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多孔骨架薄膜之相態工程與結構設計：從結晶異質介面到溶
劑揮發誘導組裝

Phase Engineering and Structural Design of Porous Framework
Thin Films: From Crystalline Hetero-Interfaces to Solvent
Evaporation-Induced Assembly

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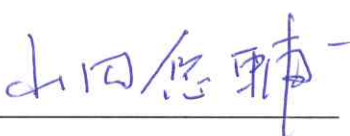
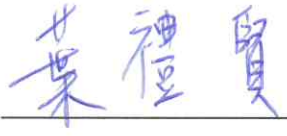
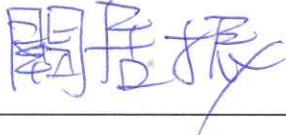
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Phase Engineering and Structural Design for Porous Framework Thin Films:
Overcoming Grain Boundaries — From Crystalline Hetero-Interfaces to Amorphous
Mesoporous Assembly

本論文係程楚仁(D11551002)在國立臺灣大學分子科學與技術國際研究生博士
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誌謝

時光匆匆，轉眼間博士班的生涯已經告一段落了。在這四年就讀博士班的期間，經歷過了非常多事情，也在這四年間因為合作的關係待過不同實驗室，從卓越大樓、凝態中心、台科大、京都大學、名古屋大學，從一個實驗室的菜鳥逐漸變成實驗室的學長。要感謝的人與事真的很多，我盡我可能的在有限的版面表達。

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於 國立臺灣大學凝態科學研究中心 中華民國 115 年 5 月 21 日



摘要

金屬有機框架 (metal-organic frameworks, MOFs) 與共價有機框架 (covalent organic frameworks, COFs) 因具有高度可設計的孔洞結構、高比表面積、可調控的表面化學性質與多樣化的框架組成，已成為近年來重要的多孔材料平台。然而，傳統 MOFs 與 COFs 多以粉末型態被合成與研究，在實際裝置應用中仍面臨許多限制，例如薄膜連續性不足、顆粒間傳輸阻力增加、界面接觸不良，以及孔道無法有效連接等問題。尤其在離子傳輸、滲透能發電與電化學感測等應用中，材料不僅需要具備內在孔洞功能，更需要形成連續且可控制的薄膜或膜材料結構。因此，本論文以「多孔骨架薄膜之相態工程與結構設計」為核心，探討如何透過異質介面設計與非晶介孔薄膜構築，將多孔框架材料從傳統粉末推進至功能性連續薄膜平台。

本論文第一部分設計並製備 MOF-on-COF 異質雙層膜，用於離子選擇性傳輸與滲透能發電。首先藉由界面縮合反應製備自由支撐 COF 膜，再利用單側暴露策略於 COF 膜表面選擇性生長 UiO-66-NH₂ MOF 層，成功建立具有孔徑與表面電荷不對稱性的異質膜結構。此設計結合 MOF 次奈米孔道所提供的離子篩分能力，以及 COF 連續孔道所帶來的離子傳輸路徑，使膜材料在濃度梯度下提升發電表現。進一步的陽離子與陰離子種類比較也顯示，MOF-on-COF 異質膜可展現高離子選擇性，並有效區分不同水合尺寸與電荷特性的離子；其整體滲透能轉換行為主要受到水合離子尺寸、離子電荷、孔徑限制與界面不對稱性等因素共同調控。

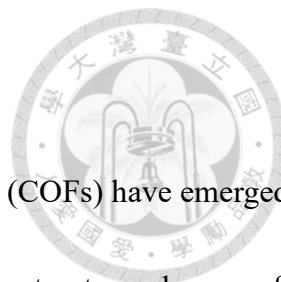
第二部分則發展溶劑揮發誘導組裝法，以 block copolymer 作為軟模板，製備連續中孔無



定形 ZIF-90 薄膜。透過調控 THF/MeOH 共溶劑環境、配體濃度、微胞形成與快速溶劑揮發過程，本研究成功抑制 ZIF-90 在薄膜形成過程中的結晶行為，同時引入可連通的中孔結構。結構分析顯示，所得 *a*ZIF-90 薄膜具有連續形貌、均勻孔洞分布與保留的 Zn-imidazolate 配位環境。進一步地，本研究亦透過理論計算探討不同溶劑環境對 ICA 去質子化與 Zn(II) 配位交換行為的影響，試圖從熱力學角度理解 THF-rich 條件下 ZIF-90 前驅物較容易維持於無定形狀態的原因。因此，本研究將無定形相作為一種有效的相態工程策略，用以避免晶粒邊界與不連續顆粒生成。進一步以尿酸電化學感測作為概念驗證，證明中孔無定形結構可改善分子擴散與活性位點可及性。

整體而言，本論文展示了結構設計與相態工程在多孔骨架薄膜材料中的重要性。透過結晶 MOF/COF 異質介面與溶劑揮發誘導之中孔無定形 MOF 薄膜，本研究提供了建構連續多孔框架薄膜的新策略，並為未來能源轉換、離子傳輸與電化學感測應用提供重要的材料設計方向。

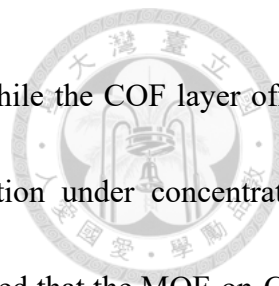
關鍵字：金屬有機框架、共價有機框架、多孔骨架薄膜、異質介面、相態工程、滲透能發電、中孔無定形 MOF



Abstract

Metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) have emerged as important porous material platforms because of their highly designable pore structures, large surface areas, tunable surface chemistry, and diverse framework compositions. However, conventional MOFs and COFs are mostly synthesized and investigated in powder form, which still presents several limitations for practical device applications, including poor film continuity, increased interparticle transport resistance, weak interfacial contact, and discontinuous pore pathways. These issues are particularly critical for ion transport, osmotic power generation, and electrochemical sensing, where porous materials must not only possess intrinsic pore functions but also be constructed into continuous and controllable thin-film or membrane architectures. Therefore, this dissertation focuses on the phase engineering and structural design of porous framework thin films, aiming to advance porous framework materials from conventional powders toward functional continuous thin-film platforms through heterointerface design and mesoporous amorphous film construction.

In the first part, a MOF-on-COF heterogeneous bilayer membrane was designed and fabricated for ion-selective transport and osmotic power generation. A free-standing COF membrane was first prepared through interfacial condensation synthesis, followed by the selective growth of a UiO-66-NH₂ MOF layer on one side of the COF membrane using a one-sided exposure strategy. This design successfully produced a heterostructured membrane with asymmetric pore sizes and surface charges.



The MOF layer provides sub-nanometer channels for ion sieving, while the COF layer offers continuous ion-transport pathways, leading to enhanced power generation under concentration gradients. Further comparison of different cation and anion systems revealed that the MOF-on-COF membrane exhibits high ion selectivity and can effectively distinguish ions with different hydrated sizes and charge properties. The overall osmotic energy conversion behavior is jointly regulated by hydrated ion size, ion charge, pore confinement, and interfacial asymmetry.

In the second part, a solvent evaporation-induced assembly strategy was developed to prepare continuous mesoporous amorphous ZIF-90 thin films using a block copolymer as a soft template. By controlling the THF/MeOH co-solvent environment, ligand concentration, micelle formation, and the rapid solvent evaporation process, ZIF-90 crystallization during film formation was successfully suppressed while interconnected mesopores were introduced. Structural analyses confirmed that the resulting *a*ZIF-90 films exhibit continuous morphology, uniform pore distribution, and retained Zn–imidazolate coordination environments. In addition, theoretical calculations were used to investigate the influence of solvent environment on ICA deprotonation and Zn(II) ligand-exchange behavior, providing a thermodynamic understanding of why ZIF-90 precursors can more easily remain in an amorphous state under THF-rich conditions. Therefore, the amorphous phase is employed in this work as an effective phase-engineering strategy to avoid grain boundaries and discontinuous particle formation. As a proof-of-concept application, uric acid electrochemical sensing further demonstrated

that the mesoporous amorphous structure can improve molecular diffusion and active-site accessibility.



Overall, this dissertation highlights the importance of structural design and phase engineering in porous framework thin films. Through crystalline MOF/COF heterointerfaces and solvent evaporation-induced mesoporous amorphous MOF films, this work provides new strategies for constructing continuous porous framework thin films and offers useful material design principles for future applications in energy conversion, ion transport, and electrochemical sensing.

Keywords: Metal–organic frameworks, covalent organic frameworks, porous framework thin films, heterointerfaces, phase engineering, osmotic energy harvesting, mesoporous amorphous MOFs.

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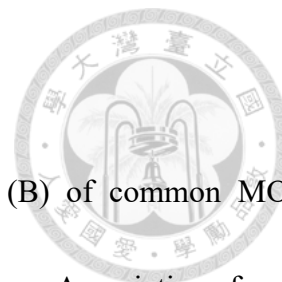
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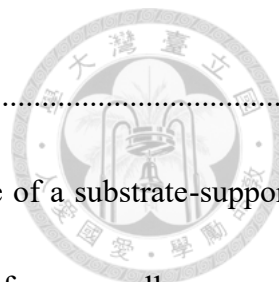


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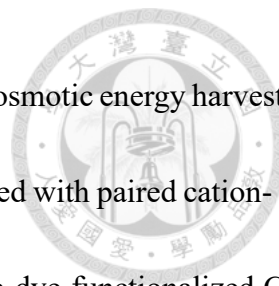


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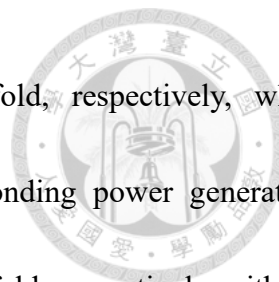
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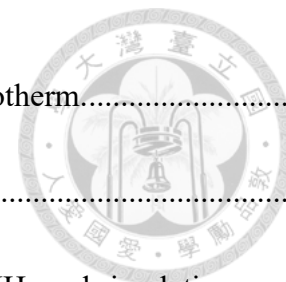
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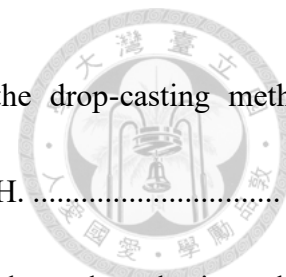


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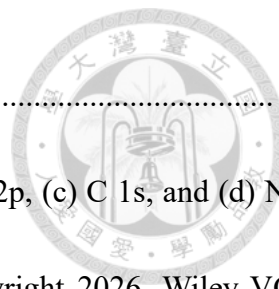
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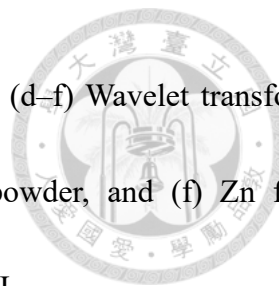
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1. Introduction

1.1. Porous Framework Materials as Designable Functional Platforms

Porous framework materials have attracted great attention because their structures can be designed from molecular building units [1-3]. Among them, metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) are two important classes of crystalline porous materials. MOFs are constructed through the coordination between metal ions or metal clusters and organic linkers (**Figure 1**) [4-6], while COFs are built by connecting organic monomers through covalent bonds (**Figure 2**) [7]. Because their components can be selected and modified at the molecular level, both MOFs and COFs provide highly tunable platforms for controlling pore size, pore shape, surface chemistry, and framework functionality [8,9].

One of the most important features of MOFs and COFs is their well-defined porous structure. These materials can contain pores ranging from the sub-nanometer scale to several nanometers, allowing molecules or ions to enter, diffuse, and interact with the internal surface [10]. In addition, their large surface areas and chemically adjustable pore environments make them useful for a wide range of applications [11], including gas adsorption [12,13], catalysis [14,15], sensing [16,17], energy storage, and energy conversion [18]. Unlike many conventional porous materials, MOFs and COFs are not

only passive porous solids; their structures can be rationally designed to provide specific chemical interactions or transport functions.



Another key advantage of MOFs and COFs is their structural diversity. By changing the metal nodes, organic linkers, functional groups, or bonding chemistry, it is possible to create frameworks with different stability, charge properties, pore dimensions, and chemical affinity [19,20]. This high degree of design flexibility makes them promising materials for addressing different scientific and technological challenges. For example, charged frameworks can be used to regulate ion transport [21], while functionalized pores can improve molecular recognition or catalytic activity [22].

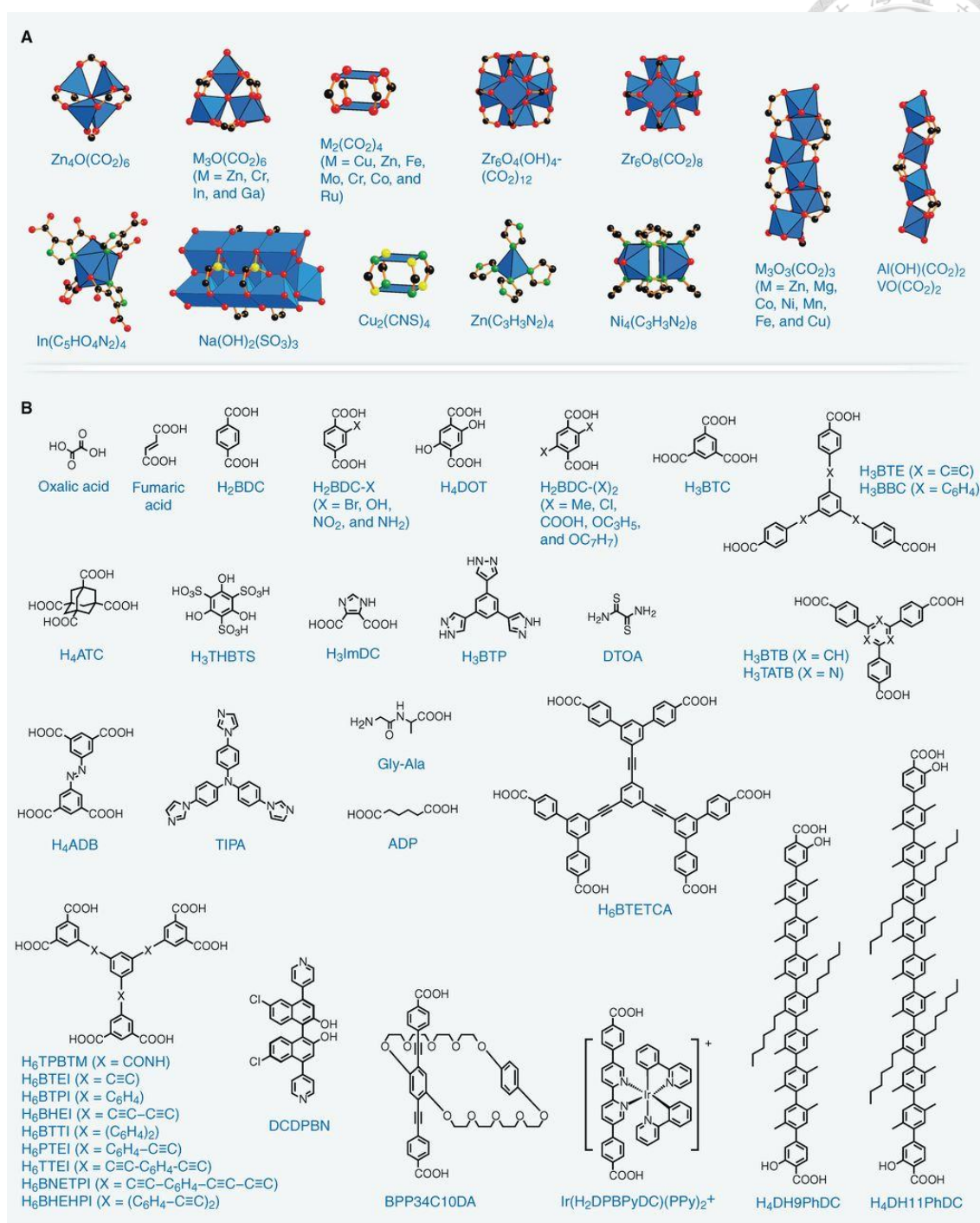
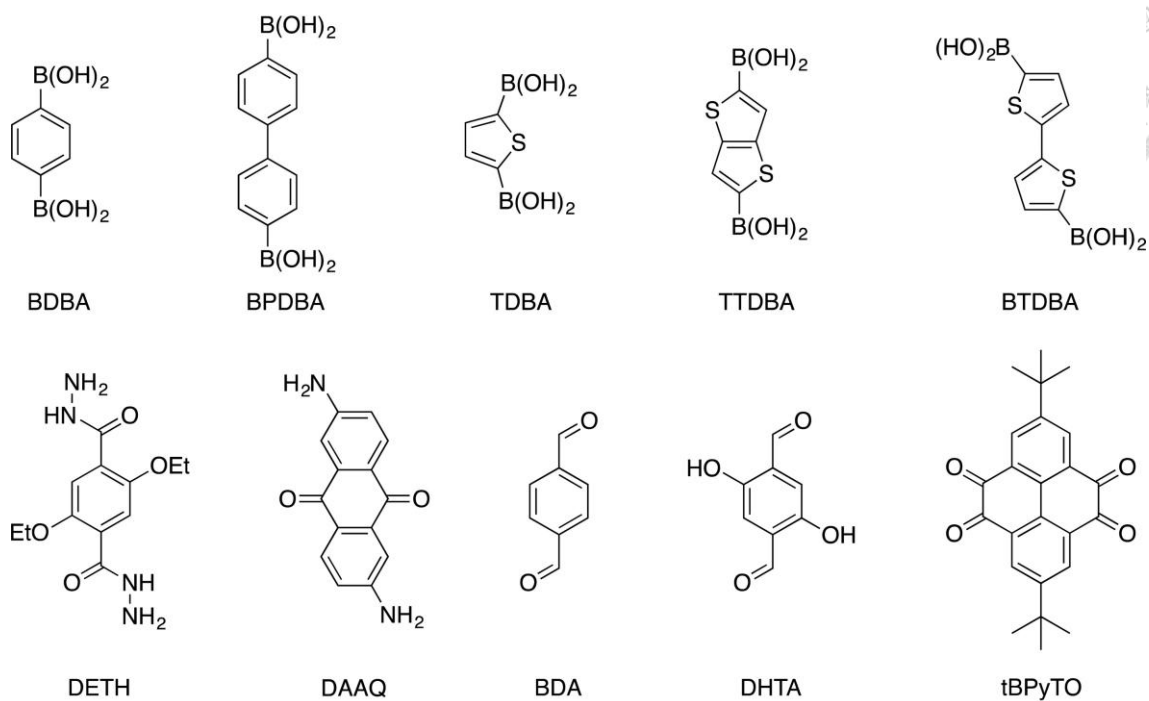
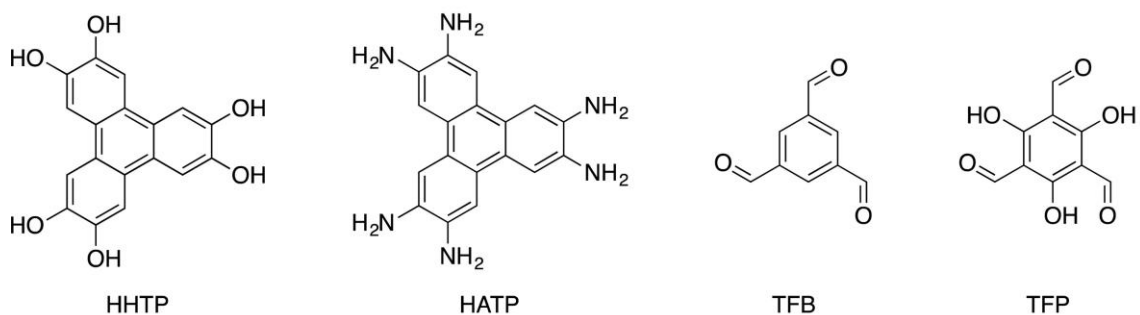


Figure 1 Inorganic secondary building units (A) and organic linkers (B) of common MOFs. Reproduced with permission [6]. Copyright 2013, American Association for the Advancement of Science.

Ditopic Linkers



Tritopic Linkers



Tetratopic Linkers

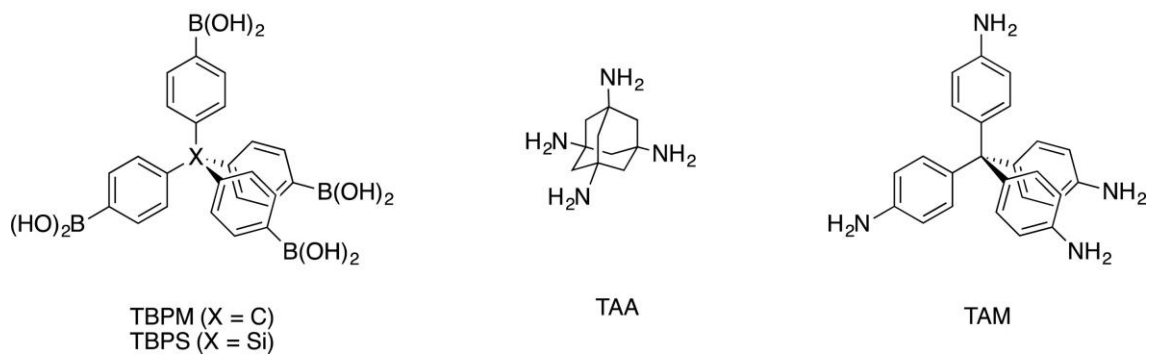
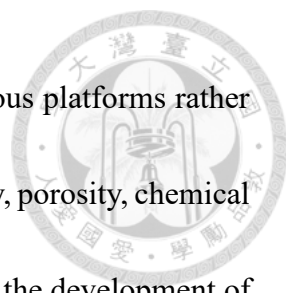


Figure 2 Linkers of common COFs. Reproduced with permission [7]. Copyright 2015,

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Therefore, MOFs and COFs can be regarded as designable porous platforms rather than simple porous powders. Their unique combination of crystallinity, porosity, chemical tunability, and structural modularity provides a strong foundation for the development of advanced functional materials. In this dissertation, these advantages are further extended from conventional framework materials to continuous thin-film and membrane architectures, with the aim of improving ion transport, energy harvesting, and electrochemical sensing performance.

1.2. From Framework Powders to Continuous Thin Films and Membranes

Although MOFs and COFs are usually synthesized and studied as crystalline powders, many practical applications require them to be processed into continuous thin films or membranes [23]. Powder-form MOFs and COFs are not inherently unsuitable for practical use. In fact, they are effective in many applications, including drug delivery [24,25], heterogeneous catalysis [26,27], and electrocatalysis [28,29], where the materials can function as dispersed particles or packed porous solids. Nevertheless, when the target application requires continuous and directional transport, such as gas separation [30,31], molecular sieving [32,33], osmotic power generation [34,35], or electrode-integrated sensing [36-38], powder-based materials become less ideal. Randomly stacked particles often create interparticle voids, weak adhesion, nonuniform film thickness, and tortuous

transport pathways. To overcome these issues, MOF and COF powders are commonly combined with substrates, binders, or supporting matrices to fabricate membranes, films, or electrodes [18,39]. However, these additional components may block pores or increase transport resistance. Therefore, the direct construction of continuous porous framework thin films is a more attractive strategy for fully utilizing their intrinsic pore structures in device-level applications [40,41].

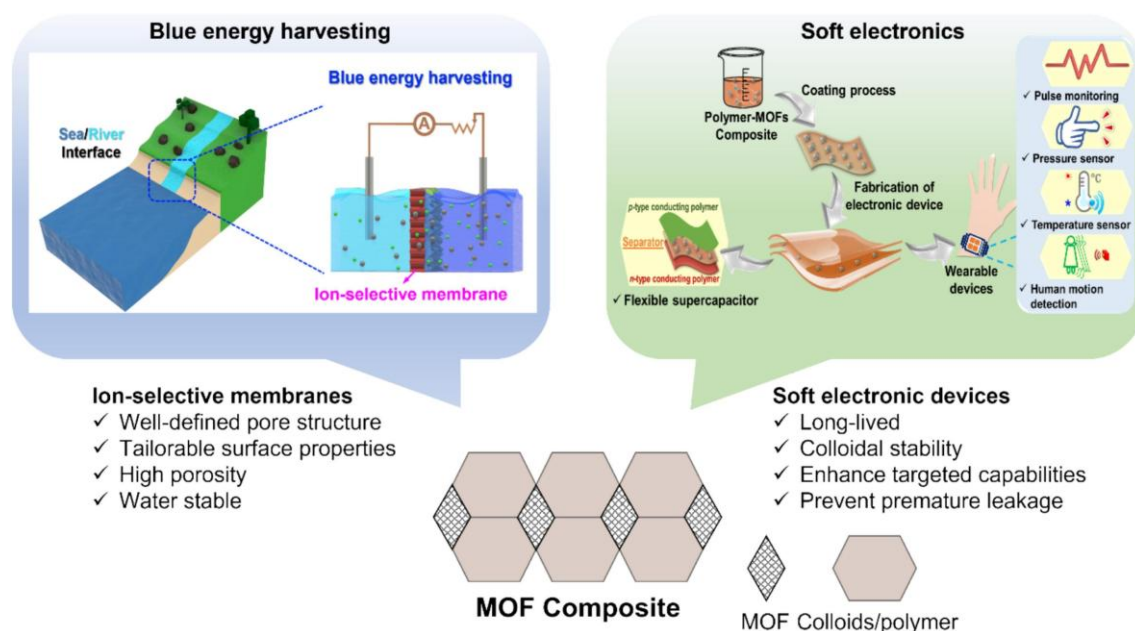
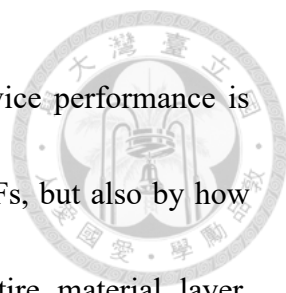


Figure 3 Schematic illustration of MOF composite and its applications in blue energy harvesting and soft electronics. Reproduced with permission [18]. Copyright 2024, Elsevier.

Compared with powder-based assemblies, continuous thin films and membranes provide more spatially integrated pathways for molecular and ionic transport. Such



structural continuity is particularly important because the final device performance is often governed not only by the intrinsic porosity of MOFs and COFs, but also by how efficiently ions, molecules, or analytes can move across the entire material layer. Therefore, developing well-defined framework thin films is essential for bridging the gap between the molecular-level design of porous frameworks and their practical device-level applications.

In this dissertation, continuous porous framework thin films are investigated in two representative forms. The first is a crystalline MOF-on-COF bilayer membrane designed for charge-asymmetric ion transport and osmotic power generation. The second is a mesoporous amorphous MOF thin film prepared through solvent-evaporation-induced assembly. Although these two systems target different applications, both highlight the importance of film continuity, pore accessibility, and structural control in framework-based thin-film materials.

1.3. Structural Challenges in Porous Framework Thin Films

Despite the attractive structural features of MOFs and COFs, the construction of functional porous framework thin films remains challenging. The first challenge is achieving continuous pore pathways across the entire film. In powder-based films or particle-assembled layers, the transport pathway is often interrupted by interparticle gaps,

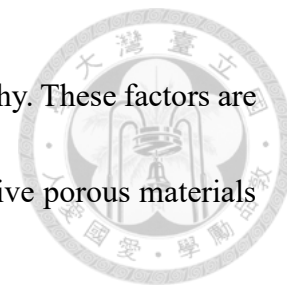
grain boundaries, or poorly connected domains. These discontinuities can increase resistance and reduce the efficiency of molecular or ionic transport [42]. Therefore, simply depositing framework particles onto a substrate does not necessarily lead to an effective porous thin-film architecture.

The second challenge is interfacial control, especially in heterogeneous framework films. When two different porous materials are combined, such as a MOF layer grown on a COF membrane, the interface must be carefully designed. Poor interfacial contact may interrupt transport across the bilayer structure, while uncontrolled growth on both sides of the membrane may destroy the desired structural asymmetry [43]. This is particularly important for ionic diode membranes, where directional ion transport relies on a well-defined asymmetric interface.

The third challenge is mass transport within the framework itself. Many crystalline MOFs are dominated by micropores, which are beneficial for molecular sieving and selectivity. However, these narrow channels may also limit the diffusion of larger molecules, slow down reaction kinetics, or reduce the accessibility of internal active sites [44]. This limitation becomes more serious in electrochemical sensing, catalysis, and high-flux transport applications.

Therefore, the rational design of porous framework thin films requires simultaneous

control over film continuity, interfacial architecture, and pore hierarchy. These factors are essential for transforming MOFs and COFs from structurally attractive porous materials into practical thin-film platforms.



1.4. Phase Engineering and Structural Design as Two Central Strategies

To address these challenges, this dissertation considers two complementary design concepts: structural design and phase engineering. Structural design focuses on controlling the spatial arrangement, interfacial connection, and charge distribution of porous framework layers, which is essential for constructing continuous and asymmetric transport pathways. Phase engineering, on the other hand, focuses on regulating the crystalline or amorphous state of framework materials to overcome the mass-transport limitations often found in conventional microporous crystalline MOFs. Together, these two concepts provide a framework for designing porous thin films with improved continuity, pore accessibility, and transport efficiency. Based on this rationale, this dissertation explores porous framework thin films from two complementary directions: crystalline hetero-interface construction and solvent evaporation-induced assembly. These two directions correspond to the structural design and phase engineering strategies emphasized in this dissertation, providing the foundation for developing functional thin-film and membrane architectures beyond conventional framework powders.



