{best} / roughness_{best}}$$

However, it is important to note that for each generation a different $roughness_{best}$ was chosen, meaning that the $fitness(roughness)$ value from different generations could not be compared without taking this into account.

6.5 Overall Fitness

Finally, to evaluate the overall performance of each synthesis condition, the average of the crystallinity and roughness fitness scores was calculated and the values were also kept in the range of 0-1. This combined fitness score was included in Table 2 and was used to rank the synthesis conditions.

$$fitness_{final} = \frac{fitness_{crystallinity} + fitness_{roughness}}{2}$$

6.6 Optimization Results

The 1st Generation and the resulting fitness for each synthesis condition of the Cu SURMOF can be seen in Table 2. To maintain clarity, only the final fitness value is shown here; the individual fitness scores for crystallinity and roughness, along with standard deviations, are included in **Annex A.1**.

Table 2: 1st Generation synthesis parameter sets with their respective fitness values.

Synthesis condition	Temperature [C]	Metal conc. [mM]	Linker conc. [mM]	Metal time [s]	Linker time [s]	Fitness
1	70	5	1	600	900	0.20
2	50	5	1	1800	900	0.20
3	70	0.5	0.1	600	900	0.61
4	50	0.5	1	600	900	0.46
5	70	5	1	1800	2700	0.28
6	50	0.5	0.1	600	2700	0.53
7	70	0.5	1	1800	900	0.33
8	70	0.5	1	600	2700	0.39
9	70	5	0.1	1800	900	0.15
10	50	5	0.1	1800	2700	0.40

The 1st generation data was fed back the SyCoFinder algorithm, which generated the following 2nd generation conditions shown in Table 3.

Table 3: 2nd Generation synthesis parameter sets with their respective fitness values.

Synthesis condition	Temperature [C]	Metal conc. [mM]	Linker conc. [mM]	Metal time [s]	Linker time [s]	Fitness
1				133		
	70.8	3.12	0.84	5	1223	0.47
2	65	1.91	1	1066	2240	0.50
3	70	4.94	0.18	600	900	0.41
4	70	3.62	1	1162	2700	0.26
5	70	0.5	0.1	600	900	0.59
6	70	0.5	0.46	600	1122	0.92
7	50	2.47	0.1	1073	2700	0.52
8	53.8	2.13	0.93	655	900	0.25
9	62	0.5	0.97	600	900	0.34
10	71.5	0.56	0.47	1258	1050	0.40

To better visualize the trends and compare performance across all tested synthesis conditions from both generations, the individual fitness scores for roughness and crystallinity, as well as the final averaged fitness score, were plotted for each sample in Figure 39.

In the first generation, crystallinity fitness scores were generally low, with most conditions falling below 0.3. However, a marked improvement was observed in the second generation. All conditions in this set achieved crystallinity fitness values above 0.2, and two synthesis conditions, S5 and S6, performed particularly well, reaching fitness scores of 0.57 and 0.84, respectively. This clear progression demonstrates that the optimization approach effectively guided the experimental conditions toward improved structural order, bringing the system closer to the targeted crystallinity reference value of 100.

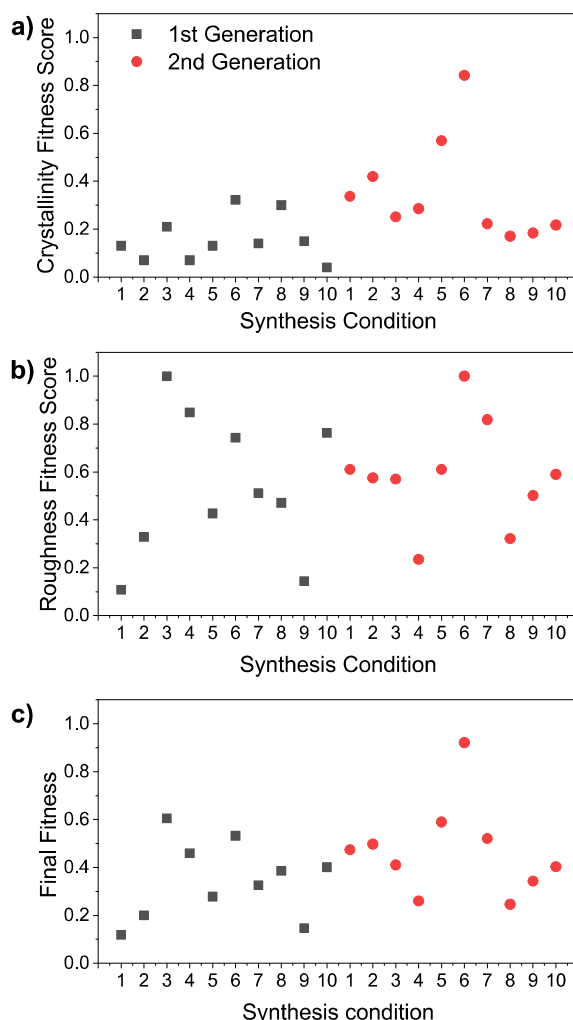


Figure 39: Fitness values for a) Crystallinity, b) Roughness and c) Final fitness for both 1st generation (gray squares) and 2nd generation (red dots) of the Cu₂(D-Cam)₂(DABCO) optimization.

In contrast, the trends in roughness fitness were less pronounced. Since the fitness for roughness was defined relative to the best-performing condition within the entire set, both generations display scores distributed across the 0.1 to 1.0 range. A closer inspection of the raw roughness values (Annex A.1) reveals that samples from the first generation actually exhibited lower roughness on average compared to those from the second generation. However, it is important to consider this observation in the broader context of the dual-objective optimization. A low-roughness film with poor crystallinity is not suitable for the intended application, as long-range structural order is essential for achieving meaningful chiroptical performance. Therefore, the increased crystallinity obtained in the second generation, combined with surface roughness values still below those of the standard condition, indicates that the optimization process was moving toward a more favorable balance of performance metrics.

This trade-off culminated in the identification of a particularly successful synthesis condition in the 2nd generation: S6. With high crystallinity and acceptable roughness, this condition reached a final fitness value of 0.92, clearly outperforming all others, none of which surpassed a score of 0.6. To provide a more intuitive view of the film morphology, representative confocal microscopy images of selected high- and low-performing samples are presented in Figure 40 and Figure 41.

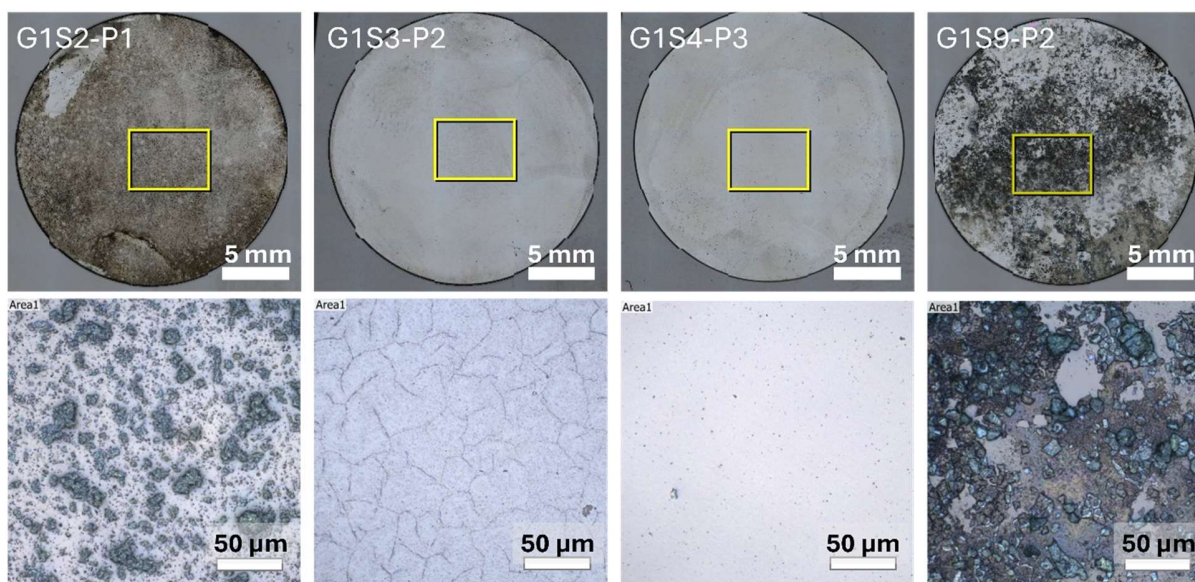


Figure 40: Confocal microscopy topography images of representative $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ films from the 1st optimization generation. For each synthesis condition, a stitched overview acquired with the 2.5 $\times$ magnification lens (top) displays the overall film coverage, while a corresponding 50 $\times$ magnification image (bottom) shows the local surface morphology used for quantitative roughness analysis. Four synthesis conditions are presented to illustrate the range of surface characteristics observed.

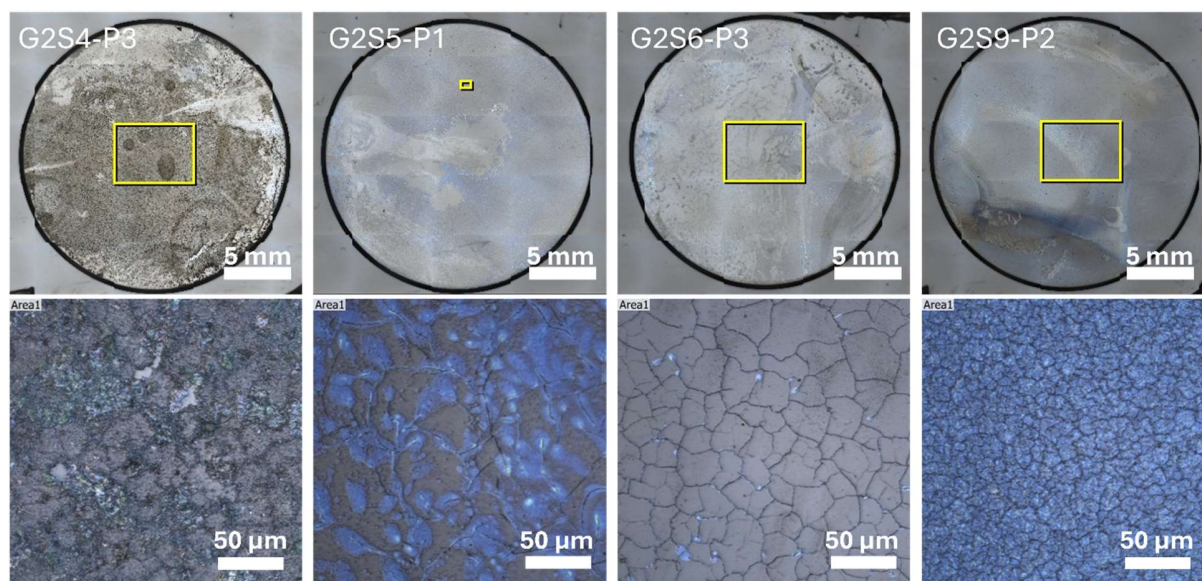


Figure 41: Confocal microscopy topography images of representative $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ films from the 2nd optimization generation. For each synthesis condition, a stitched overview acquired with the 2.5 $\times$ magnification lens (top) displays the overall film coverage, while a corresponding 50 $\times$ magnification image (bottom) shows the local surface morphology used for quantitative roughness analysis.

In the 1st generation (Figure 40), several synthesis conditions resulted in incomplete substrate coverage, with uncovered regions clearly exposing the underlying quartz substrate and the areas where the film was present often exhibited significant roughness, with prominent surface irregularities. Ideally, a quantitative metric for film coverage would further refine surface analysis, but since these poorly covered samples also exhibited low crystallinity and locally high roughness where film growth occurred, their fitness scores in general were low, as exemplified by conditions G1S2 and G1S9.

An interesting case is condition G1S4, which showed relatively low roughness, however, its low crystallinity indicated that minimal crystalline material had been deposited. This underscores the importance of jointly evaluating roughness and crystallinity when assessing film quality: a flat but nearly bare surface cannot be interpreted as a successful synthesis outcome.

In the 2nd generation (Figure 41), film coverage improved considerably, with fewer cases of exposed substrate. However, an increase in the absolute values of roughness (R_a) was also observed for many conditions (Appendix A.1, Table A.2), likely a consequence of higher material loading, consistent with the marked improvement in crystallinity across the generation. The best-

performing condition, G2S6, demonstrated a generally smooth and continuous film with elevated borders, possibly arising from inter-crystalline grain boundaries where adjacent domains converge and induce localized vertical growth.

To further understand which synthesis parameters most significantly influenced film quality, a variable importance analysis was performed using SyCoFinder. This is illustrated in Figure 42, which quantifies the relative contribution of each experimental variable to the final fitness score across both optimization generations.

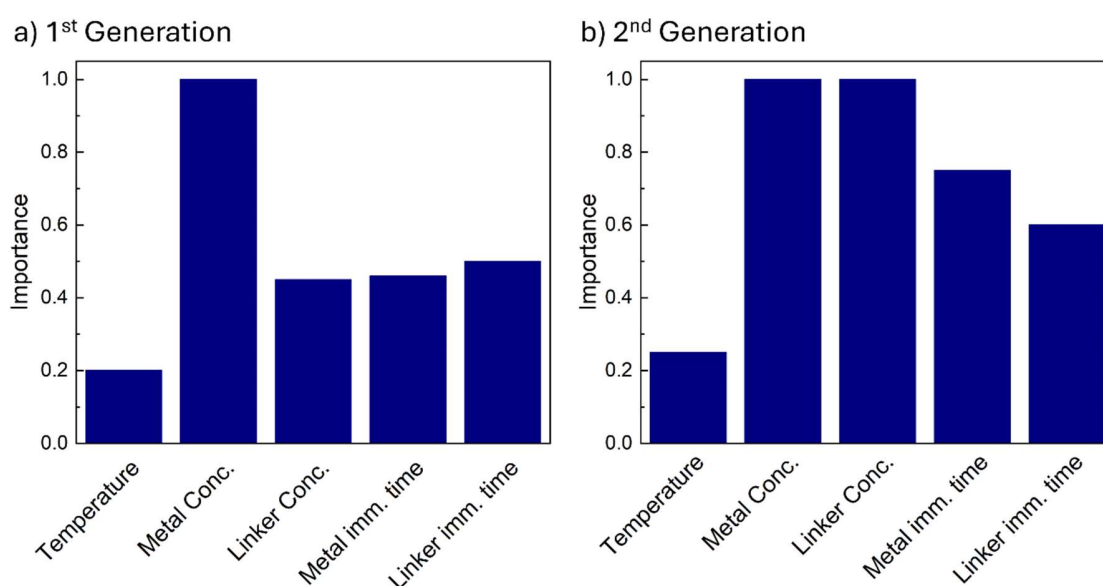


Figure 42: Importance of variables in the a) 1st and b) 2nd Generations of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$.

In the 1st generation, metal ion concentration emerged as the dominant factor by a wide margin. This can be directly attributed to the high upper limit defined for this parameter (5 mM). During the synthesis process, it became evident that such high concentrations exceeded the cleaning capacity of the ethanol steps in the pump-based system, resulting in incomplete removal of unreacted metal ions during rinsing steps. Consequently, when the linker solution was introduced, it reacted not only on the substrate surface but also within the chamber environment, triggering uncontrolled MOF formation on the chamber walls and disturbing the intended layer-by-layer growth mechanism. The resulting films were typically heterogeneous and highly rough, as reflected in the lower fitness scores for high-metal-concentration conditions.

In contrast, the 2nd generation displayed a more balanced distribution of influence among parameters. The SyCoFinder algorithm adapted to the prior generation's results and proposed generally lower metal concentrations. As a result, both metal and linker concentrations were now equally important contributors to synthesis performance, followed closely by immersion times. Temperature, however, had only a minor impact. This relatively low influence can be attributed to the narrow temperature range selected (50–70 °C). Prior knowledge had already established that room-temperature growth leads to poor film quality, and thus lower temperatures were excluded from the study. It is likely that a broader temperature window (e.g., 25–70 °C) would have increased its relative importance. This highlights an important consideration in interpreting such multivariate analyses: parameter relevance is inherently tied to the boundaries selected for exploration. Without this contextual awareness, there is a risk of misattributing significance or overlooking key process limitations.

It is important to note that all tests were conducted with 30 growth cycles of the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer to have a reasonable thickness for crystallinity comparison. However, since this is not the target material of the simulations, minimizing its contribution is desirable to avoid interfering with the spectroscopic response of the Zn-based SURMOF. Therefore, follow-up tests were conducted using the G2S6 condition but with varying numbers of deposition cycles, aiming to identify the minimum required number of cycles to ensure full substrate coverage while avoiding the formation of the grain boundaries defects between adjacent domains.

6.7 Seed Layer Thickness Tests

For the assessment of the minimum number of cycles of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ required to cover the substrate as a seed layer, five experiments were performed using the G2S6 condition:

- 0.5 cycles – metal precursor only (no linker step), to confirm that no film is formed in the absence of complete cycles;
- 1 cycle – one full metal and linker deposition step;
- 3 cycles;
- 5 cycles;
- 10 cycles.

This gradient of cycle numbers allowed us to determine the minimum required number of cycles to ensure uniform film formation across the substrate, while minimizing thickness and avoiding the emergence of defects between crystalline domains in the film.

XRD analysis was performed on all five samples to evaluate the formation and evolution of crystallinity with increasing cycle number and results are shown in Figure 43. As anticipated, the overall diffraction intensity increased progressively with the number of cycles. However, this trend does not necessarily reflect a higher degree of crystallinity, but may instead be attributed to the increased quantity of material deposited on the substrate. As expected, the 0.5-cycle sample, exposed only to the metal precursor without the linker, exhibited no diffraction peaks, confirming the absence of SURMOF formation in the absence of the full layer-by-layer process.

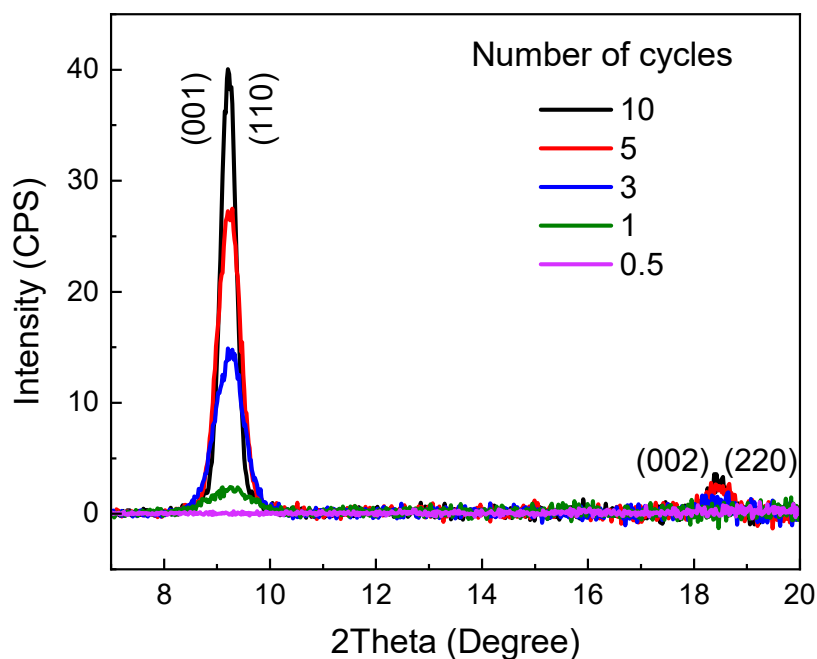


Figure 43: Diffractograms of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ films grown using the G2S6 parameters with 0.5 to 10 cycles.

Interestingly, the 1-cycle sample already displayed distinct diffraction peaks characteristic of the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ structure, indicating that reasonable crystallite formation initiates from the very first complete cycle. While the presence of peaks confirmed crystallinity, XRD alone could not determine the surface coverage uniformity, particularly at such low film thicknesses.

To assess surface morphology and continuity of the film, AFM was employed. Due to the nanometric thickness and partial transparency of the low-cycle films, confocal microscopy did not

provide sufficient contrast or resolution to yield reliable information. AFM, by contrast, enabled detailed topographical analysis to determine whether the MOF layer formed a continuous coating or isolated crystallites. The results of these measurements are shown in Figure 44.

