MOFs across Dimensions: Engineering Heterostructures and Thin Films for Catalysis and Energy Conversions

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Abstract: Metal-organic frameworks (MOFs), as a type of inorganic-organic hybrid porous materials, have attracted enormous research interests over the past two decades due to their extraordinary variability and richness of their chemistry and structures. The original design on MOFs is in pursuit of and high surface area, typically for gas storage. However, the properties in a simple MOF system could not meet the needs for a wide variety of advanced applications. Therefore, it is highly desirable to introduce multiplicities and impart functionalities into MOFs through materials design. In this regard, this dissertation focuses on engineering MOFs in two strategies, constructing heterostructures, fabricating thin films, and evaluating their impact on catalysis and energy conversions. The first chapter focuses on constructing a well-defined interface between materials with vast differences in structural dimensions. Another highlight of this study lies in developing characterization protocols to characterize interfacial structures. In the second part, a MOF-74 thin film with crack-free nature serves as a promising platform for the study of ion transport. The last part of this dissertation reports a new two-dimensional (2D) structure derived from UiO-66. The 2D structure was attained by limiting the coordination number and inducing anisotropic growth. The layered material could be further exfoliated and fabricated into thin films. This work presents strategies to impart functionality to MOFs with rational material design and elucidate their positive impacts on the performance of the whole system.

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1.0 Chapter 1

Introduction

1.1 Metal-Organic Frameworks

Metal-organic frameworks (MOFs), composed of metal ions or clusters joined by bidentate or polydentate organic bridging linkers, are a class of porous crystalline coordination materials.¹ MOFs are also known as porous coordination polymers (PCPs). We will use the terminology "MOFs" in this dissertation for unification. Taken one of the most well-known MOFs, zeolite-imidazolate framework, as an example, two zinc ions in the motif are connected through one 2-methylimidazole linker, forming the ordered three-dimensional network (**Figure 1-1**).² Ever since the first MOF was first reported by Robson *et al.* in 1989³ and the term MOF was introduced by Yaghi *et al.* in 1995,⁴ a rapid growth in the study of MOFs has been witnessed. To date, MOFs and MOF-based materials have been demonstrated to be promising in a wide range of applications, including but not limited to gas storage,⁵ chemical separation,^{6,7} heterogeneous catalysis,⁸ biomedicines,⁹ sensors,¹⁰ and (opto-)electronic devices.¹¹





As a comparably newly-developed type of porous materials, MOFs receive increasing attention mainly because of three characteristics. First of all, crystalline MOFs feature ultrahigh porosity (up to 90% volume) and enormous internal surface area, providing ordered pores and apertures for the residence and diffusion of guest species.¹² Second, the crystallization and overgrowth of MOFs could typically be synthesized under milder conditions compared to zeolites. This feature endows the fabrication of hybrid materials, such as coating MOFs on materials that are not stable under harsh synthetic conditions. In addition, MOFs combine the broad choices of organic linkers with diverse metal ions or clusters, offering a chemical versatility and designable framework. For instance, the pore apertures could be systematically expended from 14 to 98 angstroms (Å), from its original linker with one phenylene ring up to eleven.¹³ To date, the number of collected MOF structures in the Cambridge Crystallographic Data Centre (CCDC) has exceeded 10,000 (March 2021). The highly tunable structures and properties make MOFs tailorable and adjustable for the target applications.

Motivated by the unprecedentedly versatility of MOFs, tremendous efforts have been directed toward the synthesis of new MOF materials featuring new structures. Pioneered by Yaghi, the invention of new topologies relied on designing topological nets and tailoring metal nodes and linker structures, defined as reticular chemistry.¹⁴ Retaining the same topology, isoreticular chemistry endows the systemically tuning on pore dimensions by linker design.¹⁵ Some of these efforts have come to fruition, as many promising structures are attained. For instance, the zirconium cluster-based MOFs are a special subclass as one of the most robust MOFs. They are chemically and thermodynamically stable due to the strong Zr-O coordination bond between metal nodes and carboxylate groups. The rational design of reticular chemistry on Zr-MOFs by adjustable coordination and organic linkers makes them very versatile.¹⁶ Representative examples include UiO-66, NU-1000, and MOF-808 correspond to 12-, 8-, and 6-connected Zr₆ nodes, respectively (**Figure 1-2**). Another type of MOF with wide applications are zeolitic imidazole frameworks (ZIFs), tending to have zeolite-like topologies.² They combine some characteristics of MOF and zeolites, showing ultrahigh surface areas, unimodal microspores, and rich functionalities. Notably, the synthesis of ZIFs are relatively facile and controllable. They can be synthesized at room temperature in the aqueous phase and fabricated to membranes. ZIFs show great potential for gas storage and separation.¹⁷



Figure 1-2. Schematic illustration of 12-, 8-, and 6-connected Zr₆ nodes and their corresponding and representative MOFs, UiO-66, NU-1000, MOF-808, respectively.

1.2 Imparting Functionalities to MOFs

The original design on MOFs is in pursuit of high surface area with relatively high stability, which is to find materials for gas storage, typically hydrogen (H₂).¹⁸ Impressive process has been made in design material with exceptionally high gas capacity,¹⁹ whereas the efforts on improving the performance have not stopped. Later on, the applications of MOFs were extended to separation and heterogeneous catalysts.^{20,21} As studies are developed in-depth, MOFs have been demonstrated to possess huge potentials for a vast of novel applications, including but not limited to sensors, energy-conversion devices, and biomedicines. Clearly, the long-standing goals in MOF fields are to improve the performance of traditional applications and develop materials to accommodate novel applications. Therefore, engineering and modifying the existing MOF structures without altering their underlying topological net are of critical importance. For traditional applications, MOF-74 and its expanded variant M_2 (dobpdc) (M= divalent metal (Mg²⁺, Zn^{2+} , Ni²⁺ etc.); dobpdc⁴⁻ = 4,4'-dioxido-3,3'-biphenyldicarboxylate) are well-known for their CO₂ capture capability due to high concentration of open metal sites (OMSs). Long et al. remarkably improved the selectivity and capacity towards CO₂ capture by appending diamine to OMSs to form ammonium carbamate chains.^{22,23} For novel applications, Allendorf et al. reported a strategy for realizing tunable electrical in HKUST-1 who is inherently insulating by incorporating redox-active guest molecules (7,7,8,8tetracyanoquinododimethane (TCNQ).²⁴ The introduction of TCNQ bridging the meal cluster, dimeric Cu subunits, leads to strong electronic coupling.

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To date, various approaches on engineering MOFs have been reported. For some approaches, the modifications are conducted on the MOF microenvironment. For instance, post-synthetic modifications, a strategy to append functional groups onto MOF moieties via metal nodes or organic linkers, has been developed, as well as post-synthetic deprotection.^{25,26} Furthermore, MOFs can serve as hosts to confine guest molecules. For

instance, catalysts,²⁷ fluorescent dyes,²⁸ and small molecule drugs²⁹ are encapsulated in the cavity of MOFs. With Li *et al.*, our group encapsulated multiple dyes into ZIF-8 composed of multi-shells (**Figure 1-3**).^{28,30} The dyes are spatially confined in different layers, reducing the energy transfer between encapsulated dyes and attaining white-light emission. In addition, approaches that aim at engineering the dimensions and structures have also been developed. The extraordinary degree of variability makes MOFs ideal as candidates for hybrid heterostructures, which could bring synergistic multifuntionaly.³¹ In the meanwhile, the processing of MOF as films has attracted a lot of attention due to the needs of many novel applications, such as sensors,¹⁰ energy-conversion devices,³² and membranes.³³ Besides, to eliminate transport limitations, mesopore networks are incorporated in microporous MOFs to construct hierarchical pore structures.³⁴ These promising approaches mentioned above demonstrate the success in exploring new functionality and properties on the basis of simple MOF systems.



Figure 1-3. Incorporating dyes into multi-layered ZIF-8 for white-light emission.²⁸

With these toolsets, the scope of MOFs has been widely extended. This dissertation focuses on building up MOF-based heterostructures and thin film. In doing so, we aim at addressing the current challenges presenting in the engineering of MOF materials, which

limits or undermines the performance of MOF in target applications. Chapter 2 presents a strategy to construct an aligned interface between metal and MOF, which is of great importance for improving the selectivity for metal-based catalysts. In chapter 3, a crack-free MOF thin film was synthesized, serving as an ideal platform for the study of selective ion transport. Inspired by the results in chapter 3, chapter 4 discussed a strategy to attain MOF with 2D structure. The material shows the potential to be fabricated to even thinner film with controllable thickness and tunable functional groups, designed for future usage as ionic conductors.

1.3 Design and Synthesis of MOF-based Heterostructures

MOF-based heterostructures hierarchically combine multiple components with the difference in chemical composition and crystal structures into one single system. The heterostructures are also frequently referred as hierarchical materials in literature.³⁵ The structural hierarchy integrates multifunctionalities and bring cooperative effects. It has been shown that they outperform single-component material in a wide scope of applications, such as separation,³¹ catalysis,³⁶ photoelectronics,³⁷ and biomedicine.³⁸ Lee *et al.* reported an intergrown membrane by heteroepitaxial growing ZIF-67 (Co-substituted ZIF-8) on ZIF-8 for the propylene/propane separation.³⁹ The heterostructures significantly increased the separation factors from ~85 (with only ZIF-8) to ~200. Besides, the integration of two MOF materials can also lead to innovative applications. Besides the most widely discussed and investigated MOF-MOF materials discussed above, the applications of hierarchical MOFs have been greatly extended by the design of more complicated heterostructures, including MOF-COF (covalent-organic frameworks),⁴⁰ MOF-metals,⁴¹

MOF-oxides (hydroxides),^{42,43} MOF-perovskite,⁴⁴ MOF-GO (graphene oxide),⁴⁵ and MOF-cellulose.⁴⁶

For MOF-based heterostructures, their interfacial structures are of critical importance as they greatly influence the overall performance, such as mass transport,⁴⁷ ion diffusion,⁴⁸ electron transfer,⁴⁹ and electronic structures.³⁷ For example, Howard *et al.* fabricated A-B-A heterostructured MOF films (A represents Zn-ADB and B represents Zn-(Pd-DCP)) by epitaxial growth.³⁷ The photon upconversion was realized by the triplet excitons, which transferred through the chemical bonds at the heterojunctions. Xu *et al.* encapsulated Co-MOF nanocrystals in a rGO network with a strong chemical interaction at the interface, obtaining a high-performance anode for potassium ion batteries.⁵⁰ They found that the chemical bonded interface greatly promoted the charge transfer, adsorption , and diffusion of K⁺ within MOFs.

In general, the interfaces can be divided into two categories: indirect and direct interfaces. Indirect hetero-interfaces are very common between materials with a large degree of lattice mismatching. Therefore, the overgrowth of the second layer will not be directly guided or induced by core material. In order to initiate the overgrowth, surfactants or polymers were often introduced to modulate the formation process.⁵¹ For example, Kitagawa *et al.* developed a strategy hybridizing UiO-66-NH₂ and MIL-125-NH₂ into one system, with polyvinylpyrrolidone (PVP) as the structure-director agent.⁵² The PVP coated on the UiO-66-NH₂ particle and its carbonyl groups induced the overgrowth by interacting with the metal ions of MIL-125-NH₂. However, these directing reagents will remain at the interface, leading to a discontinuous pore network or crystal structure. It is also challenging to predict the potential impact on the overall properties. At direct hetero-interfaces, direct

interactions, either strong covalent bonds or weak van der Waals attraction, shall exist. There are no gaps or other chemical species at the interfaces. Direct chemical bonding could lead to a continuous pore network and crystal structure, or even tune the electronic profiles at the interface. The direct interface could be easily realized by epitaxial growth, especially for MOFs with the same topology. Typically, it features facet alignment or relative orientation between layers. Apart from that, the direct interface can be achieved between MOFs with different topologies, namely selectively epitaxial or site-specific growth.^{53,54} For example, ZIF-8 was epitaxially grown on the specific {110} facets of MIL-125 via its {020} facets.⁵⁵ The epitaxial growth could also be extended to the hybrid material composed of MOF and other materials. At the same time, it is definitely more challenging due to the large difference in structural dimensions. However, the intermarriage of MOFs and other materials could open up a new route for applying MOFs. An exciting example is an introduction of MOFs to the halide perovskites to enhance the photovoltaic properties of perovskite solar cells.^{56,57} The incorporation of MOF improves the connection at the interface, enhancing the efficiency of electron or hole efficiency.



Figure 1-4. Hetero-interfaces with lattice mismatch. Adapted with permission from ref [58]. Copyright 2014 American Chemical Society.

Despite the difficulties, MOFs hold great potential to achieve hierarchical assembles with direct interfaces. For one, MOFs possess diverse crystal topologies, and their structural dimensions can be easily altered through tuning the metal nodes or organic linker. Second, the frameworks of MOFs are highly flexible and intrinsically elastic, tolerating the lattice constant mismatch as significant as 20% (Figure 1-4).⁵⁸ Motivated by the enormous potentials, we have devoted ourselves to design the hetero-interfaces in MOF-based materials. Chapter 2 discusses a strategy to create an aligned interface between metal and MOF, featuring vast differences in structural dimensions. The challenge was addressed through mediating MOF growth on metal nanoparticles (NPs) capped by the weakly bound capping agents, which were concurrently removed during the formation of MOF coating. A well-defined core-shell structure of one metal NP in one single-crystalline MOF shell was generated. Protocols of spectroscopic analysis were conducted, revealing the direct interfacial structures. The importance of having a well-defined interface was demonstrated by using the attained materials for the hydrogenation of unsaturated aldehyde, where the selectively was significantly improved.

1.4 Integration of MOFs onto surfaces or devices: MOF thin films

In recent years, novel features of MOFs have been discovered and developed, including electronic, optical, thermoelectric, and magnetic properties. The utilization of these novel properties needs MOF thin films that are supported on various substrates. So far, several strategies have been developed to deposit and synthesize MOF thin films.

The most direct method is to deposit as-synthesized MOF particles on substrates. The MOF particles are generally synthesized with the conventional solvothermal approach and then suspended in solution prior to the deposition. Drop-casting, electrospray, spincoating will assist the deposition process.⁵⁹ To improve mechanical stability, polymers could be used as binders.⁶⁰ This method is very straightforward but lacks control in many aspects, such as orientation and morphology. In general, the thickness of the film obtained by casting MOF particles falls in the range of several to dozens of micrometers, which may not meet the needs of fabricating MOF into devices.

The solution-based approach is modified and developed based on the understanding of solvothermal synthesis for MOF particles. Typically, the substrate is immersed into MOF precursors, and MOF particles form on the substrate, resulting in polycrystalline MOF films. The early studies using this approach showed low surface coverage, poor uniformity, and inefficient thickness control.⁶¹ Modifications have been made to optimize this approach. For instance, Bein *et al.* reported the vapor-assisted conversion method to synthesize uniform UiO-66-type MOFs.⁶² The MOF precursors were directly deposited on the substrate and separated from the solvent, which served as a vapor source during synthesis. Therefore, the thickness could be controlled by adjusting the amount of precursors placed on the substrate. To date, various approaches have been reported to modify the solution-based approach, such as interfacial synthesis,⁶³ electrodeposition,⁶⁴ and microwave-assisted synthesis.⁶⁵

In contrast to the conventional solution-based approach, where reactants are mixed and reacted under solvothermal conditions, a stepwise layer-by-layer (LbL) epitaxial strategy was established by Wöll *et al.*⁶⁶ The substrate is sequentially immersed in solutions containing individual precursors. Therefore, the metal ions and organic linkers are deposited on the surface in a layer-by-layer manner. For LbL epitaxial growth, one essential requirement is that the surface of the substrate is modified with self-assembled monolayers (SAMs). SAMs expose termination groups, such as –COOH, -SH, -OH, -NH₂ moieties, anchoring the metal ions during the initial cycle.⁵⁹ The existence of SAMs also guide the anisotropic growth, leading to films with orientation. In the meanwhile, the sequential fashion enders a comparably precise thickness control. The LbL epitaxial synthesis is one of the most widely used strategies. However, the SAMs remaining at the interface, generating indirect contacts between material and substrate and create an interfacial environment hard to predict. For example, in an electron-related process, the charge transfer between the substrate and materials can be altered by the SAM layer in the middle. Another influence is the mass transport, during which the pathway of the reactants from MOF to the substrate might be interrupted.

Another approach that could realize precise thickness control is gas-phase synthesis, chemical vapor deposition (CVD), and atomic layer deposition (ALD). Ameloot *et al.* used CVD to synthesize ZIF-8 film with a controllable thickness.⁶⁷ The silicon pillar array was deposited with zinc oxide, which was then converted to ZIF-8 film by exposing in the vapor of the linker. Although CVD and ALD are well-established techniques for microdevice fabrication, they are still a new field for MOF synthesis. So far, only limited types of MOFs films are successfully synthesized by the gas-phase approach, including ZIF-8, UiO-66,⁶⁸ and Ca-BDC (terephthalic acid).⁶⁹ In the meanwhile, using volatile precursors is crucial, which may be a limiting factor for the broader usage.

MOF thin films could also be fabricated by the stacking of MOF nanosheets (MONs). MONs refer to materials possessing a continuous network composed of metal nodes linked by organic linkers in two dimensions, with non-coordinating bonds on the

third dimension.⁷⁰ They are highly anisotropic materials with large lateral sizes, while the thickness is only single or few atoms thick (typically less than 5 nm).⁷¹ There are two distinct strategies to synthesize MONs. In "bottom-up" method, MONs can be directly synthesized with the assistance of modifiers or additives, such as surfactants and modulators. MONs could also be attained by exfoliating layered MOF materials, similar to the idea of separating graphite. The suspension with dispersed MONs in solvent could be drop-casted on the substrate. The MONs tend to stack on the substrate with the preferred orientation at [001]. The transfer process could also be facilitated by the layer deposition technique. Zhang et al. assembled tetra(4-carboxyphenyl)porphine (TCPP)-based MONs into films via Laugmuir-Schäfer transfer.⁷² The strong π - π interactions aroused by TCPP between layers ensured the deposition.

In summary, the strategies are generally classified into five categories: (a) particlecasted film; (b) solution-based approach; (c) layer-by-layer (lbl) epitaxial growth; (d) gasphase synthesis; (f) films composed of deposited MOF nanosheets. These versatile approaches provide a toolbox for fabricating MOF thin films. In the meanwhile, they all have advantages and limitations. As such, further development and modifications to these methods are necessary in order to meet the needs of a specific application. In chapters 3 and 4, the focus is put on fabricating thin films as the platform for the investigation of ion transport. Chapter 3 shows that MOF-74 can enable selective Mg²⁺ transport by using the form of thin film, synthesized by a modified solution-based approach. This feature shows the potential of MOFs as the solid electrolytes for multivalent cations in conversion batteries. On the basis of chapter 3, we see the need further to improve the selectivity of MOF for ion transport. In response, Chapter 4 describes a strategy to synthesize a UiO-66derived MOF with a 2D structure by introducing coordination hindrance. The 2D structure can be further exfoliated to MONs and deposit on the desirable substrate as a film with better control in thickness.

1.5 The scope of this dissertation

While efforts are continuously devoted to the fields, a more extensive area with fascinating directions is emerging through the introduction of multiplicity and sophistication into simple MOF systems, which greatly extend the scope of MOFs. Increasing attention is attracted by exploring novel applications and creating new systems; however, nontrivial deficiencies brought by materials design are often ignored, which miss the opportunity to discover underlying properties and undermine the potential of materials. We see that the existing challenges impede the further improvement of the performance of MOF-based materials. In response, this dissertation identifies the gaps in material design that has a significant impact on the corresponding applications, and bridge them by developing rational synthetic approaches to create well-defined MOF structures. Our research interests lie in designing MOF-based heterostructures and thin film. Chapter 1 focuses on the challenge in obtaining direct interfaces between metal nanoparticle and MOFs, which is of critical importance for the selective catalysis process. A rational strategy to mediate MOF growth on metal nanoparticles, by concurrently dissociating weakly adsorbed capping agents. Combining spectroscopic analysis with conventional techniques, a direct and clean interface with ordered crystal orientation is demonstrated. The further catalytic study emphasizes the importance of a well-defined interface, as the selectivity is greatly improved. The second half of this dissertation discusses using MOF as ionic

conductors, typically for multivalent cations (Mg^{2+}) . As a nascent field, pioneer work employed powders as the study platforms. Chapter 3 presents a study on ion transport in MOF-74. Taking advantage of the film form, we are able to demonstrate its selectivity towards unwanted species and its capability as solid separators. To further improve the performance of MOF as ionic conductors, Chapter 4 is developed based on our understanding established in Chapter 3. We show a synthetic approach to attain UiO-66derived 2D structures by limiting coordination anisotropically. The 2D structure can further be engineered to MONs, composing a controllable thin film. The functional groups are able to be induced through linker exchange, tailoring the binding strength with ions, and tuning the ionic behaviors. To a larger extend, we see the opportunity to organically connect the two directions, heterostructures and MOF thin film, to construct hybrid MOF thin films with the well-defined structure for future applications.