2. Literature Review

2.1. Heterogeneous Metal-Organic Frameworks/ Covalent-Organic Frameworks

films

2.1.1. MOF Thin Films

Metal–organic framework (MOF) thin films have emerged as an important form of MOF-based materials because they allow the intrinsic porosity and chemical functionality of MOFs to be integrated into device-compatible architectures. Compared with conventional MOF powders, thin films provide better spatial control, improved substrate integration, and more continuous transport pathways, which are important for applications such as sensing, separation, catalysis, electronics, and membrane-based devices. Several comprehensive reviews have summarized the development of MOF thin films, including surface-supported MOF films, polycrystalline MOF membranes, and advanced deposition strategies for scalable fabrication [39-41]. These studies indicate that the key requirements for MOF thin-film fabrication are not only crystallinity and porosity, but also control over film thickness, coverage, orientation, adhesion, and interfacial quality.

2.1.1.1 Surface-Controlled Growth

One of the earliest demonstrations of substrate-controlled MOF thin-film growth was reported by Hermes et al. in 2005 [45]. They showed that MOF thin films could be selectively nucleated and grown on patterned self-assembled monolayers on Au (111). In this work, MOF growth occurred preferentially on COOH-terminated regions rather than CF₃-terminated regions, demonstrating that surface functionality can direct MOF nucleation and enable patterned thin-film growth. This study provided an early foundation for later surface-mounted MOF thin-film fabrication.

Following this concept, in 2007, Biemmi et al. reported oriented growth of HKUST-1, on functionalized self-assembled monolayers [46]. They demonstrated that the orientation of the MOF crystals could be tuned by changing the terminal functional groups on the substrate surface. This work clearly showed that surface chemistry is not only important for MOF nucleation, but also for controlling the orientation of crystalline MOF films.

In the same year, Shekhah et al. further developed a step-by-step route for the synthesis of surface-mounted MOF films [47]. In this method, the functionalized substrate was sequentially exposed to metal-ion and organic-linker solutions, allowing the MOF film to grow in a layer-by-layer manner (**Figure 4**). This strategy became one

of the key foundations of liquid-phase epitaxy for surface-mounted MOFs, later widely referred to as SURMOFs. The stepwise growth process enabled better control over film thickness and provided a practical route to fabricate homogeneous MOF coatings on surfaces.

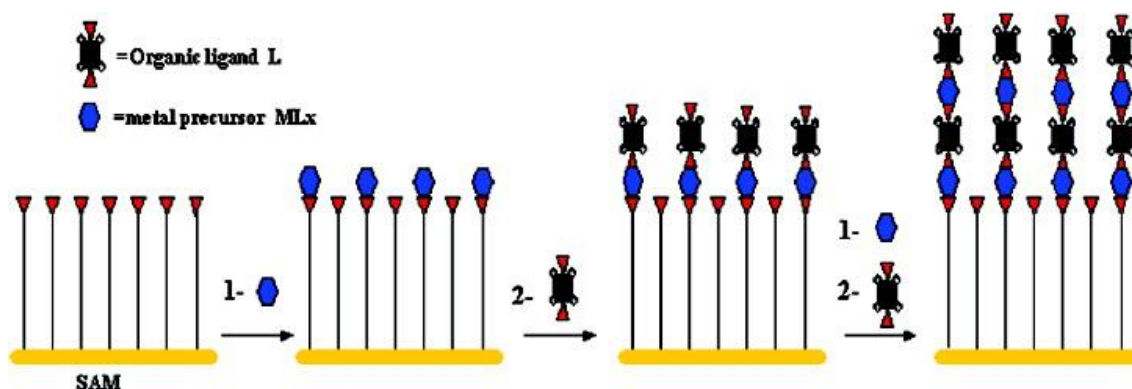


Figure 4 Schematic diagram for the step-by-step growth of the MOFs on the SAM, by repeated immersion cycles, first in solution of metal precursor and subsequently in a solution of organic ligand. Reproduced with permission [47]. Copyright 2007, American Chemical Society.

The growth mechanism of this step-by-step method was further clarified by Shekhah and co-workers in 2009. By using a layer-by-layer growth route, they investigated the nucleation and early-stage growth behavior of MOFs on functionalized surfaces [48]. This work provided important mechanistic insight into how MOF thin films form at the solid–liquid interface and helped establish liquid-phase epitaxy as a controllable method

for preparing oriented and thickness-tunable MOF thin films.



2.1.1.2 *Direct Solvothermal Growth / In Situ Growth*

Direct solvothermal growth, also known as in situ growth, is one of the most commonly used strategies for preparing MOF thin films and membranes. In this approach, the MOF layer is directly crystallized on a supporting substrate from a precursor solution, rather than being synthesized as powder first and then deposited onto a surface. This method is particularly useful for membrane fabrication because the MOF crystals can nucleate, grow, and interconnect directly on the support, leading to a continuous polycrystalline film. However, the quality of the final film strongly depends on the control of nucleation density, crystal intergrowth, substrate compatibility, and defect formation.

A representative example was reported by Kwon et al. in 2013, who developed a one-step counter-diffusion-based in situ method to prepare thin and well-intergrown ZIF-8 membranes [49]. In this method, the diffusion of metal ions and organic linkers was controlled so that ZIF-8 crystallization preferentially occurred near the porous support. This controlled reaction zone promoted the formation of a continuous ZIF-8 membrane rather than randomly precipitated MOF particles in the bulk solution. The resulting membrane exhibited excellent propylene/propane separation performance, demonstrating the importance of forming a compact and defect-minimized MOF layer for molecular

sieving applications. This work clearly showed that direct in situ growth can be an effective route to fabricate continuous MOF membranes with practical separation functions.



Another important example was reported by Liu et al. in 2014. They developed an in situ synthesis strategy for preparing MOF membranes on ZnAl-CO₃ layered double hydroxide (LDH) buffer layer-modified substrates [50]. In this design, the LDH buffer layer acted as an intermediate interface between the support and the MOF layer, improving nucleation and promoting the formation of a well-intergrown ZIF-8 membrane, as shown in **Figure 5**. This study highlights the importance of interface engineering in direct solvothermal growth. Instead of relying only on the bare substrate surface, introducing a chemically compatible buffer layer can improve MOF nucleation density, reduce intercrystalline defects, and enhance membrane continuity. Therefore, this work provides an important example of how substrate modification can be used to overcome the common limitations of in situ MOF membrane growth.

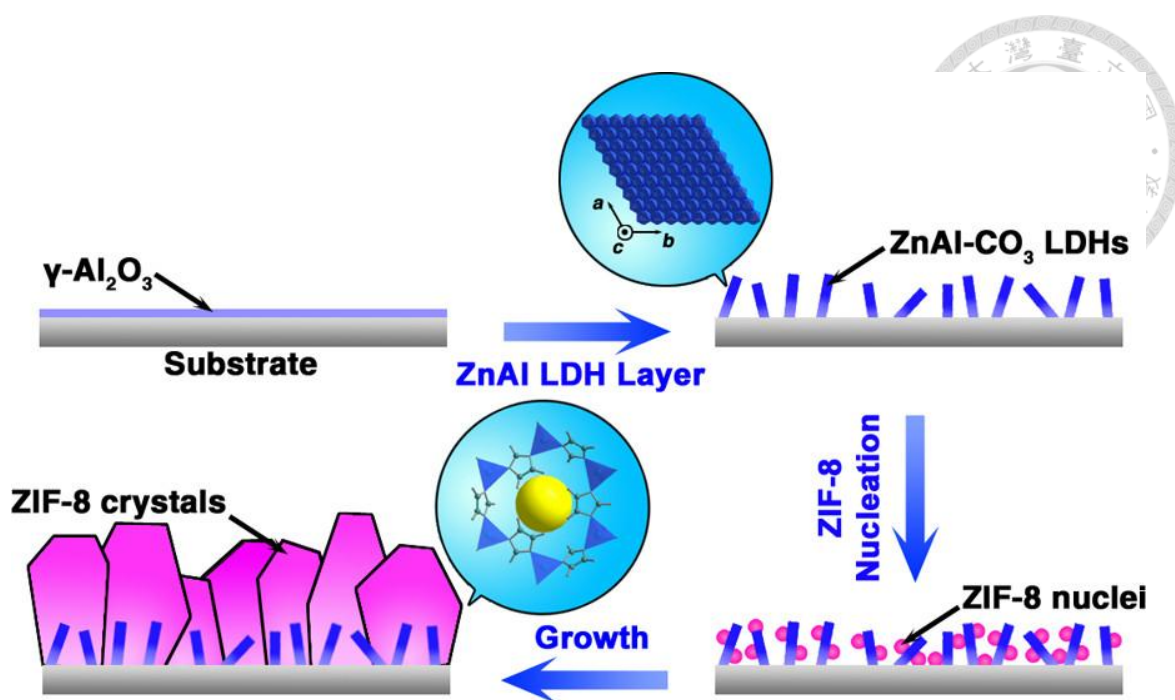


Figure 5 Schematic illustration of in situ solvothermal growth of ZIF-8 membrane on a ZnAl-LDH buffer layer-modified $\gamma\text{-Al}_2\text{O}_3$ substrate. Reproduced with permission [50].

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Overall, direct solvothermal or in situ growth is a powerful strategy for preparing continuous MOF membranes because it allows the MOF layer to form directly on the substrate. This approach is especially suitable for separation membranes, where the film must be compact, continuous, and well attached to the support. Nevertheless, the method still requires careful control over precursor diffusion, nucleation behavior, crystal intergrowth, and substrate surface chemistry. Without proper control, isolated crystals, grain-boundary defects, or discontinuous MOF domains may form, leading to poor

membrane selectivity and unstable transport performance.



2.1.1.3 Interfacial Synthesis

Interfacial synthesis is another important strategy for fabricating MOF thin films and membranes. Unlike conventional solvothermal growth, where nucleation and crystal growth may occur throughout the bulk solution, interfacial synthesis confines the framework-forming reaction to a defined interface. This interface can be a liquid–liquid, air–liquid, or liquid–solid boundary. Because the reactants meet and react mainly at the interface, MOF formation can be spatially controlled, which is beneficial for preparing thin films, membranes, and two-dimensional MOF nanosheets. This method is particularly attractive when the goal is to obtain a continuous film rather than dispersed MOF particles.

Campbell and co-workers reported a representative example of MOF thin-film fabrication through interfacial synthesis in 2015 [51]. In this work, HKUST-1 thin films were formed on polyimide P84 ultrafiltration supports to prepare MOF thin-film composite membranes for organic solvent nanofiltration. Compared with conventional in situ growth within the polymer support, the interfacial synthesis strategy enabled HKUST-1 to form as a thinner MOF layer near the membrane surface. This design improved solvent permeance while preserving the separation function of the membrane.

The study demonstrated that interfacial synthesis can be used to localize MOF growth at a desired membrane interface, which is valuable for constructing thin active layers with reduced transport resistance.



Interfacial synthesis has also been extended to the fabrication of oriented two-dimensional MOF films with controlled transport properties. In 2021, Wang et al. reported the interfacial synthesis of layer-oriented two-dimensional conjugated MOF films at the air/water interface [52]. In this work, metal-phthalocyanine-based building units were assembled with metal nodes to form p-type semiconducting 2D c-MOF films, denoted as $\text{Cu}_2[\text{PcM}-\text{O}_8]$ ($\text{M} = \text{Cu}$ or Fe). A key feature of this study is that the authors achieved an unusual edge-on layer orientation, which was guided by the preorganization of the metal-phthalocyanine ligands at the air/water interface. This orientation control is important because it enables directional charge transport through the MOF film, allowing the authors to compare lateral and vertical conductivity and demonstrate anisotropic transport behavior (**Figure 6**). Compared with conventional bulk MOF synthesis, this work highlights the unique advantage of interfacial synthesis in controlling not only film formation but also molecular orientation, layer stacking, and transport direction. Therefore, it provides a strong example of how interfacial chemistry can be used to construct functional MOF thin films with well-defined structural orientation and device-

relevant properties.

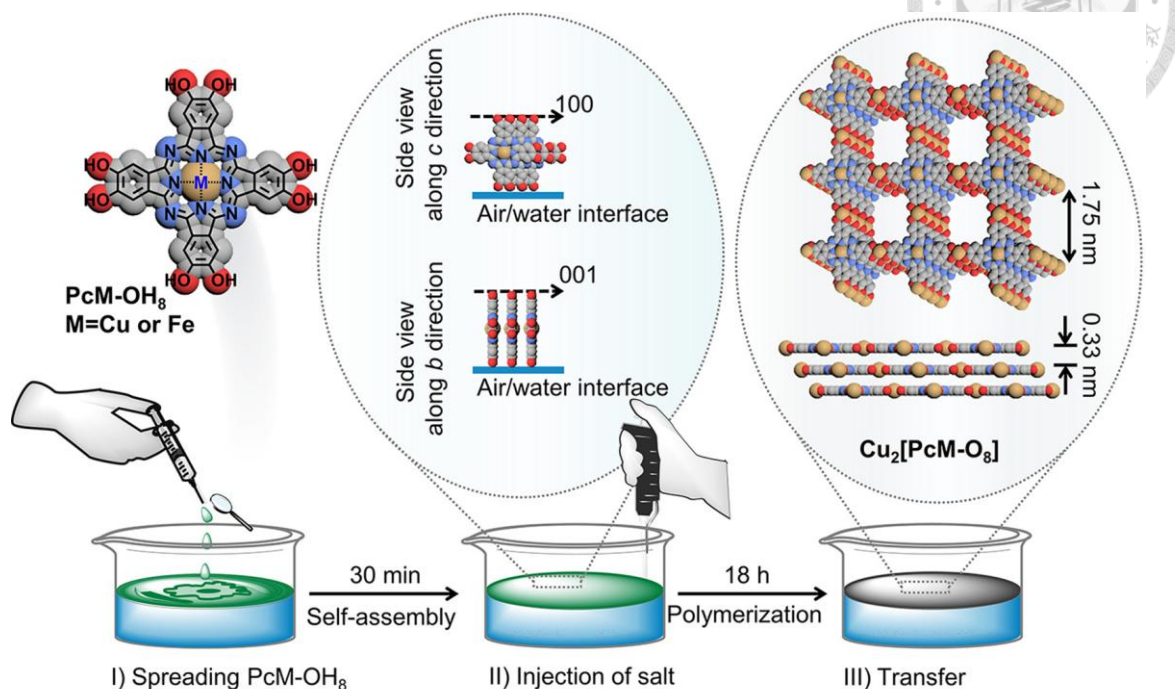


Figure 6 Synthetic scheme and atomic model of $\text{Cu}_2[\text{PcM}-\text{O}_8]$. Reproduced with permission [52]. Copyright 2021, American Chemical Society.

These examples demonstrate that interfacial synthesis is a versatile method for preparing MOF thin films, thin-film composite membranes, and two-dimensional MOF nanosheets. The main advantage of this approach is that MOF crystallization can be confined to a specific interface, reducing uncontrolled bulk precipitation and improving film uniformity. However, interfacial synthesis also has limitations. The final film quality depends strongly on the stability of the interface, precursor diffusion rate, reaction kinetics, and transfer process. For large-area membranes, maintaining uniform growth

across the entire interface remains challenging. Therefore, although interfacial synthesis provides an attractive route for MOF thin-film fabrication, precise control over interfacial chemistry and film growth remains essential.



2.1.1.4 Chemical Vapor Deposition (CVD)

Beyond liquid-phase growth, Stassen and co-workers reported a chemical vapor deposition (MOF-CVD) strategy for fabricating ZIF-8 thin films in 2016 [53]. In this method, a metal oxide precursor layer was first deposited on the substrate and subsequently converted into ZIF-8 through exposure to vapor-phase organic linkers (**Figure 7**). This vapor-phase conversion route enabled the formation of uniform and high-quality MOF films while avoiding direct immersion of the substrate in a solvothermal precursor solution. Compared with conventional solution-based methods, MOF-CVD offers better compatibility with microfabrication processes, patterned substrates, and device-integrated architectures. Therefore, this work represents an important step toward incorporating MOF thin films into electronic, sensing, and membrane-related platforms.

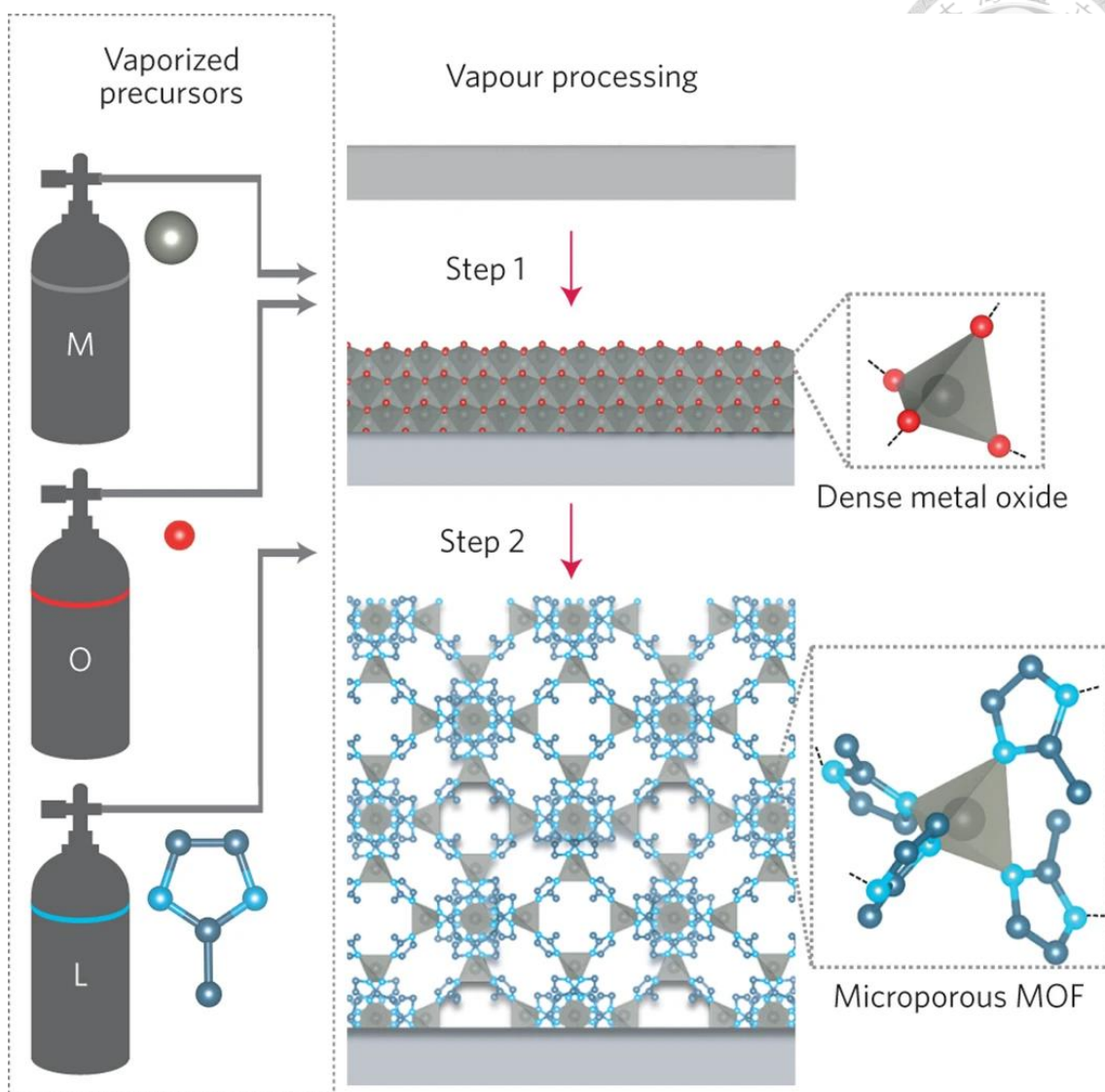


Figure 7 Chemical vapor deposition of ZIF-8 thin films. Reproduced with permission [53]. Copyright 2016, Springer Nature.

2.1.2. COF Thin Films and Free-standing COF Membranes

Covalent organic frameworks (COFs) are crystalline porous polymers constructed from organic building units through covalent bonds. Their ordered pore structures,



tunable chemical functionality, and lightweight organic frameworks make them attractive for separation, electronics, sensing, catalysis, and ion-transport applications. However, similar to MOFs, many COFs are initially synthesized as insoluble and infusible powders, which limits their direct integration into thin-film devices or membrane systems. Therefore, developing COF thin films and membranes has become an important direction for translating the intrinsic pore structures of COFs into practical functions [54]. Depending on the target application, COF films can be generally divided into two categories: substrate-supported COF thin films and free-standing COF membranes.

2.1.2.1 Substrate-Supported COF Thin Films

Substrate-supported COF thin films are particularly useful when the COF layer needs to be integrated with electrodes, optical platforms, electronic devices, or membrane supports. In this configuration, the substrate provides mechanical support and can also influence COF nucleation, orientation, film thickness, and crystallinity. Compared with randomly deposited COF powders, directly grown COF thin films offer better structural continuity and more controlled interfaces with the underlying substrate. These features are important for studying anisotropic transport, charge conduction, sensing response, or molecular diffusion through ordered COF channels.

One of the earliest representative examples was reported by Colson and co-workers



in 2011. They demonstrated the oriented growth of two-dimensional COF thin films on single-layer graphene under solvothermal conditions [55]. In this work, graphene served as a template for COF growth, and the resulting layered COF films were oriented with their aromatic units stacked perpendicular to the graphene surface (**Figure 8**). This study was important because it showed that a carefully selected substrate can guide COF film orientation and enable large-area film formation. Instead of producing randomly stacked COF powders, the use of graphene allowed the formation of oriented COF films directly on a device-relevant surface. This work provided an early foundation for substrate-assisted COF thin-film growth and demonstrated the potential of COF films for electronic and optoelectronic applications.

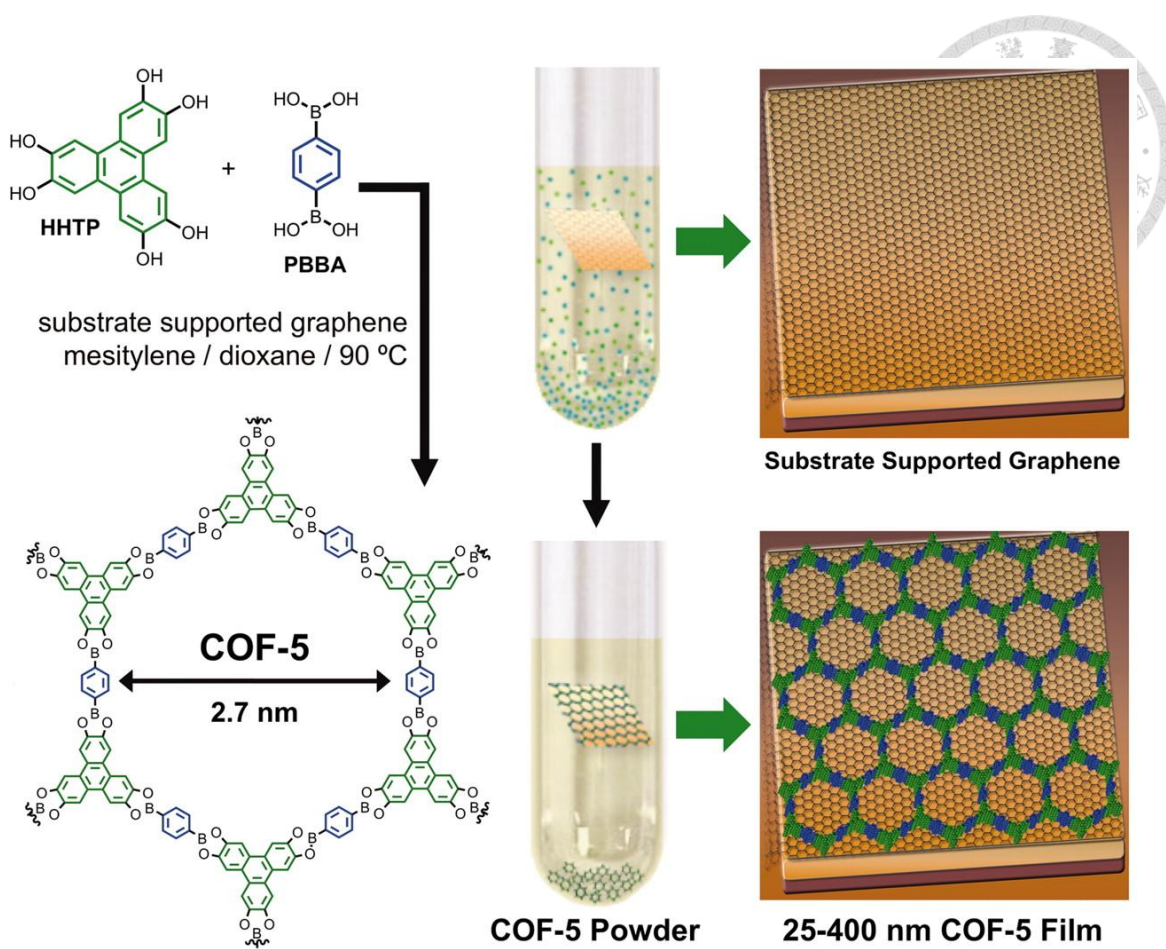


Figure 8 Solvothermal condensation of HHTP and PBBA in the presence of a substrate-supported SLG surface provides COF-5 as both a film on the graphene surface, as well as a powder precipitated in the bottom of the reaction vessel. Reproduced with permission [55]. Copyright 2011, American Association for the Advancement of Science.

Another representative example of substrate-supported COF thin-film fabrication was reported by Liu and co-workers in 2022. They developed a vapor-induced conversion strategy to prepare large-area two-dimensional imine-linked COF films directly on various substrates [56]. In this method, a pre-deposited amine-containing precursor film



was first formed on the growth substrate and then converted into a crystalline COF film by exposure to vapor-phase aldehyde monomers under controlled conditions. This approach enabled the formation of uniform COF films with tunable thickness while avoiding the direct precipitation of COF powders in bulk solutions. Importantly, the method was applicable to different substrate platforms, including wafer-scale silicon-based substrates and two-dimensional materials such as MoS₂, demonstrating its potential for constructing substrate-supported COF films and vertical heterostructures. Compared with conventional solvothermal COF powder synthesis, this vapor-induced conversion strategy provides better control over film location, thickness, and substrate compatibility, making it highly suitable for optoelectronic and device-integrated applications.

Together, these studies show that substrate-supported COF films can be prepared through different strategies, including substrate-templated solvothermal growth and vapor-induced film conversion. The first strategy highlights the role of substrate–framework interactions in controlling COF orientation, while the second demonstrates the importance of substrate compatibility and thickness control for wafer-scale device integration. However, substrate-supported COF films may still be influenced by substrate roughness, surface chemistry, and interfacial adhesion. Therefore, while they are highly useful for electronic, optical, and sensing devices, free-standing COF membranes are

often more suitable when the COF layer itself needs to serve as the main transport or separation membrane.



2.1.2.2 Free-standing COF Membranes

Free-standing COF membranes represent a more advanced form of COF thin-film architecture because they can function as independent porous membranes without relying on a dense polymer matrix or rigid substrate as the main selective layer. This is particularly important for separation, desalination, ion transport, and osmotic energy harvesting, where the membrane itself must provide continuous and selective transport pathways. Compared with mixed-matrix membranes or particle-assembled films, free-standing COF membranes can more directly preserve the ordered nanochannels of COFs and allow clearer structure–performance relationships to be established.

A representative study was reported by Liu and co-workers in 2020, where self-standing and flexible pure COF membranes were prepared through a liquid–liquid interface-confined strategy [57]. In this method, COF polymerization was spatially confined at the interface between two immiscible liquid phases, allowing the membrane to grow laterally into a continuous film (**Figure 9**). The resulting membranes were flexible and self-supported, showing that interfacial polymerization can overcome the common problem of COF powder precipitation in bulk solutions. This work is important

because it demonstrated that pure COF membranes can be fabricated without blending COF particles into polymer matrices, thereby preserving the intrinsic porous framework as the main transport medium.



In the same year, Li and co-workers reported a laminated self-standing COF membrane with uniformly distributed subnanopores for ionic and molecular sieving [58]. This work developed a scalable one-step route at an organic–organic interface to grow large-area and pliable free-standing COF membranes. More importantly, the authors showed that the pore size of the membrane could be adjusted from above 1 nm to the sub-nanometer scale by changing the stacking mode of COF layers from AA to AB stacking. The resulting AB-stacked COF membrane exhibited narrow apertures of approximately 0.6 nm and showed potential for organic solvent nanofiltration, water treatment, and gas separation. This study highlights that free-standing COF membranes are not only mechanically processable but can also be structurally engineered at the stacking level to regulate pore size and molecular sieving behavior.