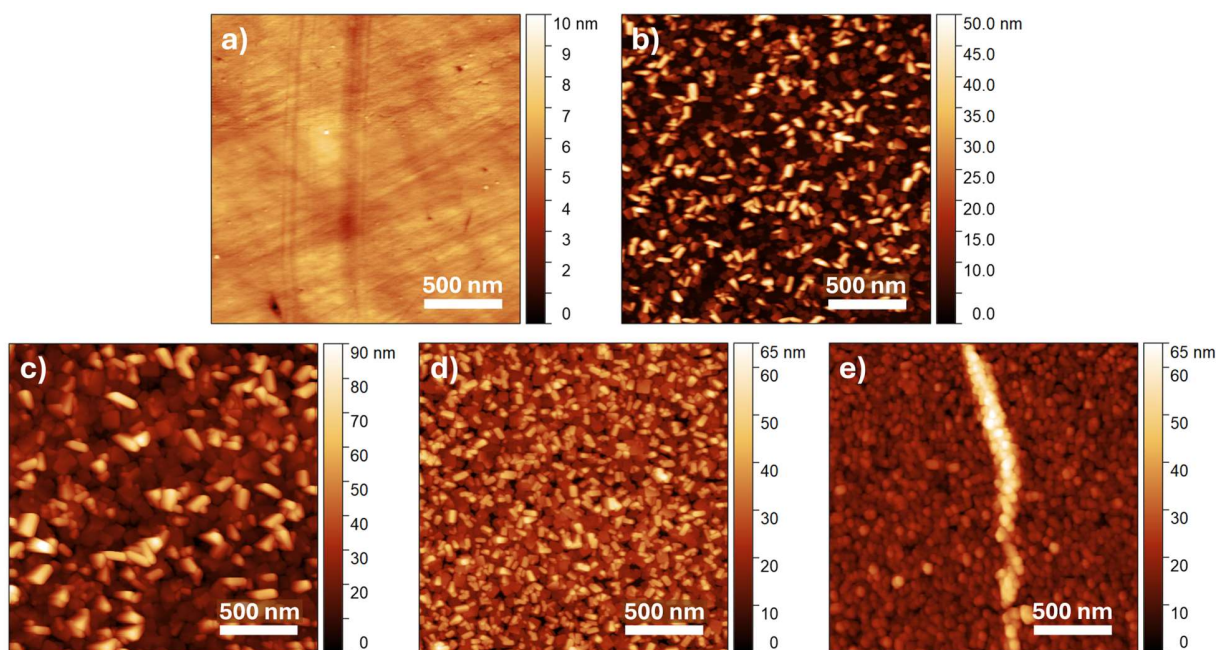


Figure 44: AFM images of Cu₂(D-Cam)₂(DABCO) seed layer tests after a) 0.5, b) 1, c) 3, d) 5 and e) 10 cycles of growth.

As expected, the 0.5-cycle sample, which had only been exposed to the metal precursor without the subsequent linker step, showed no detectable film formation. The surface topography was indistinguishable from that of the bare quartz substrate.

In contrast, the samples prepared with 1, 3, and 5 full synthesis cycles exhibited a comparable morphological profile. These films were composed of MOF crystallites predominantly lying flat on the substrate, accompanied by a fraction of crystals oriented upright. While the overall crystal orientation was not fully homogeneous, the substrate coverage was notably high. In the 1-cycle sample, the film remained somewhat discontinuous, with individual crystallites not yet forming a fully interconnected network. Nevertheless, considering the role of this layer as a seed for subsequent Zn₂(D-Cam)₂(DABCO) growth, this degree of coverage was deemed sufficient. The Zn-based SURMOF is known to form larger crystallites, and as long as adequate nucleation sites are present, the slightly incomplete coverage could even be advantageous by reducing the possible interference from the Cu-based seeding layer in spectroscopic measurements.

The sample with 10 synthesis cycles began to exhibit the characteristic elevated “border” features observed previously in the optimization stage. These raised structures likely arise from crystal overgrowth at the boundaries between adjacent domains once complete surface coverage has been achieved. Since these features are expected to increase the overall roughness of the resulting film and could compromise the homogeneity of the Zn layer, the 10-cycle condition was excluded from further consideration.

Based on these observations, 1 and 5 cycles of the Cu seed layer were selected as conditions for further testing. A final set of experiments was conducted in which 30 cycles of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ were grown on top of these two candidate seed layers to assess the impact on film morphology and structural quality and XRD analysis was performed on these samples (Figure 45a). The 3-cycle condition was not pursued further, as it displayed similar morphological characteristics to the 5-cycle sample without offering additional advantages.

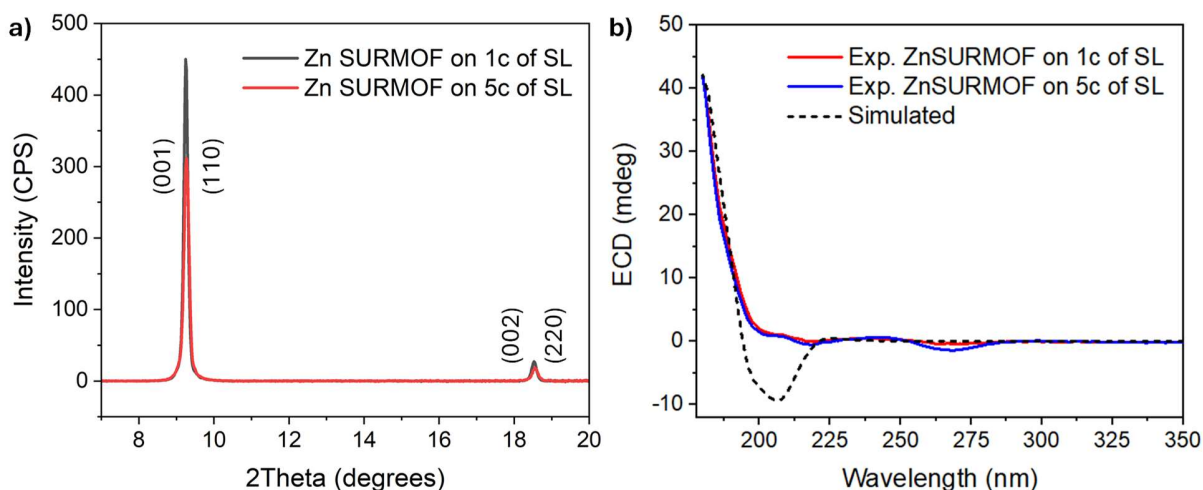


Figure 45: a) XRD and b) ECD of 30 cycles of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ with seed layer of 1 and 5 cycles of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$.

The resulting diffraction patterns shown in Figure 45a revealed comparable crystallinity for both conditions, indicating that a single cycle of the Cu-based SURMOF was sufficient to promote the oriented growth of the Zn layer. Despite the incomplete surface coverage observed in the 1-cycle seed layer, the available crystallites provided adequate anchoring sites for Zn nucleation, enabling the formation of a continuous and crystalline top layer.

Figure 45b shows the ECD spectra for these $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ samples grown on thin seed layers, along with a comparison to the simulated ECD response. The experimental spectra for both samples exhibit a strong agreement with the simulation, with a main positive band centered around 180 nm. A notable deviation occurs near 205 nm, where the simulation predicts a negative band, while the experimental curves display a weak positive feature. This discrepancy may originate from limitations in the theoretical model or simplifications introduced during the simulation process. Despite this divergence, the experimental data obtained using the optimized synthesis protocols demonstrate significantly improved consistency and alignment with theoretical expectations compared to earlier measurements obtained from films grown under standard conditions. These results show that the optimization strategy helped in improving the quality of the films and its spectroscopic performance.

Given the reduced material consumption and shorter processing time, the 1-cycle seed layer was selected for subsequent Zn SURMOF optimization experiments. Therefore, instead of using bare quartz substrates as in the Cu optimization, all Zn optimization trials were conducted on substrates pre-treated with 1 cycle of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$, grown using the optimized G2S6 synthesis condition, immediately prior to $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ deposition. It should be noted that the use of a single-cycle $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer was only feasible following the optimization process, as films prepared under standard conditions required a greater number of cycles to achieve sufficient surface coverage and provide an adequate density of nucleation sites for Zn SURMOF growth.

6.7.1.1 Optimization of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$

Building upon the insights gained from the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer optimization, a new set of synthesis conditions was designed to improve the quality of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films. Several key adjustments were made to the parameter selection process based on observed trends in the Cu optimization.

Firstly, synthesis temperature was excluded from the optimization and fixed at 65 °C. This decision was made due to the relatively minor influence temperature exhibited on the Cu

SURMOF growth within the narrow range tested. By fixing temperature, the 10 experimental conditions could instead focus on the more influential variables.

Metal precursor concentration was limited to the range of 0.05–2 mM, based on the poor performance observed in the Cu optimization for concentrations at and around 5 mM. The same limits were applied to the linker concentration. These lower ranges were chosen to avoid excessive precursor accumulation and poor film quality while exploring a range more likely to yield successful outcomes.

In terms of exposure times, the promising results obtained from reduced immersion durations in the Cu study motivated further shortening for the Zn optimization. Specifically, metal solution immersion times were set between 300 and 1200 s, and linker immersion times between 300 and 1800 s, aiming to balance quality with increased time efficiency.

All Zn SURMOF samples were grown on quartz substrates pre-treated with O₂ plasma and modified with a one-cycle Cu₂(D-Cam)₂(DABCO) seed layer prepared using the previously identified optimal condition (G2S6). With this improved seeding strategy and carefully defined synthesis window, the Zn optimization was expected to yield films with both enhanced smoothness and improved crystallinity. Table 4 summarizes the parameters and their limits.

Table 4: Parameters chosen for the roughness optimization of Zn₂(D-Cam)₂(DABCO)

Variable	Optimization limits
Metal Concentration [mM]	0.05 - 2
Linker Concentration [mM]	0.05 - 2
Metal immersion time [s]	300 - 1200
Linker immersion time [s]	300 - 1800

These conditions were fed into the SyCoFinder and 10 synthesis conditions were suggested for the 1st Generation. Each condition was made in duplicate since one of the pumps presented a problem and could not be used. The conditions and final fitness are presented in Table 5 and the individual roughness and crystallinity fitness values can be found in Annex A.2. Due to the higher crystallinity values obtained in this optimization round, some exceeding the initial target of 100, a

new crystallinity goal of 125 was established to maintain consistency in the fitness normalization scale (0-1).

Table 5: 1st Generation synthesis parameter sets and fitness values of Zn₂(D-Cam)₂(DABCO).

Synthesis condition	Metal conc. [mM]	Linker conc. [mM]	Metal time [s]	Linker time [s]	Fitness
1	2	2	513	1401	0.62
2	0.31	2	513	300	0.76
3	1.76	0.51	530	300	0.30
4	1.76	2	1200	300	0.42
5	0.52	2	1200	1585	0.53
6	0.05	1.51	300	1800	0.82
7	2	0.05	300	1800	0.11
8	0.27	0.55	1200	300	0.57
9	2	0.55	1200	1430	0.38
10	0.05	0.05	983	1800	0.15

The results of the Zn SURMOF optimization are summarized in Figure 46, which presents the fitness values for each synthesis condition, including separate bars for crystallinity, roughness, and final average fitness.

Overall, the majority of the synthesis conditions exhibited good crystallinity, with only two conditions, S7 and S10, falling significantly below the expected values. These two samples displayed negligible crystallinity and correspondingly low roughness fitness scores, indicating the formation of rough, amorphous films rather than true SURMOFs. Notably, both S7 and S10 utilized the lowest linker concentration tested (0.05 mM), which seems insufficient to support proper material formation. This outcome is clearly reflected in the confocal microscopy image of S7 in Figure 47, where a disordered and poorly formed film is evident. If no material had deposited on the surface, a very low roughness score might have been expected due to the smooth substrate. However, the presence of considerable topographical features confirms non-specific and uncontrolled growth.

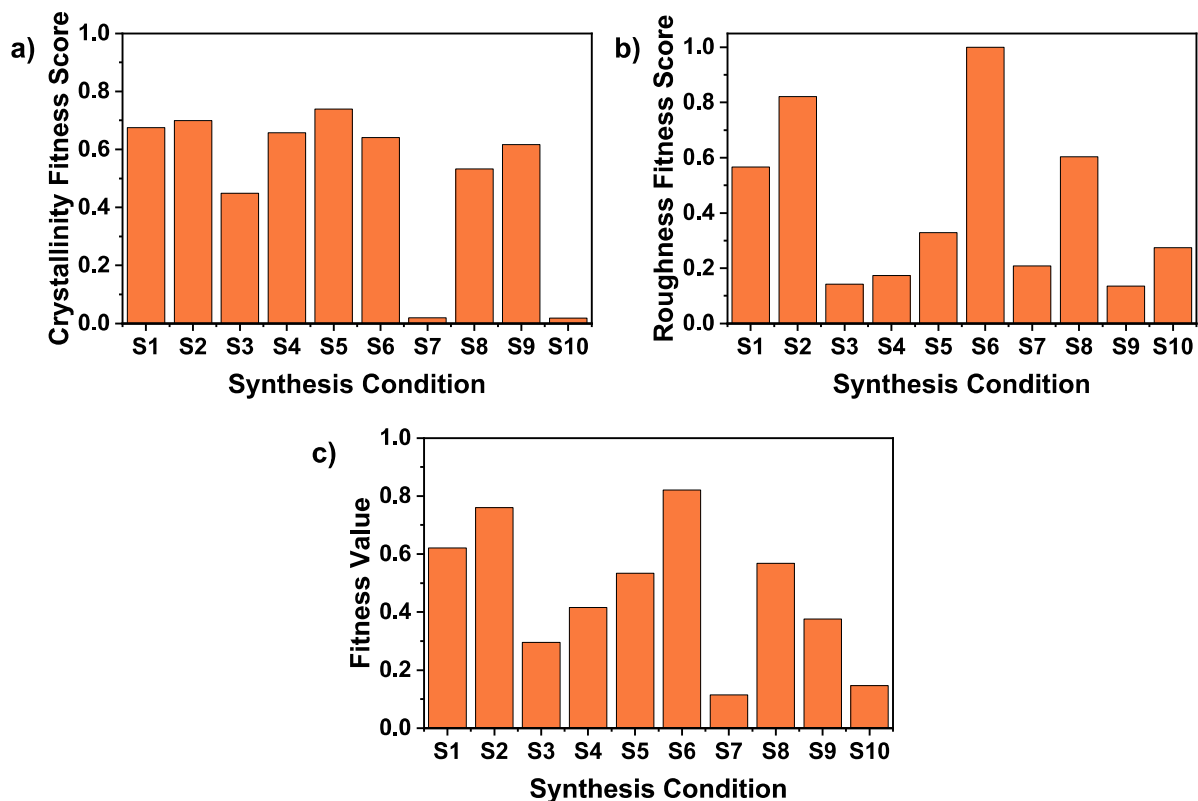


Figure 46: Fitness values for a) Crystallinity, b) Roughness and c) Final fitness for the 1st generation of the $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ optimization.

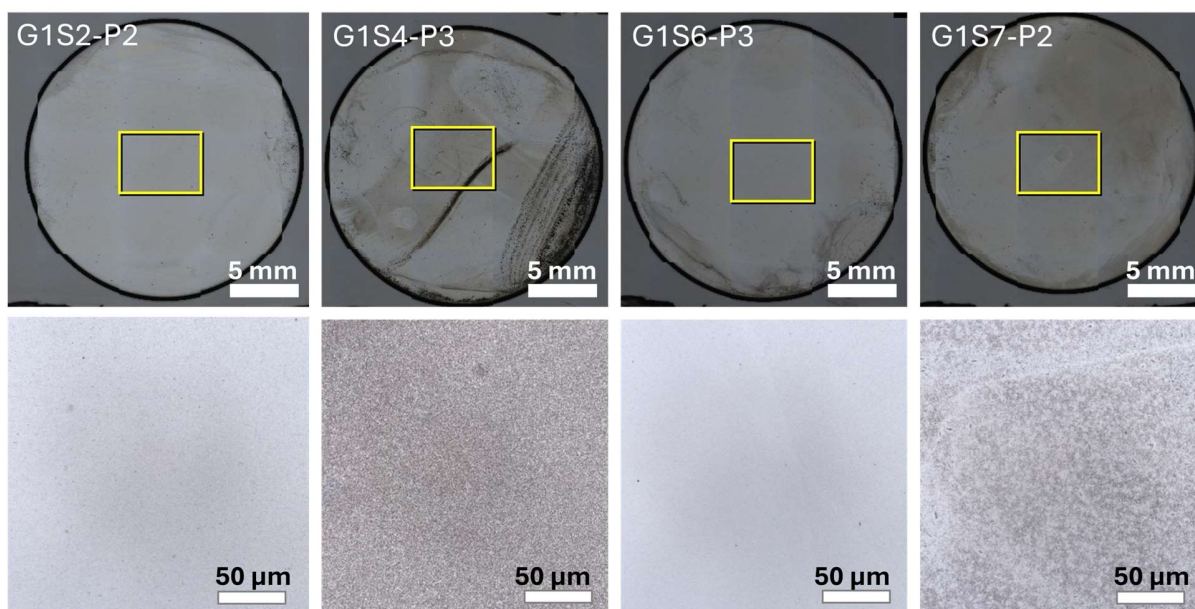


Figure 47: Confocal microscopy topography images of representative $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films from the 1st optimization generation. For each synthesis condition, a stitched overview acquired with the 2.5 $\times$ magnification lens (top) displays the overall film coverage, while a corresponding 50 $\times$ magnification image (bottom) shows the local surface morphology used for quantitative roughness analysis.

With a different performance, condition S4 yielded strong crystallinity but displayed a notably high surface roughness, further emphasizing the inherent trade-off between structural order and topographical flatness. Among all tested conditions, S6 emerged as the optimal one, offering an excellent balance between crystallinity and roughness. Although it did not achieve the highest crystallinity score, its surface morphology was clearly superior. Condition S2 also performed well and displayed similarly favorable characteristics.

Interestingly, both S2 and S6 shared a common feature in their parameter sets: low metal precursor concentration combined with relatively high linker concentration. These trends suggest that minimizing the excess of metal ions while maintaining a sufficient supply of linker molecules supports more uniform and oriented film growth.

The topography of the best-performing films (S2 and S6), as visualized by confocal microscopy, approached the resolution limit of the technique. Therefore, AFM was performed for a more accurate surface characterization. As shown in Figure 48, the AFM images of S6 revealed a homogeneous film with well-aligned platelets and minimal vertical features. The measured average roughness (R_a) was approximately 12 nm, and the root-mean-square (RMS) roughness was ~ 14 nm, in good agreement with the confocal microscopy results (~ 11 nm, Annex A.2). By contrast, films from rougher synthesis conditions could not be reliably analyzed by AFM, as the tip was frequently contaminated or damaged due to large height variations. This confirmed the utility of confocal microscopy as a high-throughput, non-contact method for roughness screening in SURMOF optimizations.

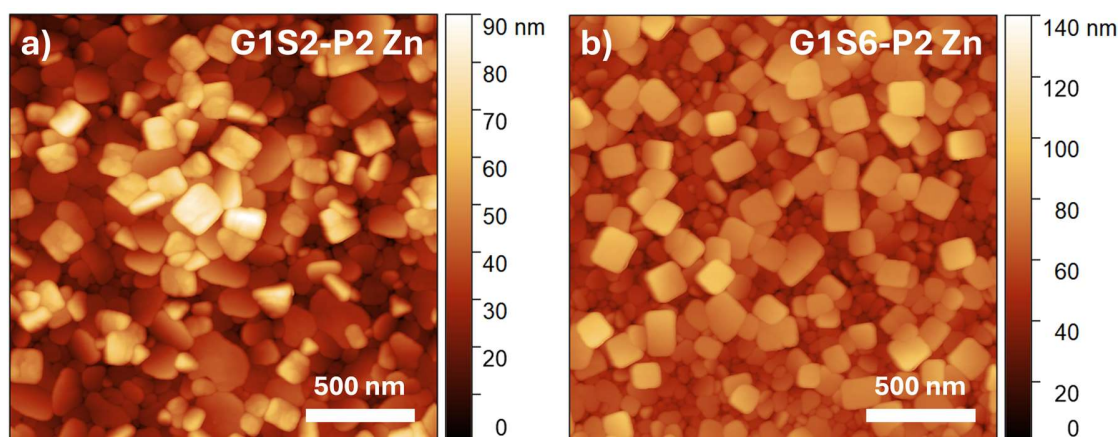


Figure 48: AFM topography images of the best synthesis conditions of the 1st generation of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ optimization: a) G1S2 and b) G1S6

To assess the functional performance of the optimized Zn SURMOF films, ECD measurements were conducted on selected samples, as shown in Figure 49. These included the two top-performing synthesis conditions (S2 and S6), one sample combining high crystallinity with elevated roughness (S5), and one condition with very low crystallinity (S10). The film grown under condition S10 displayed no discernible ECD band near 180 nm, highlighting the critical role of crystallinity for the circular dichroism property. In contrast, samples S2, S5, and S6 all exhibited pronounced ECD responses that closely match the simulated spectra, confirming the validity of the theoretical model for these thin-film systems. Notably, condition S5 shows the best agreement with the simulated feature around 200 nm, as highlighted in the inset of Figure 49. These results indicate that while surface roughness severely limits compatibility with t-SPL processing, the ECD response of the material is predominantly governed by crystallinity rather than topographical smoothness.

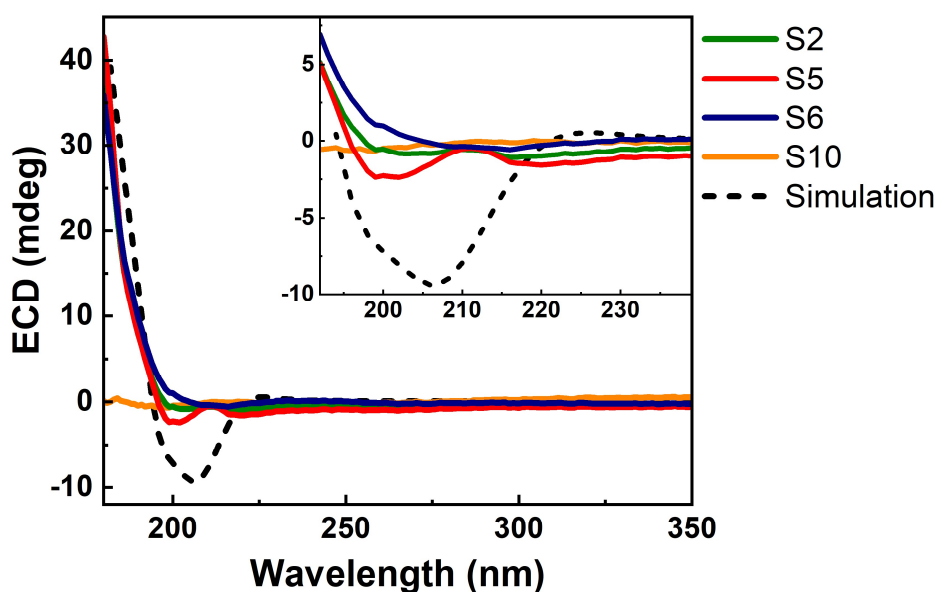


Figure 49: ECD measurements of different synthesis conditions of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ optimization compared with the respective simulation.