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2.0 Chapter 2

Creating an Aligned Interface between Nanoparticles and MOFs by

Concurrent Replacement of Capping Agents



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2.1 Abstract

Applying metal-organic frameworks (MOFs) on the surface of other materials to form multifunctional materials has recently attracted great attention; however, directing the MOF overgrowth is challenging due to the orders of magnitude differences in structural dimensions. In this work, we developed a universal strategy to mediate MOF growth on the sur-face of metal nanoparticles (NPs), by taking advantage of the dynamic nature of weakly adsorbed capping agents. During this colloidal process, the capping agents gradually dissociate from the metal surface, replaced in situ by the MOF. The MOF grows to generate a well-defined NP-MOF interface without trapped capping agent, resulting in a uniform core-shell structure of one NP encapsulated in one single-crystalline MOF nanocrystal with specific facet alignment. The concept was demonstrated by coating ZIF-8 and UiO-66-type MOFs on shaped metal NPs capped by cetyltrimethylammonium surfactants and monitored by spectroscopies. The defined interface outperforms ill-defined ones generated via conventional methods, displaying a high selectivity to unsaturated alcohols for the hydrogenation of an α,β -unsaturated aldehyde. This strategy opens a new route to create aligned interfaces between materials with vastly different structural dimensions.

2.2 Introduction: Interface Control of NP-MOF Nanocomposites

Great effort has been devoted to designing interfaces, as their structure shows a large influence on the performance of the whole system in various fields, such as electronics, biomedicines, and separations.^{1–5} Recently, focus has been extended to complicated interfaces, which are composed of materials with distinct chemical

components or crystal lattices.^{5–8} For instance, to improve the selectivity of metal nanoparticle (NP) catalysts, applying metal-organic frameworks (MOFs) to the metal surface has recently been identified as an apt strategy for this long-standing and challenging goal.^{9–12} Selectivity control in this strategy relies on the structure of the NP-MOF interface, but interfacial structure remains difficult to control because metals and MOFs have distinct chemical compositions and structural dimensions that differ by orders of magnitude.

Currently, the most common approach to generate a controlled interface is to first synthesize shaped NPs through colloidal methods and then coat them with MOFs.¹³ Compared to conventional impregnation methods,^{9,14,15} this approach indeed provides better control over the morphology and size of the metal NPs. However, it relies on adding capping agents, such as long-chain hydrocarbon surfactants (e.g., oleic acid) or polymers (e.g., polyvinylpyrrolidone), which are normally trapped at the NP-MOF interface during coating, interrupting MOF growth and preventing direct contact between the NP and MOF.^{16,17} This interfacial residue is a general dilemma in many composite materials.¹⁸ To solve this issue, we herein propose a new strategy to generate a well-defined interface in hybrid materials by introducing weakly adsorbed capping agents to mediate MOF growth (**Figure 2-1**). During growth, these capping agents gradually dissociate from the metal surface and the MOF directly grows on the gradually exposed NP surface. We hypothesize that when this in situ replacement is well mediated, a controlled interface between the MOF and NP can form.


Figure 2-1. The formation of a direct NP-MOF interface using dynamic, weakly-adsorbed capping agents.

2.3 A new approach to constructing direct NP-MOF interface

To demonstrate this concept, we first selected zeolitic imidazolate framework-8 (ZIF-8) as the MOF and shaped metal NPs with cetyltrimethylammonium bromide (CTAB) as the surfactant.^{19,20} We introduced CTAB-capped NPs into a solution with fine-tuned amounts of MOF precursors. Because it has been reported that the gradual dissociation of CTAB can be trigged by changes in the chemical environment.^{21–23} The rates of dissociation and in situ MOF growth were balanced by adjusting the CTAB and MOF precursor concentrations. Under optimized conditions, we obtained a core-shell structure with one metal NP encapsulated in one single-crystalline ZIF-8 nanocrystal, showing specific facet alignment at the inter-face. Coupling the information gained from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Raman spectroscopy, the in situ replacement of capping agents by MOFs, leading to the formation of a direct interface, was revealed. With this understanding, we then applied our approach to encapsulate NPs into a more chemically stable Zr-based MOF. UiO-66-type (University of

Oslo 66) MOFs have distinct chemical properties and crystal topologies from ZIF-8, demonstrating the generality of our method. Finally, a model reaction, the hydrogenation of an α , β -unsaturated aldehyde, was carried out over samples generated with and without the well-mediated process. The well-defined interface showed over 99.0 % selectivity toward the desired unsaturated alcohol, outperforming the sample without a well-controlled inter-face (85.1 % selectivity). This work sheds light on the process of creating well-defined interface between materials with vastly different structural dimensions.

2.4 Capping agent-mediated MOF growth

Cubic Pd NPs capped by CTAB (Pd-CTAB NPs) were synthesized through an established method that has been used to synthesize various metal NPs with defined shapes,²⁴ sizes,²⁵ and compositions.²⁶ The Pd-CTAB NPs were then added into a solution containing ZIF-8 precursors (2-methyl imidazole (2-mim) and zinc nitrate (Zn(NO₃)₂)). We found that CTAB dissociation was indeed triggered after the NPs were exposed to aqueous 2-mim (**Figure 2-2a**). The amount of CTAB in the supernatant was found to increase with time, as shown in **Figure 2-2b**, suggesting that CTAB gradually and continuously dissociates from the metal surface, finally resulting in agglomeration of the metal NPs. To control the dissociation of CTAB while avoiding the aggregation of metal NPs during the MOF coating, the concentration of each component was con-trolled to fine-tune the kinetics of each process. The detailed concentrations and procedures can be found in the supporting information (**Experimental Methods**). Under the optimized conditions, ZIF-8 was evenly coated on individual Pd NPs, forming Pd@ZIF-8 with a one-to-one, core-shell structure (**Figures 2-3 a-b**). The single-crystalline nature of ZIF-8 coating was

revealed by selected area electron diffraction (SAED) taken along the [001] zone axis (**Figure 2-3c**), where spots from the {200} and {110} planes can be clearly observed. The well-defined NP shape was also preserved after coating. Clear electron diffraction patterns indicating single-crystalline Pd was observed while decreasing the working distance, showing {200} and {220} planes along the [001] zone axis (**Figure 2-3d**). With further analysis of the relationship between two diffraction patterns, we have observed that the [100] direction of the ZIF-8 crystal aligns well with the [100] direction of the Pd nanocrystals, indicating a facet alignment along the [001] direction despite the vastly different structural dimensions (**Figure 2-3e**). This alignment was also observed by powder X-ray diffraction (XRD). When the core-shell particles are well assembled on the substrate, both Pd and ZIF-8 showed enhanced diffraction intensity corresponding to the {100} facets (**Figure 2-3f**). This unique alignment is discussed in detail later.



Figure 2-2. Pd-CTAB NPs treated with 2-mim. (a) Photographs of Pd-CTAB NP suspensions after incubation in (i) pure water, (ii) aqueous 2-mim, (iii) aqueous CTAB, and (iv) aqueous Zn(NO₃)₂. The dissociation of CTAB caused the aggregation of Pd NPs, which resulted in the loss of the brown color in solution and the formation of black precipitates. (b) Quantitative analysis of CTAB by ¹H-NMR. (c) Sample ¹H NMR spectrum for the quantitative analysis of the amount of CTAB in solution.



Figure 2-3. One-to-one encapsulation of metal NPs in ZIF-8. (a) SEM image, (b) TEM image, (c-d) SAED patterns of Pd and ZIF-8 along [001] directions, (e) 3D modeling projections at [001] directions, and (f) XRD patterns of Pd@ZIF-8.

2.5 Investigation of the interfacial structure

Since global techniques like SEM, TEM, and XRD do not provide direct evidence of the interfacial structure, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Raman spectroscopy were used to characterize the interfacial structures of Pd@ZIF-8 composites. We sought to understand the interface from two perspectives: First, is capping agent trapped at the NP-MOF interface? Second, is the MOF coated directly onto the met-al surface?

To answer the first question, we employed carbon monoxide as a probe molecule to test the metal surface through CO-DRIFTS.^{27,28} The small size of CO allows for its diffusion through the ZIF-8 shell to access the metal surface, and the vibrational stretching mode of adsorbed CO is sensitive to the nature of the metal surface.²⁹ Therefore, the characteristic CO stretching frequency can be used to determine the amount of adsorbed capping agent on the metal surface.^{30,31} To establish a reference for our system, we first carried out CO-DRIFTS on pure Pd NPs, with or without CTAB, supported on an inert substrate. As shown in Figure 2-4, three clear IR bands were observed for the clean Pd surface, which can be grouped into three binding modes: 2050-2100 cm⁻¹ for linearly bound CO (CO_{atop}), 1950-2000 cm⁻¹ for bridging bound CO (CO_{bridge}), and 1875-1925 cm⁻¹ for threefold bound CO (CO_{threefold}).^{32,33} On the other hand, when CTAB adsorbed on the Pd surface, only the CO_{threefold} band was observed. To verify that this difference can be used to monitor changes in adsorption behavior at the metal surface, we added CTAB to the clean Pd surface. We were indeed able to observe conversion from three distinct bands to one threefold band (Figure 2-4). These data clearly show that the CO_{atop} band is sensitive to the adsorbed CTAB and changes in its intensity can be used to monitor the Pd NP surface. Using CO-DRIFTS, we investigated the changes of the CTAB on Pd NP surface in the presence of ZIF-8 precursor. As shown in **Figure 2-5**, the intensity of the CO_{atop} peak (~ 2080 cm⁻¹) increased with precursor treatment time, indicating the gradual dissociation of surface CTAB, which agrees well with the previous NMR supernatant study (**Figure 2-2b**). Notably, for the Pd@ZIF-8 product after coating, a high-intensity CO_{atop} mode was seen, along with two distinct peaks at 2020 cm⁻¹ and 2000 cm⁻¹ attributed to ZIF-8. This observation fits well with our hypothesis that the weakly-adsorbed capping agent gradually dissociates from the metal surface during the formation of the MOF shell.



Figure 2-4. CO-DRIFTS spectra of Pd-CTAB NPs, the clean Pd surface, and the clean Pd surface after adding CTAB.



Figure 2-5. CO-DRIFTS study on the dissociation of CTAB. (a) Schematic illustration of CTAB dissociation during MOF coating. (b) CO-DRIFTS spectra of Pd-CTAB NPs, Pd-CTAB NPs incubated in MOF precursor (2-mim) for 5 min and 30 min, Pd@ZIF-8 with direct interface, and ZIF-8.

To further study the behavior of CTAB at the interface and determine whether there is a direct contact between the MOF shell and the metal surface, Au NPs (Au-CTAB NPs, **Figure 2-6**) were employed to allow for surface-enhanced Raman spectroscopy (SERS) studies.³⁴ As shown in **Figure 2-7**, Au-CTAB NPs showed a vibrational signal at 175 cm⁻¹, referring to the stretching of the bond between the Au surface and the adsorbed Br⁻ of the capping agent.^{35,36} After the introduction of the Au-CTAB NPs to the ZIF-8 precursor, however, the vibrational signal at 175 cm⁻¹ greatly decreased. This result indicates CTAB dissociates from the metal surface in the presence of MOF precursors, which agrees well with the IR observations (**Figure 2-5**). Interestingly, it also suggests that CTAB

dissociation is accomplished by removal of the whole surfactant molecule, including both cations and anions. A set of bands also appeared in the 800-1500 cm⁻¹ region (Figure 2-7), which was assigned to the vibrations of 2-mim in ZIF-8 (Table 2-1).³⁷ It has been reported that the 2-mim could interact with the metal surface through the imidazole "pyridine N", so we compared the spectral feature of out-of-plane bending modes of NH (γ (NH)) at around 928 cm⁻¹.^{38,39} The stretching of NH was absent in bulk ZIF-8 due to the deprotonation of 2-mim when forming Zn-N bonds (Figure 2-23). Therefore, the observation of NH bending at 928 cm⁻¹ in Au@ZIF-8 could be attributed to the 2-mim at the NP-MOF interface. After the NH moiety interacted with the metal surface, the interaction would lead to a weaker NH bending, resulting in a red-shift of the N-H bending frequency. In the spectra, Au@ZIF-8 sample showed a redshift of the NH bending mode (928 cm⁻¹) compared to free 2-mim (935 cm⁻¹), suggesting the adsorption of ZIF-8 on the metal surface through the imidazole "pyridine N" (see Experimental Methods for more detailed discussion). This result provides further evidence that ZIF-8 has direct contact with the metal surface.



Figure 2-6. Electron microscopy of Au@ZIF-8 with a direct interface by (a) SEM and (b) TEM.



Figure 2-7. in situ Raman spectra for the formation of Au@ZIF-8 with a direct interface. The capping agents were observed to dissociate during MOF coating, forming direct contact between ZIF-8 and the metal surface.

 Table 2-1. Vibrational assignments of surface-enhanced Raman spectroscopy peaks for 2

 mim on Au.

Raman Shift (cm ⁻¹)	Vibrational Assignment ^[a]
678	$\nu(\rm CCH_3)$
928	$\gamma(NH)$
1123	$\delta(ext{CH})$
1351	$\nu(\text{Ring})$

^[a] Signal assignments are based on a previous report of 2-mim on a Ag surface.³⁷

2.6 Testing the importance of efficient CTAB dissociation

Next, we investigated the correlation between the capping agent dissociation process and the resulting interfacial and material properties. To that end, we carried out a control experiment where the kinetically inefficient dissociation of CTAB was intentionally designed (see **Experimental Methods** for details) by introducing excess CTAB into the solution during the ZIF-8 coating (**Figure 2-8a**). Indeed, the dissociation of CTAB was significantly suppressed with an increased amount of exogenous CTAB as shown by the missing of CO_{atop} band in CO-DRIFTS (**Figure 2-8b**). This suggests that the sluggish desorption kinetics kept the CTAB molecules on the metal surface, trapping them at the interface in the final encapsulated Pd@ZIF-8 sample and resulting in an indirect interface.



Figure 2-8. CO-DRIFTS study on the dissociation of CTAB with high concentration. (a) Schematic illustration of CTAB dissociation with a higher concentration of CTAB present during MOF coating. (b) CO-DRIFTS spectra of Pd-CTAB NPs, Pd-CTAB NPs incubated in MOF precursor with exogenous (0.8 mM) CTAB for 5 min and 30 min, and Pd@ZIF-8 with indirect interface.



Figure 2-9. The impact of CTAB dissociation on MOF coating. Schematic illustrations, SEM images, and TEM images of Pd@ZIF-8 with (a, d, g) a direct interface and with an indirect interface obtained using an exogenous CTAB concentration of (b, e, h) 0.8 mM and (c, f, i) 1.2 mM.



Figure 2-10. Quantitative analysis of the effect of surface CTAB on MOF growth. Blue square **•**: The CTAB amount in the supernatant after treating Pd-CTAB NPs with 2-mim (50 mM) for different lengths of time, monitored by ¹H NMR. The higher amount in the supernatant, the lower amount of surface CTAB. Red diamond **•**: The ratio of single-crystalline coating in Pd@ZIF-8 samples obtained by treating Pd-CTAB NPs with 2-mim for different lengths of time before encapsulation. The numbers of the single- and polycrystalline Pd@ZIF-8 were counted through SEM images.

Notably, polycrystalline ZIF-8 coatings (Figure 2-9b, e, h) were observed with indirect interfaces formed in the presence of excess exogenous CTAB. This result is in sharp contrast with the single-crystalline Pd@ZIF-8 (Figure 2-9a, d, g). When the concentration of CTAB additive further increased, NPs were even only partially coated with ZIF-8 (Figure 2-9c, f, i). The homogeneity of the ZIF-8 shell coating, then, has a direct relationship with the amount of CTAB on the metal surface. This idea is further

supported by the positive relationship between the amount of surface CTAB and the yield of polycrystalline ZIF-8 coatings (**Figure 2-10**, see **Experimental Methods** for details; **Table 2-2**). To have a better understanding on the process, the early stages of both singleand polycrystalline formation were also investigated by EM (**Figure 2-11**). The ZIF-8 crystal growth was found to initiate at a single point to form single-crystalline Pd@ZIF-8 materials. In contrast, for polycrystalline Pd@ZIF-8, generated via Pd NPs with more CTAB on the surface, multiple ZIF-8 seeds formed and sur-rounded one NP at an early stage. We thus reason that the interfacial CTAB alters ZIF-8 nucleation and interrupts its growth, generating not only an indirect interface but also polycrystalline coatings. In other words, the dynamic replacement process allows for a capping-agent-free interface with a better-controlled crystal structure. Further impact of the interface on the engendered materials will be discussed in the next section.



Figure 2-11. Investigation of the early stages of ZIF-8 coating over Pd@ZIF-8 with (a) direct and (b) indirect interfaces.

2.7 Interface cleanliness and facet alignment

The difference between the samples with direct and indirect interfaces were additionally analyzed by thermogravimetric analysis (TGA) and a model hydrogenation reaction. As shown in **Figure 2-12a**, the resulting TGA curves showed similar features as pure ZIF-8 crystals for both samples, while the larger weight-loss for the indirect sample was credited to the trapped CTAB molecules. To further verify that the trapped CTAB is on the metal surface at the interface, we used gas-phase ethylene hydrogenation as a probe reaction (**Figure 2-12b** and **Table 2-3**). As expected, the sample with a direct interface displayed a reaction rate of $1.78 \times 10^{-3} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{Pd}^{-1}$, which is 3.5-fold higher than that of the sample with an indirect interface ($5.02 \times 10^{-4} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{Pd}^{-1}$). This indicates that the direct interface is cleaner and thus more catalytically active than the indirect interface, where a large number of active sites on the Pd surface were occupied by capping agent.



Figure 2-12. TGA analysis (a) and ethylene hydrogenation (b) of Pd@ZIF-8 with a direct interface (red) and an indirect interface (grey).



Figure 2-13. PXRD patterns of Pd@ZIF-8 with (red) a direct or (green) an indirect interface. PXRD patterns (a) from 5 to 30 degrees, displaying characteristic ZIF-8 peaks, and (b) from 35 to 65 degrees, displaying characteristic Pd peaks.

PXRD patterns of the two samples drop-casted on sub-strates were also compared (**Figures 2-13** and **2-14**). For samples with an indirect interface, the XRD patterns were in good agreement with the simulated patterns of ZIF-8 and Pd metal. For sample with direct interface, the cubic Pd@ZIF-8 particles tended to self-assemble on the substrate along the [001] direction of ZIF-8 due to their high uniformity, as evidenced by the enhanced intensity of the (200) diffraction peak. In stark contrast, the (110) peak possessed the highest intensity in the diffraction profile of the sample with the indirect interface (as seen in typical ZIF-8 powders due to its crystal structure).⁴⁰ A preferential orientation along the [100] direction of the encapsu-lated Pd NPs was also observed. The dominant peak of the sample with a direct interface was found to be (200), while the dominant peak of randomly

oriented Pd NPs should be (111).⁴¹ This concerted orientation of both ZIF-8 and Pd crystals further indicates a facet alignment between ZIF-8 and Pd. This global observation of facet alignment was consistent with the result observed via a single particle under electron microscopy (**Figure 2-3b**): six sets of {100} planes of the Pd NP aligned with six sets of {100} planes of ZIF-8, further supported by the SAED pattern. As shown in **Figure 2-3d**, the {220} planes of Pd and {110} planes of ZIF-8 were well aligned. This relative orientation suggests that the capping agent mediated growth of MOF can generate a better controlled interfaces. The detailed mechanism of alignment is currently under investigation.





2.8 Extension of Synthetic Strategies

Guided by our understanding of the mechanism, single-crystalline ZIF-8 was successfully coated on metal NPs with different morphologies. By using a similar synthetic condition, in which high concentration 2-mim facilitates the dissociation of CTAB molecules from metal NPs surface, Pd nano-spheres, Ag nano-rods have been successfully encapsulated in single-crystalline ZIF-8 in the same one-to-one manner (**Figure 2-15 a-c**). To our surprise, even Ag nano-wires with a high aspect ratio (length: 930 nm, width: 10 nm) can be encapsulated in monolithic ZIF-8 (**Figure 2-15d**). Interestingly, since the length of the nano-wire is much larger than the ZIF-8 cubes, it can be clearly seen that multiple single-crystalline ZIF-8 cubes aligned with each other and together coated the entire Ag nano-wire.



Figure 2-15. TEM images of (a) Pd sphere@SC-ZIF-8, (b) Au octahedral@SC-ZIF-8, (c) Ag nanorod@SC-ZIF-8 and (d) Ag nanowire@ZIF-8.