Overall, free-standing COF membranes provide a direct platform for utilizing the ordered and chemically tunable channels of COFs in membrane-based applications. Compared with substrate-supported films, free-standing membranes are more suitable for studying intrinsic molecular or ionic transport across the COF layer. However, their

fabrication remains challenging because the membrane must simultaneously possess crystallinity, large-area continuity, mechanical robustness, and defect-minimized structure. These requirements are highly relevant to this dissertation, where the free-standing COF membrane is further used as a continuous porous support for the construction of a MOF-on-COF heterostructure.



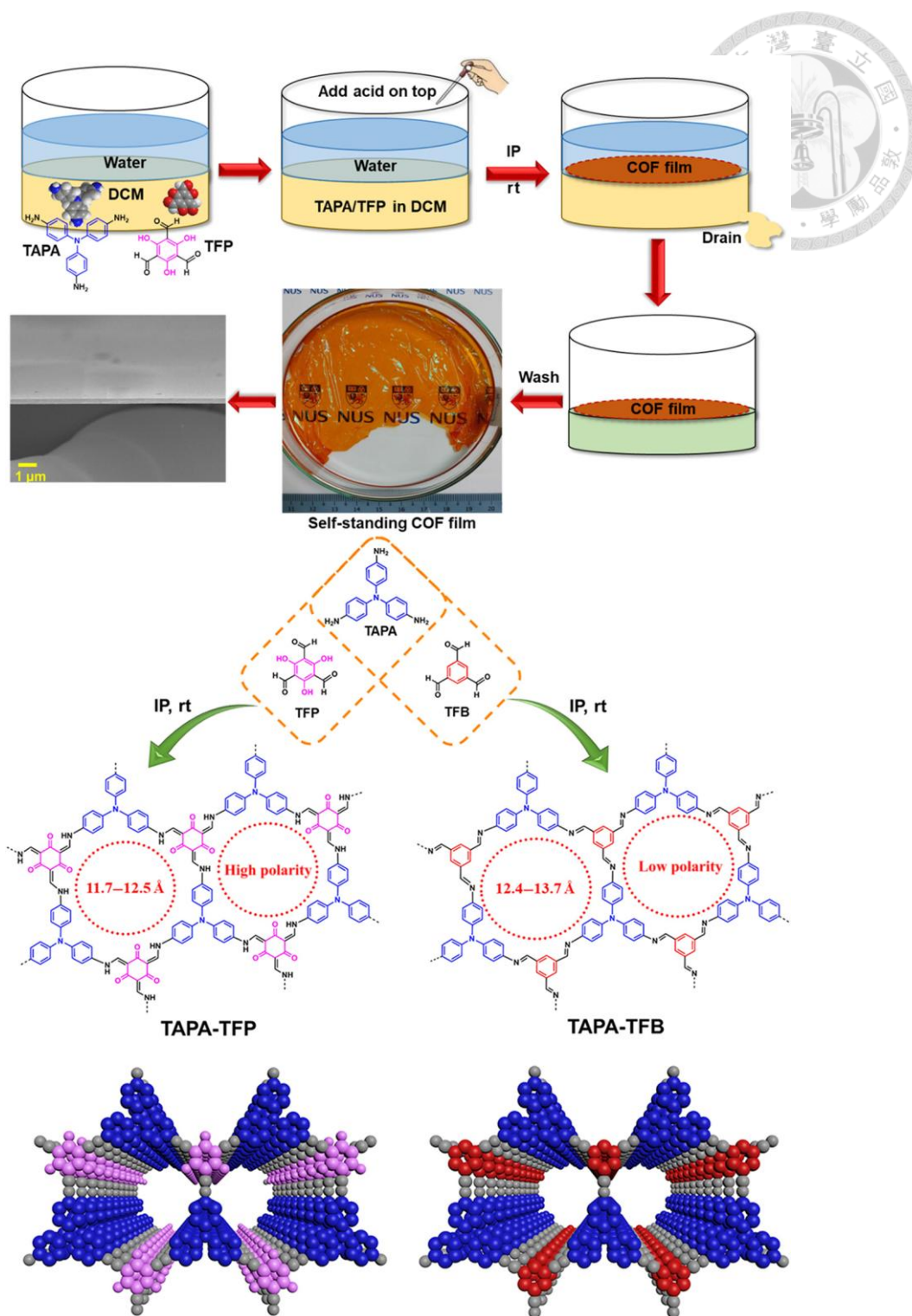


Figure 9 Fabrication process and chemical structures of the self-standing COF films.

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2.2. Framework-Based Membranes for Ion Transport and Osmotic Energy

Harvesting

Framework-based membranes have recently attracted attention as promising platforms for nanofluidic ion transport and osmotic energy harvesting. Unlike conventional dense polymeric ion-exchange membranes, porous framework membranes can provide structurally defined nanochannels, chemically tunable pore walls, and controllable surface charge properties. These features are highly important for osmotic power generation because the conversion of salinity-gradient energy into electricity relies on selective and directional ion transport across a membrane. In this context, the membrane is not only a passive separator but also an active nanofluidic component that regulates ion flux, charge separation, and transport resistance.

From a materials-design perspective, three structural parameters are particularly important: pore size, surface charge, and channel asymmetry. Pore size determines whether ions can pass through the membrane freely, partially dehydrate, or be sterically excluded. Surface charge controls the enrichment of counterions and rejection of co-ions inside charged nanochannels. Channel asymmetry, including geometric asymmetry and charge asymmetry, can further induce directional ion transport and ionic rectification. These principles provide the theoretical foundation for the design of MOF-, COF-, and



MOF-on-COF-based membranes for osmotic energy conversion.



2.2.1. Osmotic Energy and Nanofluidic Ion Transport

Osmotic energy, also known as salinity-gradient energy or blue energy, originates from the chemical potential difference between two solutions with different salt concentrations.

When seawater and river water are mixed, the spontaneous diffusion of ions releases Gibbs free energy. In conventional membrane-based systems, this energy can be harvested by pressure-retarded osmosis or reverse electrodialysis [59,60]. However, the practical power output of these systems is strongly affected by the membrane properties.

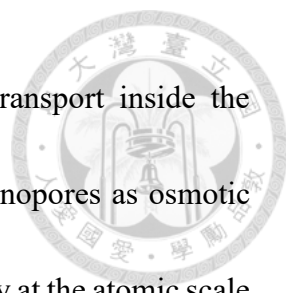
An ideal membrane should simultaneously possess high ion selectivity, high ionic permeability, low internal resistance, and good mechanical stability. These requirements are difficult to satisfy at the same time because highly selective membranes often restrict ion flux, while highly permeable membranes may suffer from poor selectivity.

Nanofluidic membranes provide a possible route to overcome this limitation because ion transport in nanoscale channels is strongly influenced by surface effects. When the channel size decreases to the nanometer or sub-nanometer scale, the surface-to-volume ratio becomes very high, and ion transport is no longer governed only by the bulk electrolyte conductivity. Instead, the surface charge of the channel walls can dominate the ion distribution and transport behavior. Stein et al. experimentally demonstrated surface-

charge-governed ion transport in nanofluidic channels, showing that ionic conductance deviates from bulk behavior under low salt concentration and becomes strongly influenced by the charged channel surface [61]. This result established an important principle: nanoscale confinement can convert surface charge into a dominant factor for ion transport.

Theoretical and computational descriptions of nanofluidic ion transport are commonly based on coupled electrokinetic models. In many cases, the Poisson equation is used to describe the electrostatic potential, the Nernst–Planck equation describes ion diffusion and electromigration, and the Navier–Stokes equation describes fluid flow. These models are useful for understanding how ion concentration, electric potential, and fluid velocity are distributed inside confined channels. They also explain why pore size is critical. When the pore diameter becomes comparable to the Debye length, electric double layers from the channel walls can overlap, leading to counterion enrichment and co-ion exclusion. This electric double-layer overlap enhances ion selectivity and is one of the key mechanisms behind nanofluidic osmotic energy conversion [62,63].

Several experimental studies have demonstrated the importance of nanoscale confinement in osmotic power generation. Siria et al. reported giant osmotic energy conversion through a single transmembrane boron nitride nanotube in 2013 [64]. The high

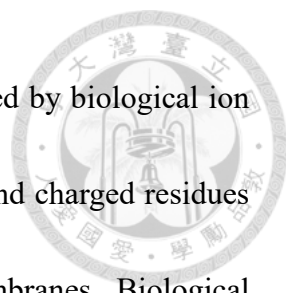


output was attributed to the strong surface charge and fast ion transport inside the nanotube. Later and co-workers demonstrated single-layer MoS₂ nanopores as osmotic nanopower generators [65]. Because the membrane thickness was only at the atomic scale, ion transport resistance was greatly reduced, leading to high power density at the single-pore level. These studies highlight two important design principles for nanofluidic osmotic energy conversion: nanoscale pore confinement is necessary for ion selectivity, while short and continuous transport pathways are required to reduce resistance.

However, conventional nanopores and nanochannels also face limitations. Large mesopores or macropores generally show weak electric-double-layer overlap under high-salinity conditions, especially when the Debye length becomes much smaller than the pore size. In contrast, sub-2 nm or sub-nanometer channels can maintain strong ion–pore interactions even at relatively high salt concentrations. This is why pore size is a central design parameter in modern nanofluidic membranes. A membrane with well-defined and narrowly distributed angstrom-scale pores can potentially achieve both high selectivity and fast transport, which provides the rationale for using crystalline framework materials such as MOFs and COFs in later sections.

2.2.2. Ionic Diode Membranes and Asymmetric Ion Transport

In addition to pore size and surface charge, structural asymmetry is another powerful



strategy for regulating ion transport. This concept is strongly inspired by biological ion channels such as electric eel, where asymmetric protein structures and charged residues allow ions to pass selectively and directionally across cell membranes. Biological channels can achieve highly efficient ion transport because their pore size, local charge distribution, and functional groups are precisely arranged at the molecular level [66]. Inspired by these natural systems, artificial nanofluidic membranes have been designed to mimic ion-channel-like behavior, including ion selectivity, gating, and rectification.

Ionic rectification refers to the phenomenon where the ionic current under one voltage polarity is much larger than that under the opposite polarity. This behavior is similar to an electronic diode, but the charge carriers are ions instead of electrons. Ion-current rectification can arise from asymmetric pore geometry, asymmetric surface charge, or a combination of both. Siwy summarized the principle of ion-current rectification in nanopores and nanotubes with broken symmetry, showing that asymmetric nanochannels can produce direction-dependent ion transport [67]. A representative experimental demonstration was reported by Vlassiouk and Siwy in 2007, where a nanofluidic diode was constructed from a single asymmetric nanopore with a sharp boundary between positively and negatively charged regions [68]. Depending on the applied voltage polarity, ion accumulation or ion depletion occurred near the charged junction, leading to strong

rectification.

Karnik et al. also reported rectification of ionic current in a nanofluidic diode based on asymmetric electrostatic environments [69]. These studies established that asymmetric charge distribution inside nanoscale channels can act similarly to a p–n junction in semiconductor diodes. Under forward bias, ions accumulate in the channel and the ionic current is enhanced. Under reverse bias, ion depletion occurs and the current is suppressed. This accumulation/depletion mechanism has become a central concept for understanding ionic diode membranes.

The concept of ionic diode membranes is highly relevant to osmotic energy harvesting. In osmotic power generation, the driving force is not an externally applied voltage but the concentration gradient between two electrolyte reservoirs. If the membrane contains asymmetric ion channels, the salinity gradient can generate directional ion diffusion more efficiently. Moreover, the rectifying structure can suppress unfavorable back-diffusion and enhance charge separation. Therefore, ionic diode membranes can improve both ion selectivity and effective ion flux, which are essential for high power output.

Before the development of MOF- or COF-based ionic diodes, many artificial ionic diode systems were constructed from polymer nanopores, track-etched membranes,

inorganic nanochannels, two-dimensional material membranes, and hybrid nanocomposite membranes. These systems provided important insights into how asymmetric geometry, charge polarity, and surface functionalization influence ion transport. For example, Laucirica et al. demonstrated that the geometry of track-etched nanochannels strongly affects osmotic energy conversion [70]. By comparing bullet-shaped nanochannels with other channel geometries and supporting the results with Poisson–Nernst–Planck simulations, they showed that asymmetric nanochannel shape can significantly influence ion selectivity, conductance, and output power (**Figure 10**). These studies demonstrate that nanochannel geometry is a key design parameter for regulating ion transport, independent of the specific material system.

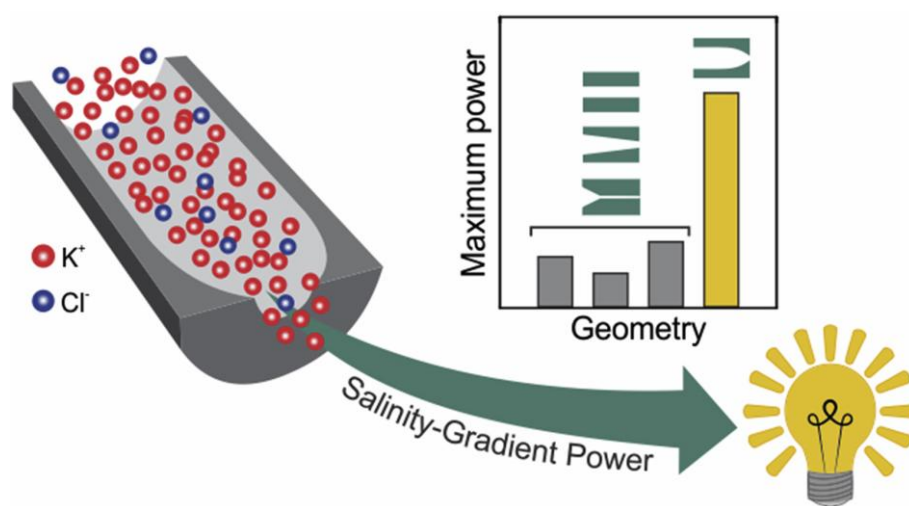


Figure 10 The influence of nanochannel shape on the osmotic energy harvesting ability.

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Nevertheless, many non-framework ionic diode membranes suffer from broad pore-size distributions, poorly defined channel structures, or limited control over pore chemistry. These limitations make it difficult to precisely correlate pore structure with ion-transport behavior. Therefore, the development of membranes with well-defined pore sizes, tunable surface charges, and ordered transport pathways is highly desirable. This requirement naturally leads to the use of crystalline porous framework materials, especially MOFs and COFs, which provide molecularly defined channels for more precise ion-transport regulation.

2.2.3. MOF-Based Ion-Transport Membranes

Metal–organic frameworks (MOFs) are highly attractive for ion-transport membranes because their pore apertures, surface functionalities, and framework charges can be designed at the molecular level. Compared with conventional polymeric or inorganic nanoporous membranes, MOFs provide well-defined angstrom-scale windows and ordered internal cavities. These structural features are particularly useful for osmotic energy harvesting, because ion selectivity depends strongly on the relationship between the hydrated ion diameter and the pore aperture. In addition, functional groups on MOF linkers can regulate the local surface charge, thereby promoting preferential transport of either cations or anions. Therefore, MOF-based membranes provide a promising platform

for constructing artificial ion-channel-mimetic systems with high selectivity and controllable ion transport.



A representative example was reported by Liu et al. in 2021 [21]. In this work, a heterogeneous subnanochannel membrane was prepared by growing a continuous UiO-66-NH₂ MOF layer on a highly ordered alumina nanochannel membrane (**Figure 11**). The UiO-66-NH₂ layer provided positively charged subnanometer windows of approximately 6–7 Å, which are comparable to the hydrated diameters of common ions. Because of this angstrom-scale confinement, the membrane exhibited strong ion-sieving ability and high Br[−]/NO₃[−] selectivity. More importantly, the MOF layer and alumina nanochannel membrane formed an asymmetric pore structure, in which the small UiO-66-NH₂ windows were coupled with larger alumina nanochannels. This design created a heterogeneous ion-transport pathway and improved osmotic power generation, reaching a power density of 26.8 W m^{−2} under a 100-fold KBr gradient (**Figure 12**). This study clearly demonstrated that the well-defined subnanometer channels of MOFs can be used to enhance both ion selectivity and osmotic energy conversion.

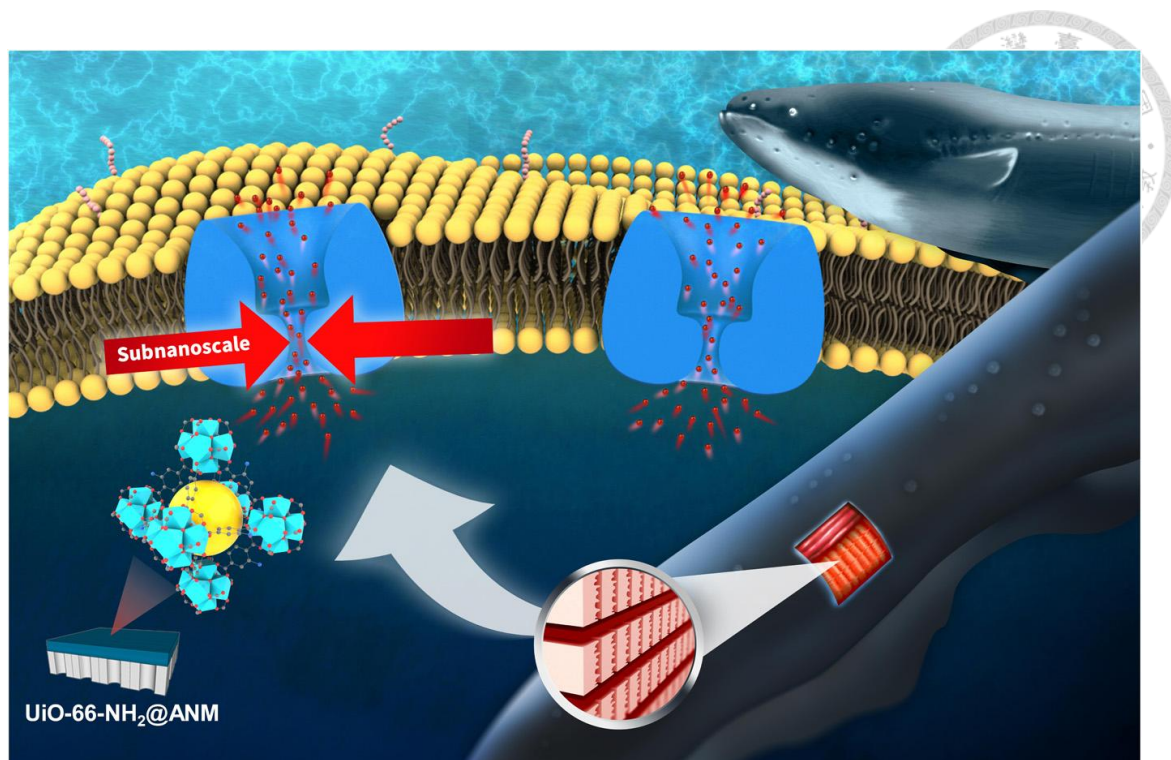


Figure 11 Schematic illustration of the electric eel–inspired heterogeneous membrane, UiO-66-NH₂@ANM, with subnanoscale channels. Reproduced with permission [21].

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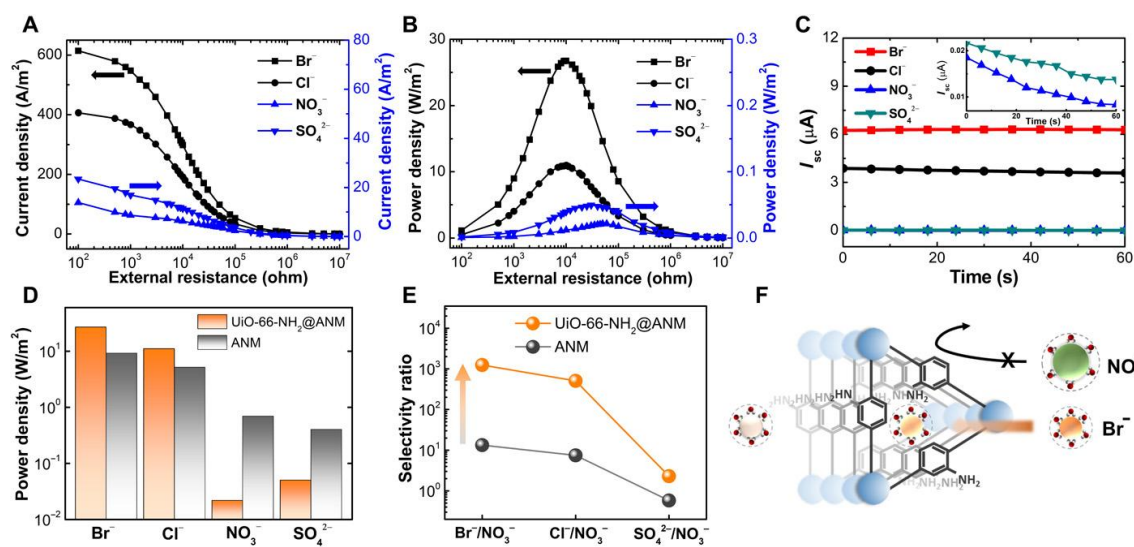


Figure 12 Highly selective and high-performance osmotic power of UiO-66-NH₂@ANM.

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Following this concept, Yang and co-workers further developed an ultrathin Zr-MOF-based heterogeneous membrane with a trilayered continuous porous structure in 2024 [71]. In this design, a dense and ultrathin UiO-66-NH₂ layer was grown on a highly aligned branched alumina nanochannel membrane. The resulting membrane contained a large pore-geometry gradient from angstrom-scale UiO-66-NH₂ windows, to nanoscale branched channels, and finally to sub-microscale alumina channels (**Figure 13**). This continuous trilayered pore architecture was designed to simultaneously improve ion selectivity and directional ion transport. The angstrom-sized UiO-66-NH₂ windows acted as selective ion-sieving sites, while the branched alumina membrane reduced transport resistance and enhanced the ionic diode effect. As a result, the membrane achieved approximately 17.1 W m⁻² with an energy conversion efficiency of 48.5% under a 50-fold KCl gradient. This work highlights the importance of combining MOF-based subnanometer selectivity with a hierarchically organized supporting membrane to balance selectivity and permeability.

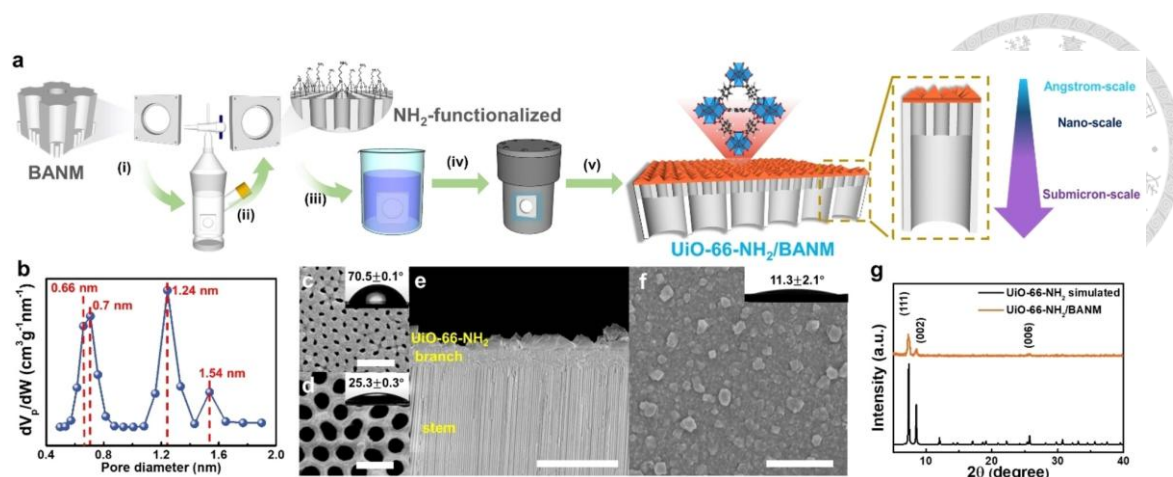
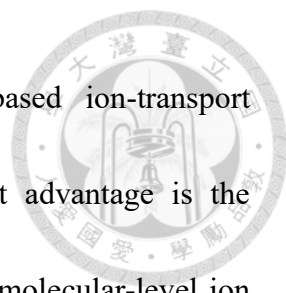


Figure 13 Construction and characterizations of UiO-66-NH₂/BANM. Reproduced with permission [71]. Copyright 2024, Wiley-VCH.

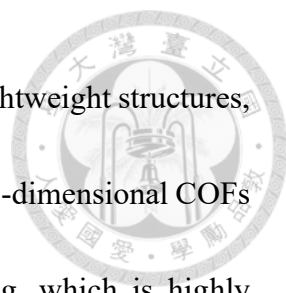
Besides UiO-66-NH₂-based membranes, other MOF systems have also been explored for osmotic energy harvesting. For example, Li and co-workers reported photoactive porphyrin MOF membranes on porous anodic aluminum oxide for light-enhanced osmotic energy harvesting [72]. The porphyrin MOF membrane was prepared through a mild cathodic deposition method, forming a crack-free MOF layer on the porous AAO substrate. The carboxyl groups in the porphyrin-based framework provided charged nanochannels for cation-selective transport, while the photoactive porphyrin units further enhanced the power output under light irradiation. The membrane delivered a power density of 6.26 W m⁻² under dark conditions, which increased to 7.74 W m⁻² upon light irradiation. This work shows that MOF membranes can serve not only as passive ion-sieving layers but also as functional channels responsive to external stimuli.



These studies demonstrate the great potential of MOF-based ion-transport membranes for osmotic energy harvesting. Their most important advantage is the presence of well-defined angstrom-scale pores, which can provide molecular-level ion sieving. In addition, MOFs offer rich chemical tunability, allowing surface charge, hydrophilicity, and ion affinity to be adjusted through linker or node modification. However, MOF-based membranes still face an important limitation: most MOFs are difficult to fabricate directly into large-area, mechanically robust, free-standing membranes. As a result, MOF layers are usually grown on supporting substrates such as anodic aluminum oxide, alumina nanochannel membranes, branched alumina nanochannel membranes, or polymeric supports. Although these substrates provide mechanical strength and directional channels, they may also introduce additional transport resistance, substrate-dependent selectivity, or interfacial defects. Therefore, the development of MOF-based ion-transport membranes requires not only precise control over MOF pore structure but also careful engineering of the supporting membrane and MOF/support interface.

2.2.4. COF-Based Ion-Transport Membranes

Covalent organic frameworks (COFs) provide another important class of framework-based ion-transport membranes. Compared with MOFs, COFs are constructed entirely



from organic building blocks through covalent bonds, giving them lightweight structures, tunable pore chemistry, and good chemical stability. In particular, two-dimensional COFs can form ordered one-dimensional channels through layer stacking, which is highly attractive for ion transport. When charged functional groups, such as sulfonic acid, ammonium, or ionic dyes, are introduced into COF channels, the membranes can regulate cation or anion transport through electrostatic interactions. Moreover, COFs are often more suitable than MOFs for preparing free-standing membranes because their organic framework structures can form flexible and mechanically processable films through interfacial polymerization or laminated assembly.

A representative example was reported by Hou et al. in 2021, who developed a free-standing TpPa-SO₃H COF membrane for salinity-gradient energy conversion [73]. The membrane was flexible and mechanically robust, with a Young's modulus of 2557 MPa, and retained its morphology after immersion in organic solvents and aqueous solutions with different pH values. Structurally, the membrane contained aligned one-dimensional nanochannels with a pore size of approximately 1.18 nm and abundant sulfonic acid groups, providing cation-selective transport and low-resistance ion pathways. Under a 50-fold NaCl gradient, the optimized COF membrane with a thickness of 10.7 μm delivered an open-circuit voltage of 115.2 mV, a short-circuit current of 5.95 μA, and a maximum

power density of 5.9 W m^{-2} . The power density further increased to 20.1 W m^{-2} under a 500-fold gradient, highlighting the potential of free-standing charged COF membranes for osmotic energy harvesting.

In the same year, Chen and co-workers reported a de novo assembly strategy to impart ion selectivity to COF membranes for blue-energy harvesting [74]. In this work, dye molecules with positive or negative charges were incorporated into COF membranes to tune their ion selectivity (**Figure 14**). This strategy showed that the ion-transport behavior of COF membranes can be regulated not only by the intrinsic framework structure but also by guest-induced charge modification. By introducing charged species into the COF channels, the authors obtained COF membranes with different ion selectivities and demonstrated their use in salinity-gradient energy conversion. This work is important because it shows that COFs can serve as chemically tunable platforms for charge-selective ion transport.