Finally, Figure 50 presents the influence of each synthesis parameter on the overall fitness as calculated by the SyCoFinder tool. In this optimization round, linker concentration emerged as the dominant variable. This is largely attributed to the fact that both synthesis conditions employing the lowest linker concentration failed entirely, drastically lowering the associated fitness scores. Metal immersion time also played a major role, surpassing the impact of metal concentration. This

shift in parameter relevance is likely due to the restricted and better-targeted concentration range used in this generation, based on insights from the Cu SURMOF study.

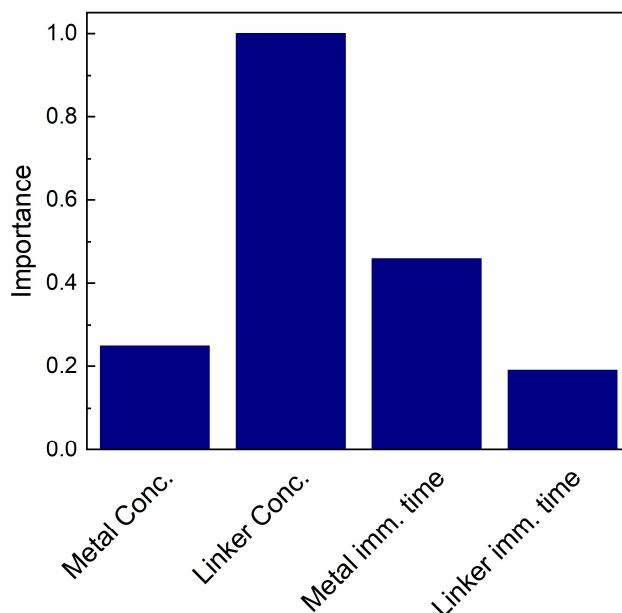


Figure 50: Importance of variables in the 1st Generation of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ optimization.

As with previous analyses, it is important to interpret these parameter weightings within the context of the selected experimental boundaries, parameters with less variation might display smaller influence.

6.8 Summary

The two-generation optimization process of the $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ seed layer proved highly effective in improving both key parameters under study, crystallinity and surface roughness, with a particularly notable enhancement in crystallinity from the first to the second generation. Beyond identifying optimal synthesis conditions, the process provided valuable insight into the influence of each varied parameter, enabling a deeper understanding of their individual and synergistic effects on SURMOF growth. Ultimately, this led to the development of a thinner and more crystalline Cu SURMOF film, characterized by better-distributed crystallites across the substrate surface. As a result, the number of required seed layer cycles could be minimized,

reducing any influence of the Cu layer on the subsequent spectroscopic characterization of the $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ films.

Building on the insights gained from the Cu optimization, the Zn SURMOF optimization was more strategically targeted, focusing on parameter ranges shown to have a greater impact, like concentration and immersion time. This led to a significant improvement in film flatness, with roughness values approaching the requirements for t-SPL. Although further optimization could still be pursued to refine surface characteristics, time constraints limited additional iterations.

Nevertheless, based on the best-performing conditions from each optimization: 1 cycle of Cu seed layer using G2S6 and 30 cycles of Zn SURMOF using G1S6, test samples were prepared for t-SPL experiments. These samples were coated with PMMA and PPA following established procedures. However, no successful patterning could be achieved using the Nanofrazor system. The equipment failed to pattern the PPA layer, potentially due to incompatibility between the system and the quartz substrate used. Unlike the typical substrates for this system, such as silicon or gold-coated silicon wafers, the quartz substrates required for CD measurements are significantly thicker (~1 mm) and possess different thermal conductivity properties. Silicon-based substrates typically act as efficient heat sinks, aiding in heat dissipation during tip heating. The lower thermal conductivity of quartz may have impaired this process, potentially hindering the tip's ability to reach the required patterning temperatures.

While a full investigation into this issue was not possible within the available time, these observations suggest that repeating the Zn SURMOF growth under optimized conditions on a gold-coated silicon substrate could help verify whether the substrate material was indeed the limiting factor. This adjustment may prove crucial for future integration of chiral SURMOF films with nanolithographic techniques such as t-SPL.

7 AZIDE-FUNCTIONALIZED SURMOFS FOR PHOTOACTIVATED REACTIVITY STUDIES

7.1 Introduction

The integration of azide groups ($-N_3$) into metal-organic frameworks (MOFs) represents a powerful approach for enabling post-synthetic modifications and unlocking a diverse range of reaction pathways. Azides are highly reactive and versatile functional groups that, under UV irradiation, can form nitrenes, transient species with a monovalent nitrogen atom and exceptional reactivity, analogous to carbenes. Nitrenes are mechanistically important intermediates in various synthetic transformations, including C–H amination, aziridination, and rearrangement reactions. However, their extremely short lifetimes, often in the nanosecond range, make them challenging to isolate or study under conventional conditions^{113,114}.

To date, much of what is known about nitrene reactivity has been derived from indirect methods such as matrix isolation, ultrafast spectroscopy, or computational studies. These methods, while valuable, typically lack the structural control and environmental confinement required for probing the reactivity of nitrenes in a defined and reproducible way. Consequently, strategies to stabilize nitrenes, either kinetically via bulky substituents or electronically through delocalization, have garnered growing attention^{115,116}. Yet, examples of long-lived nitrenes remain rare, especially under ambient conditions or in solid-state settings.

In this context, the ordered, porous architecture of MOFs, and in particular surface-anchored MOFs (SURMOFs), offers a compelling alternative platform to investigate nitrene photochemistry in a spatially controlled, solvent-free environment. The periodic arrangement of azide functionalities within the crystalline lattice allows for consistent orientation, confinement, and accessibility of reactive sites, while the thin-film geometry of SURMOFs enables the use of surface-sensitive spectroscopic tools and UHV-compatible setups.

Previous work from our group (Song *et al.*)¹⁹ explored this concept by incorporating azide-functionalized linkers into a SURMOF (Cu-DASBDC) and exposing it to UV light under UHV conditions, aiming to generate and stabilize the resulting nitrene intermediates. However, due to the presence of a reactive hydrogen atom at the carbon of the double bond ($—HC=CH—$) in the

linker structure, intramolecular rearrangements occurred leading to a rapid reaction of the formed nitrene¹⁹.

To address this challenge, a new linker was designed in collaboration with the Bräse group (IOC/KIT) and synthesized by Dr. Julian Brückel. The resulting molecule, 2,2'-diazido-4,4'-tolanedicarboxylic acid (DATDC), replaces the central C=C double bond of the stilbene-based linker with a C≡C triple bond. In this configuration, the carbon atoms are fully unsaturated and do not carry hydrogen atoms, thereby eliminating the reactive sites required for intramolecular rearrangements observed in the previous system. This structural modification was intended to suppress undesired cyclization pathways upon UV-induced azide activation and to increase the likelihood of stabilizing nitrene intermediates. The corresponding SURMOF (Cu-DATDC) preserves the crystallographic order and orientation required for surface-sensitive spectroscopic investigations and provides a well-defined platform for probing nitrene-related photochemistry.

Beyond the fundamental interest in isolating or characterizing nitrenes under solid-state conditions, azide-functionalized SURMOFs offer a compelling platform for photolithography due to its light-induced chemical reactivity. Since the azide groups can be selectively activated by UV irradiation, reactions can be spatially defined by controlled light exposure, enabling local chemical modification of the framework. This could open pathways toward patterned functionalization, including selective reactions with guest molecules or polymer crosslinking within the pores.

In this context, azide-containing SURMOFs may also serve as precursors for surface-grafted gels (SURGELS), which are obtained by transforming an ordered coordination framework into a covalently crosslinked, surface-grafted polymer network^{11,117}. Conventionally, SURGEL formation from SURMOFs relies on solution-based crosslinking reactions followed by removal of the metal nodes to yield metal-free, water-stable coatings. In the present system, however, UV irradiation alone could induce crosslinking through azide activation, eliminating the need for additional crosslinking agents. This represents a significant advantage, as it simplifies processing and enables direct, spatially resolved conversion of a crystalline SURMOF into a robust polymeric film with higher suitability for biological and medical applications, due to its stability under biological conditions and absence of metal ions.

This chapter details the synthesis, structural analysis, and spectroscopic investigation of the Cu-DATDC SURMOF before and after photochemical activation, with a view toward expanding

the utility of azide-functionalized frameworks as platforms for advanced photoresponsive materials

7.2 Cu-DATDC SURMOF growth

The synthesis of the novel linker: 2,2'-diazido-4,4'-tolanedicarboxylic acid (DATDC), designed in collaboration with the Bräse group (IOC/KIT), was carried out by Dr. Julian Brückel and the detailed synthetic procedure is described in his doctoral dissertation¹¹⁸. The first results presented here were obtained in collaboration with Dr. Yibo Tian. The new azide-functionalized linker was designed to remove the reactive vinylic C–H site associated with the central double bond in DASBDC. Substitution of the C=C unit by a C≡C bond eliminates this hydrogen and thereby prevents intramolecular reactions during UV-induced azide activation.

When coordinated with copper(II) acetate using a layer-by-layer liquid-phase deposition protocol, the DATDC linker forms the Cu-DATDC SURMOF-2, structure analogous to the MOF-2 topology¹¹⁹. In this configuration, copper paddle-wheel units coordinate to four carboxylate-terminated linkers, forming extended two-dimensional square-grid layers (Figure 51a).

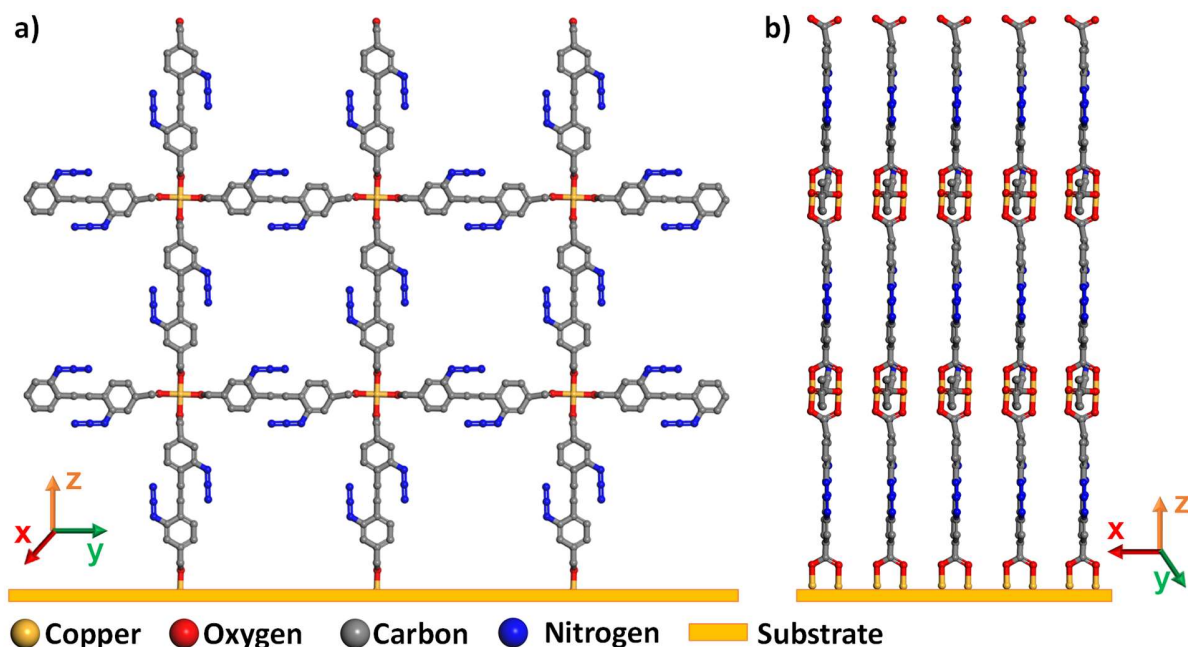


Figure 51: Schematic representation of the Cu-DATDC structure: a) planar sheets formed by four linkers connected to the SBU and b) sheets standing parallel to each other and perpendicular to the substrate.

These layers are oriented perpendicular to the substrate surface and stack in a parallel fashion, resulting in one-dimensional pores with square cross-sections (Figure 51). The anisotropic and highly ordered architecture of the Cu-DATDC SURMOF makes it a good platform for probing the photochemistry of embedded azide groups in a confined and well-defined environment.

XRD measurements were carried out in both out-of-plane and in-plane geometries to evaluate the crystallinity and preferred orientation of the Cu-DATDC SURMOF films (Figure 52). As anticipated based on the structural symmetry of the SURMOF-2 topology, the diffractograms obtained from both modes exhibited the same set of diffraction peaks. These correspond to the (001), (002), and (003) lattice planes, three successive orders along the same crystallographic direction, and are in excellent agreement with the simulated XRD pattern, thereby confirming the successful formation of the targeted crystalline phase.

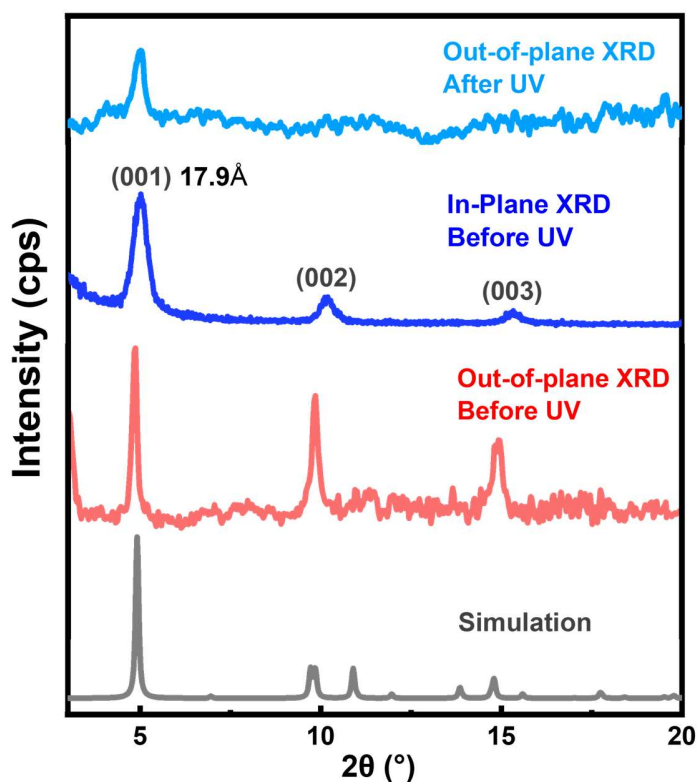


Figure 52: Diffractograms of the Simulated (grey) Cu-DATDC, experimental (red) out-of-plane and (dark blue) in-plane before UV and (light blue) out-of-plane after UV exposure ($\lambda=254$ nm).

To assess the structural stability of the SURMOF under photochemical activation, XRD analysis was repeated following exposure to UV irradiation with a mercury lamp ($\lambda=254$ nm). A

partial loss of crystallinity was observed, as indicated by the decreased intensity of the diffraction peaks. Nonetheless, the (001) reflection remained clearly visible, suggesting that while the long-range order was diminished, the overall structural framework was at least partially retained.

SEM images, presented in Figure 53, confirmed that the Cu-DATDC SURMOF was uniformly deposited across the entire substrate and the film exhibits a net-like appearance, similar to what was observed for Cu-DASBDC in previous works^{19,117}.

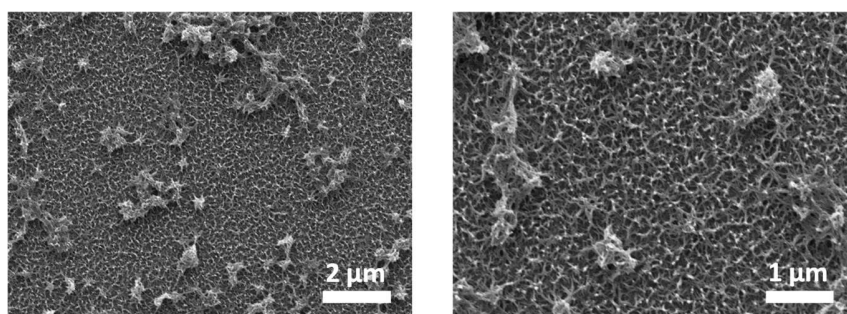


Figure 53: SEM of Cu-DATDC

7.3 Spectroscopic Analysis of Cu-DATDC SURMOF and UV Activation

The IR spectrum of the pristine Cu-DATDC SURMOF was first recorded in the range of 1200 to 2300 cm^{-1} to identify the key vibrational modes of the material. As shown in Figure 54a, the characteristic absorption bands include the azide asymmetric stretching vibration at 2127 cm^{-1} , the asymmetric stretching of the carboxylate group (COO^-) at 1602 cm^{-1} , the aromatic $\text{C}=\text{C}$ stretching at 1558 cm^{-1} , the symmetric carboxylate stretching at 1428 cm^{-1} , and the $\text{C}-\text{N}$ stretching vibration at 1287 cm^{-1} .

To study the photochemical reactivity of the azide group, the SURMOF sample was subjected to in situ UV irradiation with a mercury lamp ($\lambda=254$ nm), and IRRAS measurements were collected at regular intervals from the initial time point (0 min) up to 150 min of exposure, as shown in Figure 54b. Upon continuous irradiation, a gradual and systematic decrease in the intensity of the azide band at 2127 cm^{-1} was observed, indicating the consumption of azide groups during the course of the reaction. This spectral change confirms that a photochemical transformation is occurring within the framework, most likely involving the conversion of azide moieties into reactive nitrene intermediates and their subsequent reaction products.

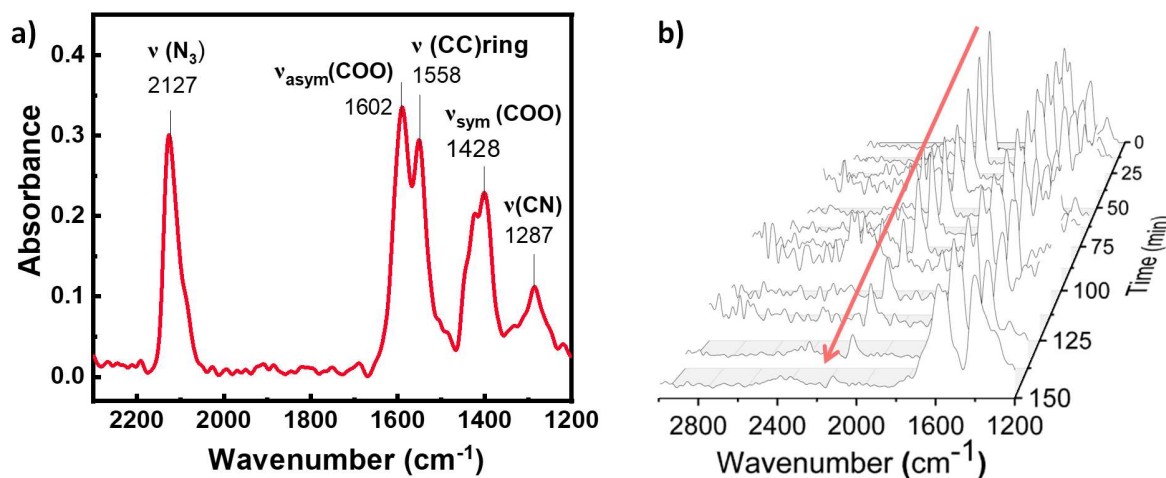


Figure 54: IRRAS spectra of a) pristine Cu-DATDC and b) in-situ measurements of the same SURMOF during UV exposure ($\lambda=254$ nm) for 150 min.

These experiments were carried out under ambient conditions, and no new absorption bands were detected below 1500 cm^{-1} , where signals from nitrene-related species are typically expected. This suggests that the highly reactive short-lived intermediates did not accumulate, and no IR signals were seen.

The photochemical behavior of the Cu-DATDC SURMOF was then investigated under conditions that could favor the stabilization of reactive intermediates, so the IR measurement during UV exposure was repeated under UHV and cryogenic conditions. These experiments were conducted in the THEO setup, where the system was cooled to approximately 70 K using liquid helium. The low temperature and UHV environment were expected to suppress side reactions and possibly allow the observation of the short-lived intermediates.

Figure 55a shows the in-situ IR spectra acquired during UV irradiation of the Cu-DATDC SURMOF under UHV conditions at 70 K, focusing on the spectral range from 1200 to 2300 cm^{-1} . As the exposure time increases, the intensity of the band at 2127 cm^{-1} , corresponding to the asymmetric stretching vibration of the azide group ($-\text{N}_3$), gradually decreases. This feature once again indicates that the azide functionalities are undergoing photochemical transformation and are being consumed over time.