2.9 Application to a more robust MOF.

To test the generality of this direct interfacial growth ap-proach, we explored the possibility of encapsulating metal NPs into another MOF with distinct chemical properties and a different topology, UiO-66. It is also more chemically and thermally robust than most current MOF materials, including ZIF-8.^{42,43} The outstanding stability of the MOF shell can significantly broaden the application of these NP@MOF materials, such as for catalytic reactions requir-ing harsh conditions.

Direct application of our coating method failed to encapsulate the NPs (Figure 2-16a). To optimize our conditions for the new MOF, we reviewed the key mechanistic requirements. Our ZIF-8 system has shown that it is important to trigger capping agent dissociation for replacement during MOF coating. We thus hypothesized that the dissociation of CTAB was not sufficient under the conditions of UiO-66 formation. To promote capping agent dissociation, the synthetic condition was modified accordingly. First, to initiate capping agent dissociation, we tried to increase the concentration of linkers. This need could be satisfied by the use of tetrafluoroterephthalic acid (BDC-F₄) as the MOF linker to synthesize UiO-66, which is chosen for its high solubility in aqueous solution.^{44,45} Second, cetyltrimethylammonium chloride (CTAC) was used as capping agents to substitute CTAB due to its weaker binding strength with metal surface than that of CTAB.⁴⁶ The kinetic capping agent exchange was conducted by exposing Au-CTAB NPs to an aqueous solution with a high concentration of CTAC. SERS spectra were collected to track the exchange process (Figure 2-17). SERS analysis indeed indicates the successful replacement of CTAB by CTAC. Compared to Au-CTAB NPs, the signal from Au-Br decreased significantly after the CTAB-CTAC exchange. In the meanwhile, a Au-Cl⁻ peak also appeared around 265 cm^{-1.47} After the capping agent exchange, the Au-CTAC NPs were then introduced into MOF precursor solution, following the previously mentioned encapsulation procedure. This optimized synthesis led to a successful encapsulation of NPs by MOF shell in a one-to-one manner, akin to that of the metal NP@ZIF-8 system (**Figure 2-16b**). With this understanding, Au NPs directly synthesized with CTAC were also used to perform the MOF coating. As shown in **Figures 2-18** and **2-19**, again, each Au NP was encapsulated into a single-crystalline MOF crystal. The PXRD pattern confirmed its identical crystallinity to the simulated UiO-66 (**Figure 2-21**). The single crystallinity was supported by SAED (**Figure 2-18d**). These results clearly demonstrate the generality of this method and the importance of controlling the dissociation dynamics of capping agents for successful encapsulation.



Figure 2-16. TEM image of UiO-66-F₄ formation in the presence of (a) Au-CTAB NPs and (b) after capping agent exchange. Au NPs are marked in red circles.



Figure 2-17. A single Au NP encapsulated in UiO-66-F₄. (a) Schematic illustration, (b) SEM image, (c) TEM image, and (d) SAED pattern from (c). See **Experimental Methods** for the discussion on the spectral shift of Au-halide features.



Figure 2-18. A single Au NP encapsulated in UiO-66-F₄. (a) Schematic illustration, (b) SEM image, (c) TEM image, and (d) SAED pattern from (c).



Figure 2-19. TEM images of UiO-66-F₄ coating of Au-CTAC NPs.

2.10 Study the influence of interfacial structure on selectivity in catalysis

We then tested the hydrogenation of an α,β -unsaturated aldehyde over NP@UiO-66 samples, with and without the direct interface. Unsaturated alcohols are the desired products of this hydrogenation, because they are critical raw materials for pharmaceuticals.⁴⁸ However, this organic transformation is challenging, as the hydrogenation of C=C bonds is more thermodynamically favorable than the hydrogenation of C=O bonds. Applying the MOF coating on metals to promote selectivity of the hydrogenation of C=O bonds has been observed in many studies,^{10,49–51} and several mechanisms have been proposed such as steric effect.⁵² While these mechanisms are different, a direct NP-MOF interface is required for the MOF layer to modulate the intermediates because the reaction takes place on the surface of metals.⁵³ With this information in mind, we carried out the hydrogenation of cinnamaldehyde over four catalysts, Au NPs with no MOF coating (Au-on-SiO₂), Au NPs on the external surface of MOF (Au-on-MOF), Au NPs with an indirect MOF interface, and Au NPs with a direct MOF interface (see **Experimental Methods** for details). To compare their selectivity, the loading of each catalyst was controlled to give the same conversion (**Table 2-3**). For the pure Au catalysts without MOF coating, the selectivity for unsaturated cinnamyl alcohol was 61.8 %, while 3-phenylpropionaldehyde and 3-phenylpropanol were both obtained (**Figure 2-20**). The sample of pure Au NPs on the MOF surface, which served as a control (Au-on-MOF), showed a 53.3 % selectivity to unsaturated cinnamyl alcohol. The catalyst with an indirect interface showed an increase in selectivity toward cinnamyl alcohol to 85.1%, indicating that the MOF coating indeed promotes selectivity. Remarkably, cinnamyl alcohol was the only product detected for the catalyst with a direct interface. As expected from the high stability of UiO-66, the crystal structures of both Au@MOF materials were well main-tained after catalysis (**Figure 2-21** and **2-22**). This result clearly highlights the importance of well-defined interfac-es for the catalytic performance of NP@MOF materials.



Figure 2-20. Selectivity for cinnamaldehyde hydrogenation over pure Au NPs without a MOF coating, Au NPs on the external surface of MOF, encapsulated Au NPs with an indirect NP-MOF interface, and encapsulated Au NPs with a direct NP-MOF interface. Cinnamyl alcohol is the preferred product, and its selectivity was determined by its ratio to the sum of all three products.



Figure 2-21. PXRD patterns of Au@UiO-66-F₄ with a direct interface (orange) before and (blue) after catalysis.



Figure 2-22. PXRD patterns of Au@UiO-66 with an indirect interface (brown) before and (green) after catalysis.

2.11 Conclusion

Here, we have developed an approach to generate well-controlled interfaces between NPs and coated MOFs. Our approach takes advantage of the *in situ* replacement of weakly adsorbed capping agents by MOF precursors during MOF coating. The concept was initially demonstrated on metal NPs capped by CTAB and coated in ZIF-8. Systematic IR and Raman spectroscopic studies showed that CTAB molecules gradually dissociate from the metal surface and are replaced *in situ* by MOFs, resulting in a direct interface between metal NPs and ZIF-8. The well-controlled interface leads to the formation of a single-crystalline MOF coating with a specific crystal facet alignment. The understanding from the ZIF-8 system was extended to coat UiO-66 type MOF on NPs with a direct interface, where NPs were again individually encapsulated in single-crystalline MOF crystals in a one-in-one fashion. The hydrogenation of an α,β -unsaturated aldehyde was employed to test the catalytic impact of interfacial structure. High selectivity towards the desired unsaturated alcohol product was achieved over the direct interface. In sum, we have demonstrated a new approach to encapsulate defined NPs into MOFs, generating a direct, clean NP-MOF interface *via* the *in situ* replacement of capping agents. This new strategy opens a new route to achieve hybrid materials well-defined interfaces.

2.12 Experimental Methods

Chemicals and Materials

bromide (CTAB, Cetyltrimethylammonium Sigma-Aldrich, >99%), cetyltrimethylammonium chloride (CTAC, Tokyo Chemical Industry Co., Ltd., > 95%), ascorbic acid (Sigma-Aldrich, \geq 99%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, Sigma-Aldrich, ~50% Au basis), hydrogen tetrachloropalladate (H₂PdCl₄, Sigma-Aldrich, 98%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, J.T.Baker, 99.6%), 2methylimidazole (2-mim, Alfa Aesar, 97%), sodium borohydride (NaBH4, Sigma-Aldrich, 98.0%), zirconyl chloride octahydrate (ZrOCl₂·8H₂O, Acros Organics, > 98%), tetrafluoroterephthalic acid (BDC-F4, Sigma-Aldrich, 97%), zirconium chloride (ZrCl4, Sigma-Aldrich, > 99.5%), terephthalic acid (BDC, Sigma-Aldrich, 98%), acetic acid (Sigma-Aldrich, \geq 99.7%), deuterium oxide (D₂O, Cambridge Isotope Laboratories, Inc., D-99.9%), methylsulfonylmethane (Sigma-Aldrich, certified reference materials), sodium citrate tribasic dihydrate (Sigma-Aldrich, \geq 99.0%), polyvinylpyrrolidone (PVP, MW 40,000, Sigma-Aldrich) were used without further purification. Ultrapure deionized water (DI water, 18.2 M Ω) was used for all solution preparations. Element standard solutions, palladium (1000.00 µg/mL) and zinc (100.00 µg/mL), for ICP-OES were purchased from Inorganic Ventures. Ethylene (Airgas, 99.995%), hydrogen (Airgas, 99.999%) and helium (Airgas, 99.999%) were used for ethylene hydrogenation. Cinnamaldehyde (Sigma-Aldrich, 99.0 %) and hydrogen (Airgas) was used for cinnamaldehyde hydrogenation.

Instrumentation

A Bruker AXS D2 Phaser diffractometer was used for the powder X-ray diffraction characterization (PXRD). Transmission electron microscopy (TEM) was performed on a JEOL JEM2010F electron microscope operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6340F and JEOL JSM-7001F scanning electron microscope. Selected area electron diffraction (SAED) was taken from JEOL JEM-1400. For sample preparation, the dry sample was dispersed in methanol by sonication. Then the dispersion was dropcast on Cu grids or silicon wafers for TEM or SEM measurements, respectively. Raman spectra were collected with a Micro-Raman system (XploRA, Horiba) with 532 nm laser excitation. Nuclear Magnetic Resonance (NMR) was collected on a Varian Unity INOVA spectrometers (500 MHz). Thermogravimetric analysis (TGA) was conducted in a NETZSCH STA 449F. Diffuse reflectance infrared Fourier transform spectroscopies of chemisorbed carbon monoxide (CO-DRIFTS) was carried out on a Bruker Tensor 27 IR spectrometer with a linearized mercury-cadmium-telluride detector, Harrick diffuse reflection accessory, and Praying Mantis high temperature reaction chamber. For ethylene hydrogenation studies, samples were diluted with low surface area quartz and loaded into glass reactors. Temperature was controlled by a furnace (CARBOLITE) and PID controller (Diqi-Sense) with a type-K thermocouple. The amount of palladium in each sample was analyzed by inductively coupled plasma optical emission spectrometry on an Agilent 5100 instrument. Gas flows were regulated using calibrated mass flow controllers (Alicat) and reactions were performed using helium as the carrier gas. The product was analyzed by mass spectrometer (MKS special V2000P). For cinnamaldehyde hydrogenation studies, the products were analyzed on a gas chromatograph with flame-ionization detection (Agilent 6850 Network GC with a autosampler, column: HP-1, 30 m \times 0.25 mm \times 0.25 µm).

Synthesis of Pd-CTAB NPs

Pd-CTAB NPs were synthesized based on a previous report.⁵⁴ 50 mg of CTAB was dissolved in 9.3 mL of deionized water (DI water), followed by adding 0.5 mL of 0.01 M H₂PdCl₄ solution. The above solution was placed in 95 °C oil bath for 5 min. Then, 200 μ L of 0.04 M ascorbic acid was added with stirring at 200 rpm. The reaction mixture was stirred for 30 min at 95 °C. After cooling to room temperature, the as-synthesized Pd-CTAB NPs were washed once with DI water via centrifugation (8000 rpm, 10 min). Normally, 10 batches of Pd-CTAB NPs were synthesized and dispersed in 5.0 mL of DI water, yielding a 10 mM Pd-CTAB NPs suspension. For the encapsulation, 0.25 mL of the Pd-CTAB NPs suspension was centrifuged (8000 rpm, 10 min) and dispersed in 0.5 mL DI water.

Synthesis of Au-CTAB NPs

The Au-CTAB NP synthesis was modified from a previous report.⁵⁵ 550 mg of CTAB was dissolved in 97 mL of DI water. Then, 2.5 mL of 0.01 M HAuCl₄ solution and 0.5 mL of 0.1 M trisodium citrate solution were added. The reaction mixture was

transferred into a 200-mL pressure vessel and heated in an oven at 110 °C for 24 h. The assynthesized Au-CTAB NPs were washed once using centrifugation (8000 rpm, 10 min) and dispersed in 2.5 mL of DI water, yielding a 10 mM Au-CTAB NPs suspension. For the encapsulation, 0.25 mL of the Au-CTAB NPs suspension was centrifuged (8000 rpm, 10 min) and dispersed in 0.5 mL of DI water.

Synthesis of Au-CTAC NPs

Au-CTAC NPs were synthesized following a seed-mediated synthesis method modified from a previous report.⁵⁶ In general, Au seeds were synthesized first and added into the growth solution to form Au-CTAC NPs. All the reactions were performed at room temperature (22.0 ± 1.0 °C). For the synthesis of Au seeds, 320 mg of CTAC was dissolved in 9.75 mL of DI water, followed by adding 250 µL of 0.01 M HAuCl₄ and 450 µL of 0.02 M NaBH₄ under stirring at 200 rpm. The above solution of Au seeds was aged for 1 hour at room temperature.

The growth step was performed using two batches of the same growth solutions. The growth solution was prepared by dissolving 320 mg of CTAC in 9.625 mL of DI water followed by adding 90 μ L of 0.04 M L-ascorbic acid, 250 μ L of 0.01 M HAuCl₄ and 10 μ L of 0.01 M sodium bromide solution. To grow the Au-CTAC NPs, 105 μ L of Au seed solution was added to the first growth solution. Upon development (~ 5 s) of a light pink color, 25 μ L of the above mixture was immediately transferred into the second growth solution. The solution was stirred for 10 s and left undisturbed for 15 min. The assynthesized Au-CTAC NPs were washed once with DI water via centrifugation (8000 rpm,

10 min). Normally, 20 batches of Au-CTAC NPs were synthesized and dispersed in 10.0 mL of DI water, yielding a 5 mM Au-CTAC NPs suspension. For encapsulation, 0.375 mL of Au-CTAC NPs suspension was washed twice with DI water via centrifugation and dispersed in 0.1 mL of DI water.

Synthesis of Ag-CTAB NPs

The synthesis was carried out following the previous report with some modifications.⁵⁷ 0.51 g of AgNO₃ was dissolved in 50 ml deionized water followed by adding 1.0 M aqueous ammonia in a dropwise manner until a clear colorless solution was obtained. Then, the solution was transferred into a 100-ml volumetric flask quantitatively and was made up to 100 ml with deionized water. Finally, the [Ag(NH₃)₂]OH solution was 30.00 mM. 2.5 ml of freshly made [Ag(NH₃)₂]OH was transferred into a 75-ml pressure vessel. 10 ml of deionized water, 2.5 ml of 20 mM glucose, and 3 ml of 50 mM CTAB solutions were added under stirring. The pressure vessel was heated at 120 °C in a furnace for 8 hours. After cooling down to room temperature, the solution was centrifuged at 8000 rpm and re-dispersed into 7.5 ml of deionized water to make the concentration 10 mM.

Synthesis of Au-PVP NPs

Au-PVP NPs were obtained using a Turkevich method with a polymeric capping agent (polyvinylpyrrolidone, PVP).⁵⁸ To form Au-PVP NPs, 1.25 mL of 0.01 M HAuCl₄ aqueous solution was introduced into 48.25 mL of DI water in a 100-mL two-neck round bottom flask. Then, the solution was stirred and refluxed at 110 °C oil bath for 20 min.

After that, 0.5 mL of the aqueous solution containing 3 wt% sodium citrate tribasic dihydrate was introduced to the above solution and the reaction was held in reflux at 110 °C oil bath for 3 min. The solution was cooled to room temperature. Then, 1.0 mL of the aqueous solution containing 150.0 mg of polyvinylpyrrolidone was added into the solution to obtain Au-PVP NPs. The formed Au-PVP NPs were centrifuged at 13000 rpm for 20 min to remove the unreacted residues. The as-synthesized Au-PVP NPs were purified by washing with methanol twice via centrifugation (14000 rpm, 20 min). The resulting Au-PVP NPs were dispersed into 0.5 mL of DMF to give a concentration of Au-PVP NPs at 5.0 mg/mL.

Synthesis of metal NP@ZIF-8 with a direct interface

The synthesis was modified from the previous method developed by our group.¹⁹ 113.52 mg of 2-mim was dissolved in 1.75 mL of 0.2 mM CTAB aqueous solution to obtain a 2-mim/CTAB solution. 250 μ L of 10 mM metal-CTAB NPs were centrifuged (8000 rpm, 10 min) and dispersed in 500 μ L of DI water. To form NP@ZIF-8 with a direct interface, 1.75 mL of 2-mim/CTAB solution was mixed with 0.25 mL of 97.5 mM Zn(NO₃)₂ solution in a 20-mL glass vial while stirring at 250 rpm at room temperature. After 10 s, 0.5 mL of metal-CTAB NPs in DI water was added into the above mixture. After stirring for 5 min, the mixture was left undisturbed for 3 h at room temperature (22.0 \pm 1.0 °C). The sample was collected by centrifugation (8000 rpm, 10 min). The sample was washed with methanol three times and was dried under a vacuum condition for 24 h.

Synthesis of metal NP@ZIF-8 with an indirect interface

For NP@ZIF-8 with an indirect interface, 2-mim was dissolved in various concentrations of aqueous CTAB solution (0.8 mM CTAB for polycrystalline shell, 1.2 mM for partially coated shell). 113.52 mg of 2-mim was dissolved in 1.75 mL of aqueous CTAB solution (0.8 mM CTAB, or 1.2 mM CTAB) to obtain a 2-mim/CTAB solution. To form NP@ZIF-8 with an indirect interface, 1.75 mL of 2-mim/ CTAB solution was mixed with 0.25 mL of 97.5 mM Zn(NO₃)₂ solution in a 20-mL glass vial while stirring at 250 rpm at room temperature. After 10 s, 0.5 mL of metal-CTAB NPs in DI water was added into the above mixture. After stirring for 5 min, the mixture was left undisturbed for 3 h under room temperature. The sample was collected by centrifugation (8000 rpm, 10 min). The sample was washed with methanol three times and was dried under a vacuum condition for 24 h.

Synthesis of Au@UiO-66-F4 with a direct interface

Based on our understanding that was built from the ZIF-8 system, the balance between the rates of dissociation and in situ MOF growth is of critical importance. To optimize our conditions for UiO-66, we propose to initiate capping agent dissociation by increasing the concentration of MOF linkers. Unfortunately, this concept is hard to realize by using the primitive linker of UiO-66, 1,4-benzendicarboxylic acid (BDC), because BDC is insoluble in an aqueous phase. To address this limitation, we make use of tetrafluoroterephthalic acid (BDC-F₄) as the MOF linker for its high solubility in an aqueous solution.

The synthesis of Au@UiO-66-F₄ was carried out in the aqueous phase by using acetic acid as the modulator. Firstly, 0.18 mmole of BDC-F₄ was mixed with 0.5 mL of 6 M acetic acid aqueous solution and denoted as the linker solution. The linker solution was then incubated at a 50 °C oil bath to facilitate the dissolving process of the MOF linker. By using the same concept, 0.18 mmole of ZrOCl₂·H₂O was dissolved in 0.5 mL of 6 M acetic acid aqueous solution and denoted as the metal solution. Before the synthesis, both linker and metal solutions were preheated at a 50 °C Oil bath for five minutes. Then, the metal solution was subjected to the linker solution in a 20-ml glass vial while stirring at a 50 °C Oil bath. 1 minute after adding the metal solution, 100 uL of the Au NPs solution was injected into the above mixture, which the metal nanoparticle solution concentrations had already been adjusted to 18.75 mmol/L (The Au NPs used here was prepared by centrifuging 0.375 mL of 5 mM as-synthesized Au-CTAC NPs suspension at 10000 rpm for 5 min. The resulting Au NPs were then washed twice with 100 µL of DI water and then dispersed in 100 μ L of DI water for further use.). The mixture was stirred for 5 minutes at a 50 °C Oil bath. Then, the reaction solution was left undisturbed at a 50 °C Oil bath for 3 hours. The resulting solid of Au@UiO-66-F4 was collected by centrifuge (3000 rpm, 8 min) and washed by DMF and methanol for three times. Then, the sample of Au@UiO-66-F₄ was dried under vacuum overnight before characterizations and catalytic reactions.

Capping agent exchange

 $375 \ \mu$ L of 5 mM Au-CTAB NPs was centrifuged down at 8000 rpm for 10 min and dispersed in 100 μ L of 100 mM CTAC aqueous solution. The suspension of Au NPs was left unstirred at room temperature overnight. Then, it was spun down at 8000 rpm for 10

min, washed with 100 μ L DI water twice and dispersed in 100 μ L DI water for the encapsulation.