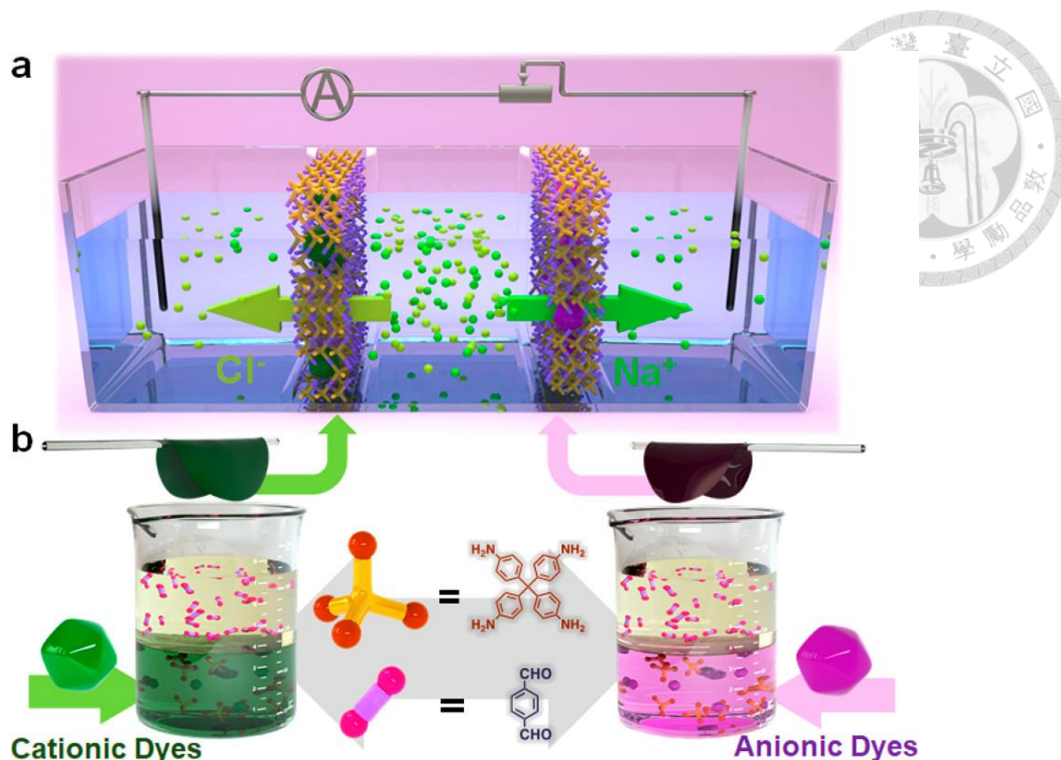
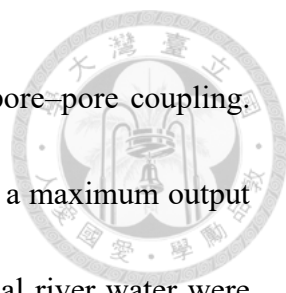


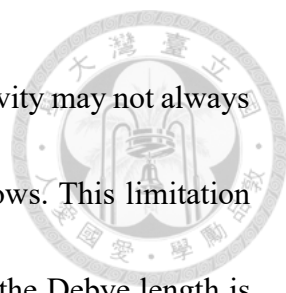
Figure 14 Schematic illustration of COF-based nanofluidic membranes for osmotic energy harvesting. (a) Configuration of a three-compartment conductive cell equipped with paired cation- and anion-selective membranes. (b) Bottom-up construction of ionic-dye-functionalized COF membranes, in which positively and negatively charged dye molecules are incorporated to generate oppositely charged COF membrane pairs. Reproduced with permission [74]. Copyright 2021, American Chemical Society.

Yang et al. further advanced COF-based osmotic power generation by using a ZnTPP–COF monolayer membrane [75]. The membrane possessed a molecularly thin thickness of approximately 1.1 nm, a highly ordered nanopore array, and a high experimental pore density. Owing to the extremely short ion-transport pathway and dense pore arrangement,



the membrane exhibited very low transport resistance and strong pore-pore coupling. Under a 0.5 M/0.01 M NaCl gradient, the COF monolayer delivered a maximum output power density of 135.8 W m⁻². When artificial seawater and artificial river water were used, the power density further increased to 203.8 W m⁻². Even higher values were obtained in divalent chloride electrolytes, reaching 267.7 W m⁻² for CaCl₂ and 317.5 W m⁻² for MgCl₂. The membrane also showed an initial power density of 294.3 W m⁻² using real seawater and river water, although the value gradually decreased to around 250 W m⁻² after four days. This work highlights the great potential of COF monolayers for ultrahigh osmotic power generation, while also indicating that large-area scaling and defect control remain important challenges.

Overall, COF-based membranes offer several advantages for ion transport and osmotic energy harvesting. First, COFs can be fabricated into free-standing membranes more readily than many MOFs, which is beneficial for constructing continuous and substrate-independent transport layers. Second, their ordered channels can provide direct ion-transport pathways across the membrane. Third, their organic building blocks allow charged groups or functional molecules to be introduced into the pores, making it possible to tune ion selectivity. However, compared with MOFs, the pore apertures of many COFs are usually larger and less strongly size-restrictive. Therefore, although COF membranes



can provide high ion permeability and low resistance, their ion selectivity may not always be as strong as that of MOF membranes with angstrom-scale windows. This limitation becomes especially important under high-salinity conditions, where the Debye length is very short, and larger COF channels may show weaker electric-double-layer overlap. Thus, COF membranes are excellent candidates for fast ion transport, but further structural or interfacial design is often required to improve their ion selectivity.

2.2.5. MOF-on-COF Heterostructures

The advantages and limitations of MOF- and COF-based membranes suggest that combining these two framework materials into a heterostructured membrane could be a promising strategy. MOFs provide angstrom-scale windows and strong ion-sieving ability, while COFs can offer continuous, chemically tunable, and potentially free-standing transport channels. If these two materials are integrated into a bilayered membrane with controlled interfacial contact, pore-size asymmetry, and opposite surface charges, the resulting MOF-on-COF membrane may behave as an ionic diode membrane for enhanced osmotic energy harvesting.

A recent example was reported by Chen and co-workers, who developed a full sub-2 nm and acid-resistant MOF-COF ionic diode membrane for efficient ionic-gradient power generation [76]. In this work, a thin and dense UiO-66-NH₂ MOF layer was

selectively grown on a β -ketoenamine-linked TFP-TPA COF membrane. The UiO-66-NH₂ layer contained positively charged windows of approximately 0.6 nm, while the TFP-TPA COF layer provided negatively charged channels of approximately 1.4 nm. Therefore, the bilayered membrane combined both pore-size asymmetry and surface-charge asymmetry within a full sub-2 nm framework architecture (**Figure 15**). The experimental and simulation results showed that this bipolar and asymmetric framework membrane induced strong diode-like ion rectification, with an on/off ratio up to approximately 350.

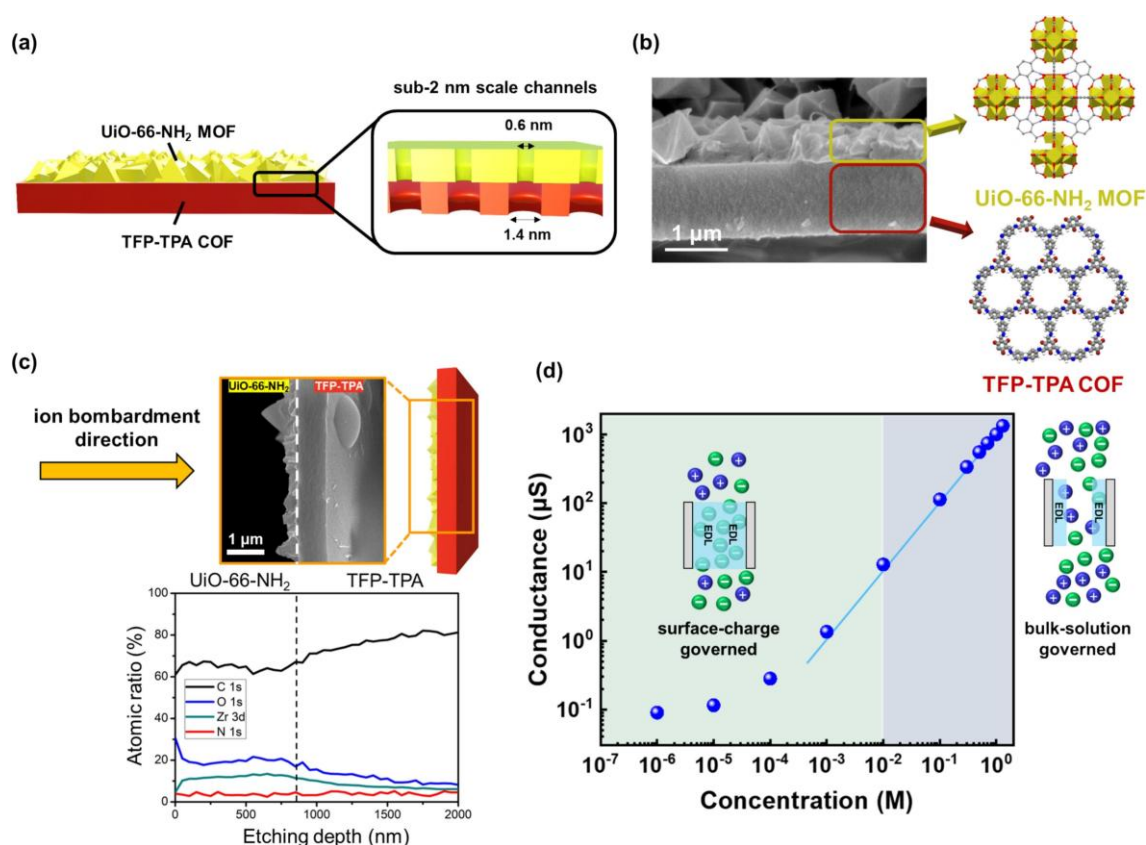
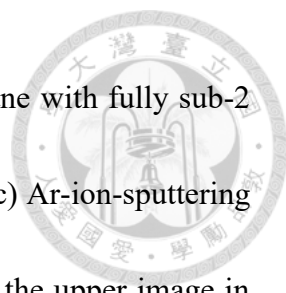


Figure 15 Structural and ion-transport characterization of the bilayer MOF-COF



membrane. (a) Schematic representation of the MOF–COF membrane with fully sub-2 nm ionic transport channels. (b) Cross-sectional SEM image and (c) Ar-ion-sputtering XPS depth profile of the UiO-66-NH₂/TFP-TPA bilayer membrane; the upper image in (c) shows the corresponding cross-sectional SEM observation. (d) Ionic conductance of the MOF–COF membrane measured under different NaCl concentrations. The solid line indicates the bulk-solution conductance behavior, while the left and right insets illustrate surface-charge-governed and bulk-concentration-governed ion transport regimes, respectively. EDL denotes the electric double layer. Reproduced with permission [76].

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The importance of this MOF-on-COF design lies in its ability to overcome the individual limitations of MOF- and COF-based membranes. Compared with MOF-on-AAO or MOF-on-ANM systems, the COF layer provides a framework-based supporting membrane with sub-2 nm channels, rather than large mesoporous or macroporous inorganic channels. This is beneficial because large support channels can weaken the electric-double-layer overlap and reduce ion selectivity under high-salinity conditions. Compared with a single-layer COF membrane, the introduction of the UiO-66-NH₂ layer provides smaller angstrom-scale windows and positive surface charge, which improves

ion selectivity and generates a stronger ionic diode effect. Therefore, the MOF-on-COF architecture integrates the fast transport capability of COFs with the strong ion-sieving ability of MOFs.



This structural advantage was reflected in the osmotic power generation performance. Under a 50-fold NaCl gradient, the MOF-COF membrane produced a higher power density than the single-layer COF membrane, and the incorporation of the MOF layer reduced the membrane's internal resistance because of the strong ionic diode effect. More importantly, the membrane exhibited excellent performance under acidic gradients. In a 1000 mM/10 mM HCl gradient, the MOF-COF membrane achieved a peak power density of approximately 192.9 W m^{-2} , which was about 7.5 times higher than that of the single-layer COF membrane (**Figure 16**). The membrane also maintained 92.7% of its initial power output after 10 days of continuous operation in a strong acidic gradient, demonstrating the durability of the acid-resistant MOF-COF framework membrane.

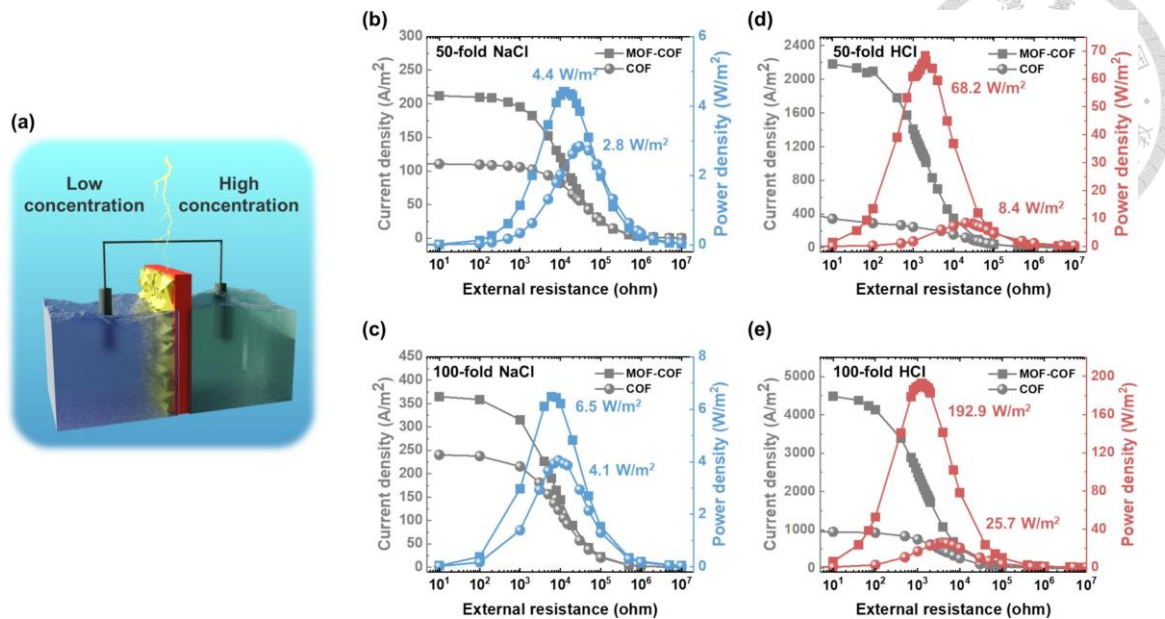


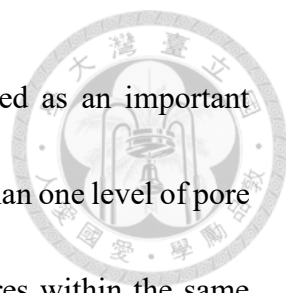
Figure 16 Ionic-gradient energy harvesting performance of the MOF–COF ionic diode membrane. (a) Device configuration for osmotic power generation. (b,c) Power output was obtained under NaCl concentration gradients of 50-fold and 100-fold, respectively, while maintaining the dilute side at 10 mM NaCl. (d,e) Corresponding power generation behavior under HCl concentration gradients of 50-fold and 100-fold, respectively, with the dilute side fixed at 10 mM HCl. Reproduced with permission [76]. Copyright 2025, Elsevier.

This MOF-on-COF system provides an important design principle for framework-based ion-transport membranes. Instead of relying on only one type of pore channel, the heterostructure uses two different framework layers to regulate ion migration across multiple structural levels. The MOF layer supplies angstrom-scale selectivity, the COF

layer provides continuous sub-2 nm transport channels, and the interface between them creates an asymmetric bipolar junction for rectified ion transport. Therefore, MOF-on-COF heterostructures represent a promising direction for developing advanced nanofluidic membranes with both high ion selectivity and efficient ion permeability.

2.3. Hierarchically Porous and Mesoporous MOFs

Hierarchically porous metal–organic frameworks (HP-MOFs) have been developed to overcome the intrinsic mass-transport limitations of conventional microporous MOFs. In general, MOFs are well known for their high surface areas, crystalline structures, and chemically tunable pore environments. Their micropores, typically smaller than 2 nm, are highly useful for molecular recognition, size-selective adsorption, and confinement effects. However, the same narrow pore structure may become a limitation when the target molecules, reaction intermediates, electrolytes, or analytes are relatively large [77,78]. In these cases, diffusion through the framework can become slow, and many internal active sites may not be fully accessible during practical operation. This problem becomes particularly important in catalysis, electrochemical sensing, adsorption, and high-flux transport applications, where molecules or ions must rapidly enter the framework, react at active sites, and leave the pore network [79,80].



To address this issue, hierarchical porosity has been introduced as an important design strategy for MOF materials. HP-MOFs usually contain more than one level of pore structure, such as micropores, mesopores, and sometimes macropores within the same material. In this architecture, micropores preserve the intrinsic molecular-level selectivity and high surface area of MOFs, while mesopores and macropores provide larger transport pathways for guest molecules, electrolytes, or reaction products (**Figure 17**). Mesopores can shorten diffusion distances and improve the accessibility of internal active sites, whereas macropores can serve as larger transport reservoirs that facilitate rapid mass transfer. Therefore, hierarchical porosity is not only a structural modification but also a functional design strategy for balancing active-site density and mass-transport efficiency [81].

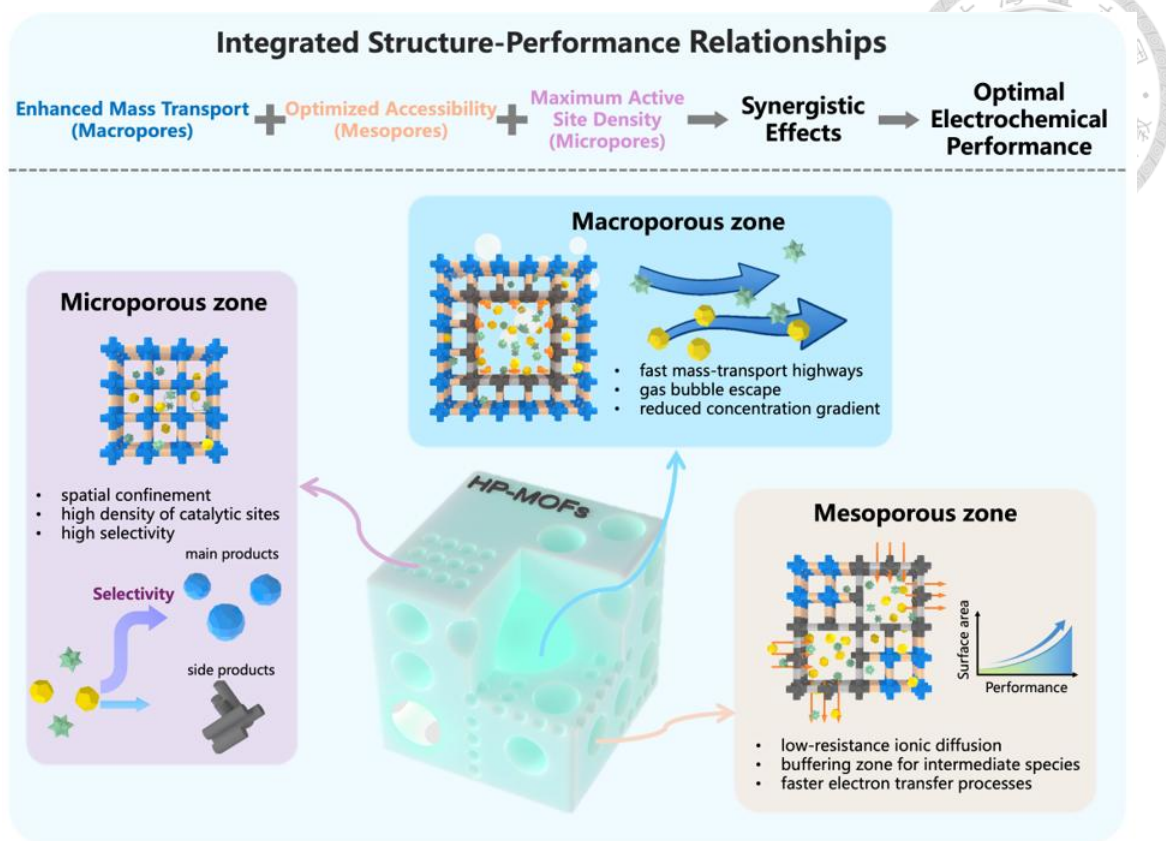


Figure 17 Schematic illustration of different pore sizes for electrocatalytic cascade reactions. (Adapted from Y. Zhao, N.C.-R. Chen, et al., [81], *under revision*)

Several excellent reviews have summarized the synthetic methodologies and applications of HP-MOFs, including ligand engineering, defect formation, hard-templating, soft-templating, and composite-derived approaches [82-84]. These studies indicate that the value of hierarchical porosity does not simply come from enlarged pore volume or higher surface area, but from the rational integration of different pore domains across multiple length scales. This concept is highly relevant to this dissertation because

the mesoporous amorphous MOF thin films discussed later are designed to address similar transport-related limitations. By introducing mesopores into a continuous MOF-based thin-film architecture, the framework can provide more accessible diffusion pathways while maintaining the chemical functionality of the MOF network.

2.3.1. Synthetic Strategies for Hierarchically Porous MOFs

2.3.1.1 *Ligand Engineering*

Ligand engineering is one of the most fundamental bottom-up strategies for constructing hierarchically porous or mesoporous MOFs. In this approach, the pore architecture is designed directly from the molecular geometry, length, connectivity, and rigidity of the organic linkers. A simple form of ligand engineering is isorecticular expansion, in which longer organic linkers are used to enlarge the pore size of a known MOF topology. However, simple linker elongation does not always generate true hierarchical porosity. In many cases, it only produces uniformly enlarged micropores or mesopores, rather than an integrated pore system containing multiple pore domains. In addition, long linkers may induce framework interpenetration, reduce structural stability, or complicate crystallization. Therefore, more advanced ligand-engineering strategies focus not only on increasing linker length, but also on controlling linker geometry,

symmetry, steric hindrance, and framework topology.

A classic example of ligand-engineered hierarchical porosity is MIL-101, reported by Férey and co-workers [85]. MIL-101 is constructed from chromium clusters and terephthalate linkers, forming a highly robust framework with two types of large mesoporous cages of approximately 2.9 and 3.4 nm. These mesoporous cages are connected through smaller microporous windows, allowing MIL-101 to combine large internal cavities with molecular-level pore openings. This multi-cage architecture provides high pore volume and good accessibility for guest molecules, making MIL-101 one of the representative examples of intrinsically mesoporous MOFs. Following a similar concept, Zhou and co-workers developed PCN-333, which contains multiple types of cages within a single crystalline framework [86]. PCN-333 integrates smaller microporous cages with larger mesoporous cavities, including giant cages with diameters of approximately 4.2 and 5.5 nm, as shown in **Figure 18**. Because of these large cage structures, PCN-333 has been used as a platform for enzyme encapsulation, demonstrating how ligand geometry and framework topology can create pore environments suitable for bulky biomolecules.

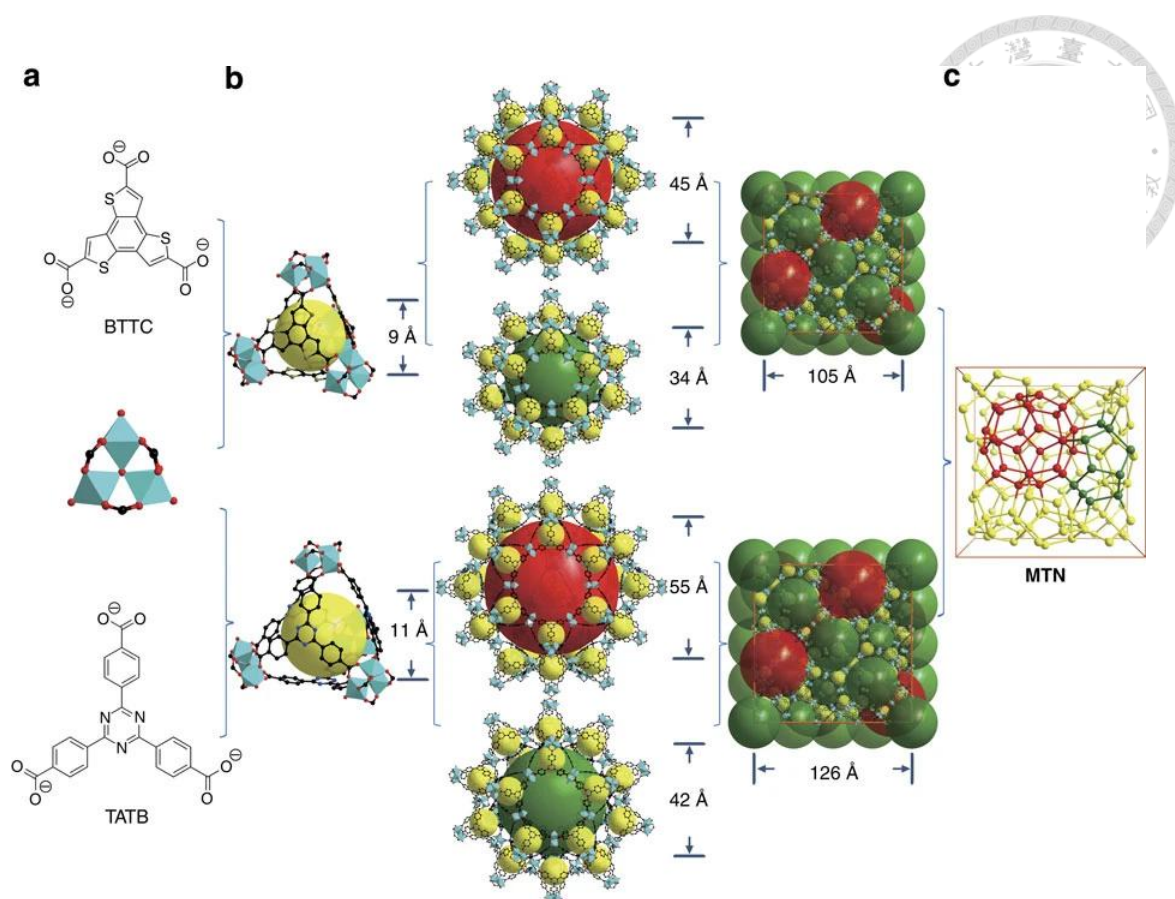
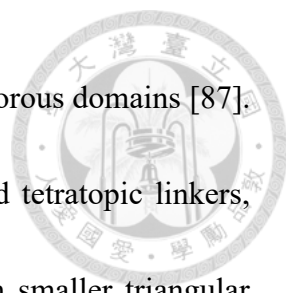


Figure 18 (a) Ligands used in PCN-332 and PCN-333. (b) Three different cages in PCN-332 and PCN-333. (c) Simplification of PCN-332 and PCN-333 into MTN topology.

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Another important direction in ligand engineering is the construction of MOFs with one-dimensional mesoporous channels. Porphyrinic and pyrene-based ligands are particularly useful for this purpose because their rigid and extended molecular structures can guide the formation of large, open channels when combined with stable metal clusters. For example, PCN-222, also known as MOF-545, is a Zr-based porphyrinic MOF with



large hexagonal mesoporous channels surrounded by smaller microporous domains [87]. Similarly, NU-1000, constructed from Zr clusters and pyrene-based tetratopic linkers, contains large one-dimensional mesoporous channels together with smaller triangular microporous channels [88]. These channel-type architectures are highly attractive because they provide relatively straight diffusion pathways, which can facilitate the transport of large molecules or reaction intermediates through the framework.

These studies demonstrate that ligand engineering can create hierarchical or mesoporous MOFs with high structural precision. Compared with post-synthetic defect formation or templating methods, ligand engineering allows the pore structure to be built into the framework from the beginning. As a result, the generated pores are often highly ordered, crystallographically defined, and closely related to the intrinsic topology of the MOF. However, this strategy also has limitations. It usually requires carefully designed organic linkers, well-matched metal clusters, and precise control over crystallization conditions. The synthesis of large or geometrically complex ligands can also be time-consuming and less general. Therefore, while ligand engineering provides one of the most elegant routes to intrinsically hierarchical MOFs, its applicability may be limited by ligand availability, framework stability, and synthetic complexity.

2.3.1.2 Defect Formation

Defect formation provides another important route to hierarchical porosity. Instead of designing a new framework from the beginning, this strategy creates additional pores by selectively removing, replacing, or weakening parts of the original MOF structure. Defects can be generated through modulator-mediated synthesis, post-synthetic ligand substitution, linker labilization, thermolysis, or chemical etching. Compared with ligand engineering, defect formation is often more practical because it can be applied to existing stable MOF platforms such as UiO-type frameworks.

A representative example was reported by Yuan et al., who developed a linker-labilization strategy to construct hierarchically porous MOFs [89]. In this approach, relatively stable bridging linkers in a parent MOF are partially replaced by more labile or terminal ligands. Because these labile ligands are more easily removed or exchanged, additional void spaces can be generated inside the framework while the overall crystal morphology and framework integrity are largely preserved. This strategy is powerful because it does not rely only on external templates; instead, it uses the coordination chemistry of the framework itself to create hierarchical porosity. By controlling the amount and type of labile ligand, the pore structure can be tuned from microporous to hierarchically porous, allowing larger molecules to access internal active sites more

efficiently.



Another representative route is controlled linker thermolysis. Feng and co-workers reported a multivariate MOF strategy in which thermally stable and thermolabile linkers were incorporated into the same framework [90]. Upon controlled thermal treatment, the less stable linker could be selectively decomposed and removed, while the more robust framework components remained intact (**Figure 19**). This process generated mesopores inside the MOF crystals without completely destroying their long-range crystallinity. The key advantage of this method is that the mesopore formation can be regulated by the ratio of thermolabile linkers, the thermolysis temperature, and the treatment time. Therefore, linker thermolysis provides a relatively controllable way to introduce mesoporosity into crystalline MOFs while retaining their original framework features.