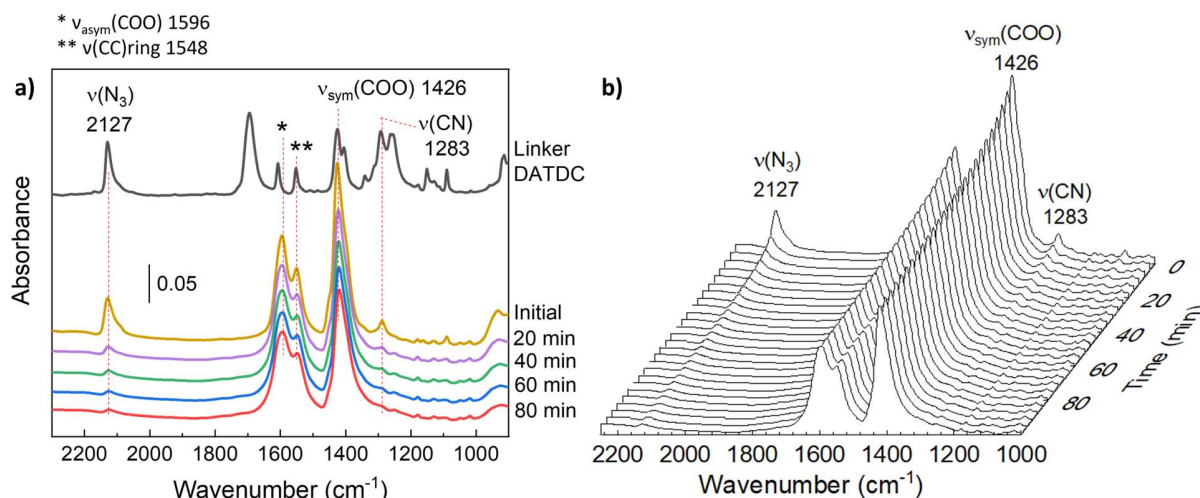


Figure 55: a) Comparison between ATR spectrum of the DATDC linker under ambient conditions and selected *in situ* IRRAS spectra recorded during UV exposure ($\lambda=254$ nm) under UHV at approximately 70 K. b) complete series of IRRAS spectra collected as a function of irradiation time (0-100 min).

Additionally, the CN stretching band at 1287 cm^{-1} also shows a decrease in intensity throughout the irradiation period. This suggests that at least some of the CN bonds adjacent to the azide moieties are disrupted during the photoreaction, reinforcing the conclusion that a structural change is occurring in the vicinity of the azide group. Despite these spectral changes, no new IR absorption bands appear in the region below 1500 cm^{-1} , where nitrene-related species are typically expected. This was observed even under ultra-high vacuum conditions, with minimized external interference and low temperature, suggesting that there is still a possible reaction between different linkers.

To further investigate whether any intramolecular transformations were taking place, as observed in the previously studied stilbene-based system (DASBDC), a closer analysis was carried out in the C–H stretching region from 2800 to 3200 cm^{-1} (Figure 56). This spectral window encompasses the aromatic C–H vibrations associated with the tolane backbone of the DATDC linker.

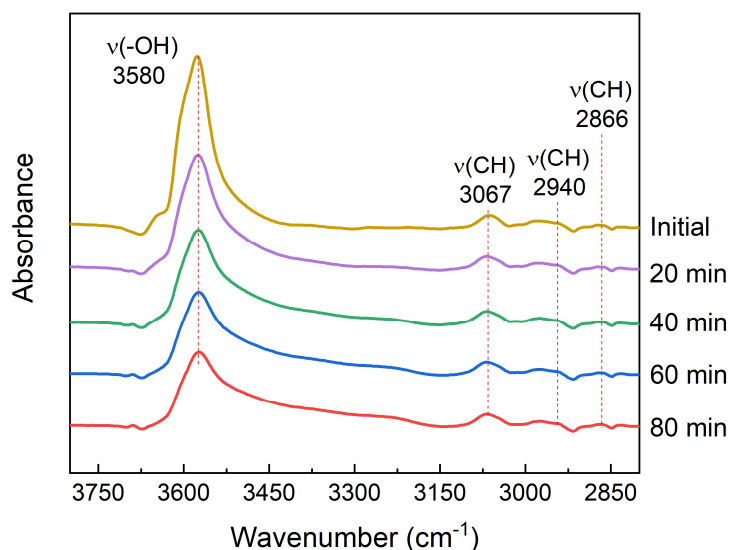


Figure 56: IR spectra under UHV at around 70 K after different times of exposure to UV light ($\lambda=254$ nm) in the spectral region of 2800-3800 cm^{-1} .

Notably, no decrease in intensity or alteration in the shape of these aromatic C–H bands was observed throughout the irradiation period. This indicates that the photochemical transformation triggered by UV exposure happens between azide functional groups in adjacent linkers and does not propagate into the aromatic framework of the linker. The preservation of these vibrational features confirms that no intramolecular cyclization or rearrangement involving the aromatic moiety occurred, in contrast to the behavior reported in the study by Song *et al*¹⁹. In the previous case, the stilbene-based linker (DASBDC) underwent undesired side reactions upon nitrene formation and that could be seen by the disappearance of the C–H vibration referent to the hydrogen in the double bond carbon ($-\text{HC}=\text{CH}-$) around 3060 cm^{-1} .

An interesting feature was observed in the region around 3580 cm^{-1} , as also shown in Figure 56. A sharp band is observed in the pristine Cu-DATDC SURMOF. This feature has previously been reported for related SURMOF-2 systems based on Cu-BDC and is assigned to OH- stretching vibrations associated with hydroxyl groups coordinated to copper centers¹²⁰.

Upon UV exposure, a gradual decrease in the intensity of the O–H stretching band is observed, suggesting that these semi-paddlewheel arrangements undergo structural reorganization during irradiation. This evolution points to changes in the local coordination environment of the copper nodes, likely driven by photochemical transformations of the azide groups and subsequent rearrangement of the framework. Importantly, while the aromatic backbone remains intact, the

observed attenuation of the OH- band indicates that UV activation affects not only the organic linker functionalities but also the metal-ligand connectivity within the SURMOF structure.

To gain deeper insight into the structural changes occurring in the Cu-DATDC SURMOF upon UV exposure, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed. MALDI-TOF is a powerful analytical technique well-suited for studying organic-inorganic hybrid materials like SURMOFs, as it enables the detection of intact molecular fragments, oligomers, or degradation products with high sensitivity and minimal fragmentation. This is particularly advantageous when investigating post-synthetic transformations, as the resulting spectra can reveal the formation of new covalent bonds, linker degradation, or polymerization phenomena within the framework.

Samples were digested in a 10% acetic acid solution in ethanol, and the matrix used was α -cyano-4-hydroxycinnamic acid (CHCA). Measurements were carried out in reflector positive ion mode over a mass range of 400–4000 Da. Two sets of samples were analyzed: a pristine Cu-DATDC SURMOF and a UV-irradiated counterpart. The corresponding spectra are shown in Figure 57a and 57b.

The MALDI-TOF spectrum of the pristine sample predominantly shows signals in the low molecular weight region, where matrix interference is more pronounced and no discernible oligomeric pattern is observed. This is consistent with the low molecular weight of the DATDC linker (~292 Da), which falls near the detection limit for well-resolved MALDI-TOF peaks without further derivatization.

In contrast, the spectrum of the UV-exposed sample reveals a distinct series of peaks that follow a regular spacing, indicative of oligomer formation. Mass signals consistent with dimers, trimers, and even tetramers (~1169 Da) suggest that the linker units underwent intermolecular coupling upon activation. This strongly implies that the azide-derived nitrenes reacted with neighboring linkers instead of remaining as isolated intermediates.

These results provide a plausible explanation for the absence of detectable nitrene signatures in the IR spectra, even under low-temperature UHV conditions. Although intramolecular rearrangements were suppressed by the tolane-based linker design (as confirmed by IR and

structural analysis), the close spatial proximity of adjacent linker molecules within the 2D SURMOF-2 structure likely facilitated rapid intermolecular coupling.

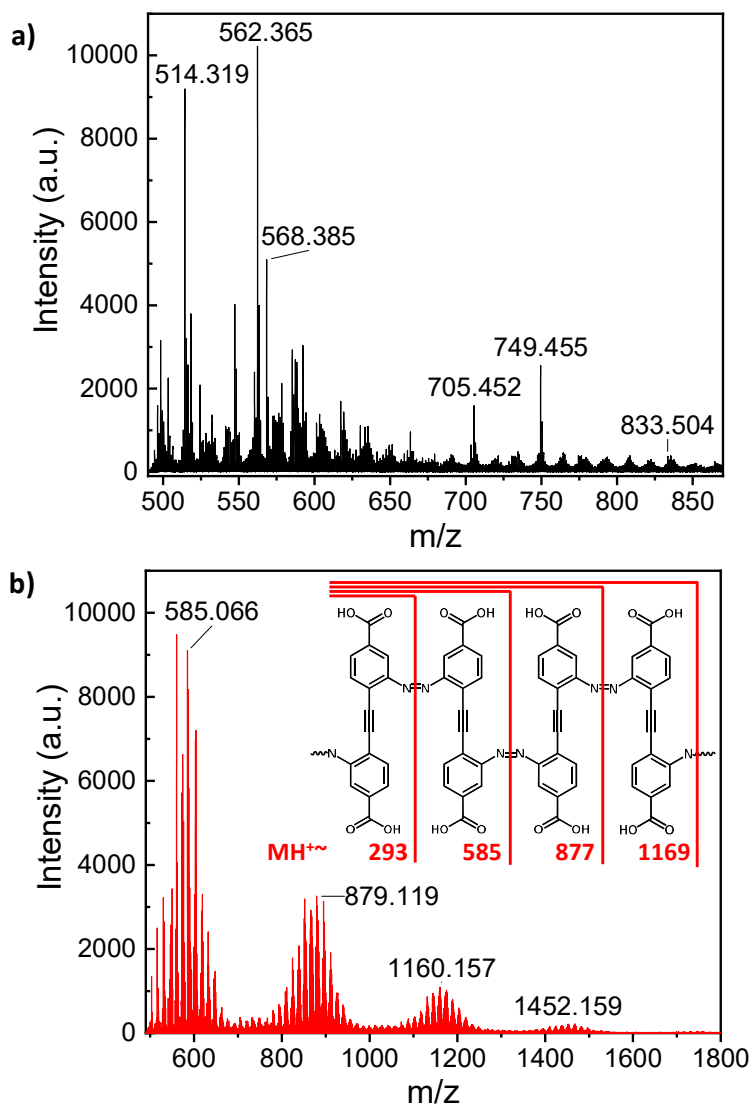


Figure 57: MALDI-TOF mass spectra of a) pristine Cu-DATDC and b) Cu-DATDC after UV irradiation ($\lambda=254$ nm). Samples were digested in 10% acetic acid solution in ethanol.

The photochemical transformation of azide groups in the Cu-DATDC SURMOF was further investigated using X-ray photoelectron spectroscopy (XPS), measured before and after UV exposure with a mercury lamp ($\lambda=254$ nm), under UHV conditions. As shown in Figure 58a, the N 1s region of the pristine SURMOF exhibits two main components centered at 403.6 eV and

400.2 eV, corresponding to the electron-deficient central nitrogen and the two terminal nitrogen atoms of the azide group, respectively¹⁹. The relative intensity ratio of these peaks is consistent with the 1:2 stoichiometry of the $-\text{N}_3$ group. A minor peak at 398.9 eV is also present in the deconvoluted spectrum, likely due to a small fraction of partially decomposed azide species already present in the as-synthesized film.

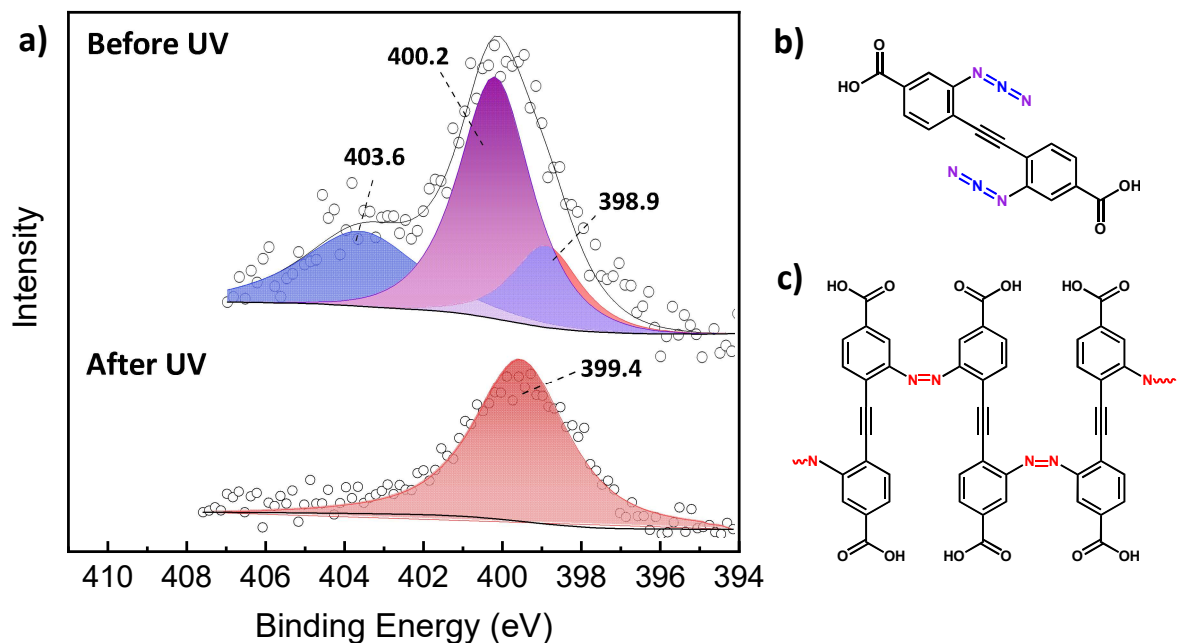


Figure 58: a) XPS results of the Cu-DATDC SURMOF and the proposed structures b) before and c) after UV exposure ($\lambda=254$ nm).

Upon UV illumination, significant changes were observed in the nitrogen chemical environment. The peaks at 403.6 eV and 400.2 eV completely disappeared, and a new feature emerged at 399.4 eV, which is attributed to the formation of azo ($-\text{N}=\text{N}-$) groups as a result of intermolecular dimerization of nitrene intermediates¹²¹. This observation supports the hypothesis proposed from the MALDI-ToF measurements, which indicate the formation of oligomeric products and supports the conclusion that nitrenes predominantly react with neighboring linker units rather than remaining isolated. A schematic representation of this intermolecular coupling is shown in Figure 59a and b.

The absence of complete crosslinking across the framework can be rationalized by the spatial distribution and relative orientation of the azide groups within the crystalline lattice. As illustrated in Figure 59a, certain azide pairs are favorably positioned for intermolecular coupling (red square),

while others are misaligned (yellow square). For the latter, nitrene-nitrene coupling would require local lattice distortions or significant reorientation of the linker units. If the SURMOF layers are assumed to be largely aligned, such distortions are energetically unfavorable and therefore limit the extent of crosslinking. This geometric constraint provides a plausible explanation for the formation of dimers, trimers, and higher oligomers up to pentamers, rather than a fully crosslinked network, as observed in the MALDI-ToF spectra.

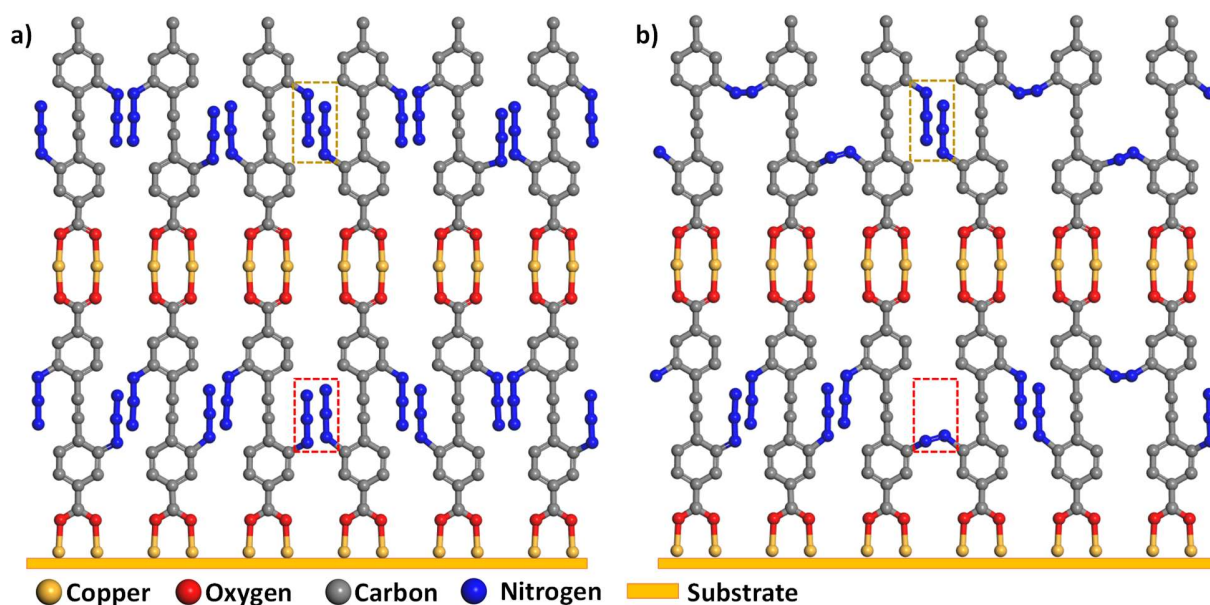


Figure 59: Representation of Cu-DATDC layers a) before and b) after UV exposure, where linkers in adjacent layers could react with each other forming oligomers.

It should be noted that azo functionalities are intrinsically difficult to identify by infrared spectroscopy. The --N=N-- group is weakly IR-active due to its low polarity, and any associated vibrations often overlap with aromatic modes, resulting in poor spectral contrast. In contrast, azo groups typically exhibit stronger signatures in Raman spectroscopy, where the N=N stretching vibration is Raman-active. Raman analysis was therefore attempted to further support the assignment of azo formation. However, under the experimental conditions used, the laser irradiation led to pronounced degradation of the SURMOF film. Instead of molecular vibrational features associated with the linker, the spectra were dominated by the appearance of broad D and G bands characteristic of carbon species, together with spectral changes at higher wavenumbers indicative of local heating effects. As a result, Raman spectroscopy could not be reliably used to probe the azo species in this system, and XPS remains the most direct evidence for their formation.

Based on these results, the next strategy was to introduce a pillar linker to expand the interlayer distance, thereby reducing the probability of linker-linker interactions. This would shift the structure from a SURMOF-2 architecture to a pillared-layer configuration, increasing the spatial separation between reactive sites and potentially enabling stabilization or even spectroscopic detection of the transient nitrene species.

7.4 Cu-DATDC-DABCO SURMOF Growth

In the attempt to mitigate the intermolecular reactivity observed in the Cu-DATDC SURMOF and facilitate spatial separation between azide-containing linker units, a pillared-layer architecture was pursued. In this type of structure, a second organic linker, known as a pillar, vertically connects adjacent 2D layers formed by DATDC and the copper paddlewheel SBUs. The inclusion of such a pillar fixes the interlayer spacing, thereby potentially preventing reactive azide groups from undergoing undesirable intermolecular coupling. Ideally for this application relatively long linkers would be desired, composed of several phenyl units, in order to maximize interlayer distance. However, the growth of SURMOFs with longer pillar linkers are often challenging so the initial proof-of-concept synthesis employed the commonly used and synthetically accessible 1,4-diazabicyclo[2.2.2]octane (DABCO) as the pillar unit. Figure 60 illustrates the structure of the Cu-DATDC-DABCO SURMOF in the desired orientation.

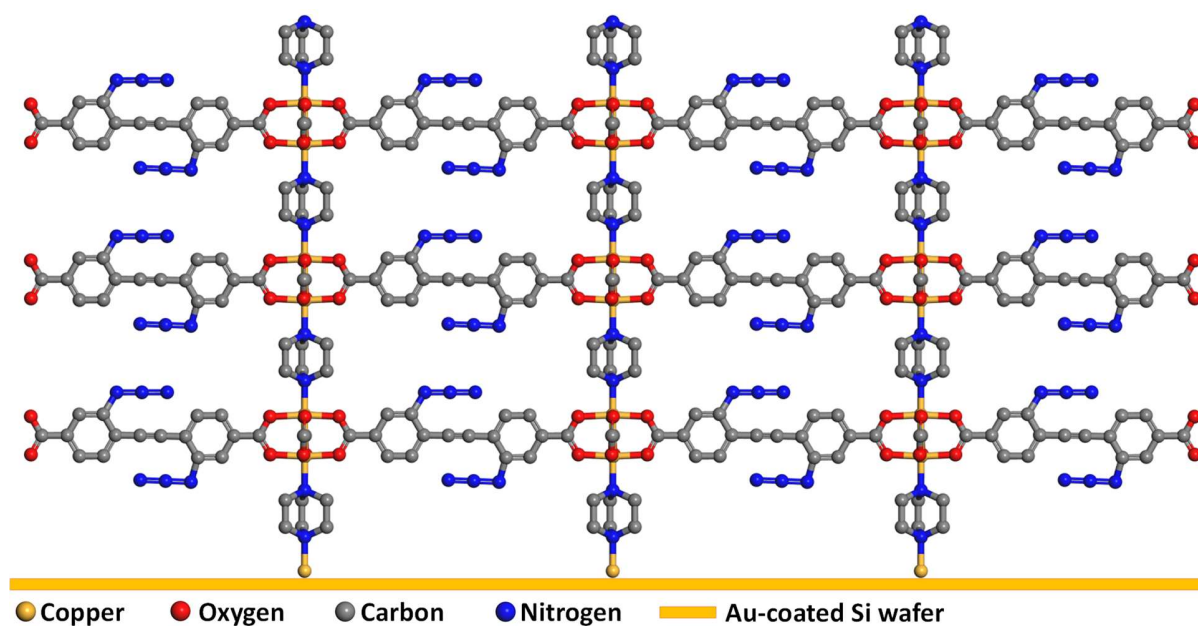


Figure 60: Schematic representation of the structure of Cu-DATDC-DABCO.