Synthesis of Au@UiO-66 with an indirect interface

The synthesis of Au@UiO-66 with an indirect interface was performed based on the previous report with minor modifications.⁵⁹ In general, 25.0 mg of BDC (0.143 mmol) was dissolved in 7 mL of DMF in a 20 mL scintillation vial. Then, 700 µL of acetic acid was added into the solution followed by adding 2 mL of DMF containing 33.4 mg of ZrCl₄ (0.143 mmol) and 150 mg PVP. The mixture was sonicated for 20 min at room temperature. Au-PVP NPs (0.25 mL, 5.0 mg Au NPs/mL) was introduced into the above mixture, and the mixture was heated at 120 °C in an oil bath for 1 h. After cooling to room temperature, the formed Au@UiO-66 sample was collected by centrifugation (8000 rpm, 10 min). The sample was washed with DMF and methanol three times. The sample was dried under vacuum for 24 h.

Study of the CTAB amount on the metal surface and its impact on forming a direct interface

In this experiment, electron microscopy was carried out to study the impact of CTAB on metal surface to the formation of a direct interface, and ¹H-NMR analysis was performed to study the CTAB amount in the supernatant. To study the impact of CTAB on metal surface to the formation of a direct interface, Pd-CTAB NPs were incubated with the 2-mim solution (50 mM) with an incubation time from 1 to 4 h. (A lower 2-mim

concentration of 50 mM was used in this study to control the dissociation of CTAB.) After incubating the NPs in the 2-mim solution, the treated Pd-CTAB NPs were introduced into the MOF precursor solution for encapsulation. The ratio of Pd@ZIF-8 with a single crystalline shell was calculated based on electron microscopy and the results are summarized in **Table 2-2**.

To study the CTAB amount in the supernatant, Pd-CTAB NPs were dispersed in 0.5 mL of deuterium oxide (D₂O) solution containing 50 mM 2-mim. The suspension of Pd-CTAB NPs was left undisturbed in D₂O/2-mim at room temperature for a given time (1, 2, or 4 h). After that, the above suspension was centrifuged and the supernatant was taken for ¹H-NMR analysis. The quantitative measurement of absolute CTAB amount in the supernatant was done using methylsulfonylmethane (20 μ L, 30.00 mM). **Figure 2-2c** shows an example of the quantitative analysis of CTAB amount from the ¹H NMR spectrum: Peak A was assigned to the six protons on methyl groups of the internal standard (methylsulfonylmethane); peak E was assigned to the 26 protons on the 13 carbons of the CTAB amount of CTAB in the solution. The results are summarized in **Figure 2-2b**.

To correlate the amount of CTAB removed from the metal surface and its impact to the formation of a direct interface, **Figure 2-2b** and **Table 2-2** were combined in one figure in **Figure 2-11**.

 Table 2-2. Calculation of the ratio of Pd@ZIF-8 with single-crystalline coating when 2

 mim (50 mM)-pretreated Pd NPs were used (treatment time: 1, 2 and 4 h, as labeled).

Time under	Ratio of Pd@ZIF-8 with single	Number of crystals used in
2-mim treatment	crystalline shell ^[a]	calculation in each trail ^[a]
0	9.3 ± 3.7	118
1 hour	31.4 ± 5.8	118
2 hour	47.8 ± 3.1	110
4 hour	74.6 ± 4.3	60

^[a] The ratio of Pd@ZIF-8 with single crystalline shell was calculated based on three independent trials, with more than 60 crystals used in the calculation for each trail.

Self-assembly of Pd@ZIF-8 samples for PXRD analysis

The assembly of the MOF samples was performed based on the previous reports.⁶⁰ Pd@ZIF-8 samples were self-assembled on a silicon wafer. In general, Pd@ZIF-8 samples were dispersed in an aqueous solution containing 0.54 mM CTAB to form a uniform suspension. Next, 10 μ L of the suspension was placed on a substrate and dried under atmosphere. The assembled samples were analyzed by SEM and PXRD (**Figures 2-13** and **2-14**). A low probe current was applied for SEM in order to minimize the charging effect.

CO-DRIFTS measurement

To carry out CO-DRIFTS analysis, the sample was packed in a sample cup and sealed in a Praying Mantis high-temperature IR reaction chamber under N₂ flow (50

mL/min). A spectrum of the sample was recorded as a background. The adsorption of carbon monoxide (CO) on the sample was performed by introducing CO (10 mL/min) into the IR reaction chamber for 20 min. Then, the CO-DRIFTS spectra were measured by flushing the samples with N_2 flow (50 mL/min) for 20 min to remove gaseous CO. All spectra were collected with 160 scans at a resolution of 4 cm⁻¹ from 1750 cm⁻¹ to 3000 cm⁻¹.



Raman spectroscopy for Au@ZIF-8

Figure 2-23. Raman spectra of Au@ZIF-8, Au NPs incubated with 2-mim, free 2-mim, Au NPs incubated with ZIF-8 in an aqueous solution and ZIF-8.
In **Figure 2-17b**, The slight shift of Au-Cl⁻ interactions between the exchanged Au-CTAC NPs and Au-CTAC NPs could be resulted from different shapes of the assynthesized Au NPs. The exchanged Au-CTAC NPs have an octahedral shape ((111) facet) and Au-CTAC NPs have a cubic shape ((100) facet). Such a geometry different could cause fluctuation on plasmonic resonance and capping agent arrangement, which may cause the shifting.

The spectrum of Au + 2-mim was measured by using the mixture of Au-CTAB NPs (100 uL, 5 mM) and 2-mim (400 uL, 790 mM). The spectrum of 2-mim was obtained by using the 2-mim aqueous solution (790 mM). The spectrum of Au + ZIF-8 was recorded by using the mixture of Au-CTAB NPs (100 uL, 5 mM) and ZIF-8 (1 mg ZIF-8 in 100 uL DI water). Raman spectrum of Au@ZIF was measured in situ during the formation of Au@ZIF-8 with a direct interface.

We are mindful that the chemicals could have different Raman spectra between solid and liquid phase, therefore, we have performed the Raman spectra for all of the samples in an aqueous solution including 2-mim. Two control samples were prepared: Au NPs incubated with 2-mim (Au + 2-mim) and Au NPs mixed with ZIF-8 in an aqueous solution (Au + ZIF-8). We compared the spectra of Au+2-mim and Au+ZIF-8 with the Au sample during the ZIF-8 coating (Au@ZIF-8), and we focused on the change of peaks from 800 to 1600 cm⁻¹. Firstly, we observed that the sample of Au@ZIF-8 exhibited a similar spectral feature with Au + 2-mim and 2-mim, suggesting that MOF interacted with the metal surfaces through the MOF ligand. Secondly, we hypothesized that the MOF ligand is mostly like to facilitate the MOF-Au interaction through the imidazole "pyridine N", so we compared the spectral feature of out-of-plane bending modes of NH (γ (NH)) at around 935 cm⁻¹. The stretching of NH was absent in bulk ZIF-8 due to the deprotonation of 2mim when forming Zn-N bonds. Therefore, the observation of NH bending at 928 cm⁻¹ in Au@ZIF-8 could be attributed to the 2-mim at the NP-MOF interface. After the NH moiety interacted with the metal surface, the interaction would lead to a weaker NH bending, resulting in a redshift of the N-H bending frequency. In the spectra, Au@ZIF-8 sample exhibits a redshift of the NH bending mode (928 cm⁻¹) compared to free 2-mim (935 cm⁻¹), suggesting the adsorption of ZIF-8 on the metal surface through the imidazole "pyridine N". In contrast, this shift for the sample of Au + 2-mim would be hard to observe because of the interference from the bulk 2-mim.

Ethylene hydrogenation

Ethylene hydrogenation is well-known for its structure-independent properties, meaning that the activity is not determined by the shape or size of the catalyst particles. It depends only on the number of active sites.⁶¹ Therefore, it is a very sensitive tool to determine the prevalence of active sites in different catalysts. In general, samples were diluted with low surface area quartz and loaded into U-shaped glass reactors. The glass reactor was then connected to a home-built gas-phase flow system for alkene hydrogenation. Gas flows, including helium, hydrogen, and ethylene, were regulated using calibrated mass flow controllers (Alicat). Gas composition was analyzed with a mass spectroscope (MKS special V2000P). Temperature was controlled by a furnace (CARBOLITE) and PID controller (Diqi-Sense) with a type-K thermocouple. Before the reaction, the catalysts were activated in the glass reactor at 60 °C under He flow for 1 h. Gas-phase ethylene hydrogenation was run at 45 °C under a continuous system. The

activity to ethylene hydrogenation in each sample was summarized by normalizing the amount of palladium in each sample. (The amount of palladium in each sample was analyzed by inductively coupled plasma optical emission spectrometry on an Agilent 5100 instrument.)

Cinnamaldehyde hydrogenation

Catalysts were dispersed in 2 mL of isopropanol solution in the 5.0-mL ampule, and then cinnamaldehyde (0.2 mmol) was added into the above solution. To compare the selectivity of our samples, the conversion of each reaction was kept at around 6 % (2.60 mg Au-on-SiO₂, 17.5 mg Au@UiO-66 with an indirect interface and 12.0 mg Au@UiO-F4 with a direct interface). Before catalysis, the high-pressure reactor vessel (Wattacas Inc., 500 mL) was preheated to 70 °C. Temperature was controlled using a hot plate (RCT basic, IKA) with a type-K thermocouple. Subsequently, the ampule was transferred into a highpressure reactor vessel. The autoclave was purged 5 times with H₂ to remove air. Then, the hydrogenation of cinnamaldehyde was carried at 30 bar H₂ at 70 °C for 24 h with magnetic stirring at 500 rpm. After that, the catalysts were separated by centrifugation, and the reaction solution was filtered through a filter membrane (0.22 μ m). The products were analyzed on a gas chromatograph with flame-ionization detection (Agilent 6850 Network GC with an autosampler, column: HP-1, 30 m × 0.25 mm × 0.25 μ m). The results are summarized in **Table 2-3**.

To prepare the control sample of Au NPs deposited on SiO_2 , 3 mL of the colloidal Au-CTAC NPs (5 mM) was mixed with 100.0 mg of mesoporous silica (SBA-15) in 5 mL

isopropanol in a 20 mL scintillation vial. The mixture was sonicated for 10 min and stirred for 3 h at room temperature. Then, the precipitates were separated by centrifugation (4000 rpm, 10 min), washed with ethanol four times, and dried in the vacuum oven overnight. The resulting sample was denoted as Au-on-SiO₂.

To prepare the control sample of Au NPs deposited on the external surface of UiO-66, 3 mL of the colloidal Au-CTAC NPs (5 mM) was mixed with 100.0 mg of UiO-66 in 5 mL isopropanol in a 20 mL scintillation vial. The mixture was sonicated for 10 min and stirred for 3 h at room temperature. Then, the precipitates were separated by centrifugation (4000 rpm, 10 min), washed with ethanol four times, and dried in the vacuum oven overnight. The resulting sample was denoted as Au-on-UiO-66.

Catalyst ^[a]	Conversion (%)	Selectivity to cinnamyl alcohol (%)	Selectivity to 3- phenylpropionaldehyde (%)	Selectivity to 3-phenylpropanol (%)
Au-on-SiO ₂ (Control)	5.0 ± 0.41	61.8 ± 0.1	30.8 ± 2.19	7.4 ± 2.17
Au-on-UiO-66 (Control)	8.0 ± 1.01	53.3 ± 2.04	28.5 ± 2.02	18.2 ± 1.73
Au@UiO-66 with an indirect interface	6.5 ± 0.66	85.1 ± 0.1	12.0 ± 0.66	2.9 ± 0.61

 Table 2-3. Summary of selectivity for cinnamaldehyde hydrogenation

Au@UiO-F4				
with a direct	6.1 ± 0.13	> 99.0 ^[b]	< 1.0 ^[c]	< 1.0 ^[c]
interface				

^[a] Selectivity was determined by its ratio to the sum of all three products (cinnamyl alcohol, 3-phenylpropionaldehyde, and 3-phenylpropanol). The standard deviation was obtained based on three independent measurements. ^[b] Cinnamyl alcohol is the only product observed in the GC-FID analysis. ^[c] Product was not observed in the GC-FID analysis.

2.13 References

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3.0 Chapter 3

Metal-Organic Framework Thin Film for Selective Mg²⁺ Transport



A significant portion of the work described in this chapter has been published in:

Luo, J.#; Li, Y.#; Zhang, H.; Wang, A.; Lo, W.-S.; Dong, Q.; Wong, N.; Povinelli, C.; Shao, Y.; Chereddy, S.; Wunder, S.; Mohanty, U.; Tsung, C.-K.*; Wang, D.* A Metal-Organic Framework Thin Film for Selective Mg²⁺ Transport, *Angew. Chem. Int. Ed.* **2019**, *58*, 15313-15317.

3.1 Abstract

As an anode material, Mg holds immense promise for post Li-ion battery energy storage applications. One critical challenge that limits its utilization is the incompatibility between the anode and the cathode chemistry. This issue may be addressed by separating the anolyte and the catholyte with a membrane that only allows for Mg²⁺ transport but blocks the solvent and/or the counterions. A potential material choice for this purpose is metal-organic frameworks (MOFs). Here we report the use of Mg-MOF-74 thin films as the separator between the anolyte and catholyte. As a separator, it was shown to meet the needs of low-resistance, selective Mg²⁺ transport. The uniform MOF thin films supported on Au substrate with thicknesses down to ca. 202 nm showed an intrinsic resistance as low as ca. 12 Ω (or 6.4 $\Omega \cdot cm^2$), with the normalized room-temperature ionic conductivity of ca. $3.17 \times 10-6$ S·cm⁻¹. When synthesized directly onto a porous anodized aluminum oxide (AAO) support, the resulting films were used as a standalone membrane to permit stable, low-overpotential Mg striping and plating for over 100 cycles at a current density of 0.05 mA/cm². Chemical and electrochemical characterization proved that the film was effective in blocking solvent molecules and counterions such as bis(trifluoromethanesulfonyl)imide (TFSI) from crossing over for extended period of time. This work demonstrates that MOF thin film is a promising choice for future Mg-battery applications.

3.2 Introduction: The challenges presenting in Mg conversion batteries

In the quest for post-Li-ion battery electrochemical energy storage technologies, Mg-battery stands out for a number of reasons. For one, Mg represents an earth abundant element whose large-scale utilization is expected to greatly reduce material-related costs

for applications such as grid-level stationary storage.¹ For another, the most outstanding issue that plagues Li-ion batteries, the dendritic growth on the anode, is believed to be absent for Mg-based batteries, promising safe operations with significantly broadened application scopes.^{2,3} Indeed, recent years have witnessed a growing body of literature on realizing the full potential of Mg-batteries.^{4–8} For instance, rechargeable Mg/S batteries have been developed and achieved long cyclability (>100 cycles).⁵ Mg/Br₂ batteries were demonstrated in a dual-electrolyte system for 20 cycles.⁶ Mg/O₂ batteries were also successfully operated with the help of redox mediators.⁸ This exciting progress notwithstanding, existing demonstrations face important issues, the most significant of which concerns the incompatibility of the anode and the cathode chemistries.^{6,9,10} That is, the types of electrolytes and chemical reactions desired for the anode reactions are often incompatible with those for the cathode and vice versa. Consider the Mg-S battery as an example. For successful practical conversion at the cathode, high potentials (e.g., >3.5 V vs. Mg/Mg²⁺) are often needed due to the kinetic overpotential requirements;¹¹ but electrolytes that could be used for such processes (e.g., organic carbonate-based ones), would form an inert passivation layer on the Mg anode, which would greatly increase the overpotentials for Mg striping and plating.¹² Conversely, chemicals such as Grignard reagents enable facile Mg stripping and plating on a Mg anode but would react with S to form phenyl disulfide and biphenyl sulfide. Similar issues were encountered in emerging Mg-Br₂ and Mg-O₂ batteries, as well.^{6,8} While some potentially promising solutions have been proposed, using, for example, non-nucleophilic electrolytes such as Mg(TFSI)₂ (where TFSI is bis(trifluoromethanesulfonyl)imide),^{11,13} Mg/AlCl_x complexes and (HMDS)₂Mg+AlCl₃ (where HMDS stands for bis(trimethylsilyl) amine) in ethereal

solvents, these electrolytes either suffer from poor stability with the Mg anode or severely corrode current collectors.¹⁰ A broadly applicable strategy to solve this issue is needed to push the field forward.

One solution to this problem lies in the ability to separate the anolyte and the catholyte,^{6,14} so as to greatly broaden the choices for each respective chemical process. For this purpose, a separator that permits selective Mg^{2+} transport but blocks the anions and the solvents would be required (**Figure 3-1**). Three types of materials have been explored to serve as separators. One type were conventional solid-state electrolytes such as MgZrPO4 and Mg-borohydride-based materials.^{15–18} While highly stable, these materials feature extremely low conductivity of 10^{-12} ~ 10^{-8} S/cm at room temperature,¹⁸ rendering their utilization as battery separators limited. The second type were polymer-based materials such as Mg salts embedded in polyethylene oxide.¹⁹ An important advantage they offered was the significantly improved ionic conductivity (up to 10^{-6} S/cm at R.T.).²⁰ However, the lack of durable selectivity due to, for example, the structural changes caused by the swelling of the polymers,²¹ made them less than ideal for practical applications.

3.3 Our Approach to adress the challenge

A third class of materials that have been explored for the purpose of selective ionic transport is metal-organic frameworks (MOFs).²² Composed of metal nodes coordinated by organic linkers, MOFs feature well-defined porous structures that could be ideal for selective ionic transport.^{23,24} Critically, since the pore sizes and the chemical compositions of MOFs can be tuned with high fidelity, tailor-designing the structures for the desired conductivity and selectivity is feasible. Indeed, MOFs have been exploited for the transport

of protons (H⁺),²⁵ Li⁺,^{26–29} and Na⁺,³⁰ and promising results have been published.^{31,32} Just within the context of Mg²⁺ transport, MOFs have been examined by Long et al. and Dinca et al., separately.^{28,32,33} Mg²⁺ conductivity up to 2.5×10^{-4} S/cm has been reported.³³ Nevertheless, these pioneering studies often employed pressed pellets of MOF powders to bring the fundamental understanding; except in rare cases where low resistance was specifically reported,³³ pressed pellets often featured resistances (>5,000 Ω) that are too high for practical applications. Furthermore, there are inevitable gaps between adjacent particles in a pressed pellet, which makes it exceedingly difficult to understand the true behavior of MOFs as selective ionic conductors.^{34,35} Clearly, there is a need to fill the gap in research on selective Mg²⁺ transport by MOFs. Here we show that this need may be met by MOF thin films, which were synthesized on a membrane that can be readily utilized.³⁶ It also eliminates interparticle gaps that are abundant in pressed pellets. Such a feature may become important in the future because it would enable studies on the inherent ionic transport properties of MOFs without confounding factors such as inadvertent transport through the gaps.



Figure 3-1. Schematic illustration of how MOF film may be used in a hybrid battery for selective transport of Mg^{2+} , where Mg metal serves as the anode and a high-potential Mg-storage materials (*e.g.*, S or O₂) as the cathode. The incompatible anolyte and catholyte (with high anodic stability) could be separated by a MOF membrane.

3.4 MOF selection and synthetic approach to MOF-74 thin film

Mg-MOF-74 is chosen as the initial study platform primarily because its structure can serve as an apt platform.³⁷ Its metal centers are coordinatively unsaturated (hence, the open metal sites (OMSs)), and the adjacent centers are ~3 Å apart in a one-dimensional channel (13 Å).^{38,39} A scenario in which how the 1-D structure and the OMSs could be utilized for study ionic transport is envisioned next. The OMSs can serve as a binding site to anchor Mg^{2+} ions via solvation shells (**Figure 3-2**). These solvent molecules can be of more than one nucleophilic functional group; one such group binds to OMS, and the other one binds to Mg^{2+} . Such a hypothesis has already been discussed in literature.^{26,33} The 1-D channel structure and close proximity of OMSs in MOF-74 ensure a relatively low activation energy barrier when Mg^{2+} ions hop between adjacent binding sites. Most importantly, the metal nodes (such as Mg, Co, Ni, Cu, Zn, etc.),⁴⁰ linkers, and nucleophilic molecules (such as solvent molecules with divalent nucleophilic sites) can be readily altered in MOF-74 system, which provides the possibility to alter the ionic behaviors in the channel.



Figure 3-2. Schematic illustration of Mg²⁺ transport in MOF-74.