Modulator-induced defect formation is also widely used to prepare hierarchically porous MOFs with high stability. In this method, monocarboxylic acid modulators or other competitive ligands are introduced during MOF synthesis to compete with the original bridging linkers. This competition can create missing-linker or missing-cluster defects in the framework. When these defects are present in sufficient density, they can merge into larger voids or mesoporous domains. For example, Cai et al. reported a modulator-induced defect-formation strategy to construct hierarchically porous MOFs

with improved stability and mass-transport properties [91]. The modulator not only regulates crystal growth but also promotes defect generation, enabling the formation of additional mesopores while maintaining the crystalline framework.

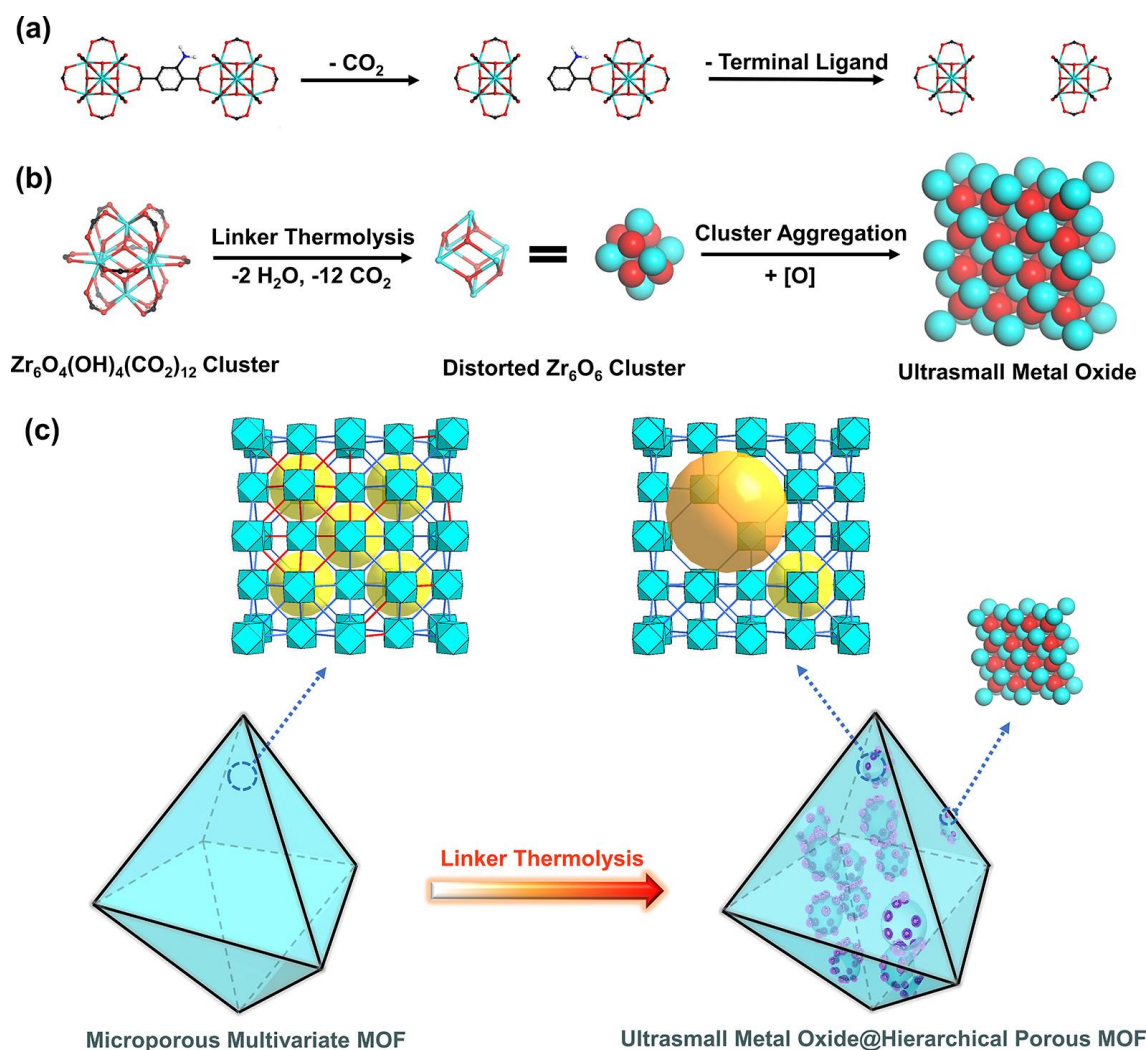
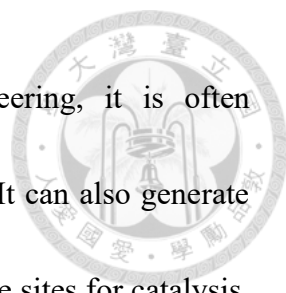


Figure 19 The mechanism of hierarchically porous structure formation. Reproduced with permission [90]. Copyright 2018, American Chemical Society.

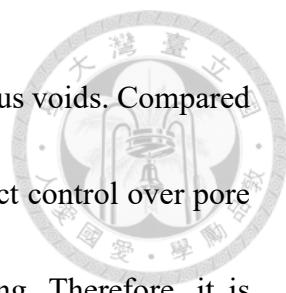
Overall, defect formation provides a practical and flexible route for introducing



hierarchical porosity into MOFs. Compared with ligand engineering, it is often synthetically simpler and can be applied to existing MOF systems. It can also generate coordinatively unsaturated sites, which may serve as additional active sites for catalysis, adsorption, or sensing. However, this strategy also requires careful control. If too few defects are introduced, the improvement in mass transport may be limited. If too many defects are generated, the framework may lose crystallinity, structural stability, or pore uniformity. Therefore, successful defect engineering requires a balance between creating sufficient mesoporous pathways and preserving the ordered framework structure of the MOF. Compared with defect formation, templating-based methods provide more direct control over pore size and pore morphology, which will be discussed in the following sections.

2.3.1.3 Hard-Templating

Hard-templating is a widely used strategy for constructing mesoporous or macroporous structures in MOFs. In this method, preformed rigid templates are introduced into the synthesis system to physically define the final pore architecture. Common hard templates include polymer spheres, silica nanoparticles, mesoporous silica, anodic aluminum oxide, carbon materials, and even sacrificial MOF crystals. After the MOF framework grows around or within the template, the template is selectively



removed or transformed, leaving behind additional meso-/macroporous voids. Compared with defect formation, hard-templating generally provides more direct control over pore size, pore shape, spatial arrangement, and long-range pore ordering. Therefore, it is particularly useful when ordered macropores or well-defined hierarchical architectures are required.

A representative example was reported by Huang et al., who developed an in situ self-assembly template strategy to prepare hierarchical-pore MOFs using MOF-5 as a sacrificial template [92]. In this design, MOF-5 served as a removable rigid template because of its relatively low stability under humid or acidic conditions. During synthesis, more stable MOFs were formed around or in association with the MOF-5 template. After selective removal of MOF-5, hierarchical-pore structures were obtained in several MOF systems, including UiO-66, ZIF-8, MIL-101, and DUT-5. This work is important because it demonstrated that sacrificial MOF crystals can be used not only as structural templates but also as chemically compatible components for constructing multilevel porosity in different MOF families. By adjusting the amount and size of the MOF-5 template, the mesopore structure of the final MOF products could be tuned.

Another important example is the preparation of ordered macro-/microporous ZIF-8

single crystals reported by Shen and co-workers [93]. In this work, ordered polystyrene sphere arrays were used as hard templates to define macroporous structures, while ZIF-8 preserved its intrinsic microporous framework. After removing the polymer template, the resulting ZIF-8 crystals contained ordered macropore arrays together with the original micropores of the framework (**Figure 20**). This architecture is particularly attractive because the macropores provide open diffusion pathways, while the micropores retain molecular-level recognition and confinement. Compared with conventional ZIF-8 crystals, the ordered macro-/microporous structure improved molecular diffusion and catalytic performance, showing the functional benefit of combining transport pores with intrinsic MOF micropores.

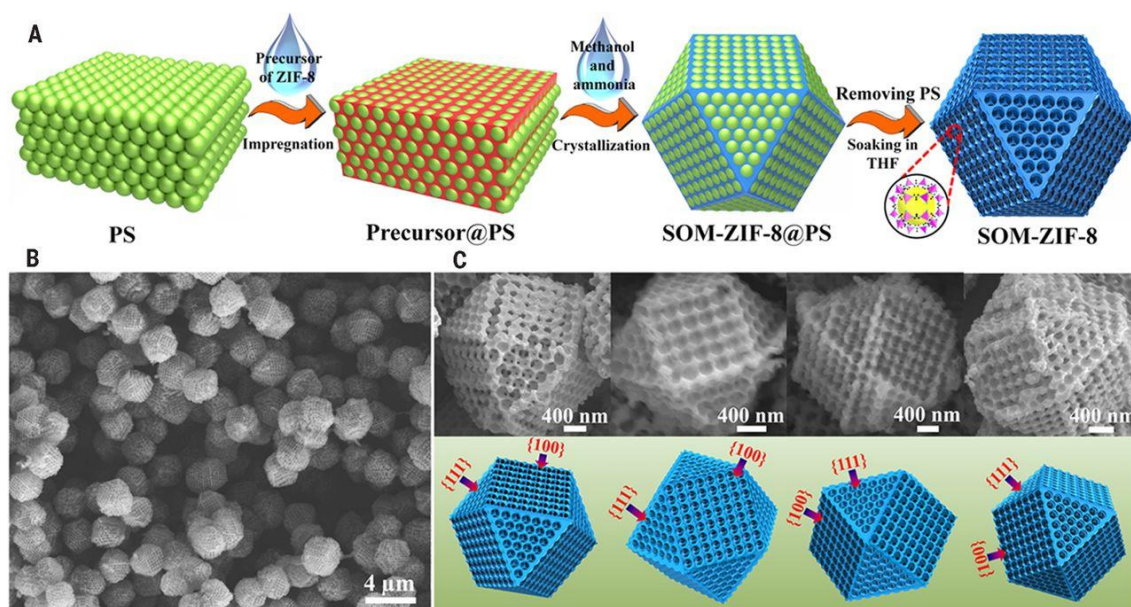


Figure 20 In situ nanocasting synthesis of SOM-ZIF-8 and its structure confirmation.

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Advancement of Science.



Overall, hard-templating is a powerful method for preparing HP-MOFs with relatively well-controlled meso-/macroporous structures. However, this approach also has several limitations. Template removal can require chemical etching or thermal treatment, which may damage the MOF framework or reduce crystallinity. In addition, precursor infiltration, nucleation, and crystal growth must be carefully matched with the template geometry. If the MOF does not grow uniformly around the template, incomplete pore replication, blocked channels, or discontinuous frameworks may be obtained. Therefore, although hard-templating offers strong structural control, it often requires careful optimization of both the template and the MOF crystallization process.

2.3.1.4 Soft-Templating

Soft-templating is another important strategy for constructing mesoporous and hierarchically porous MOFs. In contrast to hard-templating, which uses rigid and preformed solid templates, soft-templating relies on dynamic supramolecular assemblies such as surfactant micelles, block-copolymer micelles, emulsions, nanoemulsions, or other colloidal aggregates. These soft templates can guide MOF precursor organization through electrostatic interactions, hydrogen bonding, hydrophobic interactions,



coordination interactions, or interfacial assembly. After MOF formation, the soft template can usually be removed by solvent washing, activation, or mild extraction, leaving behind mesopores or hierarchical pore networks. Compared with hard templates, soft templates are more flexible and easier to tune because their size, shape, and packing behavior can be adjusted by changing the surfactant type, solvent composition, swelling agent, concentration, temperature, or ionic environment. Therefore, soft-templating is particularly attractive for preparing mesoporous MOFs under relatively mild conditions.

One early example was reported by Qiu and co-workers, who used CTAB as a soft template to synthesize hierarchically micro-/mesoporous HKUST-1 with tunable porosity [94]. In this system, CTAB molecules self-assembled into micellar structures, while copper ions and organic linkers organized around the micelles during MOF crystallization. After template removal, additional mesopores were generated within the MOF material. This study showed that surfactant micelles can be incorporated into the MOF formation process to introduce larger pores beyond the intrinsic micropores of the framework. Later, Sun et al. reported a cooperative template-directed assembly strategy for mesoporous MOFs, further demonstrating that suitable interactions between MOF precursors and supramolecular templates are essential for forming ordered mesostructures [95]. These studies established the basic concept that soft templates can direct MOF growth while

simultaneously regulating mesopore formation.



Block copolymers represent a particularly important class of soft templates because their self-assembled micelles can provide larger and more controllable mesostructures than many small-molecule surfactants. Amphiphilic block copolymers, such as Pluronic F127, P123, or PS-*b*-PEO, contain chemically distinct blocks that can selectively interact with solvents, swelling agents, and MOF precursors. In a suitable solvent environment, the solvophilic block forms the micellar corona, while the less-solvated block forms the micellar core. These micelles can then act as mesopore-directing units during MOF growth. By tuning the block length, solvent selectivity, micelle concentration, and swelling-agent content, the mesopore size and morphology of the resulting MOFs can be systematically adjusted. For example, Gu and co-workers used a Hofmeister ion-mediated F127 micellar system with hydrophobic swelling agents to continuously tune the mesopore size of hierarchical UiO-66-type MOFs from 6.4 to 12.1 nm [96]. This approach created spatially organized mesoporous domains that improved substrate diffusion, enzyme loading, and cascade sensing performance, showing the advantage of block-copolymer-based soft templating for functional biosensing platforms.

Soft templates can also be combined with emulsion or interfacial assembly to generate more complex MOF morphologies. Guan and co-workers reported asymmetric

core-shell ZIF-67 nanobowls by using a CTAB/TMB/water emulsion system, in which MOF precursors assembled at the oil-water interface to form meso-/microporous nanobowl structures [97]. In another example, dendritic UiO-66 nanoparticles with hierarchical macro-/meso-/microporosity were prepared using an emulsion-guided assembly method involving Pluronic surfactants [98]. These works show that soft-templating is not limited to simple spherical micelles; rather, the dynamic interface between surfactants, oil droplets, solvents, and MOF precursors can be used to create anisotropic or multilevel pore architectures (**Figure 21**).

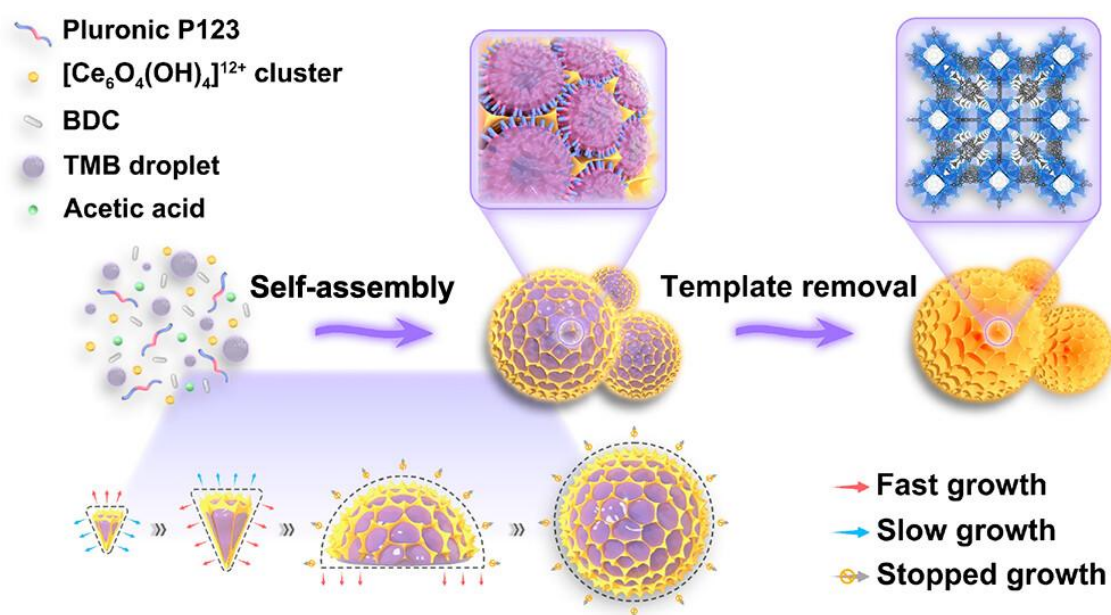


Figure 21 Schematic of the formation of UiO-66 dendritically hierarchically porous nanoparticles (DHPNPs). Reproduced with permission [98]. Copyright 2023, American Chemical Society.

2.4. Amorphous MOFs and Phase Engineering



Although MOFs are traditionally valued for their crystallinity and long-range structural order, amorphous MOFs have recently emerged as an important class of framework materials. Unlike completely decomposed or carbonized materials, amorphous MOFs can still retain local metal–ligand coordination environments similar to their crystalline counterparts, while losing long-range periodicity. This structural feature allows amorphous MOFs to combine the chemical tunability of MOFs with the isotropic, grain-boundary-free characteristics of amorphous materials. Therefore, amorphous MOFs are not simply failed crystalline products, but can be regarded as a distinct phase state of framework materials.

One of the earliest important studies was reported by Bennett, Cheetham, and co-workers, who demonstrated that crystalline ZIF-4 could undergo a crystal-to-amorphous transition upon thermal treatment [99]. Their total scattering and structural analyses showed that the resulting amorphous phase could be described as a continuous random network while retaining short-range Zn–imidazolate connectivity. This work was significant because it demonstrated that MOFs can access amorphous or glass-like states without completely losing their framework-derived local structure. Later, Bennett and co-workers further reported melt-quenched MOF glasses from zeolitic imidazolate



frameworks [100]. In this work, crystalline ZIFs were melted and then rapidly quenched to form glassy MOF phases. These MOF glasses retained basic metal–ligand connectivity while displaying properties different from conventional inorganic, organic, or metallic glasses. These studies expanded the structural landscape of MOFs from crystalline powders to amorphous solids, liquids, and glasses.

Beyond melt-quenching, amorphous MOFs can also be obtained by direct synthesis or kinetic control. Recent studies have shown that amorphous coordination polymers and amorphous MOFs can be prepared by regulating precursor coordination, nucleation rate, solvent environment, and reaction kinetics (**Figure 22**) [101]. This direction is especially important because it avoids the need to first prepare a crystalline MOF and then collapse it by thermal, mechanical, or pressure treatment. For example, Stöber-like strategies have been used to synthesize amorphous coordination polymer and amorphous MOF colloids and coatings, demonstrating that amorphous framework materials can be designed directly through controlled reaction pathways [102]. These works indicate that amorphous MOFs can be produced not only by destroying crystalline order, but also by deliberately suppressing long-range crystallization during synthesis.

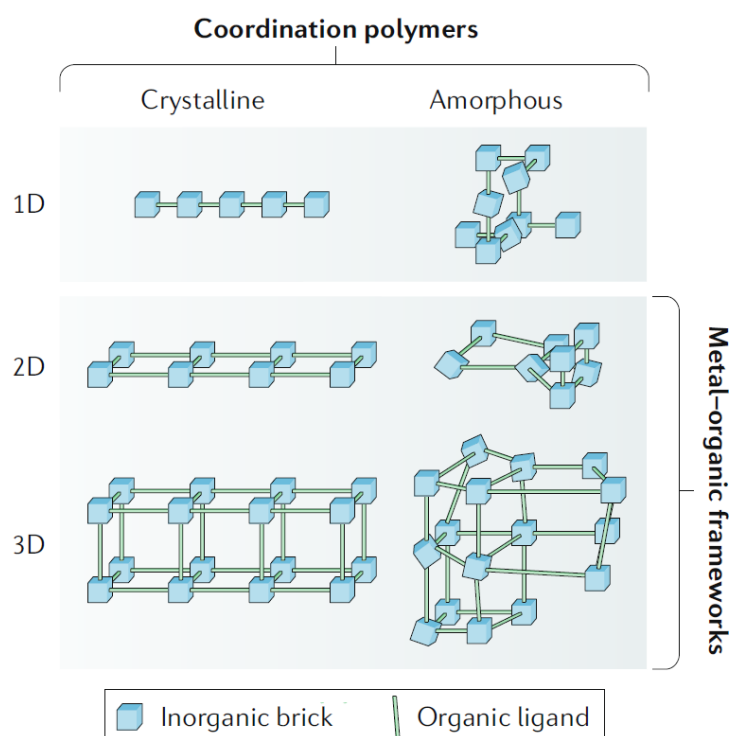


Figure 22 Terminology for crystalline and amorphous states. Reproduced with permission [101]. Copyright 2018, Springer Nature.

From a functional perspective, amorphous MOFs provide several potential advantages for thin-film materials. The absence of long-range grain boundaries may reduce discontinuous transport barriers and generate more isotropic pathways for ion, molecule, or charge transport. In addition, amorphous structures may contain distorted coordination environments, unsaturated metal sites, and flexible local networks, which can be useful for catalysis, sensing, and device integration. However, amorphous MOFs also present challenges. Because amorphous MOFs lack long-range crystallinity, their



structures cannot be fully solved by conventional diffraction methods alone. Powder X-ray diffraction is useful for confirming the loss of long-range order, but it provides limited information on the local coordination environment and may not clearly distinguish amorphous phases from nanocrystalline or highly defective structures. Therefore, complementary characterization techniques are required. Pair distribution function analysis can probe short- and medium-range atomic correlations, XAS/EXAFS provides atom-specific information on local metal coordination, and solid-state NMR, FTIR, and XPS help clarify ligand environments, bonding motifs, and chemical composition. Electron microscopy can further reveal morphology or residual nanocrystalline domains, while gas adsorption measurements are useful for evaluating porosity and pore accessibility [99,103,104].

This concept is highly relevant to the second research direction of this dissertation. As discussed in the previous section, soft-templating is an effective strategy for introducing mesopores into MOFs, but most reported soft-templated mesoporous MOFs are obtained as powders or particles. For thin-film fabrication, crystallization can become problematic because rapid crystal growth during solvent evaporation may generate isolated crystalline particles, grain boundaries, and discontinuous film morphology. These features are unfavorable for constructing continuous mesoporous MOF films. Therefore,



in this dissertation, amorphous phase engineering is introduced as a strategy to control MOF film formation. By deliberately suppressing ZIF-90 crystallization during solvent evaporation while using block-copolymer micelles as soft templates, continuous mesoporous amorphous MOF thin films can be prepared. In this design, the amorphous state is not treated as a structural disadvantage, but as a useful phase-engineering tool to avoid grain-boundary formation, improve film continuity, and integrate mesoporosity into a continuous MOF-based thin-film architecture.

3. Objective



The main objective of this dissertation is to develop continuous porous framework thin films by controlling their phase state, pore architecture, and interfacial structure. Although MOFs and COFs possess highly tunable pore structures and surface chemistries, their practical use in thin-film-based devices is still limited by several challenges, including discontinuous transport pathways in particle-assembled films, poorly controlled interfaces in heterogeneous membranes, and mass-transport limitations in conventional microporous frameworks. Therefore, this dissertation aims to establish design principles for transforming porous framework materials from conventional powders into functional thin-film and membrane architectures.

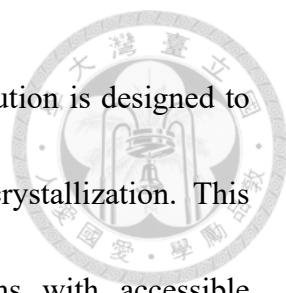
In response to these challenges, this dissertation focuses on two complementary concepts: structural design and phase engineering. Structural design emphasizes the spatial arrangement and interfacial connection of different porous framework layers. This concept is particularly important for constructing heterogeneous membranes with directional and selective ion-transport behavior. Phase engineering, on the other hand, focuses on controlling the crystalline or amorphous state of framework materials. By regulating crystallization kinetics and introducing hierarchical porosity, phase engineering provides an opportunity to overcome the diffusion limitations commonly

observed in purely microporous crystalline MOFs.



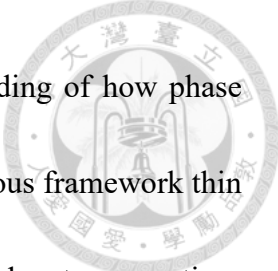
The first objective of this dissertation is to construct a crystalline MOF-on-COF heterostructured membrane for ion transport and osmotic power generation. In this part, a free-standing COF membrane is used as a continuous porous support, and a UiO-66-NH₂ MOF layer is selectively grown on one side of the COF membrane. This design aims to address the challenge of interfacial control in heterogeneous framework films. By controlling the growth position of the MOF layer, the formation of an uncontrolled symmetric structure can be avoided, allowing the construction of a directional MOF-on-COF bilayer membrane. The opposite surface charges and different pore structures of the MOF and COF layers are expected to create a charge-asymmetric ion-transport pathway, which is beneficial for ionic rectification, ion selectivity, and osmotic energy harvesting. Through this system, this dissertation investigates how crystalline hetero-interfaces, surface charge asymmetry, and sub-2 nm pore confinement influence ion transport and power generation performance.

The second objective is to develop a solvent-evaporation-induced assembly strategy for preparing continuous mesoporous amorphous MOF thin films. In this part, ZIF-90 is selected as a representative MOF system, and its crystallization behavior is deliberately controlled during rapid solvent evaporation. By using a block copolymer as a soft



template and optimizing the solvent environment, the precursor solution is designed to undergo micelle-assisted assembly while suppressing excessive crystallization. This strategy aims to form continuous amorphous ZIF-90 thin films with accessible mesoporous structures. Compared with conventional crystalline microporous MOFs, the mesoporous amorphous architecture is expected to provide shorter diffusion pathways, improved active-site accessibility, and better mass transport. The resulting materials are further evaluated using electrochemical uric acid sensing as a model reaction to clarify the relationship between pore structure, phase state, and sensing performance.

Through these two representative systems, this dissertation seeks to demonstrate that the performance of porous framework thin films is governed not only by their chemical composition, but also by their structural organization across multiple length scales. For MOF-on-COF membranes, the key design factor is the construction of a well-defined crystalline heterointerface for asymmetric ion transport. For mesoporous amorphous MOF films, the key design factor is the control of solvent evaporation, micelle assembly, and crystallization kinetics to generate continuous mesoporous films. Although the two systems are applied to different fields, namely osmotic power generation and electrochemical sensing, they share the same fundamental goal: to improve transport behavior through rational thin-film design.



Overall, this dissertation aims to provide a coherent understanding of how phase engineering and structural design can be used to create advanced porous framework thin films. By moving from crystalline MOF–COF hetero-interfaces to solvent evaporation-induced mesoporous amorphous MOF films, this work highlights the importance of film continuity, pore accessibility, interfacial architecture, and framework phase state in the development of next-generation porous framework materials for energy and sensing applications.



4. Experimental

4.1. Chemicals and Materials

Table 1 Chemicals and materials used in this work.

Chemical	Information
Zirconium(IV) chloride (anhydrous, 98%)	Acros
Zinc nitrate hexahydrate (99%)	FUJIFILM Wako
2,4,6-Triformylphloroglucinol (>98%)	Tokyo Chemical Industry
tris(4-aminophenyl)amine (>98%)	Tokyo Chemical Industry
2,5-Diaminobenzenesulfonic acid ($\geq 97\%$)	Sigma-Aldrich
Imidazole-2-formaldehyde (>98%)	Tokyo Chemical Industry
2-Aminoterephthalic acid (>98%)	Tokyo Chemical Industry
Benzoic acid (>99.0%)	Tokyo Chemical Industry
n-Octanoic acid (>98%)	Tokyo Chemical Industry
Potassium chloride (>99.5%)	Tokyo Chemical Industry
Potassium bromide (>99%)	Tokyo Chemical Industry
Potassium nitrate (99%)	Thermo Fisher
Potassium sulfate ($\geq 99\%$)	J.T.Baker
Potassium carbonate (anhydrous, 99%)	Alfa Aesar
Lithium chloride (anhydrous, >98%)	Tokyo Chemical Industry
Sodium chloride (>99.5%)	Tokyo Chemical Industry
Calcium chloride ($\geq 93\%$)	Sigma-Aldrich
Magnesium chloride (anhydrous, $\geq 98\%$)	Sigma-Aldrich
1,4-Dioxane (>99.5%)	FUJIFILM Wako
Dimethylformamide (>99.5%)	FUJIFILM Wako

Dimethyl sulfoxide (>99%)	FUJIFILM Wako
Methanol (=99.5%)	FUJIFILM Wako
Ethanol (99.8%)	Honeywell Fluka
Dichloromethane (>99.8%)	Honeywell
Tetrahydrofuran (>99.5%)	FUJIFILM Wako
Acetic Acid ($\geq 99.8\%$)	Honeywell
Potassium hydroxide ($\geq 85\%$)	Sigma-Aldrich
Sodium hydroxide (>98%)	Honeywell Fluka
Hydrochloric acid ($\geq 37\%$)	Honeywell Fluka
PEO _{5k} -b-PMMA _{22k}	Polymer Source Inc.
Polyacrylamide (99%)	Emperor Chemical
Aluminium foil, 250mm (99.9995%)	Strem Chemicals
FTO glass	AS ONE
Si wafer (100)	Matsuzaki Seisakusyo Cooperation
Deionized (DI) water with 18.20 M Ω resistance	Purified with a Milli-Q system (Millipore, Bedford, M, USA)



4.2. Equipment and Characterization Techniques

Table 2 List of Equipment used in this work.