As in other SURMOF systems, the crystallographic orientation of the film is strongly influenced by the substrate functionalization and synthesis conditions, as demonstrated in the previous chapter during the optimization of Zn-Dcam-DABCO. For the current system, our goal was to develop a synthetic protocol that promotes vertical alignment of the DABCO pillars (i.e., perpendicular to the substrate), thereby ensuring pore accessibility along the surface-normal direction. This configuration would be particularly advantageous for subsequent guest molecule intercalation and photochemical studies involving azide functional groups.

Pillared-layer SURMOFs are known to require elevated temperatures for successful growth, and are typically synthesized using a closed flow system, such as the pump-based layer-by-layer method. This approach offers improved control over solvent retention and temperature stability. However, preliminary attempts to grow Cu-DATDC-DABCO using the pump system yielded non-indexable XRD patterns, suggesting the formation of unidentified crystalline phases, as shown in Figure 61.

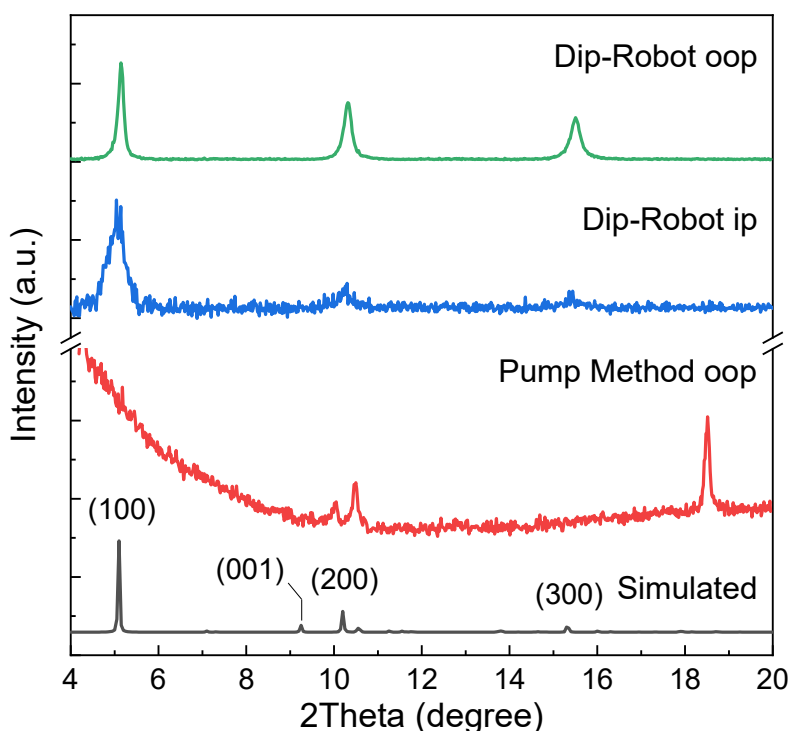


Figure 61: Comparison between simulated powder diffractogram of Cu-DATDC-DABCO and experimental diffractograms obtained after the first attempts at growing the SURMOF using the Pump method (red) and Dip robot (blue and green).

The most intense peak expected (100) was missing and the region around 10° showed two peaks, but none of them matching exactly the position of the (200) peak. An unknown peak around 18° appears and could be assigned to the (002) plane, however, in both cases it would be highly unexpected that the second order peaks appear when the first order is not even present. Given that all other components (solvents, DABCO, copper source) had previously been used in this setup without issue, it was hypothesized that the azide-functionalized DATDC linker may have reacted with the polymeric tubing material of the pump, altering the solution composition and preventing proper framework formation.

To avoid this potential incompatibility, synthesis was switched to the dipping robot. Since elevated temperatures are essential for the formation of pillared-layer SURMOFs, the protocol was adapted accordingly: the first 10 cycles of the layer-by-layer growth were carried out at 55°C , while the remaining cycles proceeded at room temperature. This compromise was necessary due to the open design of the dipping robot system, prolonged heating accelerates solvent evaporation from the beakers, making unattended overnight operation impractical. As a result, heating was limited to daytime cycles when manual refilling of the solutions could be performed.

However, the in and out-of-plane diffractograms shown in Figure 61 (blue and green) reveal that the growth of the SURMOF-2 structure was actually observed. The fact that both in and out-of-plane diffractograms show the same set of peaks and in none of them the peak at $9.2^\circ 2\theta$ expected for DABCO can be seen, indicates that during the growth process, DABCO was not incorporated in the structure.

To try and force the growth of a pillared-layer structure, we introduced a seeding layer of Cu-BDC-DABCO before growing the Cu-DATDC-DABCO. The idea was that the pillar-layer structure of the seed layer would guide the azide SURMOF to grow in the same orientation. The Cu-BDC-DABCO layer was prepared using the pump method with standard conditions, as this procedure was already well known in the group. Since the DATDC linker did not perform well in the pump system, the sample was transferred to the dipping robot for the second part of the growth.

As before, the first 10 cycles were done with heating at 55°C to help framework formation, while the remaining cycles were carried out without heating due to solvent evaporation in the open system. To increase the chances of including DABCO in the structure, the two linkers were separated into different beakers. The cycle used was: metal $\rightarrow$ ethanol $\rightarrow$ ethanol $\rightarrow$ DABCO $\rightarrow$

DATDC → ethanol. Because the robot only has six positions, the wash step after the linker was reduced to one. The XRD result of this attempt is shown in Figure 62.

The XRD results reveal distinct structural features from the two SURMOF layers. After the growth of the Cu-BDC-DABCO seeding layer, the appearance of the (001) reflection at 9.2° in the out-of-plane diffractogram and the (100) reflection at 8.3° exclusively in the in-plane measurement confirm that the SURMOF was oriented as intended, with the DABCO pillars aligned perpendicular to the substrate surface.

Following the subsequent growth of Cu-DATDC-DABCO in the dip robot, the red curves in Figure 62 show that the 9.2° peak persists, though with slightly reduced intensity, likely due to increased background signal. Importantly, the characteristic (100) reflection of DATDC at 5.1° appears only in the in-plane diffractogram and is absent in the out-of-plane mode. This anisotropic diffraction behavior strongly suggests that the azide-containing linker adopted a pillar-layer structure with the desired vertical orientation, influenced by the underlying seed layer.

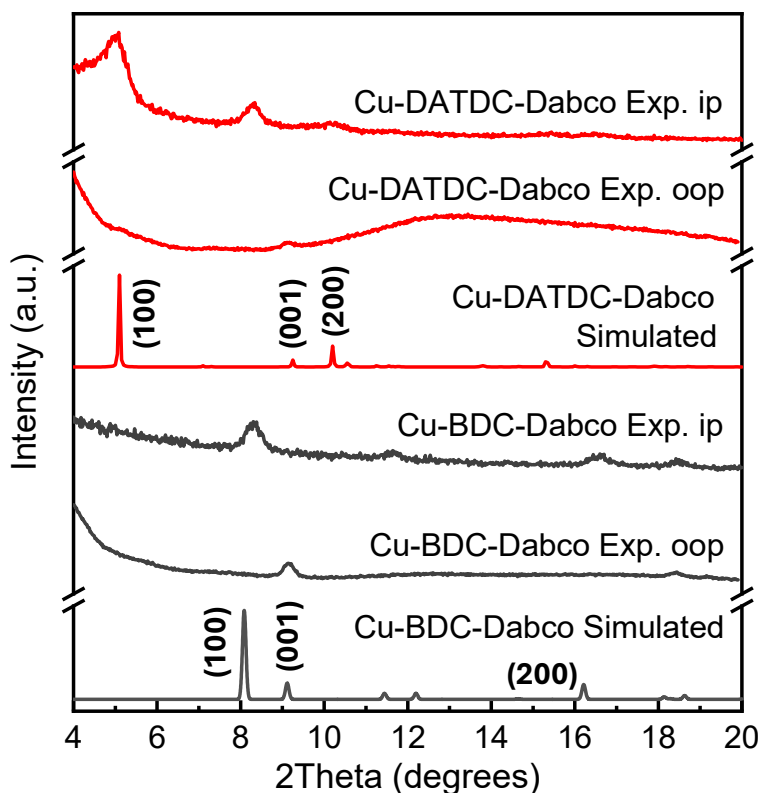


Figure 62: Out-of-plane and in-plane XRD of Cu-DATDC-DABCO grown on Cu-BDC-DABCO seed layers

The synthesis was successfully repeated, and new samples were prepared for IRRAS experiments under UHV with in situ UV irradiation under ambient temperature. Prior to UV exposure, IRRAS spectra of the pristine Cu-DATDC-DABCO SURMOF were compared with those of the Cu-DATDC SURMOF-2 structure, as shown in Figure 63. In the pillar-layer system, an additional shoulder was observed at approximately 1630 cm^{-1} that was absent in the SURMOF-2 analogue. At first glance, this feature could be interpreted as arising from a structural modification induced by pillar incorporation.

However, comparison with reference spectra of the Cu-BDC-DABCO seeding layer reveals that this shoulder corresponds to the $\nu_{\text{asym}}(\text{COO})$ vibration of the BDC linker. Since the Cu-DATDC-DABCO films were grown on top of a Cu-BDC-DABCO seed layer, contributions from the underlying SURMOF are still detectable in the IRRAS spectra. Apart from that, no other major differences were seen between the two azide SURMOFs.

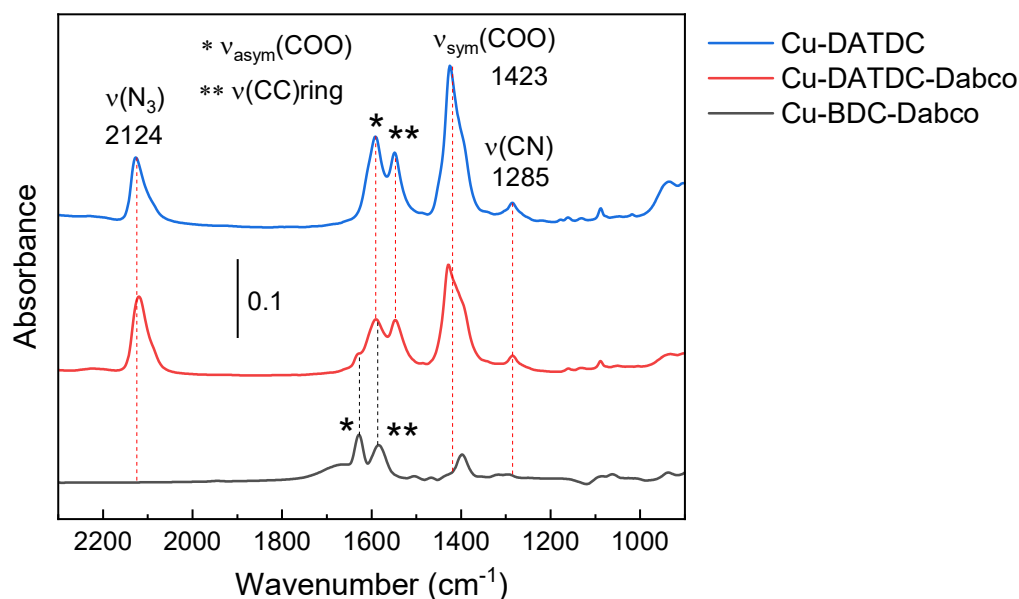


Figure 63: Comparison between IRRAS spectra of Cu-DATDC, Cu-DATDC-DABCO and seeding layer of Cu-BDC-DABCO

To slow down the photochemical reaction and increase the likelihood of resolving intermediate species, the UV irradiation ($\lambda=254\text{ nm}$) was applied in a stepwise manner during the UHV IRRAS experiment. The UV lamp power was increased incrementally, with spectra recorded at the initial time and after 5 min of exposure at each power setting. Once the maximum lamp power was reached, additional spectra were collected at 5 min intervals up to a total exposure time of 20 min.

It should be noted that the reported UV power corresponds to the nominal setting of the lamp measured at a distance of 2 cm from the source. As the sample was located inside the UHV chamber, the effective irradiance reaching the surface was lower than the nominal value; nevertheless, the reported power values provide a consistent reference for the applied irradiation conditions.

The resulting spectra are summarized in Figure 64. Figures 64a and 64b show the IRRAS spectra acquired after 5 min of exposure at each UV power setting in the ranges 900–2400 cm^{-1} and 2800–3800 cm^{-1} , respectively.

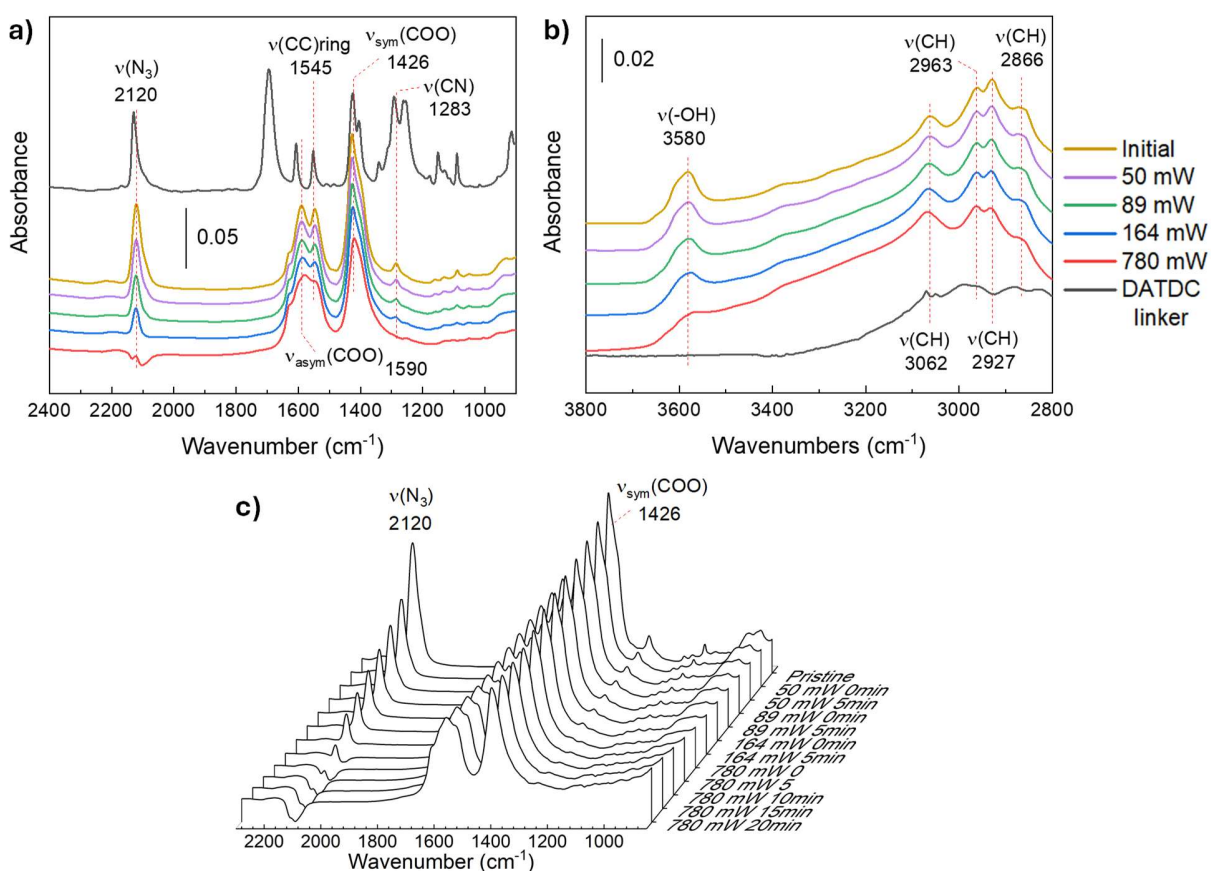


Figure 64: Comparison between ATR spectrum of the DATDC linker under ambient conditions and selected *in situ* IRRAS spectra recorded during UV exposure (UHV 298 K) in the ranges of a) 900–2400 cm^{-1} , b) 2800–3800 cm^{-1} and c) complete series of IRRAS spectra collected in the different power levels.

Overall, the spectral evolution closely resembles that observed for the Cu-DATDC SURMOF. In particular, the azide stretching band at $\sim 2120 \text{ cm}^{-1}$ progressively decreases in intensity,

indicating consumption of the azide groups under UV irradiation, while the vibrational modes associated with the aromatic backbone remain largely unaffected, showing only minor peak broadening. Once again, the C–H stretching vibrations in Figure 64b remain unchanged, in contrast to earlier studies on stilbene-based linkers, further confirming that the tolane-based DATDC linker suppresses intramolecular photochemical rearrangements.

A weak band at approximately 3580 cm^{-1} , assigned to O–H vibrations of hydroxyl groups coordinated to Cu centers and typically associated with defects or semi-paddlewheel motifs in SURMOF-2-type structures, is also observed. Compared to the Cu-DATDC SURMOF, this feature is significantly less intense, suggesting a reduced fraction of SURMOF-2-like domains and indicating that the film likely consists of a mixed structure with a dominant pillar-layer character. The lower intensity of this band supports the partial success of the pillar-layer strategy, although a perfectly homogeneous pillar-layer architecture was not achieved.

Figure 64c presents the full time-resolved dataset acquired after reaching the maximum UV power. Beyond this point, no substantial additional spectral changes were observed. As in previous experiments, no new bands emerged below 1000 cm^{-1} , where stabilized nitrene species would be expected. Since these measurements were performed at ambient temperature, repeating the experiment under cryogenic conditions using liquid helium cooling may further slow down the reaction kinetics and increase the probability of detecting nitrene intermediates. While the introduction of the pillar linker did not yet lead to observable nitrene stabilization, this approach remains promising and warrants further investigation.

7.5 Summary

In this chapter, the synthesis and characterization of azide-functionalized SURMOFs were investigated as model systems for studying solid-state photochemistry, with particular emphasis on the generation and stabilization of reactive nitrene intermediates. A newly designed linker, DATDC, was developed to eliminate undesired intramolecular reaction pathways present in earlier stilbene-based systems by replacing the central double bond with a fully unsaturated triple bond. This design strategy was successful in suppressing intramolecular cyclization, as confirmed by infrared spectroscopy, which showed preservation of the aromatic framework during UV irradiation. When incorporated into a SURMOF-2-type structure with copper paddle-wheel

secondary building units, the azide groups were found to be photoreactive, as evidenced by the gradual loss of the azide stretching vibration under UV exposure. However, even under ultrahigh vacuum and low-temperature conditions, no spectroscopic signatures of stabilized nitrene intermediates were detected. Complementary MALDI-ToF and XPS analyses instead indicated intermolecular reactivity between adjacent azide units, leading to the formation of azo-linked oligomers rather than isolated nitrenes.

To mitigate such intermolecular reactions and increase the likelihood of nitrene stabilization, a pillar-layer SURMOF architecture was pursued by incorporating DABCO as a secondary linker. Direct growth attempts without structural templating did not result in pillar incorporation; however, the introduction of a Cu-BDC-DABCO seeding layer successfully enforced the formation of a Cu-DATDC-DABCO structure with the intended crystallographic orientation. XRD and IRRAS analyses indicated a predominantly pillar-layer arrangement, although with a minor contribution from SURMOF-2-like domains. Subsequent UV-IRRAS experiments showed azide consumption similar to that observed for the SURMOF-2 system, but without evidence for stabilized nitrene species. Although full cryogenic spectroscopic evaluation of this pillar-layer system could not be completed within the timeframe of this thesis, the results demonstrate a viable structural strategy for spatially separating reactive azide groups. This establishes a solid foundation for future efforts aimed at controlling nitrene reactivity within crystalline MOF environments and for developing photoresponsive SURMOFs with tailored chemical functionality.

8 SUMMARY AND OUTLOOK

This thesis addressed the optical properties and functional structuring of surface-anchored metal-organic frameworks (SURMOFs), with a particular focus on chiroptical characterization, lithographic patterning, and photoactivated reactivity. Two complementary research directions were explored: the optical investigation and structuring of chiral SURMOFs, and the development of azide-functionalized SURMOFs as platforms for studying nitrene photochemistry in an ordered solid-state environment.

In the first part of this work, the chiral SURMOF $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ was successfully grown on different substrates and comprehensively characterized by infrared (IR), electronic circular dichroism (ECD), and vibrational circular dichroism (VCD) spectroscopy. The experimental optical responses were directly compared with multiscale theoretical simulations, showing good agreement in band positions, spectral shapes, and chiroptical signatures. This correspondence validated the theoretical workflow for thin-film SURMOF systems and confirmed the suitability of the model for predicting macroscopic optical behavior from molecular-level descriptions.