Generally, there are two strategies for synthesizing MOF thin films: vapor-based approaches and solution-based approaches.⁴¹ Vapor-based approaches, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD), could generate uniform films.^{42,43} However, the vapor-based approaches are limited due to the requirement of vaporizing linkers and volatile metal precursors.⁴⁴ The solution-based approaches are modified from conventional solvothermal methods developed for powder MOFs. To foster MOFs to grow on a substrate as a thin film via solution-based approaches, self-assembled monolayers (SAMs) were often used to guide subsequent attachment of the initial materials.⁴⁵ Nevertheless, this approach prevents direct contact between MOFs and the supporting substrate, which will be detrimental for electrochemical characterization/applications. Here, we prepared Mg-MOF-74 film using a vapor-assisted conversion (VAC) method.⁴⁶ In this approach, a layer of precursor solution, containing Magnesium nitrate, 2,5-dihydroxyterephthalic acid (dobdc), acetic acid, and sodium

hydroxide, is drop casted on the substrate and converted into continuous and unfirm film, with the system exposed to high vapor pressure of the solvents. The high vapor pressure limits the solvent evaporation during the synthesis so as to control the growth kinetics (see further discussions in the following chapter and details in **Experimental Methods**). As shown in Figure 3-3, a thin film (ca. 200 nm) with a smooth surface was grown on a Si wafer sputtered with a thin layer of Au (ca. 50 nm) that served as a conductive contact. The film was then transferred onto the Cu grid and was able to be observed under TEM. The selected area electron diffraction showed the $(2\overline{10})$ and (300) planes of Mg-MOF-74. The crystalline structure of the film was furthered confirmed by the XRD, where two characteristic peaks were assigned to $(\overline{210})$ and (300) of Mg-MOF-74, in good agreement with the simulated data and the grazing incidence XRD (Figure 3-4). The uniformity of the film was also characterized by Atomic force microscopy (AFM) (Figure 3-5), where the root mean square roughness (Rq) was calculated as 4.40nm. The absence of significant variations in the morphology and thickness is of critical importance to the targeted applications for selective Mg²⁺ transport.



Figure 3-3. Structural characterization of Mg-MOF-74 film syntheized through VAC approach. (a) Top-view and (b) cross-section SEM images. (c) TEM image and (d) selected area electron diffraction.



Figure 3-4. X-ray diffraction patterns of the Mg-MOF-74 film. (a) Powder and (b) grazing incidence XRD patterns. (210) and (300) of Mg-MOF-74 could be assigned.



Figure 3-5. Top-view AFM image of Mg-MOF-74 thin film on Au.

The introduction of modulator and assistance of vapor was found to be vital for the film's high-surface coverage and uniformness. MOF-74, featuring a 1-D structure, has the tendency to grow along the 1-D channel and form large sporadic particles, as shown in Figures 3-6 a-b. Therefore, it is challenging to form a continuous film with low thickness. To date, the thickness of the reported MOF-74 film is larger than 1 µm,⁴⁷ potentially leading to considerable resistance and not applicable as a separator in Mg-based energy storage devices. To regulate the formation and growth of MOF-74, acetic acid was employed as the modulator. In the meanwhile, the mixture was adjusted to alkaline condition by sodium hydroxide. The weak basicity could promote the deprotonation of linkers, accelerate the speed of nucleation, and lead to the formation of particles of smaller sizes. As a result, a continuous film composed of densely packed intergrown particles was obtained by the conventional solvothermal approach, where the substrate was immersed in the MOF precursor solution (Figures 3-6 c and e). However, this conventional method resulted in films with rough surfaces due to the lack of quantitive control over the amount of MOF precursors that could convert to film. In contrast, the VAC approach allows the complete conversion of the MOF precursors on the substrate, forming films with uniform thickness by exposure of a mixed solvent vapor with controlled composition (see details in **Experimental Methods**). Therefore, the film thickness can be easily alternated by tuning the concentration or droplet volume of MOF precursors. We have synthesized films on Si wafer with varying thicknesses from 800 nm to 68 nm (Figure 3-7). To the best of our knowledge, it is the thinnest MOF-74 film that has been reported. The feasible thickness control is crucial for the Mg^{2+} transport, as the conductivity is negatively associated with the thickness.



Figure 3-6. Top-view and cross-section SEM images of MOF-74 bulk particles or films synthesized through different approaches. (a) convential method, (b) solvothermal method with acetate, and (c) VAC used in this work.



Figure 3-7. Top-view and cross-section SEM images of MOF-74 films on Si wafers with different thickness. (a-b) ca. 600 nm, (c-d) ca. 266 nm, (e-f) ca. 133 nm, and (g-h) ca. 68 nm.

We further investigated the generality of the VAC approach. The film can be synthesized on various substrates, including Si, SiO₂, Au, and porous substrate, anodic aluminum oxide (AAO) (**Figure 3-18**). As shown in **Figure 3-8**, uniform films with high

surface coverage can be achieved on all the substrates. To further demonstrate the feasibility of our synthetic strategy, MOF-74 films with Co and Ni as metal centers were synthesized, respectively. The composition of the solvent mixture (vapor source) was adjusted accordingly to accommodate the formation condition (see details in **Experimental Methods**). The SEM images showed that both Co- and Ni-based continuous films with the uniform thickness could be obtained (**Figure 3-9**). The obtaining of MOF-74 analogs with different metal centers is of great importance to ion transport. The different metal centers could have different binding strengths with the solvent or anions associated with Mg²⁺, resulting in differences in terms of conductivity and selectivity. These observations and results demonstrated the power of the VAC approach employed in this work. We envisioned it could be extended to the synthesis of additional MOF topologies with 1-D structure, which are challenging to deposited as thin and continuous films.



Figure 3-8. Photographs of Mg-MOF-74 films on different substrates and the bare substrates as comparison.



Figure 3-9. Top-view and cross-section SEM images of (a, b) Co- and (c, d) Ni-based MOF-74 films, respectively.

3.5 Electrochemical properties of the Mg-MOF-74 thin film

Next, the electrochemical properties of the MOF thin film were studied. Our first goal was to show that the coverage of the resulting Mg-MOF-74 thin film on Au-coated Si was complete, and the film was crack-free. For this purpose, Co tetraphenylporphyrin (CoTPP) was employed as a probe redox specie, which is 19 Å in diameter,⁴⁸ larger than the pore of Mg-MOF-74 at 13 Å. As expected, a featureless cyclic voltammogram (CV) between -1.0 and +1.0 V (vs. Pt reference; see **Experimental Methods** for details) was recorded. In stark contrast, the same electrolyte would yield two pairs of distinct redox peaks on a bare Au electrode (Figure 2a), corresponding to the reversible $Co(I)\leftrightarrow Co(II)$ and $Co(II)\leftrightarrow Co(III)$ conversion, respectively.⁸ This set of data showed that our film is crack-free, since otherwise the Co redox peaks would show up in the CVs measured on

MOF-covered electrodes. It also confirmed that MOF-74 was indeed electronically insulating. When the redox specie was switched to ferrocene, whose diameter is 6.6 Å,⁴⁹ a clean pair of redox peaks characteristic of the Fe(II) \leftrightarrow Fe(III) conversion were observed (**Figure 3-10**). The features were almost identical to those on the bare Au electrode, highlighting the ease of ferrocene diffusion through Mg-MOF-74. Together with the CoTPP experiments, the data supported that Mg-MOF-74 permits size-selective transport of ions/molecules.



Figure 3-10. Electrochemical properties of the Mg-MOF-74 thin film. (a) Cyclic voltammograms in 1 mM CoTPP or (b) 1 mM ferrocene with bare gold substrate or MOF-74 film on Au-coated Si.

To further understand the behavior of Mg-MOF-74 as a candidate for selective Mg^{2+} transport, we carried out electrochemical impedance spectroscopic (EIS) experiments using a solid|ion-gel hybrid cell as schematically illustrated in **Figure 3-11a**. Here a hybrid cell was chosen for convenience, so that a reliable contact can be made with the MOF thin film without shorting the circuit. The ion-gel electrolyte was prepared in a 90/10 weight

ratio of ionic liquid/methyl cellulose with 0.25 M Mg(TFSI)2.⁵⁰ An alternating current (AC) voltage was applied between the two electrodes with the frequencies varying between 0.1 Hz and 1 MHz. As can be seen from **Figure 3-11b**, the rapid increase of the imaginary component of the impedance spectra was an indication of a diffusion-controlled transport mechanism,⁵¹ which was expected because with a Au blocking electrode, there was no continuous supply of Mg^{2+} to sustain a stable current. The high-frequency intersect of the Nyquist plot with the x axis reported on the bulk ionic resistance of the materials. And the Bode plots in the Figure 3-11c also showed the impedance plateau at high frequency that was characteristic of bulk ion conduction. Without the Mg-MOF-74, the value was 13.4 Ω , corresponding to the ionic resistance of the ion-gel and the resistance of the whole setup; with Mg-MOF-74, a resistance of 25.6 Ω was recorded. The difference (*ca.* 12 Ω) was attributed to the resistance of the thin Mg-MOF-74 film. Given that the film thickness was 202 nm (Figure 3-3) and using the measured cross-sectional area of 0.52 cm², we calculated the conductivity as ca. 3.17×10^{-6} S·cm⁻¹. It is in the same range as reported previously, where the MOF-74 was used as a solid electrolyte $(1.58 \times 10^{-6} \text{ S/cm})$.³³ It is also worth noting that the value reported previously was measured on pressed pellets which were rich in voids between grains. To what extent these gaps and voids contribute to the measured conductivity will require further research to understand. Our CoTPP electrochemical study showed that we have no such contribution. We are, therefore, confident that the normalized resistivity represents the inherent properties of Mg-MOF-74. The activation energy of the Mg-MOF-74 thin film was 0.53 eV, as shown in Figure 3-11d. Taken as a whole, we learned that the Mg-MOF-74 thin film provides a complete

coverage of the current collector and only allows for species smaller than its pores to pass through with a low overall resistance.



Figure 3-11. Magnesium ion conductivity of Mg-MOF-74 thin film. (a) The cell configuration of the conductivity measurements. (b) Electrochemical impedance spectra (Nyquist plots) measured at room temperature on Au with (red) and without (blue) MOF with the magnified view (inset) at the high frequency end. (c) Bode plots of the Mg-MOF-74 thin film at room temperature. (d) Arrhenius plots of the Mg-MOF-74 thin film and its calculated activation energy for Magnesium-ion conduction.

3.6 Selectivity of the Mg-MOF-74 thin film

With the inherent transport properties understood, our next task was to examine whether Mg-MOF-74 permits selective Mg²⁺ transport. An asymmetric cell as depicted in Figure 3-12 was employed. It consisted of a Mg strip as the anode, a mixture of MgCl₂ (0.1 M), AlCl₃ (0.1 M) and DME as the anolyte, and another Mg stripe as the cathode with $Mg(TFSI)_2(0.1 \text{ M})$ in bis(2-methoxyethyl) (diglyme) as the catholyte. The two electrodes were separated by a film made of Mg-MOF-74 directly grown on an anodized aluminum oxide (AAO) porous support via the same wet-chemistry procedure. Here AAO served as a non-conductive porous support to provide the needed mechanical strength to the MOF thin film. To accurately measure the potentials of the working electrode (*i.e.*, anode), we also introduced a third Mg strip in the working electrode chamber as a reference. In operating this cell, our goals were 3-fold. First, we expected to test whether Mg²⁺ can be transported through the Mg-MOF-74 thin film reliably under electrochemical conditions. Second, we hoped to study whether the Mg-MOF-74 thin film was effective in blocking solvent molecules from crossing over. Third, we wished to monitor whether the anions (e.g., TFSI⁻) could be blocked by Mg-MOF-74.



Figure 3-12. Schematics of the 3-electrode cell configuration.



Figure 3-13. Mg plating/stripping data as measured in an asymmetric cell with Mg-MOF-74/AAO as the separator. The Mg plating process took place at *ca*. -0.15 V (vs. $Mg^{2+/}Mg$), whereas the potential for Mg stripping was *ca*. 0.10 V (vs. $Mg^{2+/}Mg$).



Figure 3-14. SEM images of the Mg working electrodes (in anolyte chamber). (a) Pristine Mg electrode; (b) Mg electrode after cycling in cell with bare AAO; (c) Mg electrode after cycling in cell with MOF/AAO.

As shown in **Figure 3-13**, the Mg plating process took place at *ca.* -0.15 V (vs. Mg^{2+}/Mg ; unless noted, all potentials are relatively to this reference), whereas the potential for Mg stripping was *ca.* 0.10 V. These electrochemical features are comparable to

literature reports in similar electrolytes.⁵² In contrast, the overpotential was *ca*. 0.5 V with the bare AAO as a separator. The increased overpotential could come from the severe crossover of TFSI⁻ from catholyte to anolyte which would passivate the Mg electrode.^{10,53} The cycled Mg working electrodes were characterized by SEM and X-ray photoelectron spectroscopy (XPS). As shown in Figure 3-14, the morphologies of cycled Mg were similar in cells either with bare AAO or with MOF/AAO separator. However, the surface components varied according to the XPS spectra (Figure 3-15). Compared with the MOF/AAO system, the cycled Mg working electrode with bare AAO separator contained more MgCO₃ and MgF₂ that were likely due to TFSI⁻ decomposition, as evidenced by the Mg 1s peak shifting from MgO (1034.3 eV) to MgCO₃ (1035.0 eV), the presence of MgCO₃ (290.10 eV) in C 1s spectra and MgF₂ (685.9 eV) in F1s spectra.⁵⁴ Additionally, the Mg working electrode with the bare AAO separator showed relatively higher element intensity of N and S (Figure 3-15). This evidence proved that the Mg electrode was less passivated by TFSI⁻ with the MOF/AAO separator than with only the AAO separator, leading to lower overpotentials in the Mg plating/stripping experiments, which is desired. The asymmetric cell with Mg-MOF-74/AAO as separator operated for over 100 cycles with a low overpotential of <0.3 V, as shown in Figure 3-16. This set of experiments proved that Mg-MOF-74 as a stand-alone membrane provides adequate Mg²⁺ transport to support repeated striping/plating of Mg in a glyme-based electrolyte system and good TFSI⁻ blocking capability under electrochemical conditions. It is noted that the Mg-MOF-74/AAO platform used to obtain these results can be further optimized. For instance, the overall resistance of the Mg-MOF-74/AAO membrane was higher than what one would expect from a thin Mg-MOF-74 film (e.g., the one shown in Figure 3-3). As shown in **Figure 3-17**, the resistance of the MOF film grown on AAO was calculated as 327Ω , given 0.196 cm² of the contact area, the 64.1 $\Omega \cdot \text{cm}^2$ resistance was 10 times higher than the MOF thin film grown on Au which was 6.4 $\Omega \cdot \text{cm}^2$. This might be due to the inadvertent penetration of Mg-MOF-74 into the pores of AAO (**Figure 3-18**). We envision this issue can be addressed by depositing a layer of porous materials (such as GO) prior to the synthesis of MOF.



Figure 3-15. XPS spectra of cycled Mg working electrodes with bare AAO (top) and MOF/AAO (bottom). (a) Mg 1s, (b) C 1s, (c) F 1s, (d) N 1s, (e) S 2p and (f) O 1s. The cycled Mg working electrode with bare AAO separator showed contained MgCO₃ and MgF₂ components which were not shown in the spectra of cycled Mg electrode with MOF/AAO separator.



Figure 3-16. Electrochemical features of Mg plating/stripping in an asymmetric cell (see main text for details of the experimental conditions). Current density: 0.05mA/cm². Each plating/stripping cycle lasted 2 h.



Figure 3-17. Electrochemical impedance spectra measured of MOF/AAO(red) and bare AAO (blue) with the magnified view (inset) at the high frequency end. The resistance of the MOF film (grown on AAO) was calculated to be 327 Ω , with 0.196 cm² contact area. The large resistance possibly came from the penetration of MOF into the pores of AAO which increased the overall film thickness.



Figure 3-18. Cross-sectional SEM images of (a) bare AAO and (b)Mg-MOF-74 coated AAO. Scale bars: 1µm.

Next, we tested the capability of the Mg-MOF-74 thin film in blocking the two key species in a mixed-electrolyte battery system, namely the counter ions and the solvent molecules. Such a selectivity is critically important, especially for reduction-vulnerable compounds that are used to support the cathode chemistry but are not compatible with Mg (e.g., TFSI⁻ or ClO_4^{-}). To verify the solvent/ion blocking capability of the Mg-MOF-74 film, reduction-vulnerable electrolyte with 0.1 M Mg(TFSI)₂ in propylene carbonate (PC)¹³ was placed on one side of the Mg-MOF-74/AAO separator in an H-cell with an anodecompatible solvent, pure bis(2-methoxyethyl) ether (diglyme), on the other side. The amount of solvent (PC and Diglyme)/TFSI⁻ passing through Mg-MOF-74/AAO on both sides was measured by nuclear magnetic resonance (NMR) spectroscopy. As shown in Figure 3-19a, the Mg-MOF-74/AAO separator blocked PC for 4 days with no PC signal detected in ¹H NMR spectra on the diglyme side; the mole ratio of PC to diglyme was 0.58% after 28 days. By comparison, the ¹H NMR signal of PC was detected after only 30 min when bare AAO was used as the separator (Figure 3-21), and the mole ratio of PC to diglyme quickly reached 50% within 24 h. The TFSI⁻ anion blocking capability was shown in Figure 3-21, as well, where the ¹⁹F NMR data showed no detectable signals due to TFSI⁻ for up to 28 days. Similar blocking capability for diglyme was also observed (Figures 3-19b and 3-22). Diglyme could be completely blocked by MOF-74 within 5 days. The mole ratio of diglyme to PC was only 0.27% after 20 days. As a sharp contrast, the mole ratio of diglyme to PC reached 28% within one day. These results strongly supported that the capability of Mg-MOF-74 thin films to effectively block reduction-vulnerable PC solvents, an anode-compatible diglyme solvent and TFSI⁻ anions from crossing over while allowing for facile transport of Mg^{2+} . It is surprising that the MOF-74 can block solvent and anions

while allowing the transport of large size molecules, ferrocene. We attribute the high selectivity to the abundant open metal sites in MOF-74, as they are able to bind to the Lewis basic sites on the solvent and anions and limit their mobility.



Figure 3-19. Blocking capability measurements with bare AAO (blue line) and MOF-74 on AAO (red line) to separate PC and Diglyme in H-cell. Negligible (a) PC and (b) Diglyme crossover was measured when Mg-MOF-74 film was used as a separator; the crossover was significant when bare AAO was used.

3.7 Conclusion

In summary, we have developed a feasible and efficient synthetic strategy for the MOF-74 thin film with controllable thickness, high coverage, and unfirm surface on different supports. The films are electronically insulating but facile in allowing for Mg²⁺ transport. For Mg-MOF-74 film, when it was directly grown on a Au blocking electrode, a room-temperature resistance of 6.4 $\Omega \cdot \text{cm}^2$ and an ionic conductivity of $3.17 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ were measured. When loaded onto an AAO support, the MOF/AAO could be used as a

stand-alone membrane for electrochemical Mg striping and plating in an asymmetric cell configuration, where different chemicals were used for the anode and the cathode. Successful cycling of over 100 cycles with a low overpotential (<0.3 V) at a current density of 0.05 mA/cm² was obtained. Control experiments proved that the Mg-MOF-74 thin films were effective in blocking the solvents (*e.g.*, PC) and the anions (*e.g.*, TFSI⁻) from crossing over between the anolyte and the catholyte. The computational results revealed that the open metal sites of MOF-74 is of critical importance for the selective Mg²⁺ transport in MOF-74, and it gave a through understanding on the tranport mechanism. Taken as a whole, a promising material for Mg-battery operations where incompatible chemicals are employed for the anode and chemical chemistries is demonstrated. We envision that the outcomes of this work, including film synthesis, battery design, and mechanism study, can incite the future studies.

3.8 Experimental Methods

Chemicals and materials

MgCl₂, dimethoxyethane(DME), bis(2-methoxyethyl) ether (diglyme) and propylene carbonate (PC) (all anhydrous grade) were purchased from Sigma-Aldrich. Mg metal (Ribbon, \geq 99% trace metals basis, Sigma-Aldrich) was scraped by a blade to remove the surface passivation layer before usage. Mg(TFSI)₂ was purchased from Solvionic. Magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, Sigma-Aldrich, 99%), 2,5dihydroxyterephthalic acid (Alfa Aesar, 98%), acetic acid (Sigma-Aldrich, \geq 99.7%), sodium hydroxide (Alfa Aesar, 97.0%), dimethylformamide (DMF, Alfa Aesar, 98%), dimethyl sulfoxide-D6 (DMSO-D6; D, 99.9%, Cambridge Isotope Laboratories, Inc.), difluoroacetic acid (Sigma-Aldrich, \geq 97.0%), hydrochloric acid (Fisher), were used without further purification unless otherwise stated. Ultrapure deionized water (DI H₂O, 18.2 M Ω) was used for aqueous solution preparation. Free-standing anodic aluminum oxide wafers (size: 13 mm, thickness: 100 µm, pore size: 80 nm in diameter) were purchased from Inredox Materials Innovation.