Equipment	Information
Centrifugator	Himac, CT18R
Powder X-ray diffractometer (PXRD)	Rigaku, Ultima IV/ Rigaku SmartLab
Field Emission Scanning Electron Microscope (FE-SEM)	Hitachi, S-4800/ ZEISS GeminiSEM 560
Fourier-transform infrared (FT-IR)	JASCO FT/IR-4X



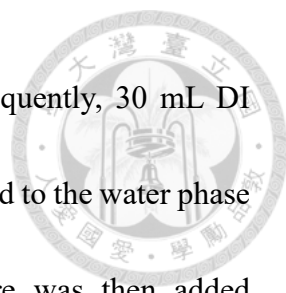
Atomic Force Microscopy (AFM)	BRUKER MultiMode 8-HR with NanoScope 6 Controller
X-ray photoelectron spectroscopy (XPS)	ULVAC-PHI PHI Quantes
BET surface area analyzer	Anton Paar Autosorb 6100/ BELSORP-II
Small/Wide Angle X-ray Scattering	NSRRC, TLS-23A1/ TPS-13A1
HAADF-STEM/ EDX	Talos F200X G2
Quick-scanning X-ray Absorption Spectroscopy (XAS)	NSRRC, TPS-44A1
High Resolution Powder Diffraction (HRPXR)	NSRRC, TPS-19A
Electronic Analytical Balance	AND, GR-200
Muffle furnace	Deng Yng, DF-202
Nuclear magnetic resonance (NMR)	BRUKER, 500MHz/AVANCE 400

4.3. Synthesis Procedures

4.3.1. Heterogeneous MOF-on-COF Membrane

4.3.1.1 Synthesis of Free-Standing COF Membranes through Interfacial Condensation

In this study, 2,4,6-Triformylphloroglucinol (Tp) and 2,5-Diaminobenzenesulfonic acid (PaSO₃H) are used as the monomers to synthesize the COF Tp-PaSO₃H as illustrated in **Figure 23**. Herein, liquid-liquid interfacial condensation was conducted to fabricate the free-standing COF membrane. Through dissolving 0.021 g Tp and 0.028 g PaSO₃H in 20 mL octanoic acid into a 20 mL vial and sonicated the mixture to achieve a



homogeneous suspension, serving as the precursor solution. Subsequently, 30 mL DI water was put into a 250 mL beaker, and 3 mL of acetic acid was added to the water phase uniformly. Afterward, the precursor solution was prepared before was then added dropwise onto the interface of water, and the beaker was kept at room temperature for 10 days. The acetic acid catalyzes the interfacial polymerization, culminating in the formation of the free-standing COF Tp-PaSO₃H membrane at the juncture of the water and organic phases (**Figure 24**).

To wash the as-synthesized COF membrane, we slightly tilted the beaker to allow the stratified water and organic solvent to decant, at which point the newly synthesized free-standing COF membrane adhered to the wall of the beaker. We then carefully introduced acetone into the beaker to wash the COF membrane, aiming to remove any unreacted monomers and residual solvents. This step was repeated several times until the solution became clear. Subsequently, the COF membrane was rinsed in the same manner with ethanol and water, in sequence. Finally, the cleaned COF membrane was stored in a 1:1 mixture of acetone and ethanol solution until further reactions were to be conducted.

Interfacial condensation

1. H_2O 30mL
2. AA 3mL

1. Octanoic acid 20mL
2. Tp 21 mg, PaSO_3H 28 mg

wash with Acetone,
EtOH, and DI water

RT, 10 days



Free-standing
TpPa- SO_3H

Figure 23 Schematic illustration of interfacial condensation synthesis of COF TpPa-

SO_3H .

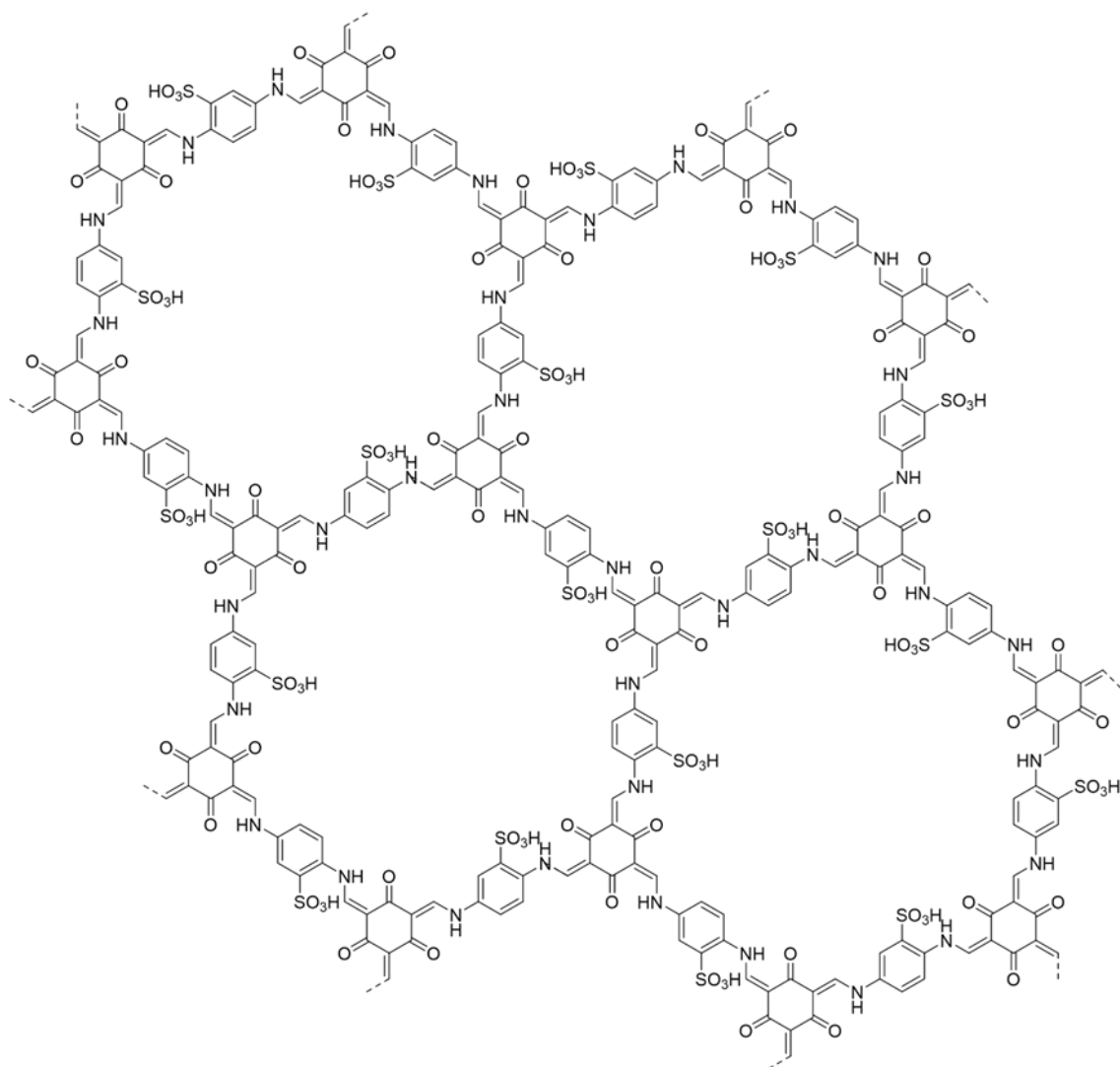


Figure 24 The molecular structure of COF TpPa- SO_3H .

4.3.1.2 Construction of Heterostructured MOF-on-COF Membranes

Before growing the MOF onto the COF membrane, we first transfer the free-standing COF membrane to the ANM (alumina nanochannel membrane) supporting layer.

The ANM supporting layer here acts as a mechanical safeguard, reducing the likelihood of COF membrane rupture due to changes in solvent surface tension during the subsequent growth of MOF. Furthermore, the ANM supporting layer also offers a homogeneous unidirectional conduit for ion conveyance (**Figure 25**).

The precursor solution for the MOF UiO-66-NH₂ was prepared by dissolving 0.58 mmol of ZrCl₄ and 48.3 mmol of benzoic acid in 35 mL of DMF within a 100 mL serum bottle. This mixture was sonicated until a clear solution was obtained. Subsequently, the precursor solution was heated to 80°C for 2 hours to facilitate the formation of the Zr₆O₄(OH)₄ moiety. Following this, 0.58 mmol of H₂BDC-NH₂ was dissolved in the solution to act as the organic linker for the MOF UiO-66-NH₂. The COF@ANM supported by a PTFE fixed mold was then immersed in the MOF precursor solution carefully and heated to 120°C for 24 hours. After the reaction, the COF@ANM with the PTFE fixed mold was transferred into fresh DMF solvent to wash away any unreacted MOF monomers, and then further washed with an acetone and ethanol solution. Finally, the PTFE fixed mold was removed, and the MOF-on-COF can be obtained (**Figure 26**).



To fabricate the asymmetric MOF-on-COF membrane, a direct MOF growth strategy was employed on the preformed COF substrate. In a typical procedure, the COF@ANM membrane was placed in the precursor solution for UiO-66-NH₂ and subsequently subjected to solvothermal treatment, allowing a MOF layer to form on the COF surface. However, without spatial control over precursor exposure, MOF nucleation may occur on both sides of the COF membrane, potentially leading to the formation of a symmetric MOF–COF–MOF trilayer structure. To prevent this undesired growth behavior, a customized polytetrafluoroethylene (PTFE) fixture was designed to expose only one side of the COF membrane to the MOF precursor solution. By limiting precursor contact to the targeted surface, this configuration enabled selective MOF growth on one side of the COF substrate, thereby producing a genuinely asymmetric MOF-on-COF membrane.

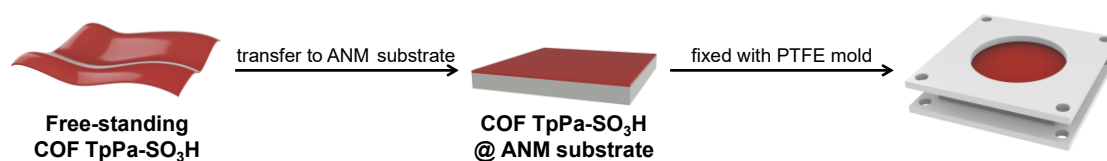


Figure 25 Transfer process of COF Tp-PaSO₃H membrane.

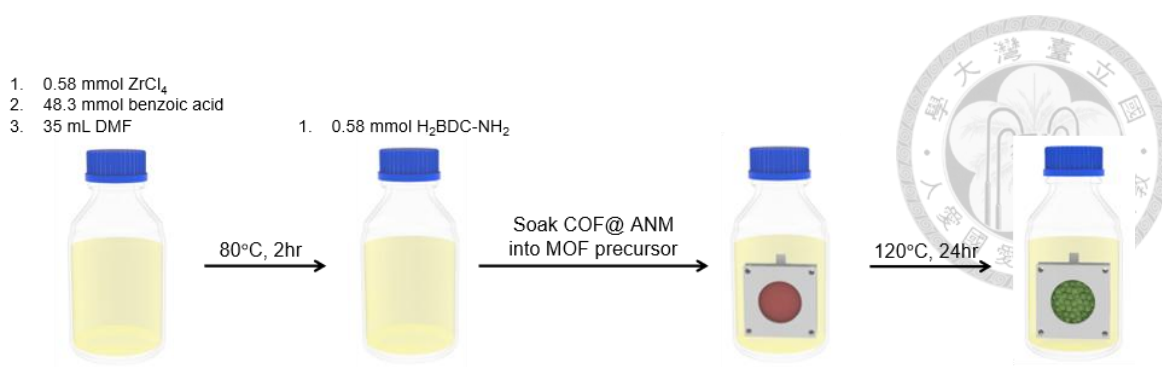


Figure 26 The synthesis protocol of MOF-on-COF heterogeneous membrane.

4.3.2. Solvent-Evaporation-Mediated Micelle Assembly for Continuous Mesoporous

Amorphous MOF Thin Films

4.3.2.1 Spin-Coating Fabrication of Mesoporous Amorphous $\alpha\text{ZIF-90}$ Thin Films

The precursor solution was formulated by first dissolving 10 mg of the block copolymer $\text{PEO}_{5k}\text{-b-PMMA}_{22k}$ in THF under continuous stirring until optical clarity was achieved. Methanol was then introduced to adjust the total solvent volume to 5 mL. Following this, 40 mg (0.134 mmol) of zinc nitrate hexahydrate was incorporated into the mixture and stirred for 2 hours. Imidazole-2-carboxaldehyde (ICA, 20 mg, 0.208 mmol) was subsequently added, with the stirring maintained for an additional 2 hours. Prior to film deposition, FTO glass substrates were washed with acetone and blown dry. A 0.7 mL aliquot of the precursor mixture was dropped onto the conductive side of the FTO glass and spin-coated at 500 rpm for 60 seconds. Thermal treatment of the resulting film

was conducted in an oven at 100 °C for 24 hours. Finally, the unreacted precursors and the polymer template were removed by washing the sample with THF and methanol subsequently.



For GISAXS analysis, silicon wafers were utilized as substrates instead of FTO glass. The wafers were pre-treated in a Piranha solution for 30 minutes to eliminate organic residues, followed by a 5-minute UV-ozone treatment to improve surface wettability. The subsequent coating and thermal steps were identical to the aforementioned procedures.

4.3.2.2 Synthesis of Bulk Mesoporous Amorphous aZIF-90 Samples

The formulation of the precursor solution followed the exact protocol described for the spin-coated aZIF-90 films. A Petri dish, rinsed with acetone, dried, and treated with ion bombardment for 3 minutes to improve surface hydrophilicity was utilized as the container. The precursor mixture was transferred into the dish and left in ambient air for 2 hours to allow for complete solvent vaporization. The dried sample was then thermally treated at 100 °C for 24 hours in an oven. Upon completion, the resulting solid was scraped off, collected in a centrifuge tube, and purified via centrifugation with THF and methanol at 11,500 rpm three times to eliminate the templating polymer and residual monomers.



4.3.2.3 Preparation of *c*ZIF-90 Powder

Crystalline ZIF-90 (*c*ZIF-90) was prepared based on a previously reported solvothermal approach [105]. Specifically, a mixture containing 296 mg (1.0 mmol) of zinc nitrate hexahydrate, 384 mg (4.0 mmol) of ICA, and 68 mg (1.0 mmol) of sodium formate was dissolved in 40 mL of methanol with the aid of ultrasonication. This homogeneous solution was transferred to a Teflon-lined stainless steel autoclave and subjected to heating at 85 °C for 24 hours. After naturally cooling to ambient temperature, the synthesized particles were washed through centrifugation with methanol at 11,500 rpm three times and subsequently dried in a vacuum oven for one day prior to use.

4.3.2.4 Synthesis of Small-Particle Crystalline ZIF-90 Reference Powders

To obtain *c*ZIF-90 powder with smaller particle size, a modified procedure from literature was employed [106]. Precursor A was prepared by dissolving 371.25 mg (1.25 mmol) of zinc nitrate hexahydrate in 12.5 mL of tert-butanol. Concurrently, precursor B was formed by mixing 480 mg (5.0 mmol) of ICA and 500 mg of polyvinylpyrrolidone (PVP) in 12.5 mL of deionized water. Precursor A was then rapidly introduced into precursor B, and the combined mixture was stirred at room temperature for 20 minutes. The resulting precipitate was collected and washed three times with methanol via

centrifugation at 11,500 rpm. The final purified solid was dried under vacuum for 24 hours.



4.3.2.5 *Spray-Coating Deposition of Mesoporous Amorphous aZIF-90 Thin Films*

The precursor solution was prepared using the same recipe as the spin-coating method. Prior to deposition, the conductive surface of the FTO glass was cleaned with acetone, blown dry, and preheated on a hot plate to 140 °C. Spray coating was executed using an airbrush equipped with a 0.3 mm nozzle, operated at a pressure of 3 bar. Approximately 2 mL of the solution was uniformly sprayed onto the FTO substrate from a working distance of ~20 cm. Upon complete solvent evaporation, the film was placed in a tubular furnace for thermal activation under a nitrogen flow (150 sccm). The temperature was ramped up at 5 °C/min to 150 °C and maintained for 2 hours. After cooling to room temperature, the film was rinsed with THF and methanol to remove residual monomers and the polymer template.

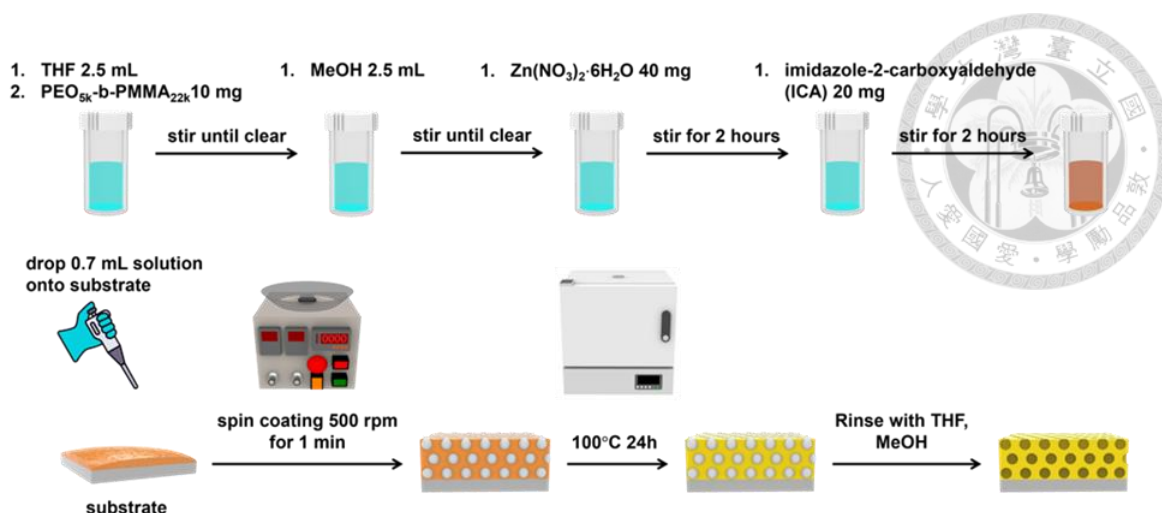


Figure 27 Schematic illustration of *a*ZIF-90 film sample preparation. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

4.4. Performance Testing Methods (Blue energy setup, Sensing protocols)

4.4.1. Blue energy generation performance test

The test of blue energy generation was evaluated using the homemade H-type electrochemical cell shown in **Figure 28**, with the COF or MOF-on-COF membrane mounted between the cells. A switchable external load resistor is connected in series in the circuit to serve as external resistance. Each side of the H-cell was filled with the ionic solution with different salinity concentrations. The current-voltage properties were recorded by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, Ohio), and with a pair of Ag/AgCl electrodes, which were put into both sides of the H-cell. The effective testing area was fixed by employing a pin-hole wafer, the area of which is

approximately $3 \times 10^{-8} \text{ m}^2$, consistent with previous work of our group [108].

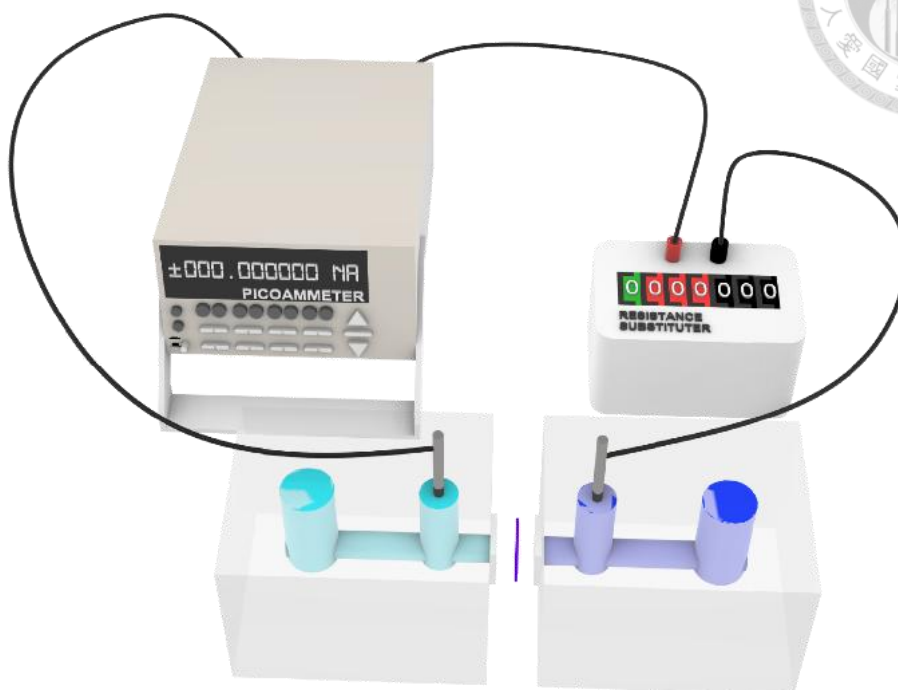


Figure 28 Electrochemical cell setup for blue energy generation performance test.

4.4.2. Uric Acid Sensor Test

- Electrode Preparation

A homogeneous MOF suspension was prepared by dispersing 4 mg of the selected MOF sample in 1 mL of deionized water containing 50 μL of Nafion solution, followed by thorough sonication to ensure uniform dispersion. Subsequently, 10 μL of the resulting suspension was drop-cast onto the working area of a screen-printed carbon electrode (SPCE) and dried under ambient conditions prior to electrochemical measurements.

- Sensor Evaluation

The sensing performance was evaluated by differential pulse voltammetry (DPV) using a PalmSens4 electrochemical workstation. DPV measurements were carried out over a potential window of 0–0.7 V at a scan rate of 10 mV s⁻¹. Uric acid solutions with concentrations ranging from 0 to 500 μM were prepared in 0.1 M phosphate-buffered saline (PBS) and used as the analyte solutions. The limit of detection (LoD) was calculated according to Equation 1 [109], where σ denotes the standard deviation of the response and S represents the slope of the calibration curve.

$$LOD = \frac{3\sigma}{S} \quad \text{Equation 1}$$

5. Heterogeneous MOF-on-COF Ionic Diodes: Structural Design and High-Performance Energy Harvesting



5.1. Characterization of COF and MOF

The free-standing Tp-PaSO₃H COF membrane was fabricated according to the procedure described in Section 4.3.1.1. As shown in the photograph, an intact membrane with an ocher-red to dark-red color and a metallic reflective sheen can be clearly observed (**Figure 29**). The obtained circular membrane has a diameter of approximately 9.5 cm and remains structurally undamaged after synthesis and transfer, demonstrating that the interfacial condensation method is capable of producing large-area, highly uniform, and mechanically self-supported COF membranes. The characteristic ocher-red or dark-red appearance is associated with the formation of the extended conjugated Tp-PaSO₃H framework during the interfacial polymerization process [110,111].

The crystallinity of the COF membrane is an important structural parameter for evaluating the quality of the synthesized film. First, crystallinity reflects the degree of periodic ordering of the COF framework over the membrane area, which is directly related to the successful formation of ordered COF nanodomains. Second, the crystalline packing quality can strongly influence ion transport behavior, because ordered pore channels generally provide more continuous pathways for ion migration, whereas poorly

ordered or defective domains may increase internal resistance and reduce ion permeability. Therefore, confirming the crystalline nature and preferred orientation of the Tp-PaSO₃H membrane is essential for understanding its subsequent ion-transport properties.

To investigate the crystallinity of the membrane, we conducted grazing-incidence wide-angle scattering (GIWAXS) measurements to examine the crystallinity of the COF Tp-PaSO₃H membrane. Grazing-incidence wide-angle X-ray scattering (GIWAXS) is a powerful synchrotron-based technique for analyzing the crystalline ordering, molecular packing, and preferential orientation of thin-film materials. Compared with conventional powder X-ray diffraction, GIWAXS is particularly suitable for thin membranes because the grazing-incidence geometry enhances the scattering signal from the film while reducing interference from the substrate [112,113].

In the GIWAXS 2D pattern (**Figure 30**), there are two obvious diffraction rings can be found. The inner ring belongs to the COF nanodomain, (100) direction, and the outer ring belongs to π - π interlayer stacking of COF layers, (001) direction. In the 1-D line-cut profile, both in-plane and out-of-plane integrated directions (**Figure 31**) show two peaks that correspond to the 2D pattern inner ring (100) and outer ring (001), which represents certain COF crystalline structures may not packing unidirectionally. Nonetheless, the (001) signal is stronger in the out-of-plane direction, indicating that the majority of the

layer-by-layer stacking is parallel to the substrate.



Figure 29 The photograph of COF Tp-PaSO₃H.

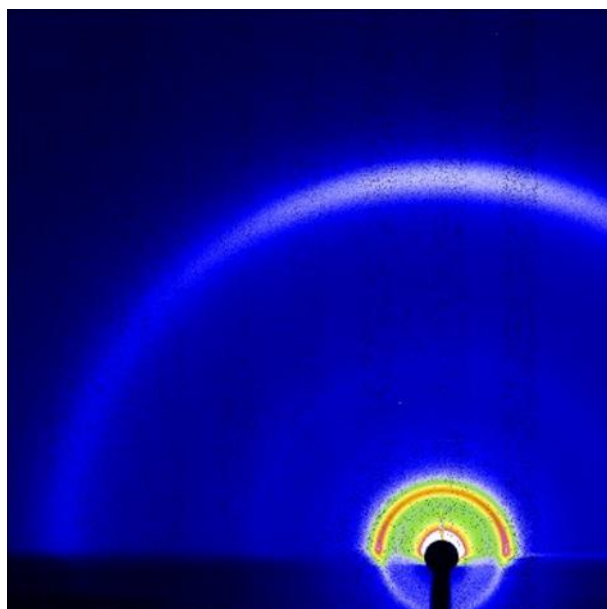


Figure 30 GIWAXS patterns of free-standing COF Tp-PaSO₃H.

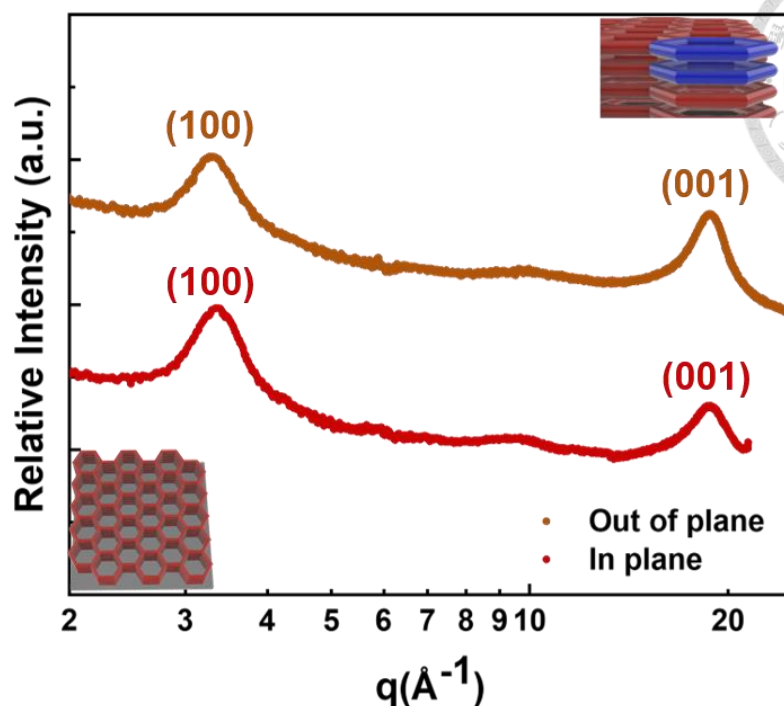


Figure 31 GIWAXS 1-D line-cut profiles of COF Tp-PaSO₃H membrane with in-plane and out-of-plane direction.

Figure 32 shows the FTIR spectra of monomer Tp, PaSO₃H, and as-synthesized COF Tp-PaSO₃H. The 3330 cm⁻¹ and 3303 cm⁻¹ peaks that appear in PaSO₃H indicate to primary amine stretch (-NH₂). The 1283 cm⁻¹ peak that appears in COF Tp-PaSO₃H belongs to the C-N stretch of β-ketoenamine bond [114]. The attenuated primary amine stretch peak and the presence of the β-ketoenamine bond both signify a high degree of polymerization in the COF Tp-PaSO₃H membrane. Vibration bands associated with O=S=O stretching both appear at 1082 cm⁻¹ and 1028 cm⁻¹ in PaSO₃H and COF Tp-

PaSO₃H, and these two spikes didn't appear in Tp. This suggests that the O=S=O stretching originates from the sulfonic group (-SO₃H) and is preserved within the structure of the COF Tp-PaSO₃H.

In solid-state ¹³C nuclear magnetic resonance (¹³C NMR) measurements (**Figure 33**), we can further identify the COF Tp-PaSO₃H bonds with corresponding peaks, especially the peak at 184.0 ppm, which represents the keto form of the carbonyl carbon [115]. Based on the comprehensive characterization results of GIWAXS, FTIR, and ¹³C NMR, it can be inferred that the COF Tp-PaSO₃H membrane has been successfully synthesized.