A particularly significant result of this work is the experimental realization of VCD measurements on SURMOF thin films directly grown on transparent substrates. Unlike conventional powder MOF studies, which require embedding in KBr pellets and often suffer from reduced signal-to-noise ratios, the SURMOF geometry enabled non-destructive transmission-mode VCD measurements on CaF_2 substrates. This approach provided improved spectral quality and established SURMOFs as highly attractive model systems for solid-state chiroptical spectroscopy.

Motivated by theoretical predictions of enhanced chiroptical responses in structured architectures, two lithographic approaches were investigated to pattern chiral SURMOF films into defined geometries. Although a fully reproducible and general patterning route could not be established within the scope of this work, important insights were gained. Direct laser writing (DLW) revealed that the use of in-house PMMA formulations for the spin coating of a layer to protect the SURMOF from the developer, ended up in too many residues left over at the end of the plasma process. To improve that, commercially available PMMA/MA solutions could be used, which would significantly reduce the thickness of this protective layer, potentially minimizing

residual material after etching. Additionally, even though the regular O₂ plasma was able to etch away parts of the SURMOF film, reactive ion etching (RIE) used after t-SPL proved superior to the non-directional oxygen plasma etching in terms of pattern fidelity and vertical resolution, indicating a more promising direction for future SURMOF structuring strategies.

Thermal scanning probe lithography (t-SPL) enabled the development of a viable patterning route for HKUST-1 thin films, demonstrating that SURMOF materials can be structured with micrometer-scale precision. Sub-micrometer structures revealed limitations related to lift-off efficiency and mechanical stability of the protective layer. As seen in SEM images, the protective layer detached from the surface of the SURMOF in some cases. Improvements such as extended lift-off times, solvent optimization, or the use of sonication are expected to enhance pattern quality. For the chiral SURMOF system, the lack of successful patterning on quartz substrates suggests that substrate thickness and thermal conductivity play a critical role. Future experiments on thinner substrates, such as gold-coated silicon wafers, may clarify whether the limitations arise from insufficient heat dissipation. Further reductions in surface roughness through additional optimization cycles could also improve compatibility with t-SPL.

In the second part of this thesis, azide-functionalized SURMOFs were developed to explore photoactivated chemistry in a spatially ordered framework. The introduction of a triple bond in the DATDC linker successfully eliminated intramolecular cyclization pathways observed previously for stilbene-based systems, confirming the effectiveness of the molecular design strategy. However, the SURMOF-2 structure formed by Cu-DATDC did not stabilize nitrene intermediates sufficiently to allow their direct observation by IR spectroscopy under ultrahigh vacuum conditions. Instead, spectroscopic and mass-spectrometric analyses revealed intermolecular reactions between adjacent azide units, leading to oligomerization. MALDI-TOF measurements indicated the formation of oligomers up to pentamers, while XPS results supported the formation of azo-type nitrogen species after UV exposure ($\lambda=254$ nm).

To suppress these intermolecular reactions, a pillar-layer architecture was pursued through the synthesis of Cu-DATDC-DABCO SURMOFs. This approach aimed to maintain a fixed interlayer distance and reduce the probability of azide-azide interactions between neighboring layers. Initial structural characterization confirmed the successful incorporation of the pillar linker and the desired crystallographic orientation. However, subsequent spectroscopic investigations under

UHV at 298K still did not reveal clear signatures of stabilized nitrene species. Repeating these experiments under cryogenic conditions may increase the lifetime of photo-generated nitrenes and improve their detectability. In addition, the use of longer pillar linkers, such as bipyridine derivatives, could further increase the interlayer distance and thereby enhance nitrene stabilization. Achieving such architectures will likely require alternative synthesis strategies, for example pump-based growth systems with independently addressable channels for layer and pillar linkers. Finally, machine-learning-assisted optimization could be employed to systematically refine growth parameters, improve crystallinity, and ensure the formation of a fully pillar-layer structure, providing a promising route toward controlled photoactive SURMOFs.

Overall, this work demonstrates the versatility of SURMOFs as platforms for both optical characterization and controlled chemical reactivity. The results advance the understanding of chiroptical phenomena in MOF thin films, establish VCD as a powerful tool for SURMOF analysis, and provide valuable guidance for future lithographic structuring and photoresponsive SURMOF design. The insights gained here open new pathways toward SURMOF-based optical materials, metamaterials, and spatially controlled photochemical systems.

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10 ABBREVIATIONS

Abbreviation	Full name
AFM	Atomic Force Microscopy
BDC	1,4-benzenedicarboxylate
BTC	1,3,5-benzenetricarboxylate
Cam (D or L)	D or L Camphoric acid
DABCO	1,4-Diazabicyclo[2.2.2]octane
DASBDC	2,2'-Diazido-4,4'-stilbenedicarboxylic acid

DATDC	2,2'-Diazido-4,4'-tolanedicarboxylic acid
DLW	Direct Laser Writer
ECD	Electronic Circular Dichroism
EDX	Energy-Dispersive X-ray Spectroscopy
EtOH	Ethanol
HKUST-1	Hong-Kong University of Science and Technology [Cu ₃ (btc)]
IR	Infrared
IRRAS	Infrared Reflection-Absorption Spectroscopy
KBr	Potassium Bromide
LbL	Layer-by-Layer
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry
MOF	Metal-organic Framework
PMMA	Poly(methyl methacrylate)
PMMA/MA	Poly(methyl methacrylate-co-methacrylic acid)
PPA	Poly(phthalaldehyde)
RIE	Reactive Ion Etching
SAM	Self-Assembled Monolayer
SEM	Scanning Electron Microscopy
SURMOF	Surface-anchored Metal-Organic Framework
SyCoFinder	Synthesis Condition Finder
t-SLP	Thermal Scanning Probe Lithography
UHV	Ultra-High Vacuum
VCD	Vibrational Circular Dichroism
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

11 ACKNOWLEDGMENTS

Institutional and Resource Acknowledgments

I would like to acknowledge the assistance of ChatGPT (OpenAI), which provided support in refining the language and improving the clarity of selected parts of this thesis. I would also like to thank the 3DMM2O Graduate School for providing enriching scientific courses and for organizing events that greatly supported networking and professional development throughout my doctoral studies.

Personal Acknowledgments

First, I would like to thank my supervisor, Prof. Christof Wöll, for the opportunity to pursue my PhD in his group, and for his continuous support and the valuable scientific discussions throughout the course of these projects.

I would further like to thank Prof. Stefan Bräse for accepting to serve as co-reviewer of my doctoral thesis and for the extensive support in linker synthesis provided by him and his group.

I also thank Prof. Carsten Rockstuhl and his group member Dr. Marjan Krstić and Dr. Benedikt Zerulla for the fruitful collaboration.

I would like to thank all the members of the IFG for their help and advice. Special thanks go to Hartmut Gliemann for all his support, both scientifically and with all the organizational matters. Our regular Friday morning meetings were essential for the completion of this work. And for that, I would also like to thank Matthias Schwotzer, who not only provided interesting ideas and support during these meetings, but also shared his extensive expertise in SEM. This knowledge is invaluable and I really appreciate it. I also thank Peter Weidler, whom I have disturbed way too many times with PC and XRD problems (RIP in-plane machine). Thank you for all the explanations about crystal planes and my peculiar diffractograms. If you have any questions about Portuguese, I am always willing to help.

I extend my gratitude to Angela Weiss for the warm smile and uplifting chats in the morning, to Alex Welle for all the interesting conversations and humor, you were a great office mate, even

if only for a short time. To my other short-time office mate, Stefan Heissler, I thank you for all the training and support in all the different spectroscopy techniques and all the tips of interesting things to see in the region and beyond. To Peter Krolla for the support and sharing his knowledge in AFM. And all the other COOI or RIMS members.

To my IFG colleagues who also became friends: Bruno Kanj, I would never have finished this PhD without having you to listen to my complaints about life and partially support me and partially mock me for it, bringing the necessary balance to life. To Chatrawee Scheiger (or as I prefer: Cuckoo), thank you for being a great friend and support in all times, it was always good to have someone sharing the pains of machine learning and MOFs. To Ariadna Lázaro, for all the lunch breaks, the support chasing a healthy life and all the gossip over beers we shared, I cannot thank you enough. To Lena Pilz, who I got close only later in the PhD, I have to admit I was intimidated by your efficiency and competence in the beginning, but you have become a dear friend throughout this journey and have taught me so much in the last stretch of this process, I will be forever grateful.

I would never have finished this PhD without the support of my amazing family, Ana Maria, Silas, Aline and Lucas, thank you all for the support from far away. Thanks for all the Sunday calls (that I have to make, or you forget me) and the warm welcome and even spoiling me a little bit when I come to visit. Sadly, these visits are not often enough due to the lack of teleport technology, maybe we'll get there someday. To Florian, my favorite German, but also the least German of them. Thanks for all the random walks, for all the vegan meals and the general companionship. To all my Brazilian friends, especially Pedro who was one of my first friends here and a mentor of life in Europe, Phono and summer of 2022 will never be forgotten. To Camila, for providing a great house for reality show watch parties and for all the venting about our PhDs. To Bibi, for all the gossip, aesthetic photos and great company. Our little secret society will live on. To the other Ana C, for sharing my sense of humor and taste in TV shows. What can I say? We just clicked.

To all my friends still in Brazil or around the world, specially Thamy, Caio, Marlon, Gui and Denise, for all the support from afar. Our conversations were essential for keeping my mental health, muito obrigada.

I would not have enough space to thank everyone who was important to me in these years of my PhD, but I thank God for that. I have met more nice people than I can count and I found friends everywhere I went.

APPENDIX

A.1. Optimization of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ thin film towards Roughness and Crystallinity

1st Generation - Fitness

Table A. 1: Fitness values of crystallinity, roughness and overall fitness for the Generation 1

	Crystallinity	Fitness _{crystallinity}	Roughness - Ra (nm)	Fitness _{Roughness}	Final Fitness
S1	13 ± 3	0.13	108 ± 97	0.26	0.20
S2	7 ± 2	0.07	88 ± 110	0.33	0.20
S3	21 ± 1	0.21	29 ± 12	1.00	0.61
S4	7 ± 2	0.07	34 ± 49	0.85	0.46
S5	13 ± 4	0.13	67 ± 39	0.43	0.28
S6	32 ± 21	0.32	38 ± 18	0.74	0.53
S7	14 ± 6	0.14	56 ± 19	0.51	0.33
S8	30 ± 17	0.30	61 ± 41	0.47	0.39
S9	15 ± 3	0.15	198 ± 178	0.14	0.15
S10	4 ± 1	0.04	37 ± 24	0.76	0.40

2nd Generation - Fitness

Table A. 2: Fitness values of crystallinity, roughness and overall fitness for the Generation 2

	Crystallinity	Fitness _{crystallinity}	Roughness - Ra (nm)	Fitness _{Roughness}	Final Fitness
S1	34 ± 12	0,34	113 ± 6	0,61	0,47
S2	42 ± 33	0,42	120 ± 27	0,58	0,50
S3	25 ± 3	0,25	121 ± 41	0,57	0,41
S4	29 ± 16	0,29	294 ± 25	0,23	0,26
S5	57 ± 12	0,57	113 ± 6	0,61	0,59
S6	84 ± 23	0,84	69 ± 4	1,00	0,92
S7	22 ± 8	0,22	84 ± 20	0,82	0,52
S8	17 ± 11	0,17	214 ± 44	0,32	0,25
S9	18 ± 11	0,18	138 ± 20	0,50	0,34
S10	22 ± 11	0,22	117 ± 12	0,59	0,40

1st Generation – Diffractograms and confocal microscopy images

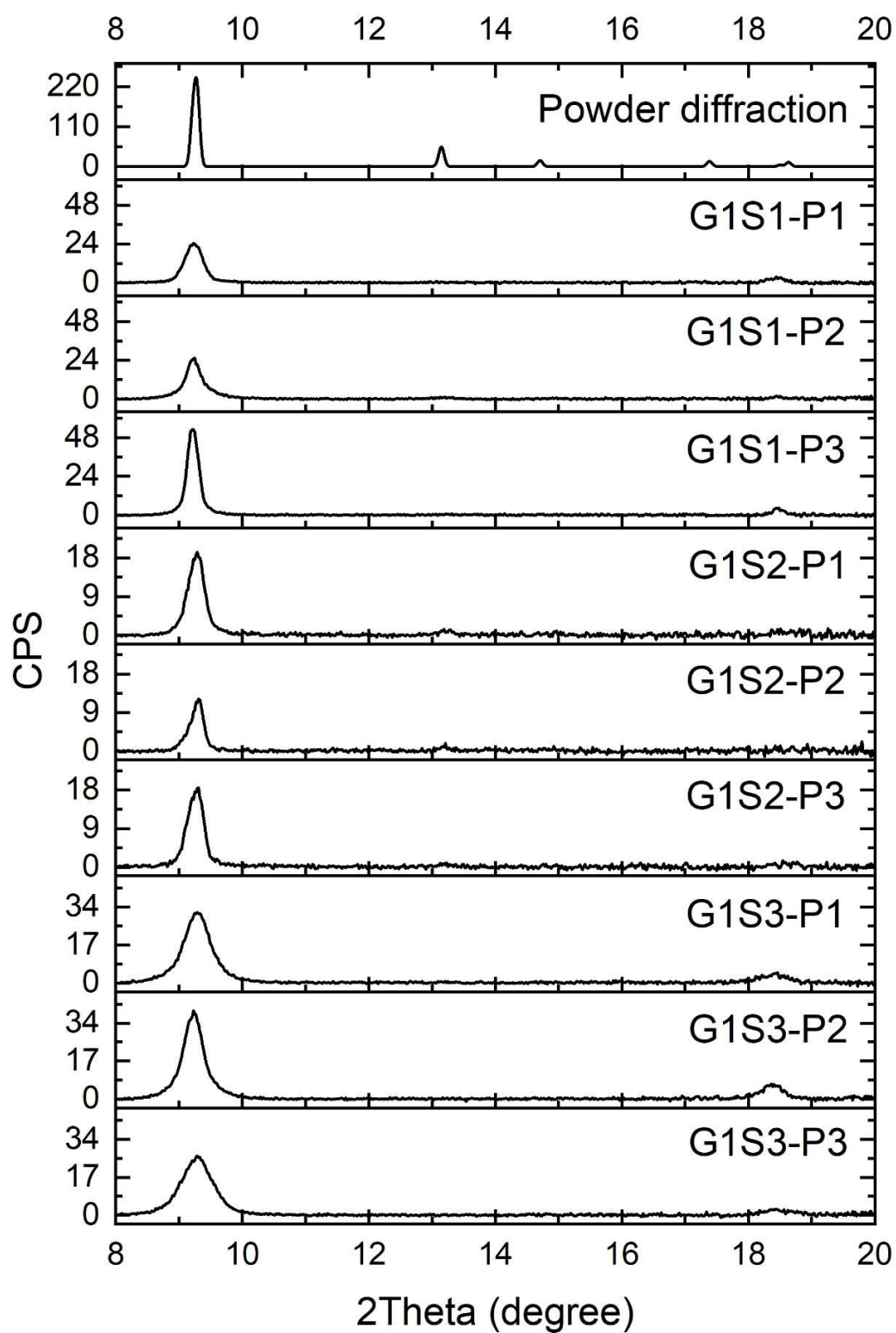


Figure A. 1: X-Ray Diffractograms of Generation 1 for synthesis conditions 1 to 3

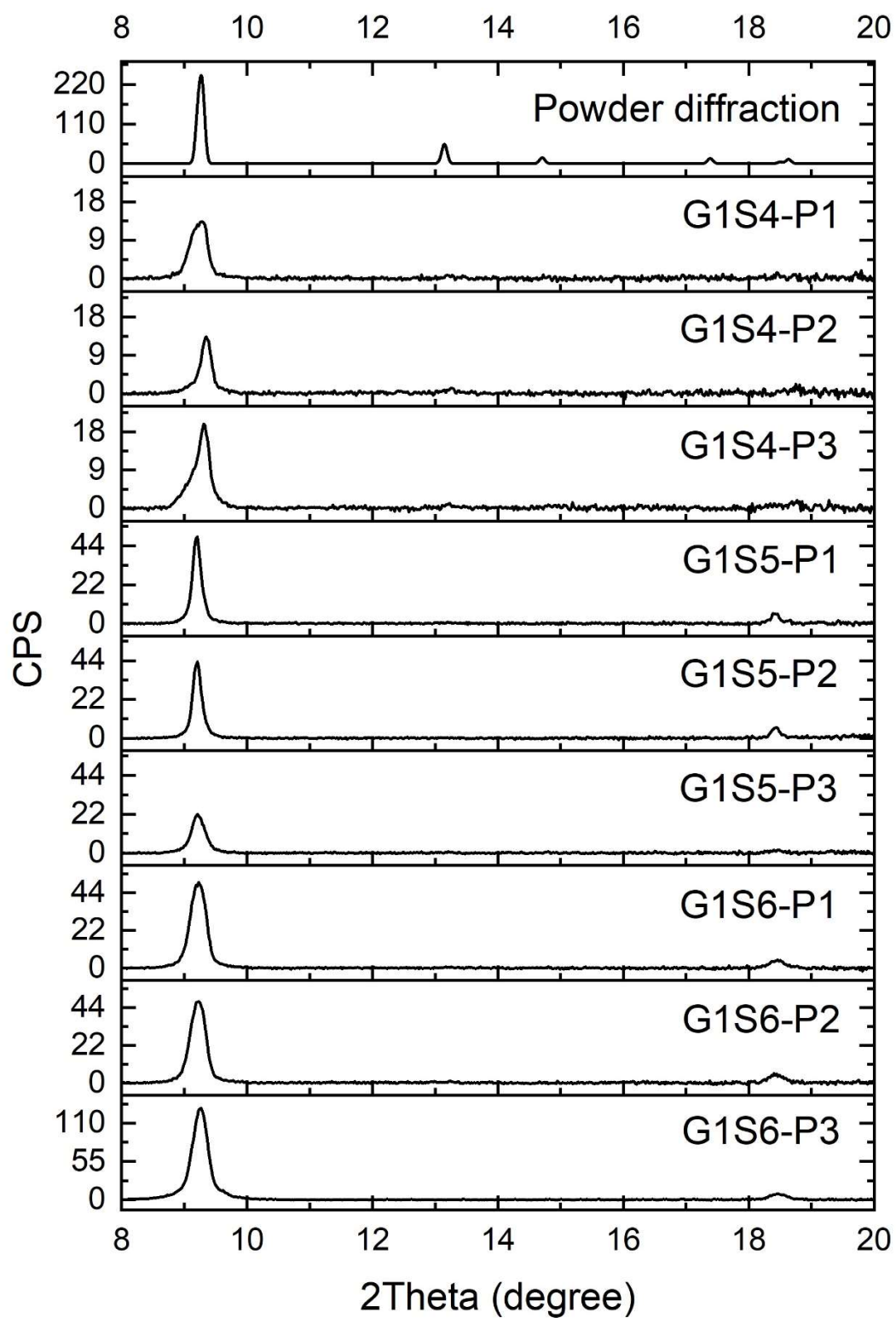


Figure A. 2: X-Ray Diffractograms of Generation 1 for synthesis conditions 4 to 6.

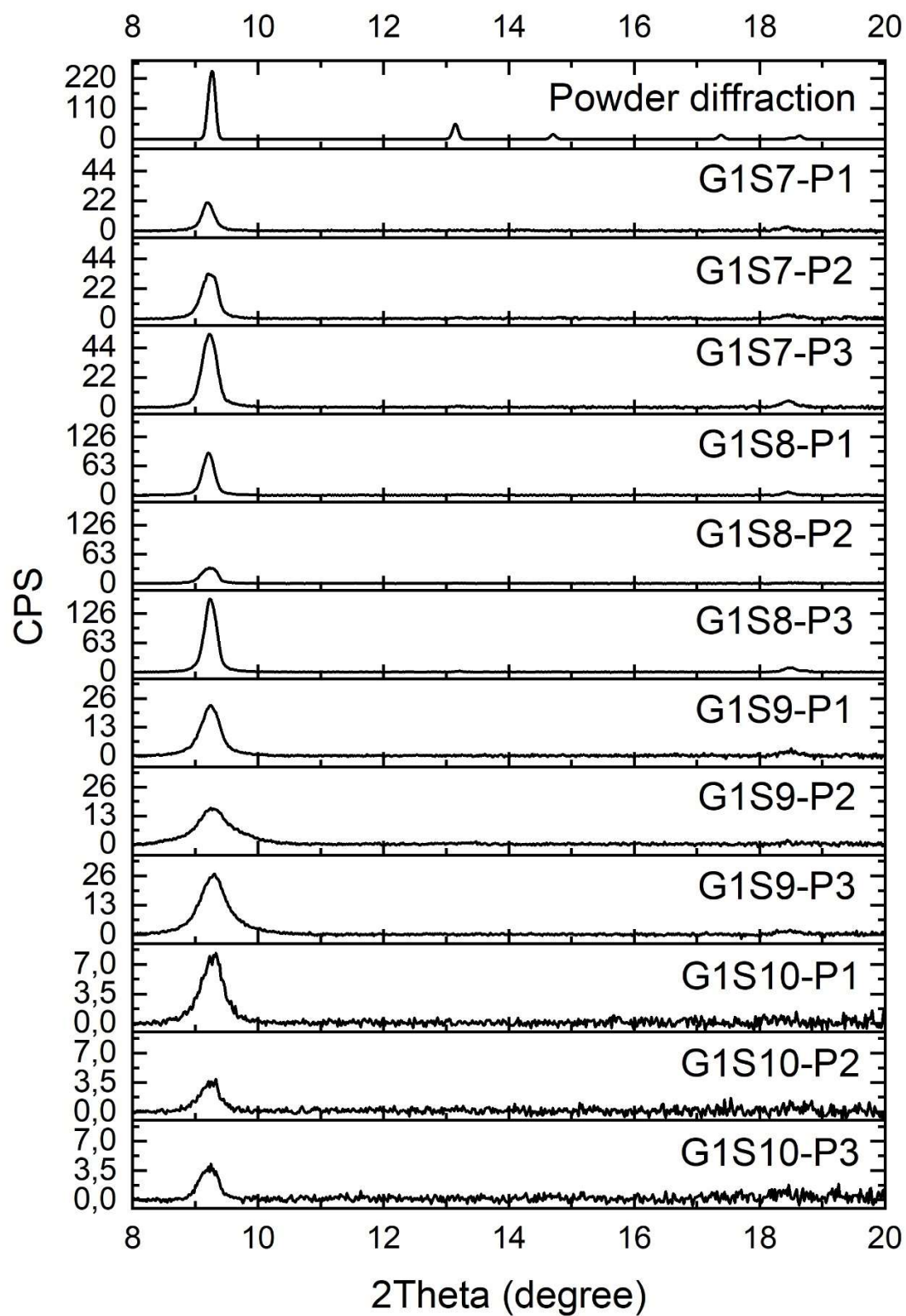


Figure A. 3: X-Ray Diffractograms of Generation 1 for synthesis conditions 7 to 10.