Instrumentation

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6340F and JEOL JSM-7001Fscanning electron microscope. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D2 diffractometer with Cu K α radiation (λ =1.5418 Å). AJA International Orion 8 sputter deposition system was applied to make substrate. An adhesive layer of Ti or Cr with 5 nm was firstly sputtered on Si wafer, and then a thin layer of Au with 50 nm was sputtered. ¹H NMR and ¹⁹F NMR spectra were collected on a Varian Unity INOVA spectrometers (500 MHz, or 600 MHz) with chemical shifts reported in ppm. Mg plating/stripping and CV measurements were performed in an Argon glovebox (Mbraun, O₂ and H₂O <0.1 ppm) at room temperature and data collected on a VMP3 BioLogic potentialstat. Impedance spectra were recorded by using a ModuLab® XM potentiostat. The EIS data were measured by a 25 mV perturbation from 1MHz to 0.1 Hz. The atomic force microscopy (AFM) measurement was performed using ezAFM equipment (Nanomagnetic Instruments), with BM-10 Bench Top Vibration Isolation Platform (Minus K Technology). The images were taken with 512 × 512 Pixel resolution.


Figure 3-20. The configuration of VAC approach for the synthesis of MOF-74.

Mg-MOF-74 thin film synthesis

The configuration of VAC approach was shown in **Figure 3-20**. The film was synthesized in the autoclave, where the substrate was placed in a holder separated from the vapor source. The precursors were cast on the substrate. Before use, the substrates will be washed with acetone, methanol, and isopropanol while sonicated in sequence. The precursor solution was prepared by dissolving 40 mg of 2,5-dihydroxyterephthalic acid (0.2 mmol) and 461.54 mg of Mg(NO₃)₂·6H₂O (1.8 mmol) in the mixture of DMF (5.5 mL), ethanol (5.5 mL), and deionized water (3.6 mL). Then 57.2 µL of acetic acid (1 mmol) was added. The precursor was adjusted to basic condition by adding 1.9 mL of 0.763 M NaOH aqueous solution. The ratio among DMF, ethanol, and water ended up with 1:1:1. 50 µL of the as-prepared precursor solution was cast on the substrate (Si, SiO₂, and Au). 4 mL of the vapor source, composed of DMF, ethanol, and water (volume ratio: 12:1:1), was

added in autoclave. The autoclave was then transferred into a oven preheated to 100 °C. After 24 h, the as-synthesized film was taken out and washed by DMF and methanol. The thickness of the film was ca. 600 nm (**Figure 3-7 a-b**). The thinner films were obtained by diluting the original precursors with the mixture of DMF, ethanol, and water (1:1:1). Taken the film on Si substrate with thickness at ca. 266 nm (**Figure 3-7 c-d**) as an example, the precursor was prepared by adding 1 mL of the original precursors to 9 mL of solvent mixture. When the substrate was switched from Si to Au (**Figure 3-3**), the thickness was found to change slightly due to the different binding strength with the substrate. The 133 nm and 68 nm film was obtained by diluting the original precursors 10 and 30 times, respectively.

Mg-MOF-74/AAO

The synthesis of MOF-74/AAO was similar to the synthesis MOF-74 thin film on Au/Si. An AAO substrate was washed thoroughly with methanol before use. 75 μ L of precursor solution was added on the AAO. The following methods are the same as the synthesis of MOF-74 thin film. The concentration of the precursor solution used in this case is the same as the 266 nm film on Si wafer.

Synthesis of Co- and Ni-MOF-74 thin film

The synthesis of Co- and Ni-based film was modified from the synthetic condition of Mg-MOF-74. For Co-MOF-74, 523.85 mg of Co(NO₃)₂·6H₂O (1.8 mmol) was used to replace Mg(NO₃)₂·6H₂O in the recipe for Mg-MOF-74. The vapor composition was adjusted to the mixture of DMF, ethanol, and water with a volume ratio 1:1:1. The film could form at 100 °C for 3 days. In the case of Ni-MOF-74, 523.42 mg of Ni(NO₃)₂·6H₂O (1.8 mmol) was used to replace Mg(NO₃)₂·6H₂O in the recipe for Mg-MOF-74. The vapor source was pure DMF. The reaction also took place at 100 °C for 3 days.

Solvent Exchange and Activation of MOF-74 thin film

Sample was soaked in methanol and change with fresh methanol every 3 h. The solvent exchange continues two days. And then the sample was placed under 150 °C in vacuum oven for 3 d before any measurements.

Electrochemical measurements

The exposed portion of the Au contact was connected to a wire using silver paste. Silver paste was cured at 80 °C for 30 min. The surface was further covered by an insulating epoxy resin but leaving a small area (3 mm in diameter) of MOF exposed. The epoxy resin was cured at 80 °C for 15 min.

For Fc measurements, 1 mM Fc was dissolved in 10 mL acetonitrile with 0.1 M TBAP6F as the supporting electrolyte. Mg-MOF-74/Au was used as the working electrode (exposed area was \sim 3 mm in diameter). FTO (Fluorine-doped tin oxide) was used as counter electrode (\sim 1 cm² immersed into the solution). Ag/AgCl was used as the reference electrode. In glove box, cyclic voltammograms were conducted with a scan rate of 50 mV/s. The voltage range was -0.3 V– 0.5 V vs. Ag/AgCl.

For CoTPP measurements, 1 mM CoTPP was dissolved in 10 mL DMSO with 0.1 M TBAP6F as the supporting electrolyte. Mg-MOF-74/Au was used as working electrode. FTO was used as counter electrode (\sim 1 cm² immersed into the solution). Pt was used as reference electrode. CV scans were conducted with a scan rate of 50 mV/s. The voltage range was -1.0 V - 1.0 V vs. Pt.

Conductivity measurements

The Mg salts were filled into the MOF-74 thin film by electric field. The Mg-MOF-74/Au was employed as working electrode and it was exposed to in 0.25 M Mg(TFSI)₂ / $0.5 \text{ M} \text{ MgCl}_2$ /DME liquid electrolyte with applied potential (-0.5 V) for 4h to uptake Mg²⁺ before usage (two Mg stripes were used as the counter electrode and the reference electrode, respectively). A Swagelok cell was used in the EIS measurement. The Au blocking electrode was connected to the cell with silver paste. The Cu foil was used as the other blocking electrode with a contact area of ca. 0.5 cm². A thin layer of Mg²⁺-conducting iongel electrolyte (prepared in a 90/10 weight ratio of EMIMTFSI ionic liquid and methyl cellulose with 0.25M Mg(TFSI)₂ salt) was placed between Cu and Mg-MOF-74 to ensure the contact. An alternating current (AC) voltage was applied between the two electrodes with the frequencies varying between 0.1 Hz and 1 MHz. After the EIS measurement, the Mg-MOF-74/Au electrode was taken out and etched by 0.5 M HCl for 2 h to fully dissolve the Mg-MOF-74 layer. After drying, the electrode was subjected to the same EIS measurements with only the ion-gel electrolyte in between the two blocking electrodes. All cell assemblies were performed in a glovebox (Mbruan, O_2 and $H_2O < 0.1$ ppm) at room temperature.

The conductivities at different temperature were obtained by same method as described above. The Swagelok cell was rested at the certain temperature for over 2 hours before the EIS measurement. The temperature ranged from 25°C to 65°C. The activation energy (E_a) was calculated using the equation $\sigma_T = \sigma_0 \exp(-E_a/k_BT)$, where σ_T is the conductivity, σ_0 is the pre-exponential parameter, T is absolute temperature, E_a is the activation energy, and k_B is the Boltzmann constant.

The EIS data of MOF/AAO was measured with two stainless steel as blocking electrodes in H-cell with dual electrolytes. The contact area is 0.196 cm². An AC voltage was applied between the two blocking electrodes with the frequencies varying between 0.1 Hz and 1 MHz.

Mg asymmetric cell measurements

Three different Mg stripes were used as the working electrode, the counter electrode and the reference electrode, respectively. MgCl₂ (0.1 M) and AlCl₃ (0.1 M) were dissolved in DME as the anolyte. Mg(TFSI)₂ (0.1 M) was dissolved in diglyme as the catholyte. The volumes of the electrolytes were both 2 mL in each chamber. The two electrolytes were separated by a Mg-MOF-74 /AAO membrane. All electrochemical measurements were performed in a glovebox (Mbruan, O₂ and H₂O < 0.1 ppm) at room temperature.

Solvent (Diglyme and PC)/TFSI⁻ blocking capability measurements

 $0.1 \text{ M Mg}(\text{TFSI})_2$ dissolved in PC was placed on one side of the Mg-MOF-74/AAO separator in an H-cell. Pure diglyme was placed on the other side of the H-cell with Mg-MOF-74/AAO placed between as a separator. For NMR analysis on the diglyme side, 20 μ L solvent was taken out. Then it was mixed with 600 μ L DMSO-D6 and 3 μ L F₂CHCOOH (as a comparison in ¹⁹F NMR). For the NMR analysis on the PC side, 20 μ L solvent was taken out and mixed with 600 μ L DMSO-D6.



Figure 3-21. Selected regions of ¹H NMR (left side) and ¹⁹F NMR (right side) spectra for the PC/TFSI⁻ selectivity measurements of bare AAO (blue) and Mg-MOF-74/AAO (red) at (a), 30 min, (b), 3 h, (c) & (d), 24 h, and (e) & (f), 28 d.



Figure 3-22. Selected regions of ¹H NMR spectra for the diglyme selectivity measurements of bare AAO (blue) and Mg-MOF-74/AAO (red) at (a), 30 min, (b), 3 h, (c) & (d), 24 h, and (e) & (f), 28 d.

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4.0 Chapter 4

Bottom-up Synthesis of a Two-Dimensional UiO-66 Structure by Coordination

Hindrance on Zr₆ Clusters



A significant portion of the work described in this chapter is from the manuscript that is in preparation:

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4.1 Abstract

A two-dimensional (2D) UiO-66-F₄ structure with tetragonal 4-coordination Zr₆ clusters, derived from the regular fcu-UiO-66-F₄ MOF, has been synthesized under conditions with restricted linker-node coordination. From several different syntheses, it was proposed that such a coordination hindrance could be achieved by adding polymers (Pluronic) to cause steric barricades around metal nodes, increasing the amount of coordination-competing modulators, or decreasing the linker (BDC-F₄) amount to restrict linker-node coordination probability. Demonstrated with this 2D-UiO-66-F₄, the design and syntheses reported in this work establish a new strategy to derive 2D-MOF structures from existing 3D MOF materials without trying different linker-node combinations.

4.2 Introduction

Two-dimensional (2D) nanomaterials have received keen interest in the past decade because of their unique dimension-related properties in separation, catalysis, and energy storage compared to their bulk counterparts.^{1–4} Metal–organic frameworks (MOFs), a class of crystalline porous materials, have emerged as a new member of the 2D-material family. Because MOFs combine high diversities of organic linkers with wide choices of metal ions or clusters, which allows rational design and great tunability of the structure and motif. In the past decade, remarkable progress has been made on constructing MOFs with 2D structures,^{5,6} a lot of which showed promising utilities in applications such as separation, catalysis, and energy storage.^{7–9} Among them, layered Zr MOF materials with Zr₆(oxo) as metal clusters are particularly thermally and chemically stable due to strong Zr-O bridging, making them great candidates for practical applications under harsh conditions.¹⁰ The

strong linker-node connection in Zr MOFs also tolerates the presence of a decent amount of defects and brings coordination vacancies as active sites for sorption and catalysis.^{11,12} However, the syntheses of 2D Zr MOFs are still very challenging as it requires an anisotropic restriction of the crystal growth along the vertical direction without affecting the other two lateral directions.⁸ Such an anisotropic control of growth is especially difficult in Zr-based MOFs, as the Zr_6 cluster has multiple coordination modes (4-, 6-, 8-, 10-, and 12-coordinated), which makes it easily form multiple 3D topologies even with the same linker.^{13,14}

To form 2D Zr MOF structures with the Zr₆ cluster as the metal cluster, the key is to lower its coordination number (≤ 6), which may allow all linkers to form in-plane coordination bonds with the node and thus form 2D Zr MOFs (Figure 4-1). In metal nanoparticle syntheses, surfactants and polymers that can preferentially interact with the crystal facets/precursors have been widely used to induce anisotropic growth.^{15,16} Polymers have also been applied in MOF syntheses to change the morphology of resulted material¹⁷ or to incorporate mesopores into the structure acting as templates.¹⁸ For example, we have previously used Pluronic polymers that have an affinity to Zr₆ clusters as templates to synthesize hierarchically mesoporous UiO-66 MOFs,¹⁹ a prototypical family of Zr MOFs with 12-coordinated Zr₆ clusters. Notably, we also noticed an unknown side product induced by the polymer additive, which showed crystallinity but low porosity, resembling characteristics of 2D-layer materials with close packing. These polymer-assisted studies on crystal growths lead us to a hypothesis that the new phase we observed previously was a 2D structure with low-coordination Zr₆ clusters caused by coordination hindrance caused by the Pluronic polymers.



Figure 4-1. Three possible coordination modes of the Zr_6 cluster that can form 2D networks and the 2D network (1) formed by the tetragonal, 4-coordinated cluster.

Herein, we further resolved the structure of this lately discovered material as a new 2D cpp UiO-66 structure, based on which we demonstrated a coordination-hindrance design to acquire this 2D MOF material. In this study, diffraction experiments by X-ray (regular PXRD, SAXS, and WAXS) and electron microscopes (SAED under HRTEM) were carried out to characterize the materials, which suggest a tetragonal net-work composed of 4-coordinated Zr₆ clusters, connected by tetrafluoroterephthalic acid (BDC-F₄) linkers, forming a cpp topology. Resulted from such a 2D network, flexibility in structure (~7% lattice parameter change) was also observed upon activation. During the formation of this 2D-UiO-66 structure, Pluronic block-co-polymers were proposed to act

as steric barricades to the coordination sites and result in this 2D network (**Figure 4-1c**). Based on this hypothesis, an excess of monocarboxylate modulators (acetic acid, AcOH) were introduced to the synthesis as the coordination-hindrance agents, which also engendered this 2D-UiO-66-F₄ structure. As another method to suppress linker-node coordination, a linker-deficient environment was created by using a hydrophobic porous membrane to separate Zr and BDC-F₄ solutions, but allow BDC-F₄ slowly to diffuse to the other side. This enabled the growth of this 2D-UiO-66-F₄ structure on the Zr-side surface of the membrane and engendered a MOF-membrane hybrid material. Demonstrated by a model UiO-66 MOF, a coordination-hindrance strategy was established to derive 2D MOF structures from existing 3D MOF materials without looking for new metal nodes or linkers.

4.3 Pluronic induced formation of a 2D UiO-66-F4 material

As mentioned earlier, polymers have been introduced in UiO-66 MOF syntheses as mesopore-formation templates^{19,20} or morphology-control agents.¹⁷ These effects are proposed to result from the Zr-O coordination interaction between oxygens on the organic backbone and the Zr clusters.^{17,20} Using this strategy, our group previously have successfully used Pluronic F-127 as templates to grow hierarchically-mesoporous (HM) UiO-66 shell materials on UiO-66 nanoparticle (NP) seeds in an aqueous solution.¹⁹ However, while the HM-UiO-66 growth was guided by pre-synthesized UiO-66 NP seeds, an unknown phase with little porosity was observed when the seed was absent. Its low porosity and few PXRD diffraction signals at the low-20 region led us to propose that this material is a 2D network rather than a 3D matrix (generally with high porosity and many high-index (20) diffraction signals, both resulted from one more spatial dimension). Such

speculation of forming a 2D material with the presence of Pluronic polymers is not unreasonable due to the strong affinity observed between the Pluronics and UiO-66 MOFs,^{17,19} which could block some coordination sites on the Zr₆ cluster and cause an anisotropic growth.



Figure 4-2. PXRD profiles and schematic illustration of 2D-UiO-66-F₄|_{Plu}. a) PXRD profiles of the 2D-UiO-66-F₄|_{Plu} with the 2 θ labelled. The inset table lists the d spacing calculated from the experimental 2 θ , ideal fcu-UiO-66 (orange text) and the derived tetragonal 2D-UiO-66 structure (blue text) with the (hkl) plane as subscript. b) Structures of fcu-UiO-66 and 2D-UiO-66 viewing from [010] and [001] direction (unit cells are circled in dashed squares in the images on the bottom). c) A proposed interaction manner between the Pluronic polymers and the 2D-UiO-66-F₄ structure during its growth.



Figure 4-3. PXRD profiles of simulated structure and as-synthesized materials, and three potential coordination modes. a) PXRD profiles of simulated fcu-UiO-66 structure (black), simulated 2D-UiO-66 structure (cyan), UiO-66-F₄ synthesized without Pluronic F-127 (grey), the unknown material reported previously (blue), and the 2D-UiO-66-F₄|_{Plu} (green). b) Zr₆ clusters with three coordination modes that can from 2D networks, along with a table listing the (010) diffraction signals resulted from the possible 2D networks. aThe diffraction signals of (010) planes resulted from 2D networks constructed by the corresponding Zr₆ clusters (4-c(1), 4-c(2), or 6-c), which were calculated based on Cu Ka source (wavelength 1.5406 Å).

Due to the high-temperature growth condition (90 °C, 1-day growth), the weak crystallinity of the unknown side product in the previous work gave only three visible diffraction peaks (6.05, 8.55, 12.16° (2 θ)). To obtain materials that can provide more structural insights, a slow crystal growth (50 °C, 3-day growth) was employed, which resulted in white-powder products with sharper PXRD signals and the presence of highindex diffractions (Figures 4-2 and 4-3), the material was named as $2D-UiO-66-F_4|_{Plu}$). Micron-size particles with a hollow, "coffee-bean" morphology were observed under EM (Figure 4-4). This hollow spherical morphology has been observed in other 2D materials. For example, a morphology evolution model has been proposed for the growth of SnS_2 hollow spheres.²¹ With a close examination od the particle edges, a morphology of stacking layers was also observed. From an attempt of indexing all detectable diffraction peaks, it was found that they aligned well with the diffraction signal resulted from (hk0) planes of the fcu-UiO-66 structure (see inset Table in Figure 4-2). Notably, the 1st prominent signal is corresponding to (110) diffraction of fcu-UiO-66, which should not be allowed for the fcu structure due to the diffraction extinction of the cubic crystal lattice. All the findings indicate that this new phase retains the lattice parameter from the parent fcu-UiO-66 structure but possibly has a structure losing the long-range order in one direction, which breaks the diffraction extinction rule and allows the presence of (110) diffraction. According to these reasonings, we thus derived a 2D network from the fcu-UiO-66 structure as a possible construction of this material (Figure 4-2b), which is a network composed with 4-coordinated Zr₆ clusters with a C4 symmetry and cpp topology (Figure **4-5**). This layered structure could be obtained by slicing the fcu-UiO-66 layer-by-layer at the z axis. A simulated PXRD profile resulted from the ideal structure 1 indeed well matches with the experimental data (Figure 4-3).



Figure 4-4. SEM images of 2D-UiO-66-F₄|_{Plu}.



Figure 4-5. Schematic illustration on 4-coordinted Zr₆ cluster and its corresponding 2D network with cpp topology.

It was noticed that two other possible 2D networks could be formed by Zr_6 clusters with other coordination modes (4-c(2) or 6-c, **Figure 4-1**). According to the simulated structures, the 1st prominent diffractions of the two materials resulted from the (010) plane are corresponding to ~6.75° and 6.87° (2 θ) under the diffraction condition, which is in stark contrast with the experimental data (**Figure 4-3b**). In addition, despite its scarcity, we also considered the possibility of Zr_{12} clusters being the metal nodes, which could also form 2D structures, demonstrated by Grey and her co-workers with an hns-UiO structure built by 12-coordinated Zr_{12} clusters (**Figure 4-6**).²² However, due to the orientation of the cluster, it can only form hexagonal networks with a d(010) at ~12.83 Å, corresponding to a diffraction signal at ~6.8° (2 θ) (**Figure 4-6**), which is also far away from the experimental result. Based on the stark contrasts between the experimental PXRD data and predicted profiles of these alternative structures, we further consider that structure 1 is the most probable construction for this new phase (additional characterization on the structure will be discussed in the later sections).



Figure 4-6. A potential 2D-network composed of Zr_{12} cluster. a) PXRD profiles of the simulated hns-UiO-66 (red), hns-UiO-66 (violet), and 2D-UiO-66-F₄|_{Plu} (black). The first

two were plotted on raw data requested from Firth, which were reported previously.²² b) Left panels: A polygon demonstration of the 12-coordination Zr_{12} cluster (top) and the corresponding hns network formed using it as building blocks; Right panels: Crystal structure of the hns-UiO-66 viewing from [100] (top) or [001] (bottom).