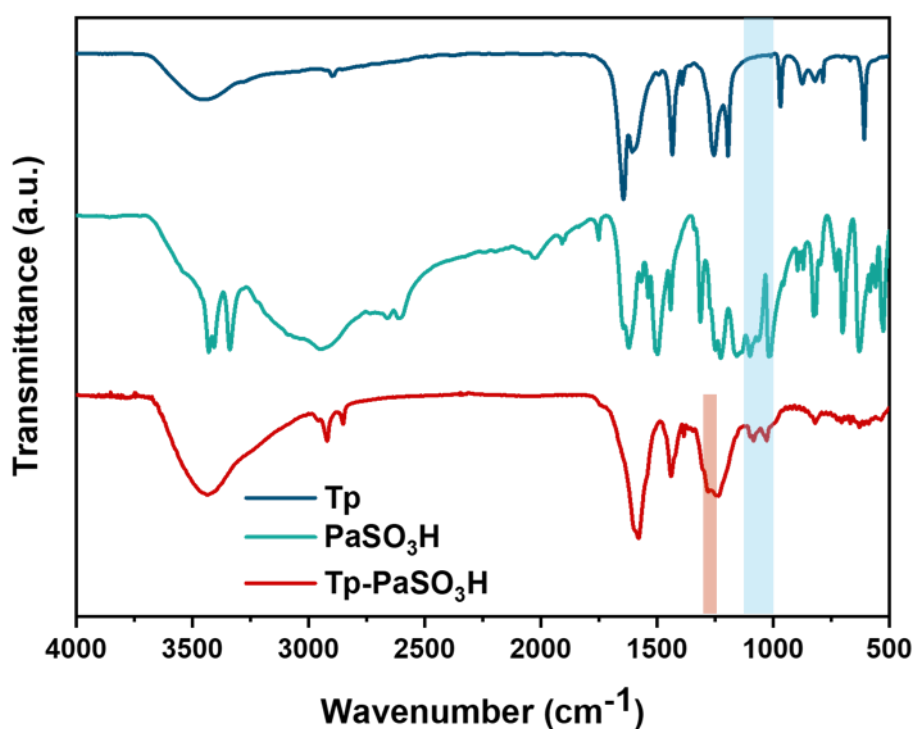


Figure 32 FTIR spectra of Tp, PaSO₃H, and COF Tp-PaSO₃H.

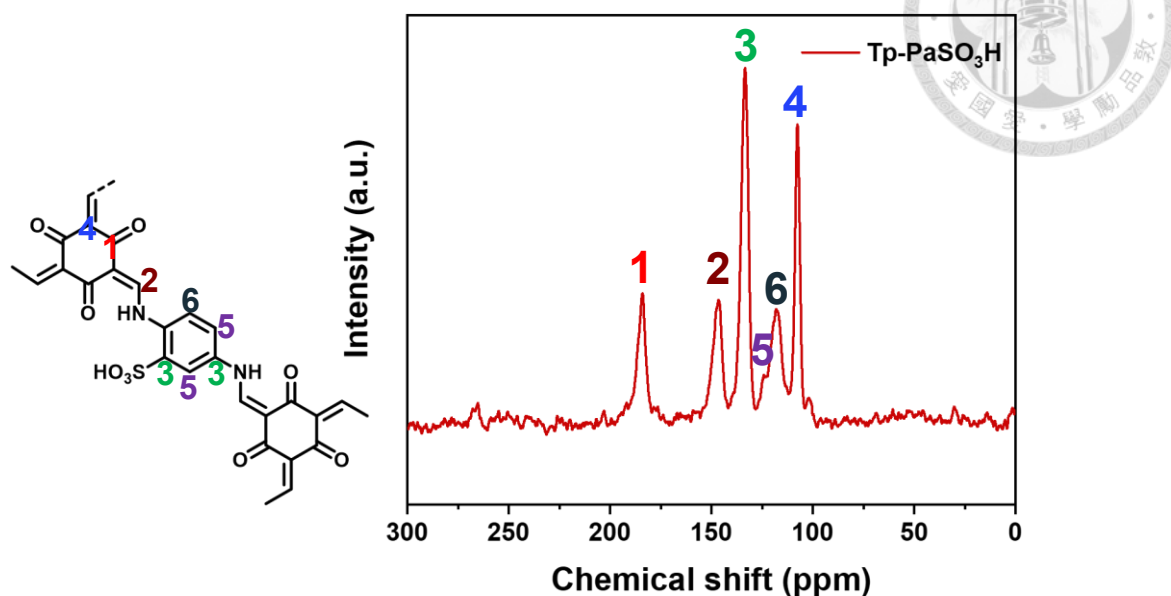


Figure 33 Solid-state ^{13}C NMR spectrum of the free-standing COF Tp-PaSO₃H membrane.

For MOF UiO-66-NH₂, the octahedron morphology can be observed through SEM observation which is shown in **Figure 34**, which is a characteristic morphology of UiO-66-NH₂ [116]. MOFs are a kind of well-defined porous material with a high surface area, the N₂ adsorption-desorption isotherm can confirm the high surface area of MOF. The surface area of the MOF UiO-66-NH₂ was found to be 1118 m²/g (**Figure 35**), this value was calculated by the BETSI method [117]. The pore size distribution shows two peaks at 0.6 nm and 1.1~1.2 nm, corresponding to the window aperture and pore size of the standard UiO-66-NH₂ model respectively (**Figure 36**). MOFs usually have high

crystallinity, the crystallinity of MOFs is important as it represents the structure's uniformity and regularity. The crystallinity of UiO-66-NH₂ is confirmed by X-ray Powder Diffraction (PXRD). There are lots of peaks that can be found in the XRD profile, especially three main peaks, which correspond to (111), (200), and (442) Miller indices. To compare the position and intensity of the crystallization signals with the standard MOF UiO-66-NH₂, we plot the measurement profile with the simulation profile. **Figure 37** shows that the peaks shown in the PXRD measurement are coincidental with the simulation profile, showcasing the high quality of as-synthesized UiO-66-NH₂.

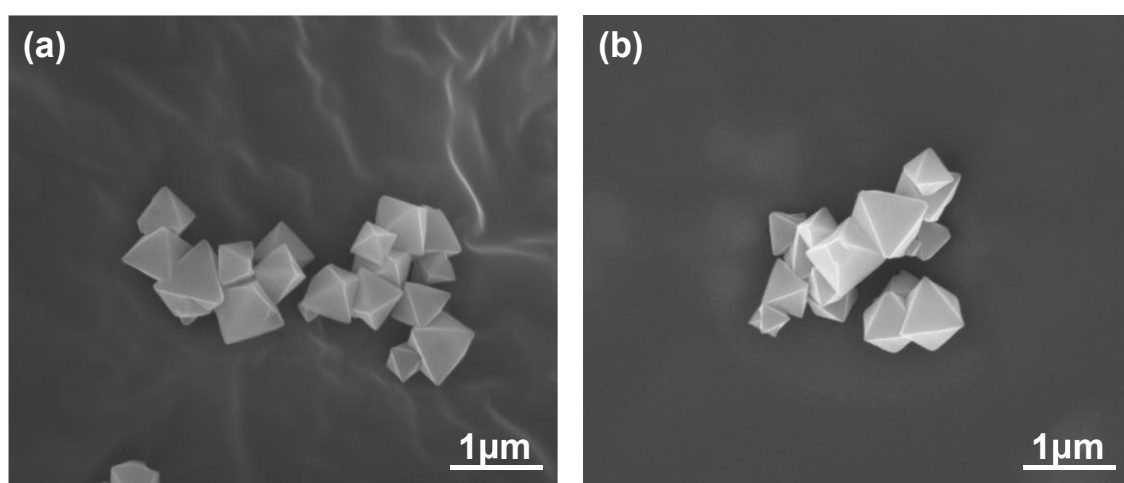


Figure 34 SEM images of as-synthesized MOF UiO-66-NH₂.

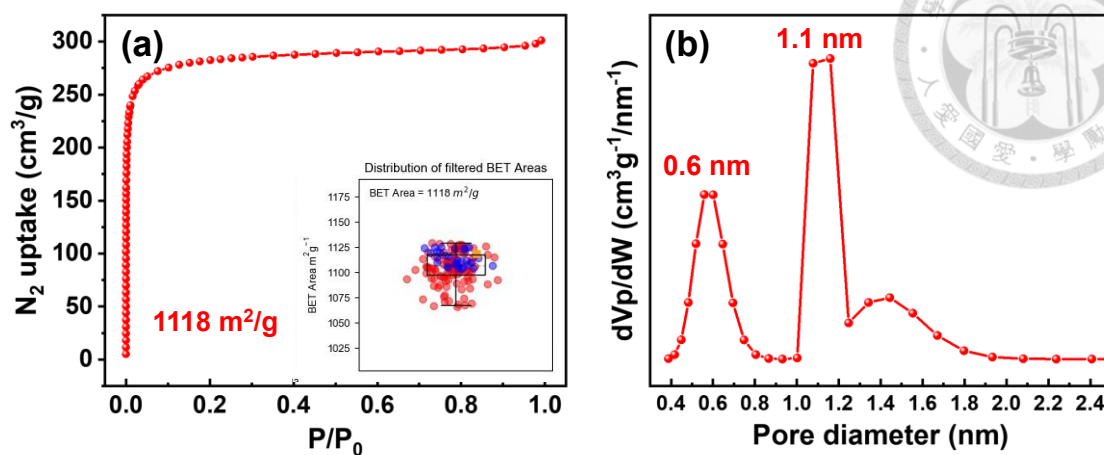


Figure 35 Porous-structure analysis of UiO-66-NH₂. (a) N₂ adsorption–desorption profile and corresponding BETSI surface area evaluation shown in the inset. (b) NLDFT-derived nominal pore-size distribution obtained from the N₂ sorption isotherm.

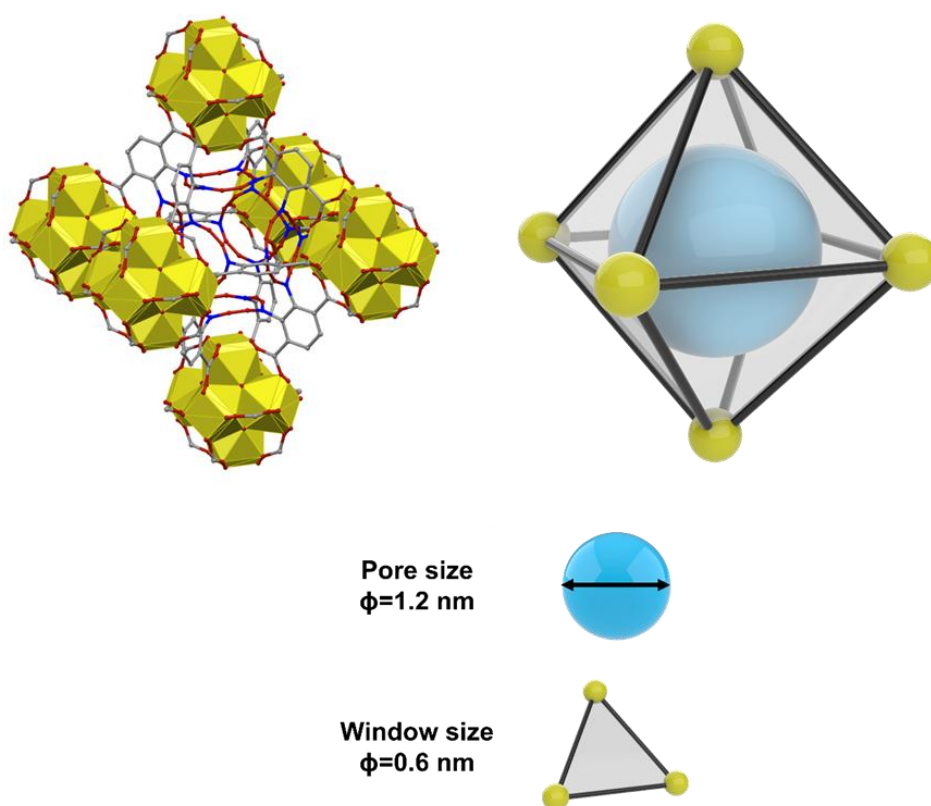


Figure 36 Schematic illustration of UiO-66-NH₂ octahedron.

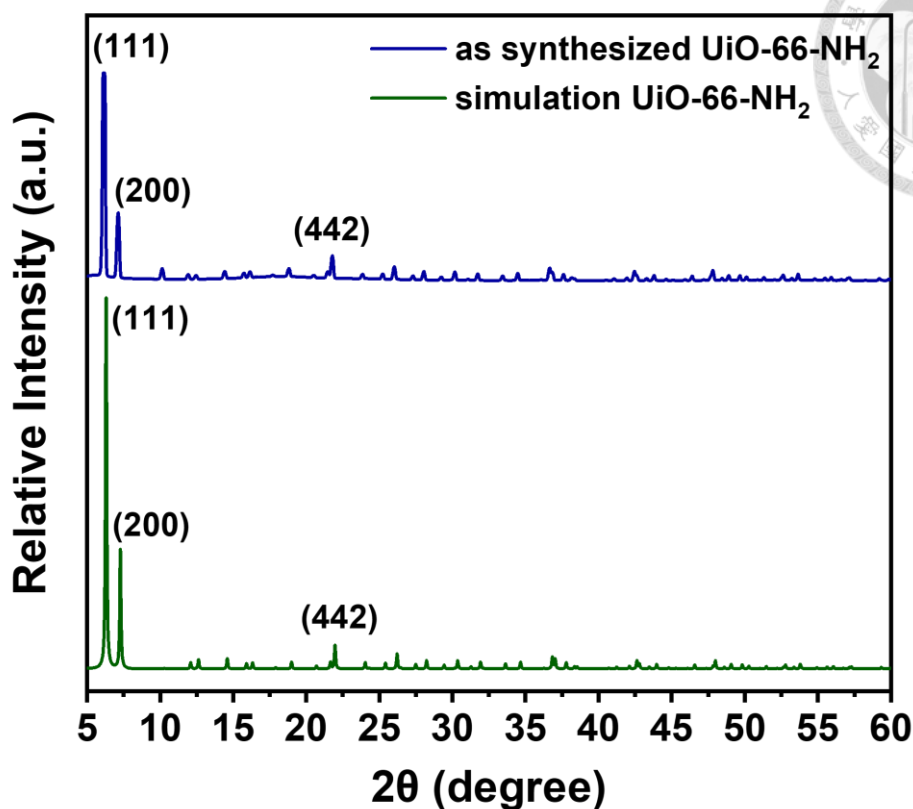


Figure 37 The comparison of the XRD profile of as-synthesized UiO-66-NH₂ and simulation profile.

The zeta potentials of UiO-66-NH₂ MOF and Tp-PaSO₃H COF were measured in 10 mM KCl solution to evaluate their surface charge properties (**Figure 38**). UiO-66-NH₂ exhibits a positive zeta potential of 12.7 ± 3.2 mV, whereas Tp-PaSO₃H shows a much stronger negative zeta potential of -32.2 ± 5.7 mV. This clear difference in surface charge confirms the formation of a charge-asymmetric MOF/COF system, in which the positively charged MOF layer and negatively charged COF layer can provide a bipolar

ion-transport environment.

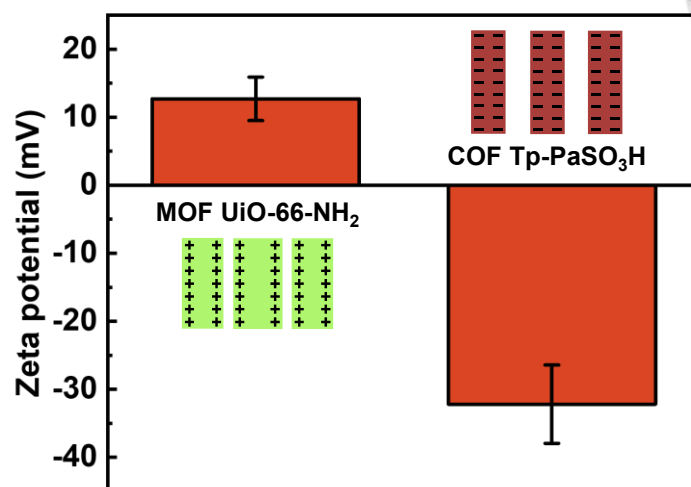


Figure 38 The zeta potential of MOF UiO-66-NH₂ and COF Tp-PaSO₃H in 10 mM KCl solution.

5.2. Fabrication of Heterogeneous MOF-on-COF Membrane

The heterogeneous MOF-on-COF membrane was fabricated according to the procedure described in Section 4.3.1. . The successful construction of the bilayered membrane was first examined by SEM. As shown in **Figure 39a**, one side of the membrane exhibits a continuous and relatively smooth COF morphology. Notably, almost no UiO-66-NH₂ MOF crystals can be observed on this side, indicating that MOF growth was effectively suppressed on the protected surface. This result confirms the effectiveness of the one-sided exposure strategy, in which a polytetrafluoroethylene (PTFE) barrier was

used to selectively expose only one side of the COF membrane to the MOF precursor solution.



In contrast, **Figure 39b** shows the opposite side of the membrane after MOF growth. A continuous layer composed of densely packed octahedral UiO-66-NH₂ crystals can be clearly observed, confirming the successful formation of the MOF layer on the targeted COF surface. The use of the COF membrane as a supporting substrate is particularly important because it helps overcome the difficulty of directly preparing a continuous free-standing MOF thin film from UiO-66-NH₂ alone [118]. Instead of forming isolated MOF particles or discontinuous domains, the MOF crystals are closely assembled on the COF surface to generate a compact and continuous MOF layer.

The cross-sectional SEM image further verifies the successful fabrication of the heterogeneous MOF-on-COF membrane (**Figure 39c**). The MOF and COF layers are clearly distinguishable and well attached to each other, indicating intimate interfacial contact between the two framework components. Such a well-integrated bilayered structure is essential for constructing an asymmetric ion-transport pathway, because the selective ion transport behavior relies not only on the individual properties of the MOF and COF layers but also on the continuity and integrity of their heterointerface.

To gain more insight into the crystal structure of heterogeneous MOF-on-COF

membrane, we further conducted Wide-angle X-ray scattering (WAXS) measurements.

In the WAXS profile (**Figure 40**), we can find there is a small peak at $q=0.4 \text{ \AA}^{-1}$ which belongs to the COF nanodomain (100) plane. It is worth mentioning that the broad peak located below $q = 0.4 \text{ \AA}^{-1}$ corresponds to the Kapton tape used to fix the sample during the measurement. We also observed numerous sharp peaks at q values higher than $0.5 \text{ \AA}^{-1}$, which are attributed to the MOF UiO-66-NH₂. The three strongest peaks, labeled in the figure, correspond to the (111), (200), and (442) planes, respectively. This characterization offers us two important information. First, the crystallinity of COF Tp-PaSO₃H is retained after the MOF growth reaction in DMF solvent, as evidenced by the unchanged peak positions, indicating that the well-defined pore structure of COF Tp-PaSO₃H is preserved. However, the relatively low-intensity peaks of COF are due to its composition of lighter elements, whereas the MOF contains heavier metallic elements (Zr) with higher scattering length density (SLD) [116]. Consequently, when both are present in the X-ray scattering observations, the signal from the COF appears significantly weaker.

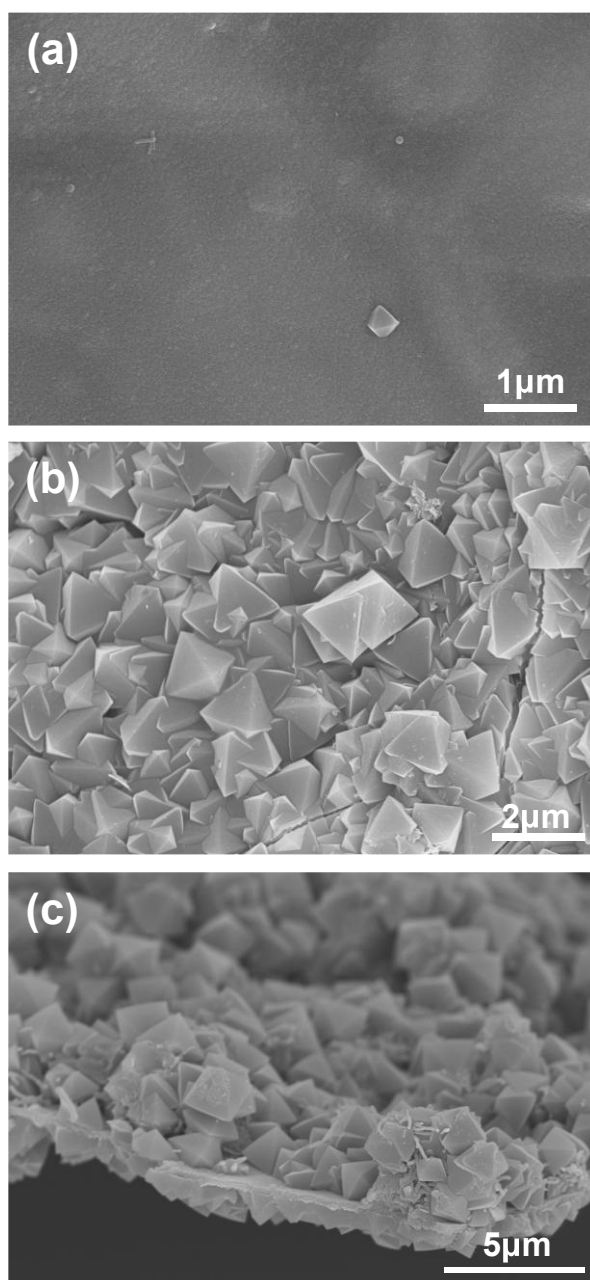


Figure 39 SEM images of MOF-on-COF membrane. (a) COF-side, (b) MOF-side, (c) cross-section.

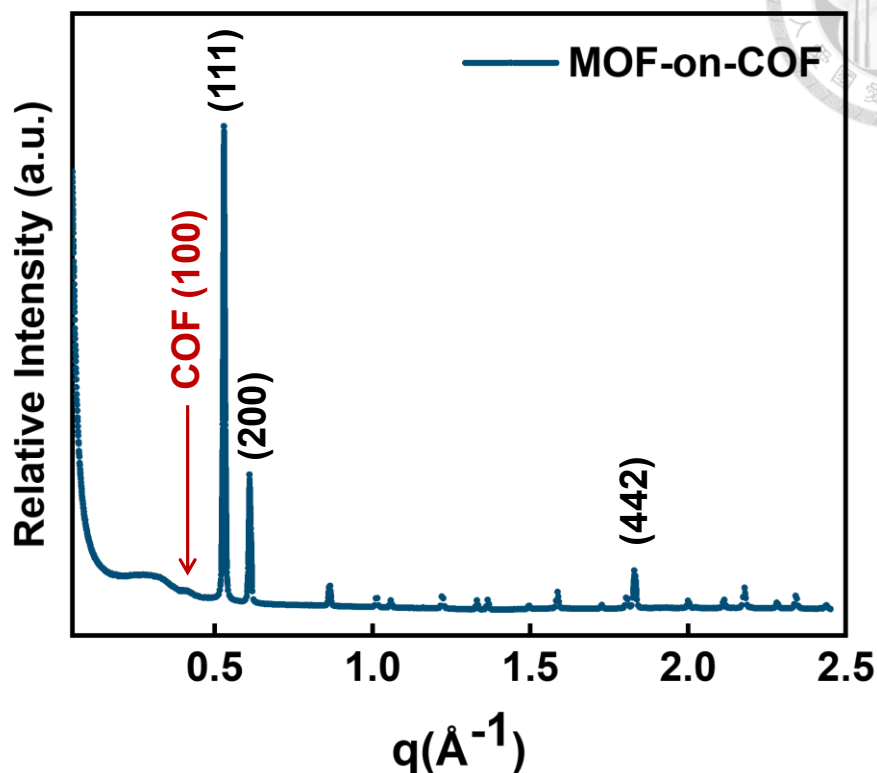


Figure 40 WAXS profile of heterogeneous MOF-on-COF membrane.

5.3. Blue Energy Harvesting of MOF-on-COF Membrane

The blue energy generation performance of the MOF-on-COF membrane was tested in the homemade H-cell which was filled with electrolytes in different salinity gradients, in series with an external load resistor as an external resistance. (**Figure 28**). Due to the geometry asymmetry of the MOF-on-COF membrane, two opposite configurations can be realized. The forward configuration refers to the setup where the COF side faces the

high-concentration electrolyte and the MOF side faces the low-concentration electrolyte, whereas the backward configuration refers to the setup where the MOF side faces the high-concentration electrolyte and the COF side faces the low-concentration electrolyte.

As shown in **Figure 41**, which records the I-V curve under 50-fold KCl concentration gradient. The intercepts on the voltage axis are representative of open-circuit voltage (V_{OC}) and the intercepts of the current axis are representative of short-circuit current (I_{SC}). In the forward configuration, the V_{OC} and I_{SC} values are 93.6 mV and 9.90 μ A, respectively, while the V_{OC} and I_{SC} values of the backward configuration are 87.4 mV and 6.46 μ A.

The internal resistance (R_{internal}) of the membrane can be calculated by using the formula:

$$R_{\text{internal}} = V_{OC}/I_{SC} \quad \text{Equation 2}$$

The calculated internal resistance in the forward configuration is 9454 Ω , whereas it is 13529 Ω in the backward configuration. The internal resistance was reduced by 30.1% in forward configuration, which demonstrates the preference for forward configuration.

These results show the preferential direction of ionic diffusion through the COF Tp-PaSO₃H with a larger ion transportation channel into the MOF UiO-66-NH₂ with a relatively smaller pore size. Hereafter, we introduce electrolytes of higher concentration into the COF side while placing electrolytes of lower concentration into the MOF side to maximize the harvest of blue energy.

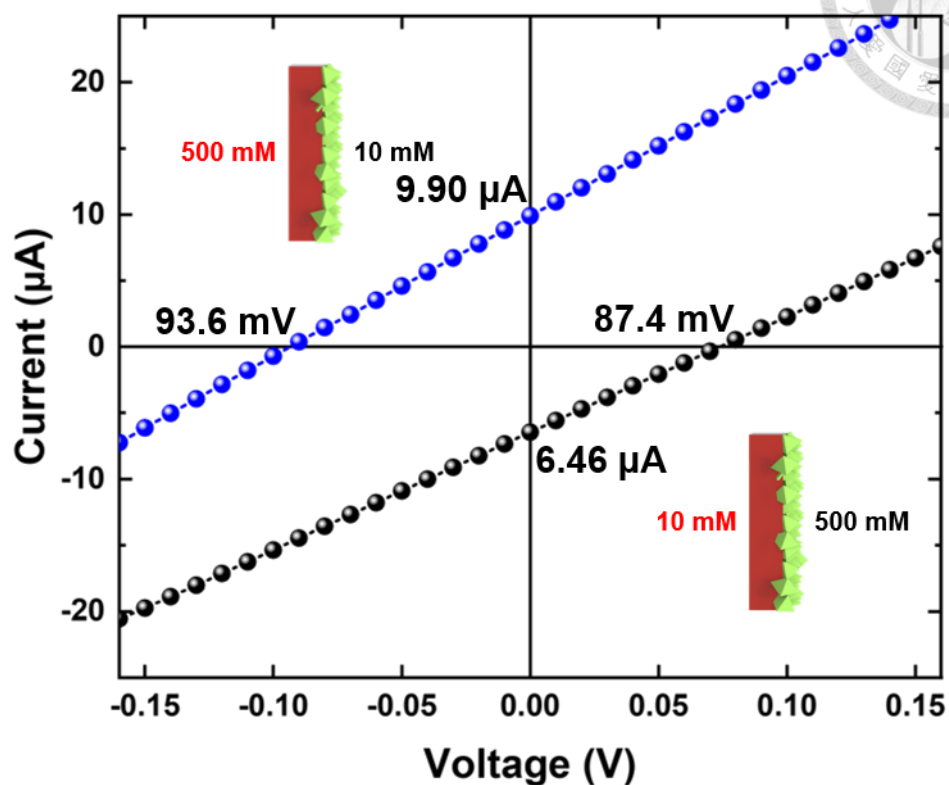


Figure 41 I–V curves of the MOF-on-COF membrane recorded under two opposite configurations of the 50-fold KCl concentration gradient.