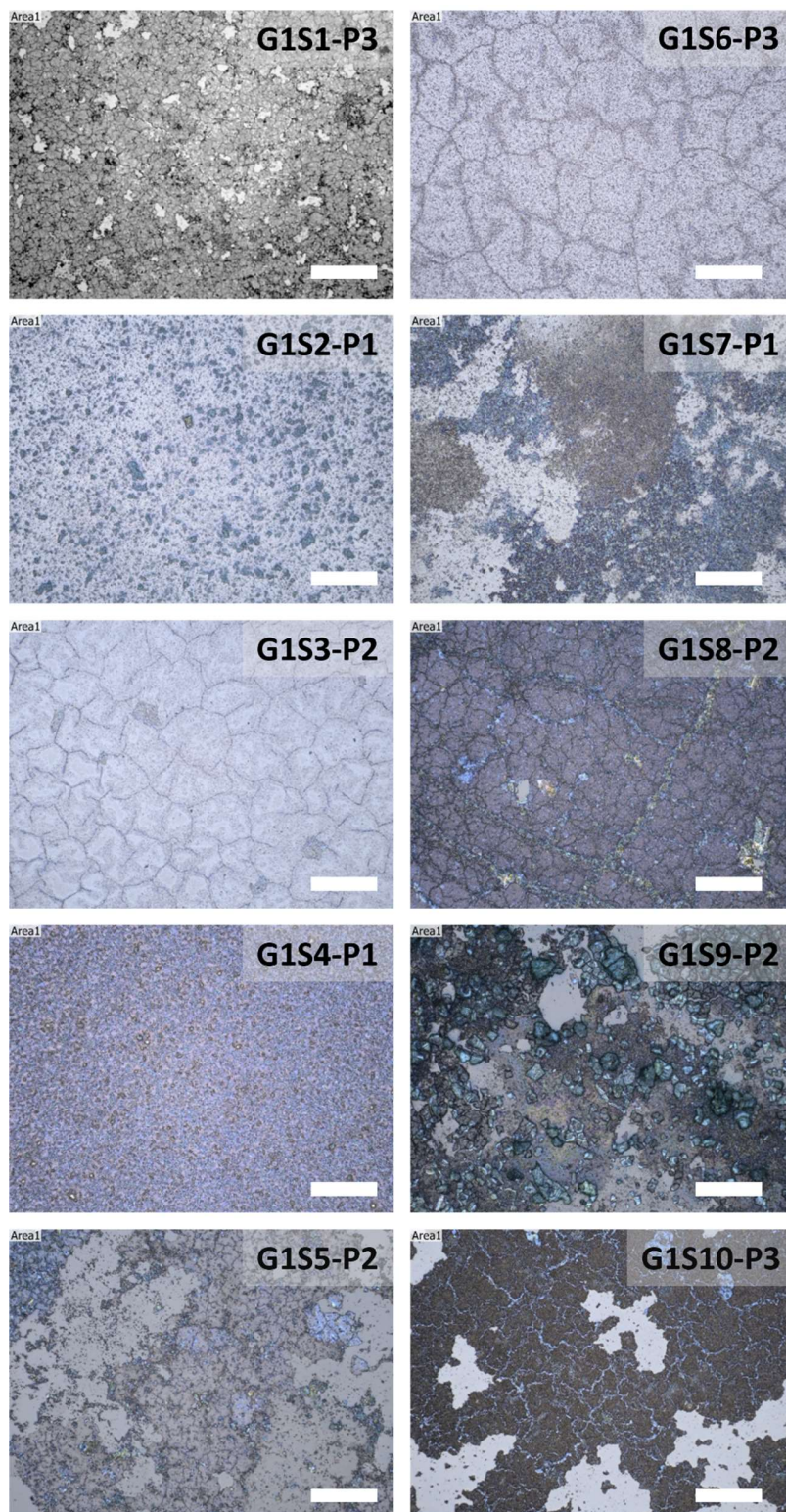


Figure A. 4: Representative confocal microscopy images of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ from all the synthesis conditions in Generation 1. Scale bar: 50 μm .

2nd Generation – Diffractograms and confocal microscopy images

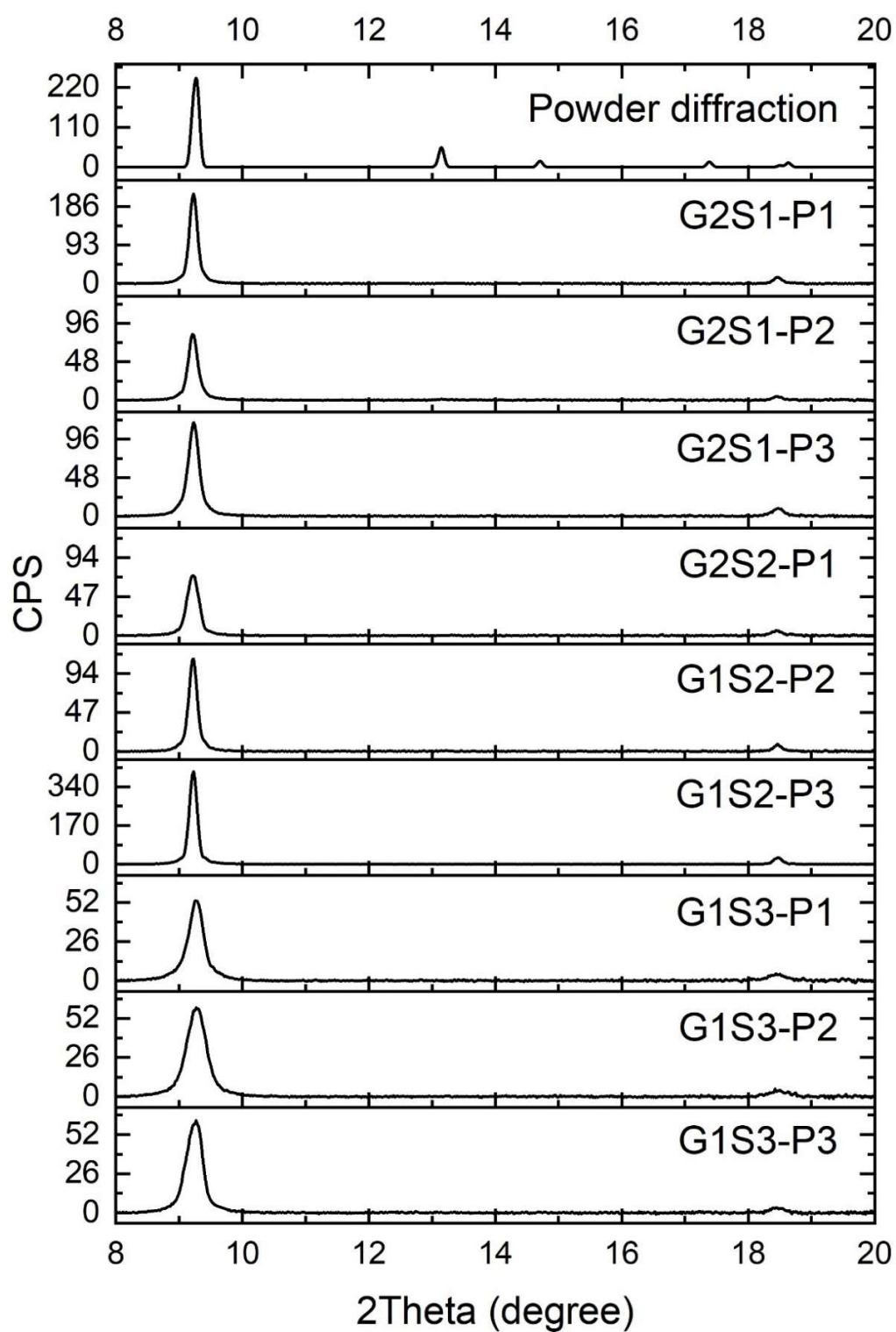


Figure A. 5: X-Ray Diffractograms of Generation 2 for synthesis conditions 1 to 3.

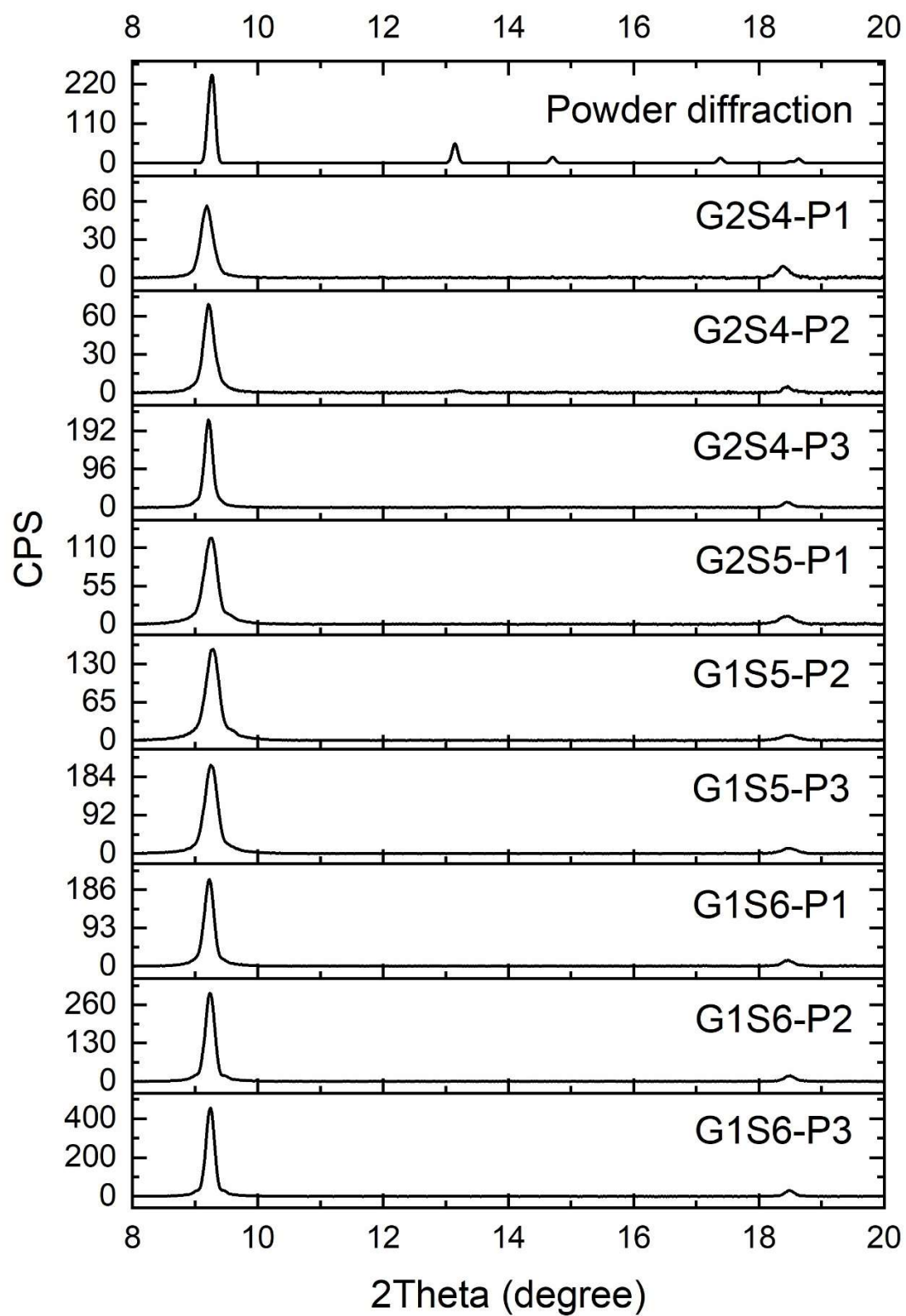


Figure A. 6: X-Ray Diffractograms of Generation 2 for synthesis conditions 4 to 6.

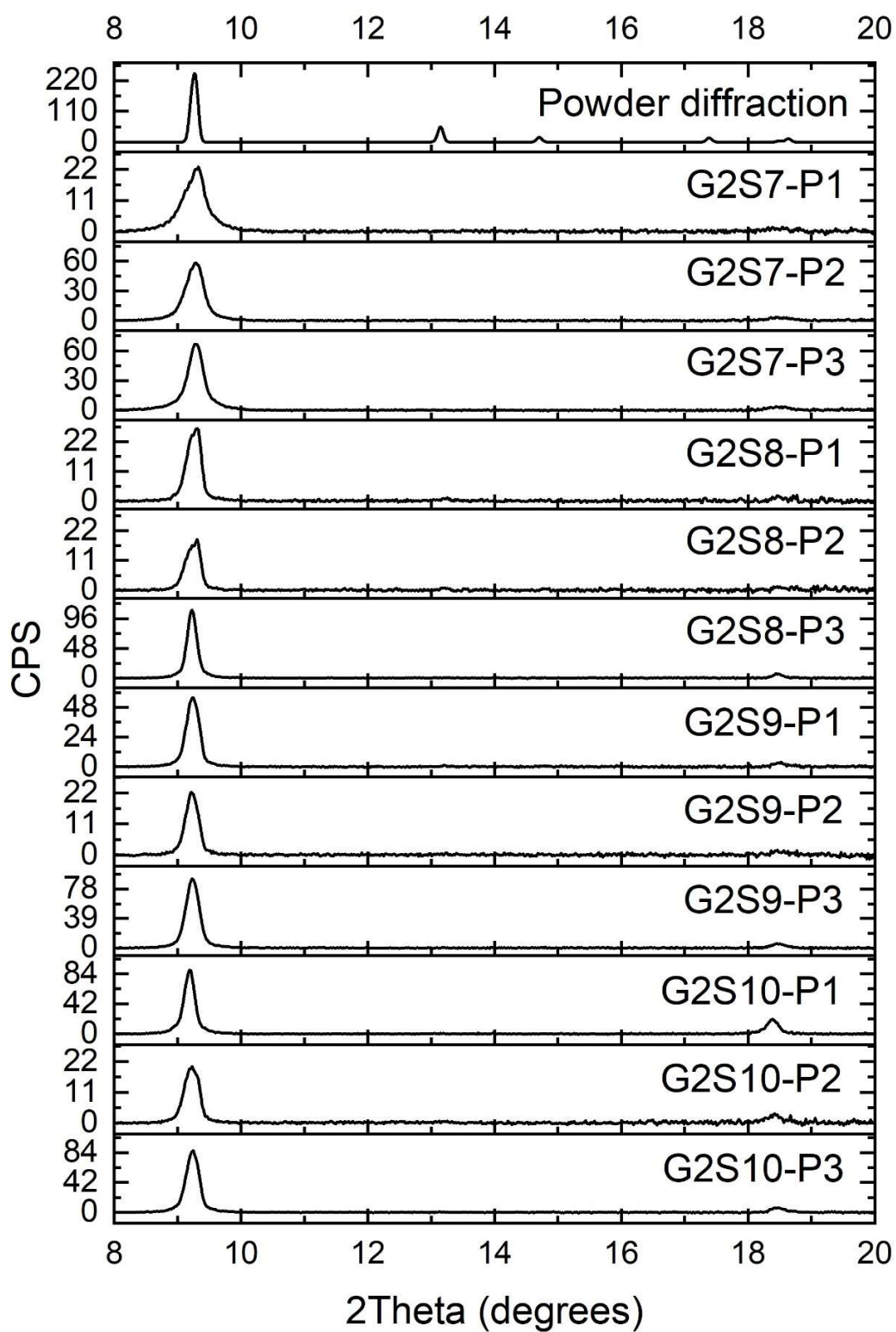


Figure A. 7: X-Ray Diffractograms of Generation 2 for synthesis conditions 7 to 10.

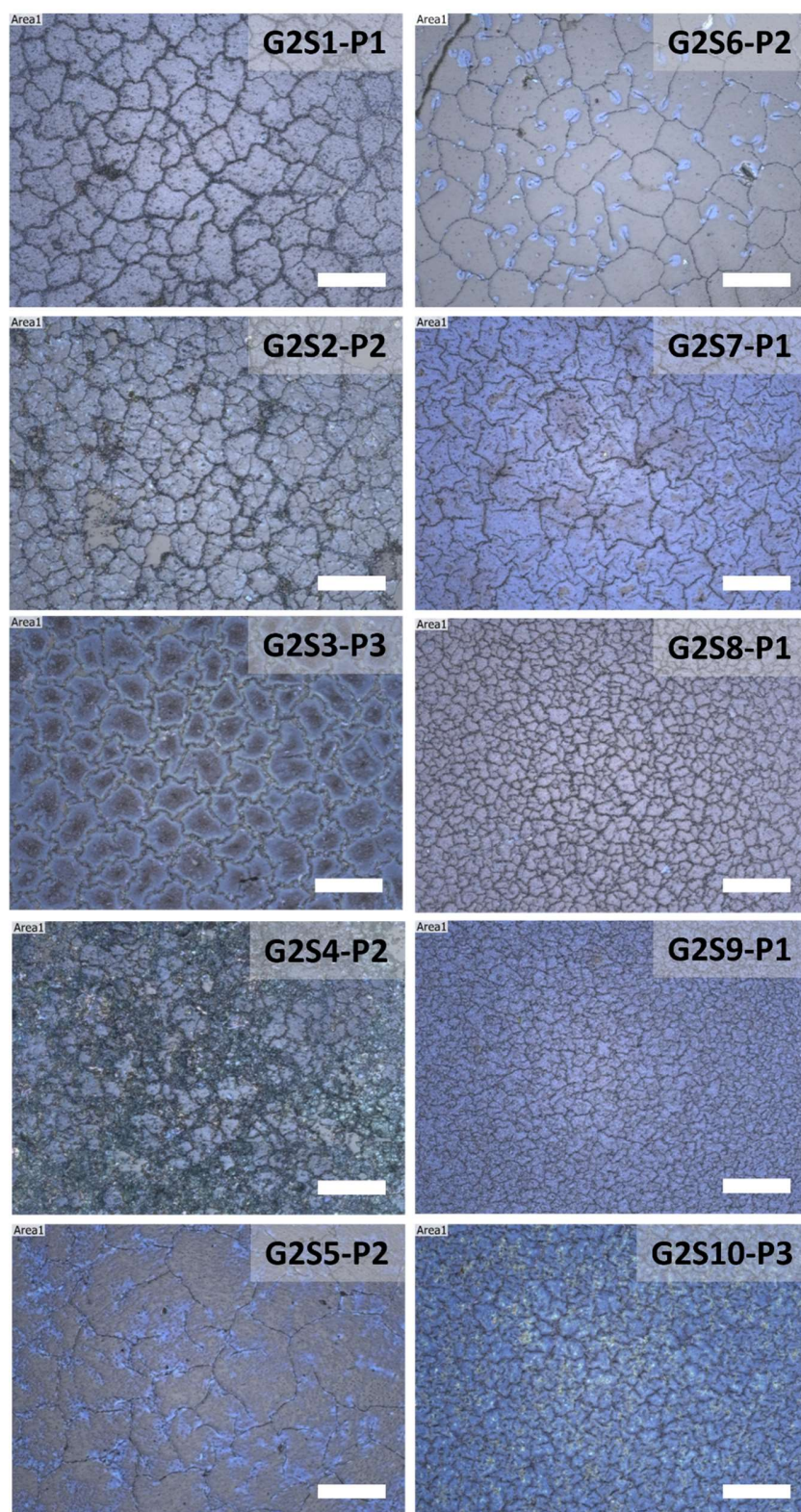


Figure A. 8: Representative confocal microscopy images of $\text{Cu}_2(\text{D-Cam})_2(\text{DABCO})$ from all the synthesis conditions in Generation 2. Scale bar: 50 μm .

A.2. Optimization of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ thin film towards Roughness and Crystallinity

1st Generation - Fitness

Table A. 3: Fitness values of crystallinity, roughness and overall fitness for the Generation 1.