In such a Pluronic-polymer-induced synthesis, it has been found that the hydrophobic interaction between the linker (BDC- F_4) and the poly(propylene oxide) (PPO) portion of Pluronic played a critical role to form the 2D-UiO-66-F4|Plu material. In a set of syntheses, when Pluronic polymers with low PPO molar ratio were used in the syntheses (i.e., F-127, F-68, F-108), the fcu-UiO-66's most prominent PXRD signal at $\sim 7.3^{\circ}$ (20) was observed (Figure 4-7). However, this peak is much less noticeable when L-31 or P-123 was used in the synthesis, which contains ~ 90 and ~ 70 mol% PPO in the polymer backbone (Figure 4-7). In addition, we previously made an attempt to grow this 2D-UiO-66-F₄|_{Plu} with F-127 but using four different linkers (BDC-NH₂, BDC-(OH)₂, BDC-(COOH)₂, and BDC-F₄), where only the growth with BDC-F₄ resulted in the 2D-UiO-66- $F_{4|Plu}$ material. The syntheses with the other linkers gave either fcu-UiO-66 materials (BDC-NH₂ and BDC-(OH)₂) or products with little crystallinity (BDC-(COOH)₂), suggesting the importance of the fluorine species on the linker to the formation of this 2D network. Together, these data indicate that the growth of the 2D-UiO-66-F₄|_{Plu} material is preferred with coexistence of BDC-F₄ and PPO-rich Pluronic. Considering a higher hydrophobicity of BDC-F₄ linker compared to that of other linkers,²³ it is proposed that BDC-F4 interacts with the hydrophobic PPO chain of the Pluronic while the PEO end coordinates with the Zr_6 cluster during the MOF growth (Figure 4-2c). Such an interaction between the Pluronic polymers and the UiO-66-F₄ building blocks could bring a steric coordination hindrance to the vertical sites on the Zr_6 cluster and thus results in the formation of such a tetragonal 2D network (**Figure 4-2c**).



Figure 4-7. 2D UiO-66-F₄|_{Plu} materials synthesized with different Pluronic polymers. a) PXRD profiles of a series of 2D UiO-66-F₄|_{Plu} materials synthesized on the same day with different Pluronic polymer; Plu = L-31 (black), P-123 (blue), F-68 (green), F-108 (purple), or F-127 (orange). b) Plot of relative PXRD peak integration ratio [fcu-UiO-66 (111) : 2D-UiO-66-F₄|_{Plu} (100)] and the PPO molar mass % in the Pluronic during the synthesis. It shows a positive trend between the PPO molar mass% in the Pluronic and the relative 2D-UiO-F₄ diffraction, which indicates that the hydrophobic chain of the Pluronic facilitates the formation of this 2D-UiO-66-F₄.

4.4 AcOH induced formation of the 2D UiO-66-F4 material

Under the same vein, we hypothesized that the introduction of coordination competitors could also restrict the binding of BDC linkers on the Zr_6 node and shift the coordination number on Zr_6 clusters from 12 (that of 3D fcu-UiO-66) to 4, leading to the

same 2D material resulted from the Pluronic-assisted syntheses. Monocarboxylate modulators (such as AcOH), unlike bidentate BDC linkers, could only form coordination bonds with metal nodes/clusters on one end. Therefore, they could compete with MOF linkers and regulate the MOF growth, controlling the particle size and morphology.²⁴ Also, considering its high solubility in water compared with other organic monocarboxylate modulators, AcOH is chosen as the coordination competitor in this synthesis. The synthesis was first carried out in an aqueous solution with a regular and moderate amount of AcOH modulating the crystallinity (1:44.4).²⁵ As expected, the resulted material showed a fcu-UiO-66-like PXRD pattern (Figure 4-8) and a cubic morphology (Figure 4-9 a-b). As the acetic acid-to-BDC-F₄ ratio increased (1:88.9 to 1:177.8), an intensive peak at $\sim 6.08^{\circ}$ (20) appeared along with other peaks aligning well with that of 2D-UiO-66-F₄|_{Plu}, indicating a formation of the 2D-UiO-66-F4 material. When the amount of AcOH was further elevated (AcOH : BDC = 1:355.2), the new peak at ~6.08° (2 θ) dominated, and the peaks belonging to fcu-UiO-66 was completely suppressed, giving a PXRD profile the same as that of the 2D-UiO-66-F₄|_{Plu} (the resulted material here is noted as 2D-UiO-66-F₄|_{AcOH} onwards). Interestingly, a morphology of rods with stacking layers was observed under SEM (Figures 4-8b and 4-9 g-h), resembling that resulted from screw-dislocation-driven growth of 2D plates with a high growth rate at the dislocation core.²⁶ These data suggest that the increasing amount of AcOH modulator indeed drives the formation of the proposed 4coordination 2D-UiO-66-F₄ materials rather than the 12-coordinated fcu-UiO-66-F₄, mimicking the coordination hindrance brought by Pluronics (Figure 4-8c).



Figure 4-8. UiO-66-F₄ synthesized under different amount of AcOH. a) PXRD profiles of simulated fcu-UiO-66 (black), products resulted from 2D-UiO-66-F₄ synthesis with a AcOH : BDC-F₄ ratio of 44.4 (grey), 88.9 (light green), 177.8 (green), and 355.2 (dark green), and simulated 2D-UiO-66-F₄ (blue). b) SEM images of the product synthesized with a AcOH : BDC-F₄ ratio of 355.2. c) A cartoon showing the proposed 4-coordinated Zr₆ cluster formed with acetic acid modulators.



Figure 4-9. SEM images of fcu-UiO-66-F₄, mixed phase of 2D-UiO-66-F₄ and its 3D counterparts, and pure 2D-UiO-66-F₄ that were synthesized with the presence of AcOH. The ratio of BDC-F₄ to AcOH was gradually increased from top to bottom. (a), (b) fcu-UiO-66-F₄ (BDC-F₄:AcOH=1:44.4). (c), (d) mixed phase (BDC-F₄:AcOH=1:88.9). (e), (f) mixed phase (BDC-F₄:AcOH=1:177.8). (g), (h) 2D-UiO-66-F₄|AcOH (BDC-F₄:AcOH=355.2).



Figure 4-10. Structure analysis of 2D-UiO-66-F₄|_{AcOH}. (a) TEM images of ground 2D-UiO-66-F₄|_{AcOH}. (b) ED pattern taken at [001] with (010) and (010) facets assigned, showing the C4 symmetry. (c) HRTEM image with lattice distance at 1.45 nm, corresponding to (100) facets. (b) and (c) were taken from the selected area marked in (a).

4.5 Structural characterizations of the 2D UiO-66-F4 materials

As a further confirmation of the tetragonal 2D structure, a direct visualization of the crystalline fringes and diffraction pattern were acquired under HRTEM with mildlyground 2D-UiO-66-F₄|_{AcOH} material (**Figure 4-10**). Grinding was applied to obtain the thin sample and avoid scattering across multiple crystals in bulk materials. The same PXRD patterns of the materials before and after grinding suggest that the grinding did not affect the crystallinity of the material (**Figure 4-11**). Clear crystal fringes (d = 1.45 nm) were observed under HRTEM (**Figure 4-10c**), which matches with the d-spacing of (100) in the proposed structure 1 (14.67 Å). The corresponding selected-area diffraction pattern revealed a pattern with apparent C4 symmetry, aligning well with diffractions resulted from $\{100\}$ and $\{010\}$ planes of structure 1 along [001] zone axis. Notably, the other potential 2D structures formed by either Zr₆ or Zr₁₂ clusters with other coordination modes do not possess a C4 symmetry and thus cannot give such a tetragonal diffraction pattern (**Figure 4-12**). The evidence further supported the proposed lamellar structure composed of 4-c(1) Zr₆ clusters, each of which is linked by four in-plane BDC-F₄ linkers with a ~90° angle between two adjacent ones.



Figure 4-11. PXRD patterns of as-synthesized 2D-UiO-66- $F_4|_{AcOH}$ and 2D-UiO-66- $F_4|_{AcOH}$ after ground in mortar for 1 min.



Figure 4-12. Zr_6 or Zr_{12} clusters and their simulated SAED patterns. Clusters with specific coordination mode (top), the corresponding structure viewing from [001] direction (middle), and the simulated SAED patterns from [001] zone axis (bottom).

Composition analysis was also carried out to quantify the linker to node (L/N) ratio in the 2D-UiO-66-F₄ materials by carrying out NMR and ICP analysis on digested samples (see **Experimental Methods**). A low L/N ratio (~3) was deter-mined for both 2D-UiO-66-F₄|_{Plu} and 2D-UiO-66-F₄|_{AcOH}, which was much lower that of an ideal fcu-UiO-66 structure (L/N = 6) or that (L/N = 5) in an fcu-UiO-66-F₄ sample (**Table 4-1**). However, it is slightly higher than the L/N ratio of the proposed structure 1 (L/N = 2), which indicates that there could be additional dangling BDC-F₄ linkers with one carboxylate group coordinating on the axial/vertical coordination sites in our materials.

Table 4-1. Chemical Compositions of 2D-UiO-66 materials as determined by NMR andICP-OES quantitative analyses.

UiO-66 sample	Zr ₆ - cluster content (µmol/mg of MOF)	BDC-F ₄ content (μmol/mg of MOF)	Molecular formula ^{<i>a</i>}
Ideal fcu-UiO-66-F ₄	-	-	Zr ₆ O ₄ (OH) ₄ (BDC-F ₄) ₆
2D-UiO-66-F4 Plu	0.62	1.92	Zr ₆ O ₄ (OH) ₄ (BDC-F ₄) _{3.1} (CH ₃ COO) _{0.4} (OH) _{5.4} (H ₂ O) _{5.4}
$2D-UiO-66-F_4 _{AcOH}$	0.62	2.02	Zr ₆ O ₄ (OH) ₄ (BDC- F ₄) _{3.3} (CH ₃ COO) _{0.6} (OH) _{4.8} (H ₂ O) _{4.8}

Consistent with the 2D structure composed of low-coordination Zr₆-clusters, high flexibility in terms of aperture size and structural dimensions was observed upon high-temperature activation, which has also been observed for other 2D MOF materials.^{8,27} When the 2D-UiO-66-F₄|_{AcOH} sample was activated at two different temperatures to gradually remove solvent molecules from the aperture (120 °C and 150 °C), a gradual shifting of the entire PXRD pattern toward high 20 range was observed (**Figure 4-13**). Particularly, the most prominent (100) peak shifted from 6.08° (no activation) to 6.52° (after 150 °C activation). (It was noted that the sample had been fully activated at 150 °C, as further shift was not observed when activation temperature was increased to 180 °C.) Such a shifting of PXRD profile was also consistently observed on the 2D-UiO-66-F₄|_{Plu} material (**Table 4-2**). This directly reflects an obvious decreasing in lattice parameter on both materials (from 14.52 to 13.55 Å), which potentially result from the bending angle between Z-O-C and ab plane (~28°; **Figure 4-14**). Similar twisting was observed in other 2D Zr MOFs, such as NU-1400 and PCN-700.^{20,28}



Figure 4-13. PXRD patterns of as-synthesized 2D-UiO-66-F₄|_{AcOH} and 2D-UiO-66-F₄|_{AcOH} samples that were activated at 120 °C and 150 °C, respectively. The peak position was calibrated by NaCl or Au powder.

Table 4-2. The peak position in PXRD and d-spacing of (100) planes for as-synthesized 2D-UiO-66-F₄, activated 2D-UiO-66-F₄, and simulated structures.

Materials or simulated structures	(100) Diffraction (2θ°)	d-spacing of (100)
Simulation with distortion at 28°	6.48	13.62
2D-UiO-66-F ₄ _{AcOH} (activated at 150 °C)	6.52	13.55
2D-UiO-66-F ₄ _{AcOH} (activated at 120 °C)	6.33	13.95
2D-UiO-66-F ₄ _{Plu} (activated at 120 °C)	6.35	13.90
As-synthesized 2D-UiO-66-F ₄ _{AcOH}	6.08	14.52
As-synthesized 2D-UiO-66-F ₄ _{Plu}	6.06	14.57
Simulation with distortion at 11°	6.04	14.61
Simulation with no distortion	5.94	14.87



Figure 4-14. Simulated structures of undistorted structure (ideal structure), as-synthesized structure with a tilt angle at 10.8°, and fully activated structure with a tilt angle at 28.2°.

4.6 Formation of the 2D-UiO-66-F4 on membrane surface driven by linker-deficiency

Given that this 2D-UiO-66 was synthesized with Pluronic polymer as coordination barricade or with an excess of coordination competing agent (AcOH), we recapitulate that the critical factor to inducing the 2D growth was a local linker-deficient environment around the Zr₆ cluster. To create such a circumstance in a macroscopic scale, we separately place the Zr-precursor and BDC- F_4 (aqueous) solutions in two chambers of a twocompartment cell with a hydrophobic PEEK microfiltration membrane in between (PEEK stands for polyether ether ketone) (Figure 4-15a). With the hydrophobic nature of PEEK, the membrane does not allow permeation of water under room temperature, whilst it should allow the diffusion of BDC-F₄ to Zr solution under a diffusion-facilitating condition, for example, a moderate heating (for example, 60 °C). After one day, the solution on the Zr side turned cloudy while that on the BDC-F₄ side stayed clear. Rod-like particles with a stacking-layer morphology were observed in the Zr-solution supernatant after the synthesis (Figure 4-16), which resemble that of 2D-UiO-66- $F_4|_{AcOH}$ (Figure 4-8b). On the Zr-side surface of the resulted membrane (named as $2D-UiO-66-F_{4|Mem}$), a thick crust was observed (Figures 4-15b and 4-17). Importantly, the PXRD profiles of both the solid products collected from the Zr solution and a strip cut from the 2D-UiO-66-F₄|_{Mem} showed signals majorly from the 2D-UiO-66 material (Figure 4-15c and 4-18). A top view of the crust under SEM shows micron-size spikes with pyramid-like morphologies (Figure 4-15b), which are commonly seen for 2D plates formed by a screw-dislocation driven growth under conditions with a low precursor supersaturation level.²⁶ These observations clearly suggest that the 2D-UiO-66-F₄ material preferentially formed on the Zr-side of the twocompartment cell, where BDC-F4 linker was deficient, favoring the structure with lowcoordination Zr₆ clusters.



Figure 4-15. Mechanism study on the formation of 2D-UiO-66-F₄. a) A two-compartment cell design to grow 2D-UiO-66-F₄ on a PEEK microfiltration membrane, where the BDC- F_4 linker could preferentially diffuse across the PEEK membrane. b) A top view of the Zr-side surface of the 2D-UiO-66-F₄|_{Mem} product. c) PXRD profiles of simulated fcu-UiO-66 structure (black), simulated 2D-UiO-66 structure (cyan), and the 2D-UiO-66-F₄|Mem (purple).



Figure 4-16. SEM images of the product formed in the Zr-side solution in the 2D-UiO- $66-F_4|_{Mem}$ synthesis.



Figure 4-17. Cross-section SEM images of the 2D-UiO-66- $F_4|_{Mem}$ membrane with the BDC-F₄ side facing up and Zr side facing down. The right panel shows a zoom-in SEM image corresponding to the area circled in white dash box in the left panel (right).


Figure 4-18. PXRD profiles of simulated fcu-UiO-66 (grey), simulated 2D-UiO-66 (green), powder product collected from Zr-side supernatant after the synthesis of 2D-UiO-66-F₄|_{Mem} (blue), and a strip sample cut from the 2D-UiO-66-F₄|_{Mem} (violet). A slight shifting toward high-angle region observed for the 2D-UiO-66-F₄|_{Mem} trip sample could be resulted from the particle activation after MeOH soaking and overnight drying in an 80 °C oven. Please see the section (titled "Structural characterizations of the 2D UiO-66-F₄ materials") in the manuscript for discussions on how activation could affect the lattice parameter and diffraction profile of the materials.

Not surprisingly, the PXRD profile of the 2D-UiO-66-F₄|Mem also gave noticeable signals (for example, (110) dif-fraction at 7.3° 2 θ) from fcu-UiO-66 structure, indicating that some 3D fcu-UiO-66-F₄ also formed on the surface or/and inside the membrane. To

qualitatively determine the spatial distribution of fcu-UiO-66-F4 and 2D-UiO-66-F4 material across the membrane, X-ray diffraction experiments were performed on different areas of the membrane product (with or without the surface crust). Interestingly, a significant decrease of the 2D-UiO-66-F₄ diffraction signals was observed when the diffraction area did not contain the crust, while the experiment performed on the area with the crust gave suppressed fcu-UiO-66 signals (Figure 4-19). Considering tge direct diffraction of the crust powder mostly gave 2D-UiO-66 diffraction pattern (Figure 4-19), it is concluded that the crust product is attributed to the 2D-UiO-66-F₄ material and that the fcu-UiO-66-F₄ is majorly located inside the PEEK porous membrane. Since it is obvious that there would be more $BDC-F_4$ linker inside the membrane than on the Zr-side surface of the membrane during the growth, the 2D-UiO-66-F₄ growing as a crust layer on the Zr-side surface highlights the importance of a linker-deficiency condition to its formation. Thus, demonstrated by UiO-66-F₄, decreasing the amount of link-er used in the synthetic condition of a 3D porous MOF could limit the coordination number on the metal node and induce the formation of a 2D network.



Figure 4-19. PXRD profiles collected from a diffractometer (Cu K α , 1.5406 Å) with the 2D-UiO-66-F₄|_{Mem} material piece and the crust powder on its surface. a) the diffraction pattern acquired on an area without crust (black), with obvious crust (blue), and the crust powder scraped from the membrane surface (orange). b, c) Photograph collected under an optical microscope in the diffractometer on the corresponding exposure area with and without the crust for the data collection in panel a) (the approximate exposure areas in the experiment are highlighted in semi-transparent squares).

4.7 Conclusion

In this work, we have found new 2D-UiO-66-F₄ material and demonstrated a coordination-limiting strategy to shift the growth of an existing 3D Zr MOF to a 2D network. From PXRD, WAXS, PDF, and HRTEM data, we resolved the new structure as a tetragonal network composed of 4-coordinated Zr₆ clusters and BDC-F₄ linkers. (Note: At the point when the thesis was being written, additional structural characterization was undergoing, which includes synchrotron-based wide-angle X-ray scattering and X-ray total scattering. The data would be coupled with Pawley/Rietveld refinement and pair-distribution function analysis to have additional evidence of the proposed 2D cpp structure.) From polymer- and modulator-assisted syntheses, we have established that a low linker concentration around the metal cluster is critical to limit its coordination and initiate 2D anisotropic growth. Guided by this coordination-limiting design, a polymer membrane material containing the 2D-UiO-66-F₄ was synthesized under a linker-deficient, template-free environment. With the conditions we have explored in this work, three synthetic routes are recapped here that could be taken to achieve such a coordination hindrance: 1)

adding "barricade" agents such as polymers that can interact with building blocks, 2) using an excess amount of coordination-competing agents, such as monocarboxylate modulators for Zr MOFs, and 3) keep a low linker amount in the synthetic solution during the material growth. The rational design and synthesis of this 2D-UiO-66 material show an untouched route to develop new 2D MOF materials - restricting coordination sites on the secondary building units without trying new linker-node combinations.

4.8 Experimental Methods

Unless otherwise stated, all reagents were used as received. Zirconium chloride (ZrCl4) and Hafnium chloride (HfCl4) were purchased from Strem Chemicals, Inc. (Newburyport, MA, USA). Hydrogen peroxide (H₂O₂, 30 wt % in water), naphthalene, formic acid (FmOH), acetic acid (AcOH), 1,4-benzene dicarboxylic acid (BDC), tetrafluoro terephthalic acid (BDC-F4), Pluronic® F-127, maleic acid, pyromellitic acid (BDC-(COOH)₂), 2-amino terephthalic acid (BDC-NH₂), and zirconium ICP standards were purchased from Sigma-Aldrich Co., LLC. (St. Louis, MO, USA) and used as received. 2,5-dihydroxyterephthalic acid (BDC-(OH)₂) was purchased from TCI America (Portland, OR, USA) and used as received. Deuterated dimethylsulfoxide (DMSO-d6, 99%) was purchased from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA). Ultrapure deionized (DI) water (18.2 M Ω •cm resistivities) was obtained from a Millipore Milli-Q Biocel A10 instrument (Millipore Inc., Billerica, MA, USA). Solvents were purchased from either Sigma-Aldrich Co., LLC. (St. Louis, MO, USA) or Fisher Scientific, Inc. (Pittsburg, PA, USA) and used as received.

Powder X-ray diffraction (PXRD) patterns of the materials (except for 2D-UiO-66-F₄|_{AcOH}) were collected on a STOE's STADI-MP powder diffractometer (STOE & Cie. Ltd, Darmstadt, Germany) equipped with an asymmetrically curved Germanium monochromator (Cu K α 1 radiation, $\lambda = 1.54056$ Å), a one-dimensional silicon strip detector (MYTHEN2 1K from Dectris AG, Baden, Switzerland), and a line-focused Cu Xray tube operated at 40 kV and 40 mA. The as-received powder was sandwiched between two acetate foils (polymer substrate with neither Bragg reflections nor broad peaks above 10 degrees) and measured in transmission geometry in a rotating holder. Prior to the measurement, the instrument was calibrated against a NIST Silicon standard (640d). Measurements were made over the range 5° < 20 < 60° in 6° steps of the detector and an exposure time of 20 s per step. Powder X-ray diffraction (PXRD) analyses of 2D-UiO-66-F₄|_{AcOH} materials were conducted at Boston College on a Bruker AXS D2 Phaser diffractometer (Cu K α radiation, λ = 1.5406 Å) (Bruker Biospin Corp., Billerica, MA, USA). Sodium Chloride or Au powder was mixed with the samples and served as standard.

 N_2 adsorption and desorption isotherms were measured on a Micromeritics 3Flex (Micromeritics Instrument Corporation, Norcross, GA, USA) at 77 K. Before each run, samples were activated in a National Appliance Laboratory Bench Vacuum Oven-model M5831 (National Appliance Co., Portland, OR, USA) that was connected to house vacuum (~20 in Hg), and then at 120 °C for 12 h on a Micrometrics Smart VacPrep (Micromeritics Instrument Corporation, Norcross, GA, USA) sample degas station. About 20-50 mg of sample was used in each measurement and the BET area was calculated in the region P/P₀ = 0.005-0.01, which is selected to satisfy the first consistency criterion for materials containing micropores, as recommended by Walton and Snurr.²⁹ The pore-size-distribution functions (PSDFs) of the MOFs were calculated from the adsorption-desorption isotherms by density functional theory (DFT) using the carbon slit-pore N₂-DFT model in the range of $0 < P/P_0 < 1$.

Scanning electron microscopy (SEM) images were obtained at Northwestern University's EPIC/NUANCE facility on an SU8030 FE-SEM microscope (Hitachi High Technologies America, Inc., Dallas, TX, USA) with an acceleration voltage of 10-15 kV or at ShanghaiTech University on a field emission scanning electron microscope (FE-SEM) JEOL JSM-7800F or JEOL-6340F (JEOL Shanghai Semiconductors Ltd., Shanghai, China) with an accelerating voltage of 5-10 kV. Size measurements were obtained from sample populations of >100 particles, which were used to construct the standard normal distribution plots (mean \pm 3 standard deviation units) and the histograms.

Transmission electron microscopy (TEM) images were obtained at Shanghai on JEOL JEM-2100 (JEOL Shanghai Semiconductors Ltd., Shanghai, China) plus with an accelerating voltage of 200 kV.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on a computer-controlled (QTEGRA software v. 2.2) Thermo iCap 7600 Duo ICP-OES (Thermo Fisher Scientific, Waltham, MA, USA) instrument equipped with a SPRINT valve and a CETAC 520ASX autosampler (Teledyne CETAC, Inc., Omaha, NE, USA).

For obtaining MOF compositions, 1H NMR and 19F NMR spectra were recorded on a Bruker Neo 600 MHz spectrometer (Bruker Biospin Corp., Billerica, MA, USA) equipped with a triple-resonance (HCFN) cold probe w/ Z-gradient and the following manufacturer-reported sensitivities: ${}^{1}\text{H} = 5000$, 19F = 7000, and 13C = 800. 1H NMR chemical shifts are referenced in ppm downfield from tetramethylsilane (TMS, δ scale) using the residual solvent resonances as internal standards. ${}^{19}\text{F}$ NMR chemical shifts are referenced in ppm downfield from trichlorofluoromethane (CFCl₃, δ scale). Trifluoroacetic acid (TFA) was used as an internal standard.

A Mettler ToledoTM Micro-Analytical Balance (Mettler-Toledo, LLC., Columbus, OH), located in the IMSERC facility of Northwestern University, was used to weigh samples ≤ 10 mg. To minimize static, samples were weighed into Al sample pans; the weighing apparatus and sample containers were also de-staticized with a Milty Zerostat 3 anti-static gun when necessary.

An IKA-Werke RCT Basic S1 Magnetic Stirrer (IKA Works, Inc., Wilmington, NC, USA) was used to carry out the experiments that require heating and stirring. The stirring rate was kept at a relatively vigorous rate (~ 800 rpm) to maintain nanoparticle dispersion and favors overgrowth on the seed instead of undesirable self-nucleation. To maintain a consistent temperature throughout the reaction volume, the reaction vial was immersed in a mineral oil bath in a manner that the top of the reaction volume is below the level of the oil bath.

For the synthesis experiments, centrifugation was carried out in an Eppendorf Centrifuge 5804 R, Model AG 22331 (Eppendorf AG, Hamburg, Germany) equipped with an F34-6-38 rotor or a centrifuge from Thermo Scientific, Model CL 2 (MA, USA). All centrifugations were carried out at 25 °C and 8000-11000 rpm (8228-15557 g) for 10-30 minutes on Eppendorf and 2900 rpm for 8-10 min on Thermo Scientific. The drying of MOF samples after synthesis was routinely carried out at 120 °C for 24 h in a National Appliance Laboratory Bench Vacuum Oven-model M5831 (National Appliance Co., Portland, OR, USA) that was connected to house vacuum (20 in Hg).

Volume measurements were carried out using mechanical pipets (professionally calibrated every 3 months) for convenience. However, the volume accuracy does not need to be maintained at the \pm 0.005 mL level of accuracy that is intrinsic to these instruments.

Synthesis of Materials

2D-UiO-66-F4[Ptu. This material was synthesized by F.Z. via a protocol modified from reported literature by us (the material was named as [Zr+BDC-F4]* in that article).¹⁹ A BDC-F₄ solution was prepared by dissolving F-127 (3000 mg, 240 μ mol) with AcOH_{aq} (100 mL of a 1.75 M aqueous solution), followed by dissolving BDC-F₄ (238 mg, 1 mmol) under sonication (~5 min). Another ZrCl₄ solution was prepared by dissolving F-127 (3000 mg, 240 μ mol) with AcOH_{aq} (100 mL of a 1.75 M aqueous solution), followed by dissolving ZrCl₄ (233 mg, 1 mmol) under sonication (~5 min). For the synthesis, an aliquot (5 mL) of the BDC-F4 solution was mixed with an aliquot (5 mL) of the ZrCl₄ solution in an 8 dram vial, which was then placed into a 50 °C pre-heated oven for 72 h. For each synthesis, 20 vials were used and they were allowed to cool down to rt after being taken out from the oven. The resulted solution in all the vials was combined together in a 250 mL beaker, which was then evenly dispensed into six 50 mL centrifuge tubes and subjected to centrifugation (10000 rpm, 10 min); the supernatant was removed by decantation to remove unreacted reagents and F-127. MeOH (~25 mL) was added to each centrifuge tube and the tube was sonicated (~10 min) to homogenize the mixture. The resulting MeOH suspension was subjected to centrifugation (10000 rpm, 10 min) and the supernatant was removed by decantation. This MeOH-washing procedure was repeated twice more, after which the product was left to air-dry inside the tube. The dry product was then subjected to Soxhlet extraction with MeOH. The product was then collected from the Soxhlet thimble, air-dried, and further dried for 12 h inside a 60 °C oven. Yield = ~165 mg.

2D-UiO-66-F₄|Mem. This material was grown inside and on top of synthesized in a commercially available PEEK microfiltration membrane (Sterlitech, WA, USA) by using a two-compartment setup (Figure 4-20). The as-received PEEK membrane (10×10 cm²) was firstly evenly cut into four pieces ($5 \times 5 \text{ cm}^2$). Clamp one PEEK membrane ($5 \times 5 \text{ cm}^2$) in between the cell with a joint clamp (45/50). A BDC-F4 solution was prepared by dissolving BDC-F⁴ (476 mg, 2 mmol) with AcOH_{aq} (40 mL of a 1.75 M aqueous solution), under sonication (~5 min). Another ZrCl₄ solution was prepared by dissolving ZrCl4 (466 mg, 2 mmol) with AcOH_{aq} (40 mL of a 1.75 M aqueous solution) under sonication (~5 min). The two solutions (30 mL each) were simultaneously decanted into the two chambers correspondingly. A rubber stopper (size) poked with a needle (size) was then place on the mouse on each side (the needle was to avoid building pressure in either side which might push the solution to the other side unintentionally during the capping process). Then the cell with one cap (with a needle) on each side was then placed into a 60 °C pre-heated oven for ~ 30 min, after which the needles were removed from the caps and the cell was heated in the oven for another 23.5 h. After the reaction, solid products were observed in the solution of ZrCl₄ side, while little was seen on the BDC-F₄ side. Similarly, through the

glass, membrane surface on the ZrCl₄ side turned rough/powdery, while the other side remained smooth. The cell was taken out from the oven and cooled down to rt, after which the joint clamp was removed. The solution from the ZrCl₄ side was decanted into a 50 mL centrifuge tube and collected by centrifugation (10000 rpm, 10 min). The supernatant in the tube was decanted and replaced with fresh MeOH (~25 mL). The tube was subjected to sonication (~5 min) and centrifugation (10000 rpm, 10 min). This washing process of decantation, MeOH soaking, sonication, and centrifugation was repeated twice more. Then the palette in the tube was air-dried (~1 h), oven-dried (60 °C, overnight), and transferred into a 2-dram vial for later characterizations. The membrane was then transferred into a petri dish having MeOH (~20 mL) and allowed to be soaked for 1 h. The MeOH was replaced by fresh MeOH (~20 mL) and the membrane was soaked in MeOH for another 1 h. Then the membrane was air-dried (for ~1 h) and oven-dried (60 °C, overnight).





66-F₄|mem synthesis on each side were noted with the arrow. b) The photograph of the two-compartment cell with PEEK membrane, rubber cap, and the joint clamp (the setup was vertical for the ease of taking the photo, and it was put horizontally flat in a container inside the oven during the reaction (beaker or petri dish)). The upper chamber was filled with water and the bottom chamber was empty (air). The PEEK membrane was clamped in between, which hold the water well overnight without obvious permeation.

fcu-UiO-66-F4. The synthesis of fcu-UiO-66-F4 was carried out in an aqueous phase with acetic acid as the limiting agent. Specifically, a BDC-F4 solution A was prepared by dissolving BDC-F4 (0.183 mmol, 43.5 mg) in an acetic acid aqueous solution (0.5 mL, 8 M) in a 20-mL glass vial, which was heated in an oil bath (50 °C) with stirring until the BDC-F4 solid fully dissolved. A ZrOCl₂ solution was prepared by dissolving ZrOCl₂·H₂O (0.18 mmol, 58.01 mg) with an acetic acid aqueous solution (0.5 mL, 8 M) in another 20 mL glass vial. The ZrOCl₂ solution was preheated in the oil bath (50 °C) for 5 min before being added to the other vial in the oil bath with the BDC-F4 solution (in this synthesis, the ratio of BDC-F4 to AcOH in the mixture was 1:44.4). The mixture was stirred for 1 min and then left undisturbed in the 50 °C oil bath for 24 h. After 24h, the vial was taken out and cooled down to rt before washing. The supernatant was removed from the resultant product by centrifugation (3000 rpm, 8 min) and decantation. The sample was firstly washed by DMF once and followed by methanol (3 times). The sample was dried overnight under a house vacuum at room temperature, which gave solids in a white powder form.

2D-UiO-66-F4|AcOH. The materials were synthesized following the same protocol as that for fcu-UiO-66-F4 synthesis, but with different BDC-F4-to-AcOH ratios (1: 88.9 and 177.8). At the ratio of 1: 88.9 (BDC-F4 : AcOH), the BDC-F4 solution was prepared by adding BDC-F4 (0.183 mmol, 43.5 mg) with acetic acid aqueous solution (1 mL, 8 M). While the ZrOCl₂ solution was prepared by dissolving of ZrOCl₂·H₂O (0.18 mmol, 58.01 mg) with acetic acid aqueous solution (1 mL, 8 M). At the ratio of 1: 177.8 (BDC-F4 : AcOH), the same amount of BDC-F4 and ZrOCl₂·H₂O was dissolved separately in an additional amount of acetic acid aqueous solution (2 mL, 8 M). Typically for 2D-UiO-66-F4|AcOH, the BDC-F4 solution was made by using 4 mL acetic acid aqueous solution (8 M), and the ZrOCl₂ solution was also made by using 4 mL acetic acid aqueous solution (8 M). All the other synthetic conditions and workup steps are the same as that of the fcu-UiO-66-F4 synthesis.

Sample Activation. The sample was dispersed in methanol by sonicated for about 5 min and was soaked in methanol for 3 h. Then the solid was collected by centrifugation (3000 rpm, 8 min). Fresh methanol was added to soak the sample for another 3 h. This solvent exchange process was repeated 8~9 times. The supernatant was removed, and the sample was activated at different temperatures under house vacuum (~20 in Hg) for about 48 hours before testing. The activation temperature was 120 °C or 150 °C.

Compositional analyses of the 2D-UiO-66-F4 materials

Procedure for the quantitative analysis of the Zr content in UiO-66 materials. In a 15 mL polypropylene centrifuge tube, conc. HNO₃ (750 µL), HCl (250 µL), and HF (250 µL) were added to a small amount of sample (~1 mg) to be analyzed. The resulting mixture was sonicated until the solution became clear (~2 h) albeit sometimes small white flakes could still be seen on the bottom. After the sonication, DI H₂O (2.750 mL), HNO₃ (750 µL), and H₂O₂ (250 µL, 30 % (w/w) in H₂O) were added into the tube, which was then capped and placed into a 70 °C oil bath for 12 h. In the end, the solution was clear, and no solid was visible. The resulting solution was then transferred into a 50 mL polypropylene centrifuge tube and diluted with DI water to a final volume of 50 mL. This solution was then analyzed for Zr and Hf by ICP-OES (λ Zr = 343.823, 327.305, 349.621, and 339.198 nm) against a calibration curve of standards with known [Zr].

Caution: HF is very toxic and dangerous to handle without proper safety training. PPE must include Silvershield gloves and goggles. Acid digestions and subsequent dilutions should be carried out in a well-ventilated hood.

Procedure for the quantitative analyses of BDC-F4, and acetic acid in MOF. The ¹H NMR/¹⁹F NMR spectra of the digested MOFs can quantitatively reveal the composition of the organic ligands and acetic acid present in each digested sample, and the ICP-OES data can yield the weight percentage of Zr composition in the sample. Thus, the linker to node (L/N) ratio and chemical formula can be determined for the materials.

AcOH (¹H NMR). In a 2-mL polypropylene centrifuge tube, HF (10 μ L) and DMSO-d6 (90 μ L) were added to a small sample (~2 mg) of the material to be analyzed. The resulting mixture was sonicated until the solution became clear (~1 h). Then an aliquot (10 μ L, corresponding to ~0.2 mg of the sample) of the resulting solution was transferred to a 2 mL polypropylene centrifuge tube along with an aliquot of maleic acid (MA) solution in DMSO-d6 (12 mM, 50 μ L) and fresh DMSO-d6 (540 μ L). This combined solution was transferred into an NMR tube and then analyzed by ¹H NMR spectroscopy with a 90° pulse using a 50-s delay between scans. The amount of each substrate was calculated by comparing the integration against a calibration curve of standards with known concentrations (see Figure **4-21** for calibration curve, and **Figure 4-22** for NMR spectra).



Figure 4-21. NMR (¹H and ¹⁹F) calibration curves for AcOH (left), and BDC-F₄ (right) against the internal standards (MA for ¹H; TFA for ¹⁹F).



Figure 4-22. ¹H NMR spectrum of the digested 2D-UiO-66-F₄|_{Plu} (bottom) and 2D-UiO-66-F₄|_{AcOH} (top) with MA as the internal standard.

BDC-F4 (¹⁹**F NMR**). In a 2-mL polypropylene centrifuge tube, HF (10 μ L) and DMSOd6 (90 μ L) were added to a small sample (~2 mg) of the material to be analyzed. The resulting mixture was sonicated until the solution became clear (~1 h). Then an aliquot (10 μ L, corresponding to ~0.2 mg of the sample) of the resulting solution was transferred to a 2 mL polypropylene centrifuge tube along with an aliquot of 4.0 mM trifluoroacetic acid (TFA) solution in DMSO-d6 (50 μ L), and fresh DMSO-d6 (540 μ L). This combined solution was transferred into an NMR tube and then analyzed by 19F NMR spectroscopy with a 90° pulse using a 5 s delay between scans, which exceed the T1 relaxation time for BDC-F4 (435 ms), and TFA (107 ms). The amount of each substrate was calculated by comparing the integration against a calibration curve of standards with known concentrations (see Figure 4-21 for calibration curve, and Figure 4-23 for NMR spectra).



Figure 4-23. ¹⁹F NMR spectrum of the digested 2D-UiO-66-F₄|_{Plu} (bottom)and 2D-UiO-66-F₄|_{AcOH} (top) with TFA as the internal standard.

Computational Methods

To assess the chemical stability of the proposed 2D structures (4-c(1) Zr₆, 4-c(2) Zr₆, 6-c Zr₆, and 12-c Zr₁₂) and predict their corresponding experimental spectra (PXRD, SAED, etc.), theoretical models of the structures were constructed (**Figure 4-24**). For the 4-c(1) Zr₆ structure, a 2D single layer sheet was generated by cutting the conventional unit cell of fcu UiO-66-F₄ (20.7 × 20.7 × 20.7 Å) along the (001) plane.³⁰ The unit cell of the 2D sheet was then further reduced based on symmetry considerations (14.7 × 14.7 Å).

Open metal sites exposed on the surface of the Zr₆ cluster due to removal of linker molecules were capped with hydroxide/water, in a way consistent with the chemical formula of the experimental structure. Similarly, the 4-c(2) Zr₆ and 6-c Zr₆ structures were constructed by cutting the primitive unit cell of fcu UiO-66-F₄ (14.8 × 14.8 × 14.8 Å) along the [001] direction,³¹ and also capping exposed open metal sites with hydroxide/water. In the case of 4-c(2) Zr₆, two additional linkers in the plane of the 2D sheet were removed. Finally, the 12-c Zr₁₂ structure was constructed by cutting the conventional unit cell of hcp UiO-66-F₄ (14.7 × 14.7 × 37.0 Å) along the [001] direction.³²



Figure 4-24. Four possible 2D networks could be formed by BDC-F₄ linkers and Zr clusters (Zr_6 or Zr_{12}).

For each generated structure, density functional theory (DFT)-based structure optimization was performed using a plane-wave basis set, and the projector augmented

wave (PAW) method through the Vienna Ab Initio Simulation Package (VASP version 5.4.4).³³ The Perdew-Burke-Ernzerhof exchange-correlation functional revised for solids (PBEsol) was applied, with dispersion effects accounted for by Grimme's D3 correction with Becke-Johnson damping (D3BJ).^{34–36} The cutoff energy was set to 500 eV, and the smearing parameter to 0.05 eV to facilitate SCF convergence. Because of the 2D nature of the structures, a 15-Å vacuum layer was used and a dipole correction was applied in the z-direction. From this, the optimized structures of the 2D sheets were obtained. The lattice parameters of the optimized 2D structures did not deviate significantly from their initial values (<1% change), which are based on the parameters of 3D bulk UiO-66.

To account for the discrepancy in PXRD d-spacing values among the activated, unactivated, and 4-c(1) Zr₆ theoretical structures, we hypothesized a decrease in the lattice parameter induced by distortion in the angle between the O_{linker} -Zr-Zr- O_{linker} and O_{linker} -C- O_{linker} planes (**Figure 4-14**).²⁸ To test the feasibility of this hypothesis, theoretical structures were constructed in which the planar angle of the 4-c(1) Zr₆ structure is distorted such that its initial lattice parameter is reduced by factors of 0.975, 0.950, 0.925, 0.912, and 0.900. Following optimization of each distorted structure (using the protocol described above), the optimized lattice parameters were found to be 14.61, 14.15, 13.88, 13.62, and 13.42 Å, respectively, with corresponding distortion angles of 11, 21, 25, 28, and 31°. The optimized structure with 11° distortion angle best approximated the unactivated samples with respect to PXRD d-spacing, while the structure with 28° distortion angle best approximated the activated samples. Moreover, the electronic energy differences between the undistorted structure and structures with 11 and 28° distortion angles were calculated to be 0.19 and 0.97 kcal/mol per distorted Zr-O_{linker} bond, respectively. These results suggest that Zr-

O_{linker} angle distortions are a plausible explanation for the discrepancy in d-spacing observed between the unactivated and activated samples.

4.9 References

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