	Crystallinity	Fitness_{crystallinity}	Roughness - Ra (nm)	Fitness_{Roughness}	Final Fitness
S1	84 ± 5	0.68	19 ± 1	0.57	0.62
S2	87 ± 22	0.70	13 ± 1	0.82	0.76
S3	56 ± 24	0.45	75 ± 3	0.14	0.30
S4	82 ± 22	0.66	61 ± 15	0.17	0.42
S5	92 ± 17	0.74	33 ± 4	0.33	0.53
S6	80 ± 10	0.64	11 ± 1	1.00	0.82
S7	2.5 ± 0.3	0.02	51 ± 3	0.21	0.11
S8	66.5 ± 0.6	0.53	18 ± 3	0.60	0.57
S9	77 ± 8	0.62	79 ± 4	0.14	0.38
S10	2.4 ± 0.7	0.02	49 ± 1	0.27	0.15

1st Generation – Diffractograms and confocal microscopy images

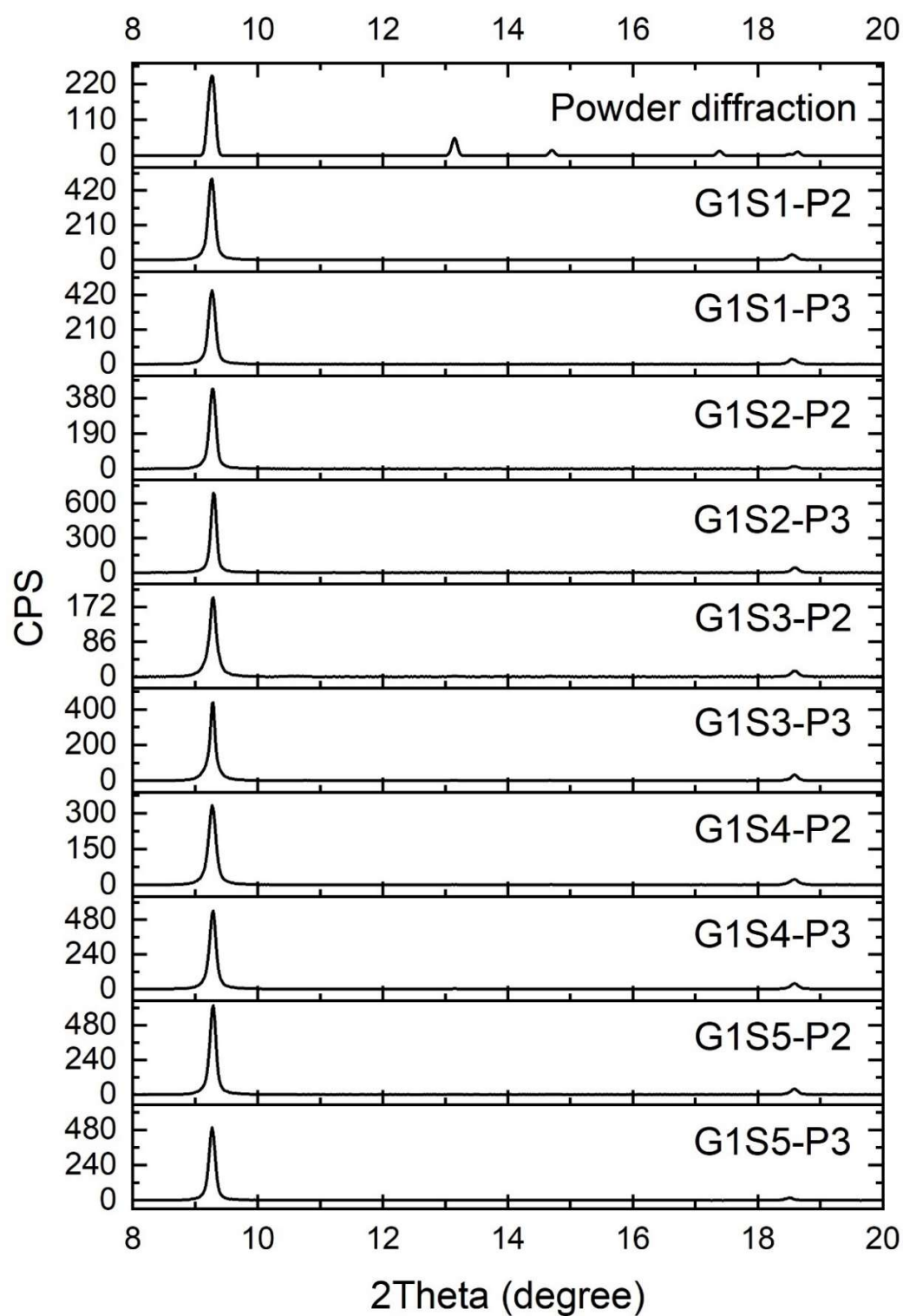


Figure A. 9: X-Ray Diffractograms of Generation 1 for synthesis conditions 1 to 5.

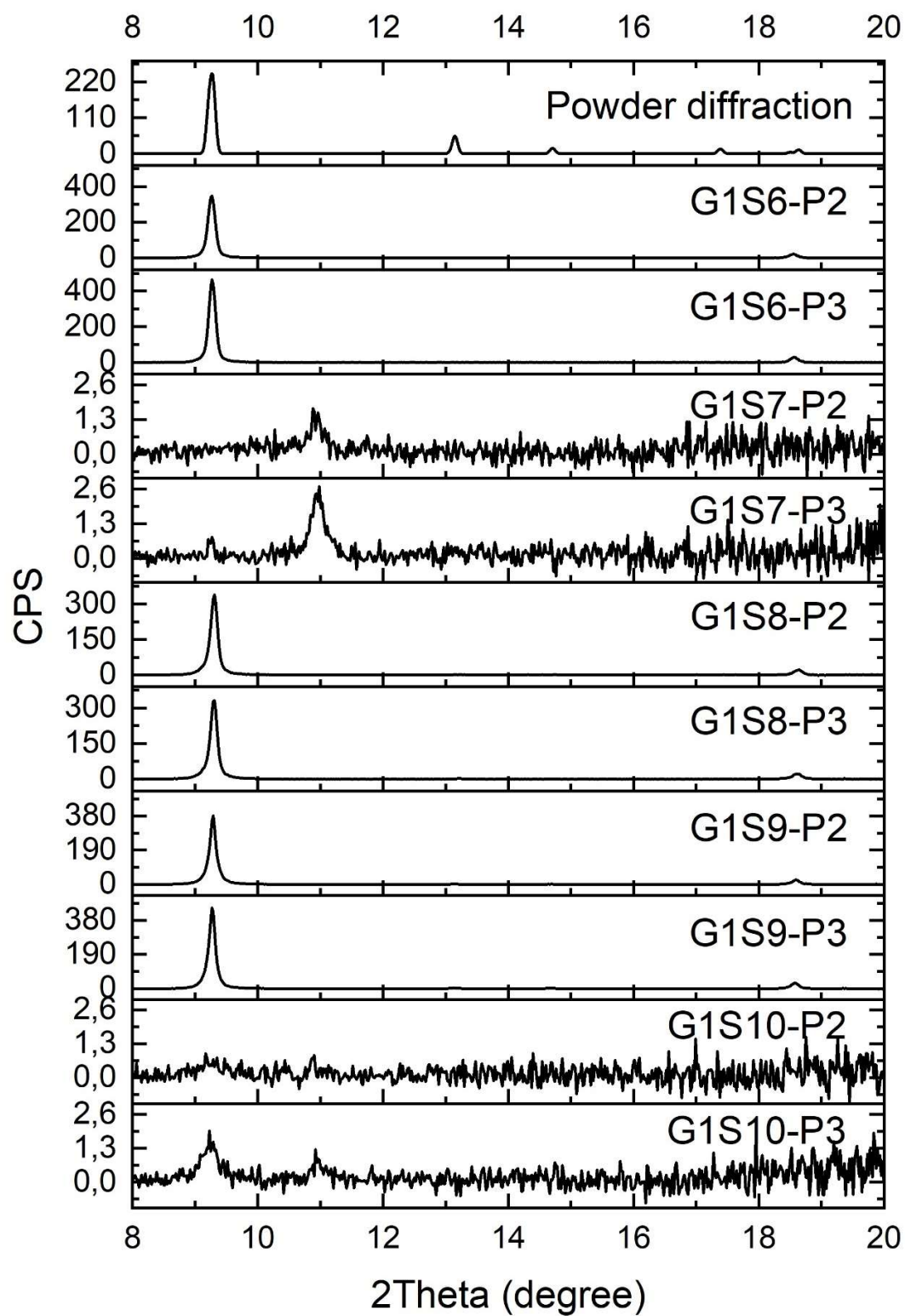


Figure A. 10: X-Ray Diffractograms of Generation 1 for synthesis conditions 6 to 10.

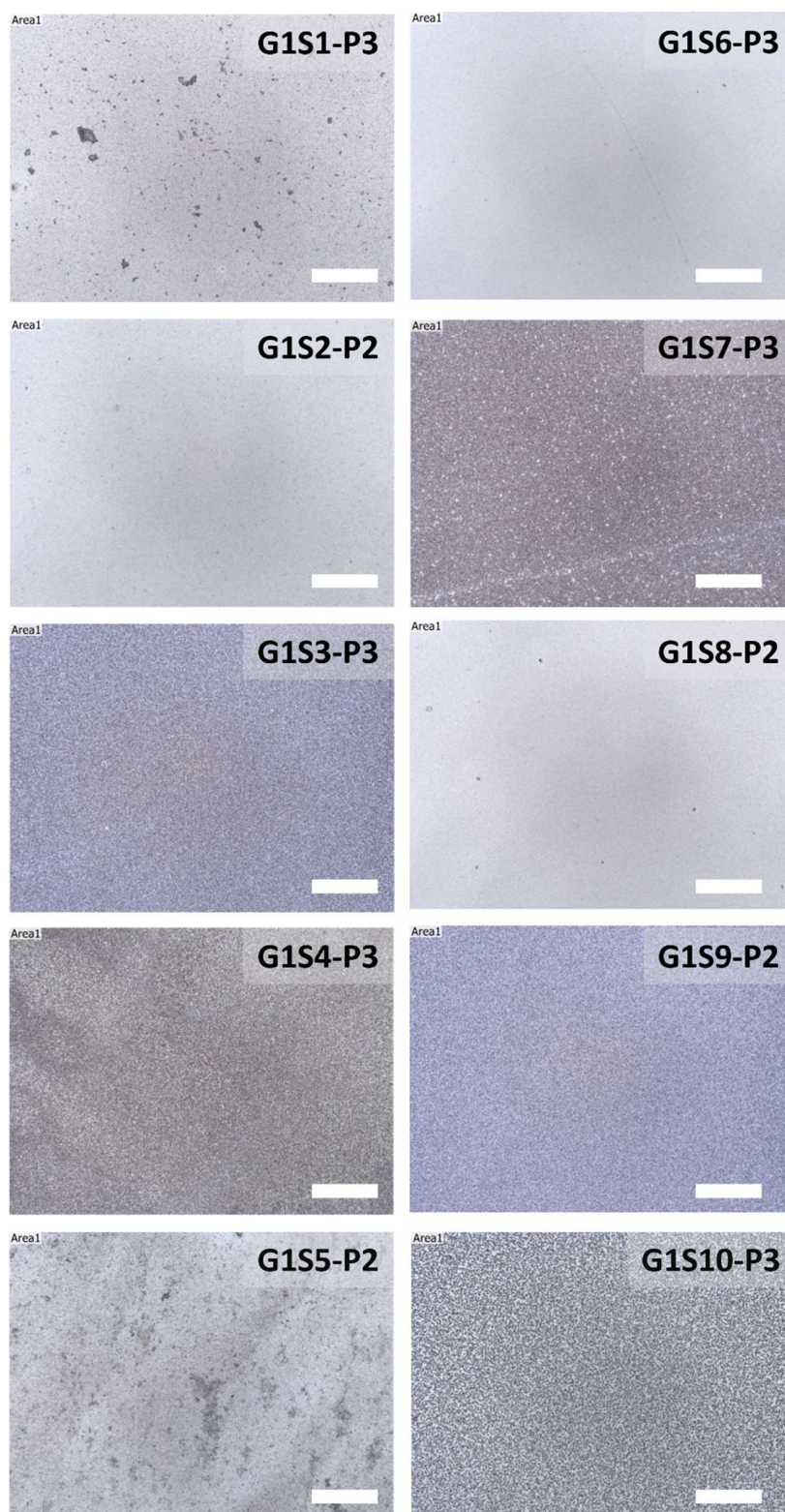


Figure A. 11: Representative confocal microscopy images of $\text{Zn}_2(\text{D-Cam})_2(\text{DABCO})$ from all the synthesis conditions in Generation 1. Scale bar: 50 μm .

A.3. Chemotion labels

Figure 20	a) wi9563-90, b) wi9563-89 c) wi9563-44 d) wi9563-74
Figure 21	a) wi9563-94 b) wi9563-94-1
Figure 22	Cu ₂ (D-Cam) ₂ (DABCO) on CaF ₂ wi9563-99 Zn ₂ (D-Cam) ₂ (DABCO) on CaF ₂ wi9563-99-1 Cu ₂ (D-Cam) ₂ (DABCO) on Quartz wi9563-149 Zn ₂ (D-Cam) ₂ (DABCO) on Quartz wi9563-149-1 Cu ₂ (D-Cam) ₂ (DABCO) on Au wi9563-100 Zn ₂ (D-Cam) ₂ (DABCO) on Au wi9563-100-1
Figure 23	a) wi9563-97-1 b) wi9563-94-1
Figure 25	a) wi9563-141-1 b) wi9563-149-1
Figure 26	a) .Reflectance IR b) .Transmittance IR c) wi9563-140-1 d) wi9563-141-1
Figure 28	wi9563-89-1 wi9563-89-1-1
Figure 29	wi9563-92-1-1
Figure 31	a) wi9563-59-1 b) wi9563-59-1-2
Figure 32	wi9563-59-1-5
Figure 33	a) wi9563-114-1-1 Zn-Dcam-DABCO b) wi9563-141 HKUST-1
Figure 43 and 44	0.5 cycles: wi9563-358 1 cycle: wi9563-355 3 cycles: wi9563-351

	5 cycles: wi9563-352 10 cycles: wi9563-356
Figure 45	1 cycle of seeding layer: wi9563-359-1 5 cycles of seeding layer: wi9563-348-1
Figure 61	a) wi9563-368 b) wi9563-361
Figure 62	wi9563-411 Cu-BDC-DABCO wi9563-411-1 Cu-DATDC-DABCO
Figure 40, A.1, A.2, A.3 and A.4	wi9563-173 Cu-Dcam-DABCO G1S1-P1 wi9563-174 Cu-Dcam-DABCO G1S1-P2 wi9563-175 Cu-Dcam-DABCO G1S1-P3 wi9563-182 Cu-Dcam-DABCO G1S2-P1 wi9563-183 Cu-Dcam-DABCO G1S2-P2 wi9563-184 Cu-Dcam-DABCO G1S2-P3 wi9563-176 Cu-Dcam-DABCO G1S3-P1 wi9563-177 Cu-Dcam-DABCO G1S3-P2 wi9563-178 Cu-Dcam-DABCO G1S3-P3 wi9563-188 Cu-Dcam-DABCO G1S4-P1 wi9563-189 Cu-Dcam-DABCO G1S4-P2 wi9563-190 Cu-Dcam-DABCO G1S4-P3 wi9563-205 Cu-Dcam-DABCO G1S5-P1 wi9563-206 Cu-Dcam-DABCO G1S5-P2 wi9563-187 Cu-Dcam-DABCO G1S5-P3 wi9563-197 Cu-Dcam-DABCO G1S6-P1 wi9563-198 Cu-Dcam-DABCO G1S6-P2 wi9563-215 Cu-Dcam-DABCO G1S6-P3 wi9563-179 Cu-Dcam-DABCO G1S7-P1 wi9563-180 Cu-Dcam-DABCO G1S7-P2 wi9563-181 Cu-Dcam-DABCO G1S7-P3 wi9563-208 Cu-Dcam-DABCO G1S8-P1 wi9563-209 Cu-Dcam-DABCO G1S8-P2 wi9563-202 Cu-Dcam-DABCO G1S8-P3 wi9563-194 Cu-Dcam-DABCO G1S9-P1

	wi9563-195 Cu-Dcam-DABCO G1S9-P2 wi9563-196 Cu-Dcam-DABCO G1S9-P3 wi9563-191 Cu-Dcam-DABCO G1S10-P1 wi9563-192 Cu-Dcam-DABCO G1S10-P2 wi9563-193 Cu-Dcam-DABCO G1S10-P3
Figure 41, A.5, A.6, A.7 and A.8	wi9563-228 Cu-Dcam-DABCO G2S1-P1 wi9563-229 Cu-Dcam-DABCO G2S1-P2 wi9563-230 Cu-Dcam-DABCO G2S1-P3 wi9563-232 Cu-Dcam-DABCO G2S2-P1 wi9563-233 Cu-Dcam-DABCO G2S2-P2 wi9563-234 Cu-Dcam-DABCO G2S2-P3 wi9563-218 Cu-Dcam-DABCO G2S3-P1 wi9563-219 Cu-Dcam-DABCO G2S3-P2 wi9563-220 Cu-Dcam-DABCO G2S3-P3 wi9563-235 Cu-Dcam-DABCO G2S4-P1 wi9563-236 Cu-Dcam-DABCO G2S4-P2 wi9563-237 Cu-Dcam-DABCO G2S4-P3 wi9563-221 Cu-Dcam-DABCO G2S5-P1 wi9563-222 Cu-Dcam-DABCO G2S5-P2 wi9563-223 Cu-Dcam-DABCO G2S5-P3 wi9563-238 Cu-Dcam-DABCO G2S6-P1 wi9563-239 Cu-Dcam-DABCO G2S6-P2 wi9563-240 Cu-Dcam-DABCO G2S6-P3 wi9563-224 Cu-Dcam-DABCO G2S7-P1 wi9563-225 Cu-Dcam-DABCO G2S7-P2 wi9563-226 Cu-Dcam-DABCO G2S7-P3 wi9563-241 Cu-Dcam-DABCO G2S8-P1 wi9563-242 Cu-Dcam-DABCO G2S8-P2 wi9563-243 Cu-Dcam-DABCO G2S8-P3 wi9563-244 Cu-Dcam-DABCO G2S9-P1 wi9563-245 Cu-Dcam-DABCO G2S9-P2 wi9563-246 Cu-Dcam-DABCO G2S9-P3 wi9563-247 Cu-Dcam-DABCO G2S10-P1 wi9563-248 Cu-Dcam-DABCO G2S10-P2

	wi9563-249 Cu-Dcam-DABCO G2S10-P3
Figure 47, 48, 49, A.9, A.10 and A.11	wi9563-378 Zn-Dcam-DABCO G1S1-P2 wi9563-379 Zn-Dcam-DABCO G1S1-P3 wi9563-380 Zn-Dcam-DABCO G1S2-P2 wi9563-381 Zn-Dcam-DABCO G1S2-P3 wi9563-396 Zn-Dcam-DABCO G1S3-P2 wi9563-397 Zn-Dcam-DABCO G1S3-P3 wi9563-394 Zn-Dcam-DABCO G1S4-P2 wi9563-395 Zn-Dcam-DABCO G1S4-P3 wi9563-382 Zn-Dcam-DABCO G1S5-P2 wi9563-399 Zn-Dcam-DABCO G1S5-P3 wi9563-390 Zn-Dcam-DABCO G1S6-P2 wi9563-391 Zn-Dcam-DABCO G1S6-P3 wi9563-392 Zn-Dcam-DABCO G1S7-P2 wi9563-393 Zn-Dcam-DABCO G1S7-P3 wi9563-388 Zn-Dcam-DABCO G1S8-P2 wi9563-389 Zn-Dcam-DABCO G1S8-P3 wi9563-398 Zn-Dcam-DABCO G1S9-P2 wi9563-385 Zn-Dcam-DABCO G1S9-P3 wi9563-386 Zn-Dcam-DABCO G1S10-P2 wi9563-387 Zn-Dcam-DABCO G1S10-P3

A.4. List of publications

Ana C. Fingolo, Nadine von Coelln, Benedikt Zerulla, Marjan Krstić, Christian Huck, Thomas G. Mayerhöfer, Christoph Krafft, Petra Tegeder, Carsten Rockstuhl, Christof Wöll. **Chiral SURMOFs for Vibrational Circular Dichroism: Multiscale Modeling and Experimental Insights**. *Advanced Functional Materials*, 2025, e24088. DOI 10.1002/adfm.202524088.

A.5. Conference contributions

Oral Presentations

“Experimental validation of a multi-scale simulation model for optical properties of chiral SURMOFs.” **6th European Conference on Metal Organic Frameworks and Porous Polymers (EuroMOF)**, Heraklion, Greece, September 2025.

“Top-Down Approaches for SURMOF Patterning”. **Symposium Nano-BW 2023**, Bad-Herrenalb, Germany, December 2023.

“Short Introduction in Thermal Scanning Probe Lithography (t-SPL) and Nanostructuring of SURMOFs with t-SPL”. **KNMFi User Meeting 2023**, Ettlingen, Germany, September 2023.

“Lithographic Structuring of SURMOFs”. **Summer Cluster Meeting 3DMM2O**, Heidelberg, Germany, October 2022.