5.3.1. High-performance blue energy harvesting of MOF-on-COF membrane

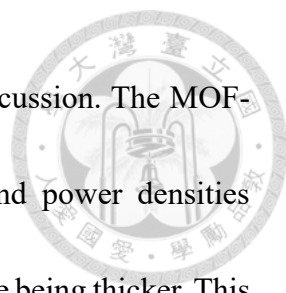
To evaluate the blue energy performance of the MOF-on-COF membrane and compare it with that of the COF membrane, we test the power generation performance under a 100-fold salinity gradient. The osmotic current densities decrease as the external load increases, as shown in **Figure 42** (a) and (c). Taking KCl as a solute, when the

external resistance is negligible, the osmotic current densities of the MOF-on-COF membrane reach 776 A/m², this value is 83.9% higher than the value of the COF membrane at 422 A/m² (**Figure 42 (a)**). The energy harvesting ability is measured through an external load circuit that includes a series of resistances (R_e). By using the electric power formula (Equation. 1) [117], the current density was directly converted to the power density, which evaluates the osmotic power generation performance of the membrane.

$$P_e = IV = I^2 R_e = \frac{V^2 R_e}{(R_m + R_e)^2} = \frac{V^2 R_e}{(R_m - R_e)^2 + 4R_m R_e}$$

where P_e: output power (W); I: current (A); V: voltage (V); R_e: external resistance (Ω); R_m: internal resistance of membrane (Ω). Based on the information derived from Equation 3-1, it can be observed that the P_e reaches its maximum value when R_m is equal to R_e. The power generation capability of the MOF-on-COF membrane peaks at 18.93 W/m², while the COF membrane reaches its maximum value at 9.23 W/m² (**Figure 42 (b)**).

Using NaCl as the solute shows a similar trend to the KCl case. The osmotic current densities of the MOF-on-COF membrane reach 588 A/m², which is 82.6% higher than the COF membrane's value of 322 A/m² (**Figure 42 (c)**). The power generation capability of the MOF-on-COF membrane peaks at 11.42 W/m², while the COF membrane reaches its maximum value at 6.82 W/m². (**Figure 42 (d)**)



Here, we can find an interesting phenomenon that deserves discussion. The MOF-on-COF membrane consistently shows higher current densities and power densities compared to the COF membrane, despite the MOF-on-COF membrane being thicker. This phenomenon seems contrary to the general belief that thinner films achieve higher current densities and power densities due to their lower internal resistance. However, in our study, we observed that the internal resistance of the MOF-on-COF membrane is lower than that of the COF membrane in both KCl and NaCl solutes. Specifically, the resistance decreases from 7800 Ω to 5000 Ω in KCl solute and from 9000 Ω to 4500 Ω in NaCl solute. This can be attributed to the

To summarize this section, the heterogeneous MOF-on-COF structure exhibits higher power generation performance compared to the COF film. This improvement is attributed to the combination of two geometrical and surface charge asymmetric sub-2 nm ion transportation channels.

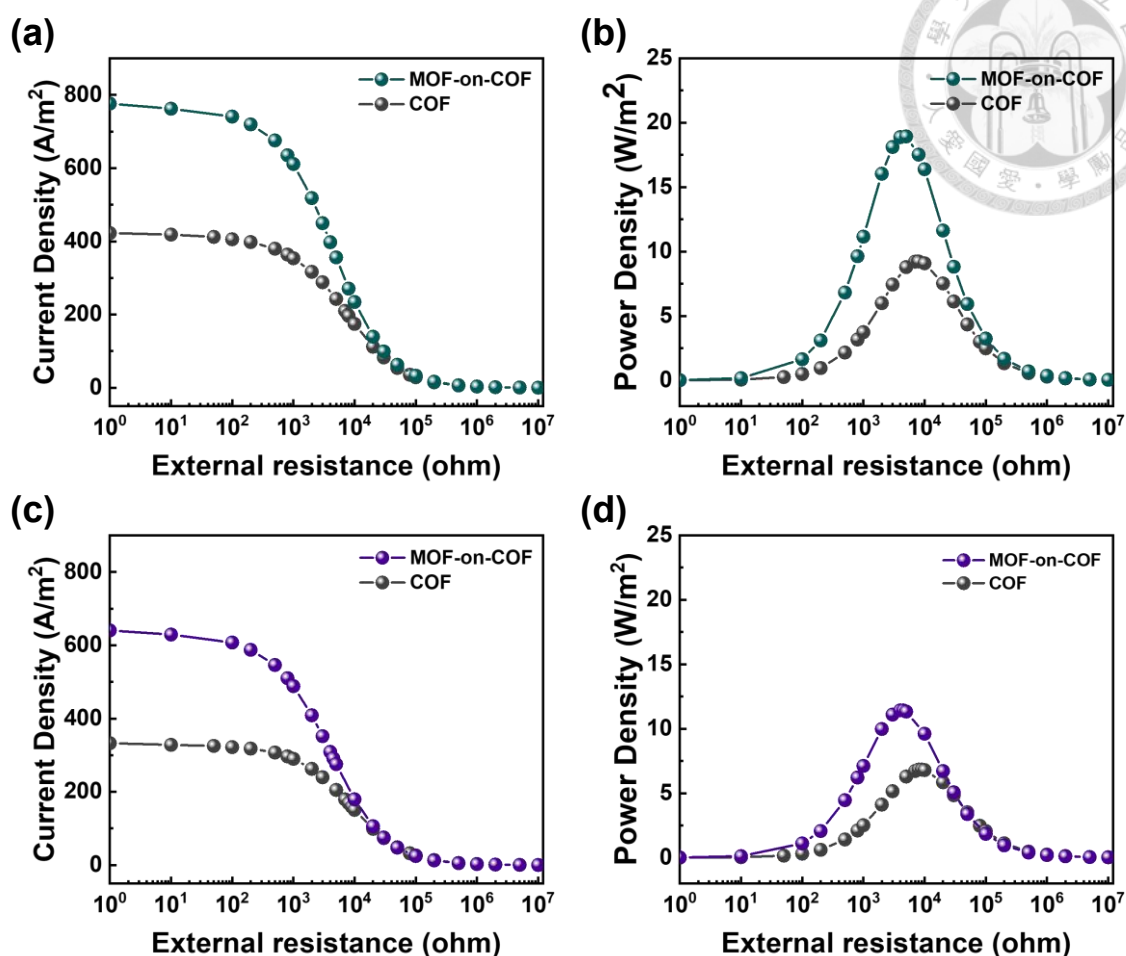
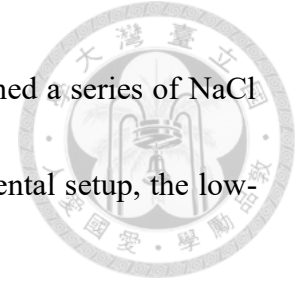


Figure 42 Comparison of ionic-gradient power generation performance between the MOF-on-COF membrane and the pristine COF membrane. (a,b) Current density and power density obtained under a 100-fold KCl salinity gradient for the MOF-on-COF membrane (green) and COF membrane (gray). (c,d) Corresponding current density and power density measured under a 100-fold NaCl salinity gradient.

In real environments, the salinity gradients at the interfaces between river water and seawater vary significantly depending on the location. To investigate the relationship

between salinity gradients and osmotic power generation, we designed a series of NaCl salinity gradients ranging from 10-fold to 500-fold. In this experimental setup, the low-concentration side was consistently maintained at 10 mM NaCl.



In **Figure 43** (a), the results demonstrate that the area enclosed by the open-circuit voltage (V_{OC}) on the x-axis, and the short-circuit current (I_{SC}) on the y-axis increases progressively with the increasing salinity gradient. This observation indicates that larger salinity gradients are associated with enhanced power generation capabilities. In **Figure 43** (b), we can find that current densities decrease with increasing external load, reaching their highest values when the external load is negligible. Furthermore, higher salinity gradients result in higher peak current densities, which are 163 A/m², 412 A/m², 641 A/m², and 1672 A/m², respectively. In **Figure 43** (c), we observe that the power density increases with the salinity gradient, reaching peak values at 1.85 W/m², 7.23 W/m², 11.42 W/m², and 45.28 W/m², respectively. The power generation ability peaks when the internal resistance equals the external resistance. Additionally, the figure illustrates a trend where the internal resistance, at the peak power generation value, gradually decreases as the salinity gradient increases.

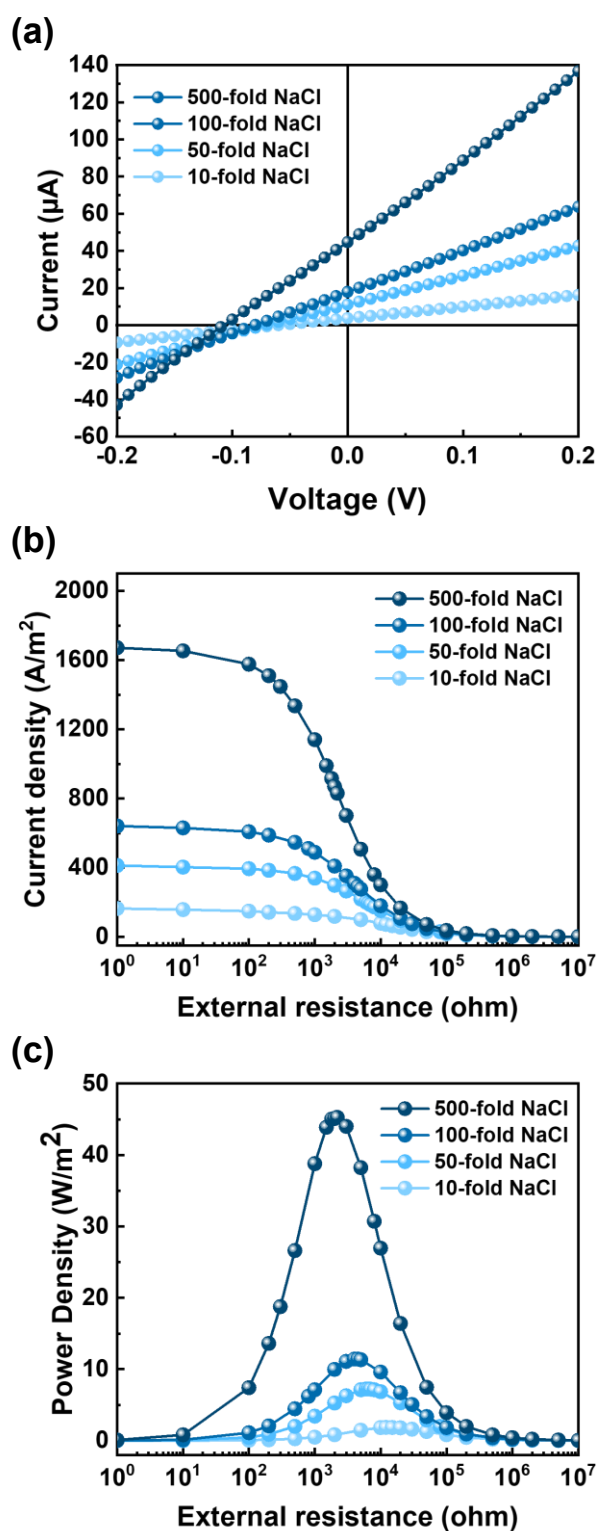


Figure 43 (a) I-V curve, (b) current density, and (c) power density of MOF-on-COF

membrane in different NaCl salinity gradients.

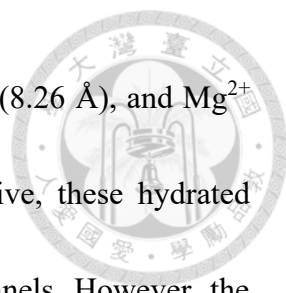
5.3.2. Effect of Ion Types on Blue Energy Harvesting Performance of the MOF-on-COF Membrane



In practical applications, natural river water and seawater contain a diverse array of cations and anions. Understanding the transport behavior of these ions is essential for evaluating the feasibility of osmotic power generation. To systematically investigate the impact of cation species on performance, we conducted a series of experiments using five different chloride salts (KCl, NaCl, LiCl, MgCl₂, and CaCl₂) under a 50-fold salinity gradient (500 mM vs. 10 mM).

As shown in **Figure 44a**, the peak current densities obtained from the five salt systems with different cation species, namely KCl, NaCl, LiCl, MgCl₂, and CaCl₂, are 776, 641, 370, 173, and 166 A m⁻², respectively. The corresponding maximum power densities are 18.93, 11.42, 7.51, 1.71, and 1.40 W m⁻², respectively (**Figure 44b**). This clear performance sequence indicates that the cation species plays a significant role in determining the ion-transport efficiency and osmotic energy conversion behavior of the heterogeneous MOF-on-COF membrane.

Because Tp-PaSO₃H COF possesses negatively charged sulfonic acid groups, the COF layer preferentially promotes cation transport. The nominal pore diameter of Tp-PaSO₃H COF is approximately 1.4 nm, which is larger than the hydrated diameters of the



investigated cations: K^+ (6.62 Å), Na^+ (7.16 Å), Li^+ (7.64 Å), Ca^{2+} (8.26 Å), and Mg^{2+} (8.56 Å) [118]. Therefore, from a simple size-exclusion perspective, these hydrated cations should be able to enter and migrate through the COF channels. However, the overall ion transport across the bilayered membrane is not governed solely by the COF layer, but is also strongly affected by the smaller window aperture of UiO-66-NH₂, which is approximately 6–7 Å.

For monovalent cations, the observed trend of $K^+ > Na^+ > Li^+$ can be reasonably attributed to their hydrated size and ion mobility. K^+ has the smallest hydrated diameter and a relatively weak hydration shell, allowing it to migrate more efficiently through the confined framework channels. In contrast, Li^+ possesses a larger and more strongly bound hydration shell, resulting in slower transport and lower power output. For divalent cations such as Ca^{2+} and Mg^{2+} , the transport resistance becomes much more pronounced. Their larger hydrated diameters are comparable to or even larger than the UiO-66-NH₂ window size, making their passage through the MOF layer highly restricted. In addition, their stronger hydration shells and possible stronger electrostatic interactions with the negatively charged COF channels may further hinder their migration. These combined effects likely account for the substantially lower current densities and power densities observed in the $MgCl_2$ and $CaCl_2$ systems compared with the monovalent salt systems.

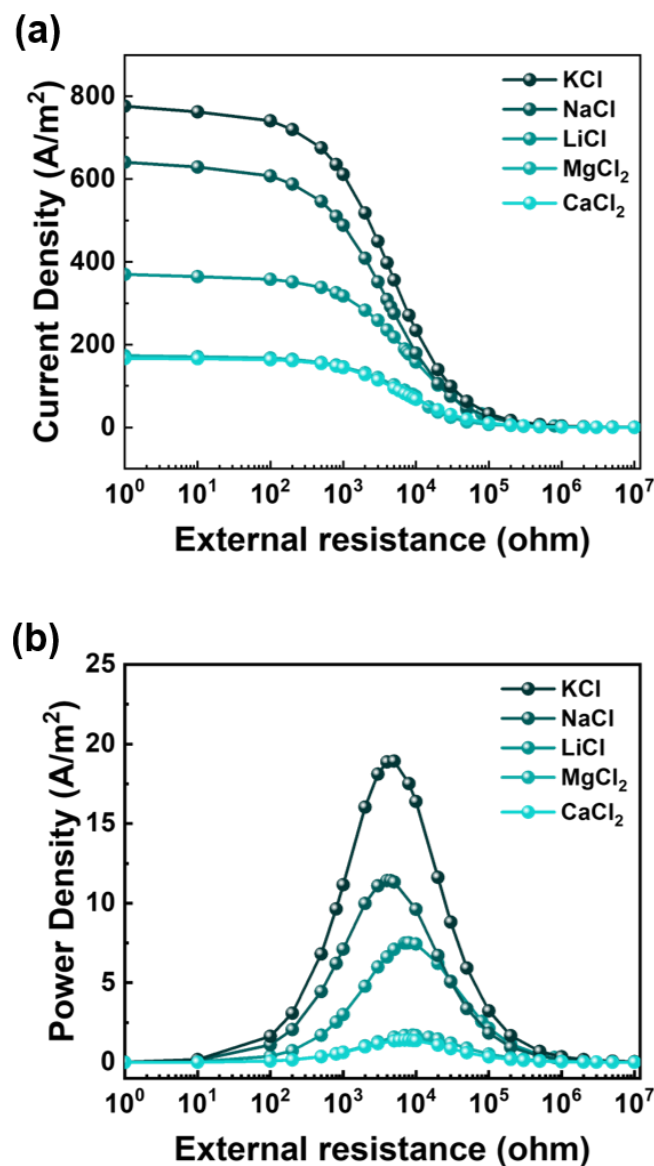


Figure 44 The effect of different cation types on the (a) current density, and (b) power density of MOF-on-COF membrane in the 50-fold salinity gradient.

In the second part of this study, the influence of anion species on osmotic power generation was investigated by fixing the cation as K^+ while varying the anions, including Br^- , Cl^- , SO_4^{2-} , CO_3^{2-} , and NO_3^- . For all measurements, a 50-fold salinity gradient was

applied, with the high-concentration side maintained at 500 mM and the low-concentration side at 10 mM. As shown in **Figure 45**, the anion type has a pronounced effect on the ion-transport behavior of the heterogeneous MOF-on-COF membrane.

When Br^- and Cl^- were used as the anions, relatively high current densities were obtained, whereas the current densities became significantly lower for SO_4^{2-} , CO_3^{2-} , and NO_3^- containing electrolytes.

This difference becomes even more evident in the power density analysis. The maximum power densities obtained with Br^- and Cl^- are 36.64 and 10.23 W m^{-2} , respectively. In contrast, the power densities for SO_4^{2-} , CO_3^{2-} , and NO_3^- are much lower, reaching only 1.58, 1.16, and 0.015 W m^{-2} , respectively. These results indicate that although the cation is fixed as K^+ , the counter anion still plays a critical role in determining the overall ion migration behavior and energy conversion efficiency. This phenomenon can be attributed to the combined influence of hydrated ion size, ion mobility, valence state, and ion–framework interactions within the charged sub-nanometer channels of the MOF-on-COF membrane.

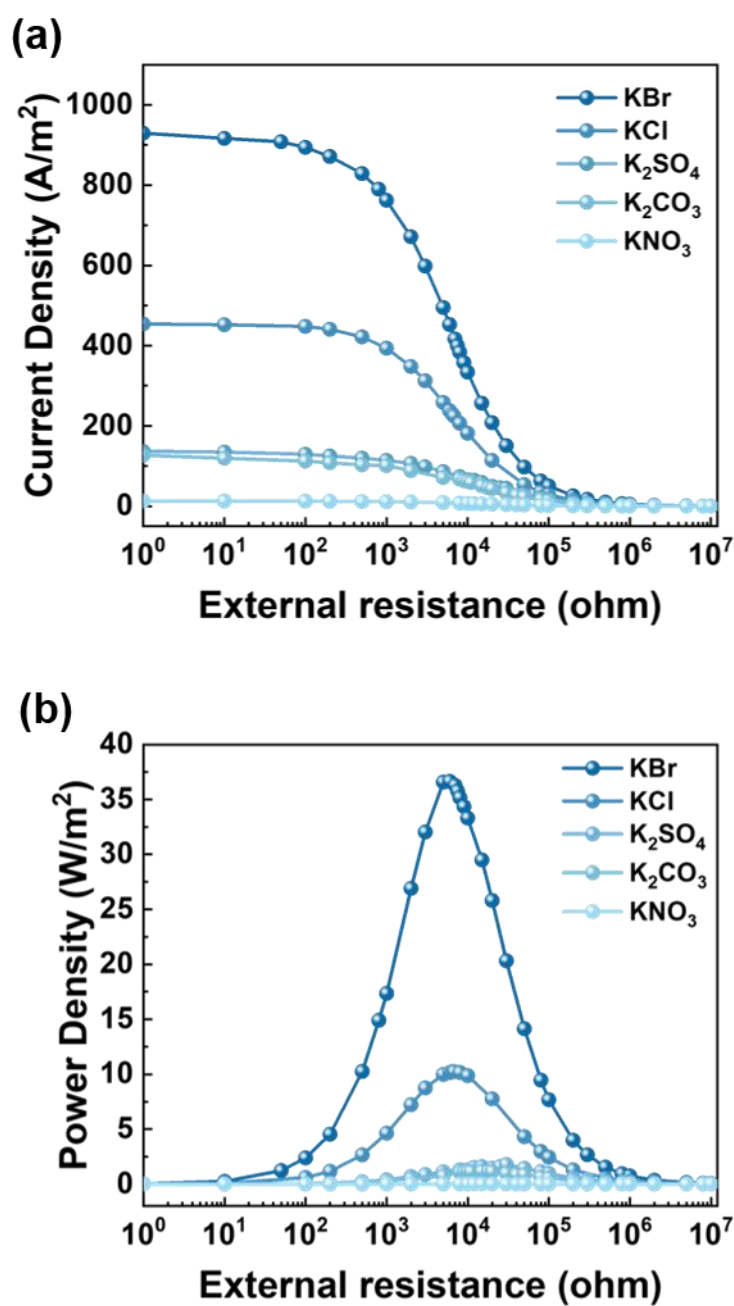
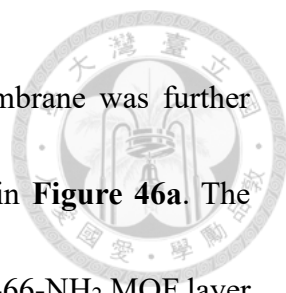


Figure 45 The effect of different anion types on the (a) current density, and (b) power density of MOF-on-COF membrane in the 50-fold salinity gradient.



The power generation performance of the MOF-on-COF membrane was further compared with that of the single-layer COF membrane, as shown in **Figure 46a**. The results clearly demonstrate that the heterogeneous growth of the UiO-66-NH₂ MOF layer on the COF membrane improves the osmotic power output. Specifically, when Br⁻ is used as the anion, the MOF-on-COF membrane shows a 34.8% enhancement in power generation compared with the COF membrane alone. When Cl⁻ is used, the enhancement becomes even more pronounced, reaching 78.2%. These improvements suggest that the MOF layer does not simply increase the membrane thickness or transport resistance. Instead, the MOF-on-COF heterostructure provides an additional charge-asymmetric and size-confined transport environment, which can regulate ion migration and improve osmotic energy conversion.

Among the five tested anions, NO₃⁻ exhibits the lowest current density and power density. This poor performance is likely related to the restricted transport of NO₃⁻ through the UiO-66-NH₂ layer. The hydrated diameter of NO₃⁻ is approximately 6.70 Å, which is very close to the window size of UiO-66-NH₂, approximately 6–7 Å. Therefore, NO₃⁻ migration through the MOF layer may be strongly hindered by the narrow framework aperture. In addition, the transport behavior may also be affected by the specific hydration structure, ion mobility, and possible interactions between NO₃⁻ and the positively charged

UiO-66-NH₂ channels. These combined factors likely contribute to the much lower power output observed in the KNO₃ system.



Because NO₃⁻ gives the lowest power generation performance among the investigated anions, it was used as the reference to estimate the selectivity ratios (calculated by output power) of the MOF-on-COF membrane (**Figure 46b**). Remarkably, the Br⁻/NO₃⁻ and Cl⁻/NO₃⁻ selectivity ratios reach 2442 and 682, respectively. The SO₄²⁻/NO₃⁻ and CO₃²⁻/NO₃⁻ selectivity ratios are also calculated to be 118 and 85, respectively. It is worth noting that the selectivity ratios of the MOF-on-COF membrane are higher than those of the single-layer COF membrane in all cases. This comparison further highlights the unique advantage of integrating MOF and COF layers into a heterogeneous membrane architecture. The combination of the negatively charged COF layer and the positively charged, size-restrictive MOF layer provides a more selective and asymmetric ion-transport pathway, thereby enhancing ion discrimination and improving blue-energy harvesting performance.

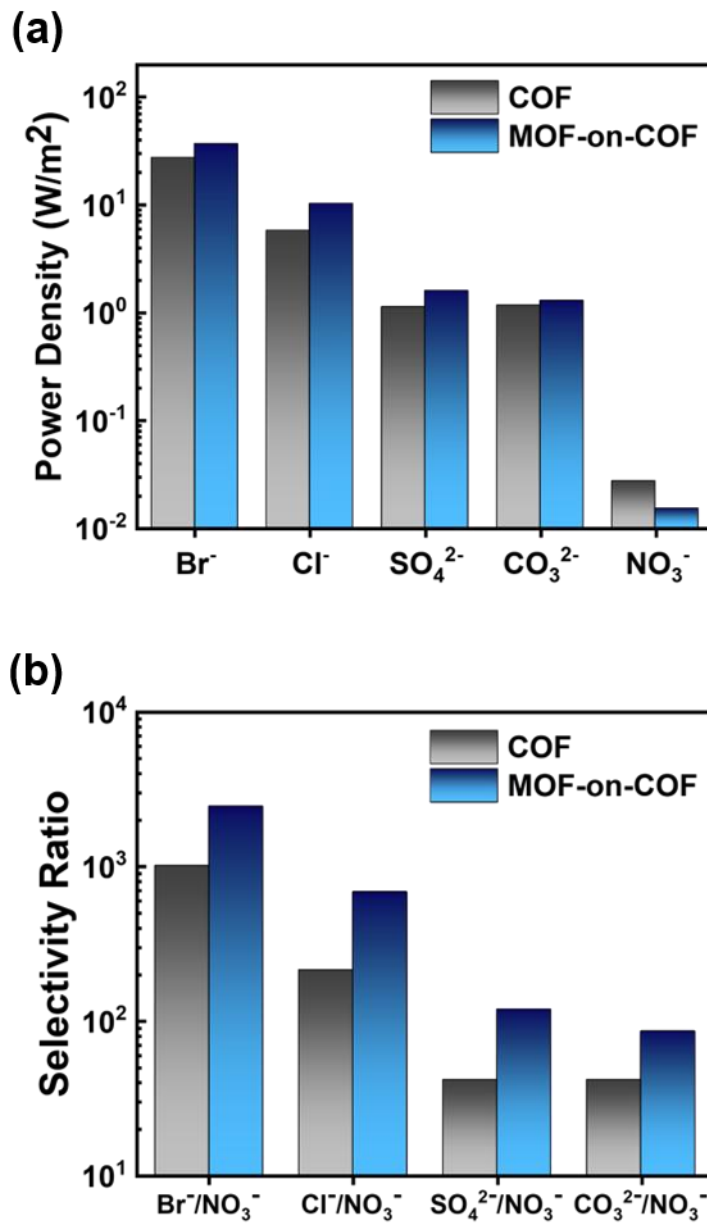


Figure 46 (a) Comparison of the power generation ability between COF membrane and MOF-on-COF membrane in different anion types in the 50-fold salinity gradient. (b) The selectivity ratio between the COF membrane and the MOF-on-COF membrane. The selectivity ratio between the COF membrane and the MOF-on-COF membrane is calculated through the ratio of peak power generation ability.

5.4. Summary



In this chapter, a heterogeneous MOF-on-COF membrane was developed as a crystalline bilayered framework platform for ion transport and osmotic energy harvesting. A free-standing COF membrane was first prepared through interfacial condensation synthesis and then used as a continuous porous substrate for the confined growth of UiO-66-NH₂. By selectively exposing only one side of the COF membrane to the MOF precursor, a bilayered MOF-on-COF heterostructure was successfully obtained. SEM, WAXS, and chemical characterization confirmed the successful integration of the crystalline MOF and COF layers.

The structural advantage of this membrane arises from the combination of two framework layers with different pore sizes and opposite surface charges. The positively charged UiO-66-NH₂ layer provides sub-nanometer windows for ion sieving, while the negatively charged COF layer offers continuous sub-2 nm transport channels. This pore size and charge asymmetry create a framework-based ionic diode membrane, enabling directional ion transport and enhanced ion selectivity.

The osmotic power generation tests showed that the MOF-on-COF membrane exhibits improved performance compared with the single-layer COF membrane. Ion-type-dependent measurements further revealed that both cation and anion species strongly

affect the power generation behavior. The results indicate that the MOF-on-COF heterostructure regulates ion transport through the combined effects of hydrated ion size, charge interaction, pore confinement, and interfacial asymmetry.

Overall, this chapter demonstrates that crystalline hetero-interface engineering is an effective structural design strategy for constructing ion-selective porous framework membranes. However, the presence of crystalline domains and interfacial boundaries also suggests that a continuous porous framework film without obvious grain boundaries could be an important next target. This consideration leads to the next part of this dissertation, where mesoporous amorphous MOF thin films are developed through solvent evaporation-induced assembly.

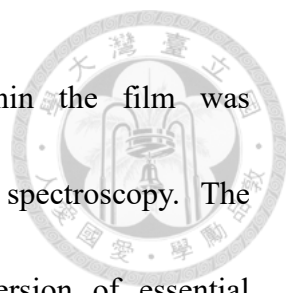
6. Solvent-Evaporation-Driven Formation of Mesoporous Amorphous MOF Thin Films



6.1. Characterization of Mesoporous Amorphous Films

6.1.1. Formation of Continuous Mesoporous *a*MOF Thin Films through Spin Coating

The surface morphology of the prepared film, as observed through scanning electron microscopy (SEM) (**Figure 47**), exhibits a highly distinct mesoporous network. This structural architecture is characterized by relatively uniform pore dimensions predominantly ranging from 20 to 30 nm, indicating a well-controlled structural evolution during the film formation process. To further investigate the internal structural features, cross-sectional analysis was conducted via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). As demonstrated in **Figure 48** and **Figure 49**, the cross-sectional micrographs reveal that this homogeneous mesoporosity is not merely a surface phenomenon but spans continuously throughout the entire bulk of the film, extending from the underlying FTO substrate interface directly to the upper boundary. Additionally, these images indicate an overall film thickness of approximately 100 nm. Notably, the *a*ZIF-90 layer forms a conformal coating over the rough, pyramidal features of the FTO substrate (visible in the Sn map), maintaining its structural integrity without obvious interfacial gaps or macroscopic defects.



The spatial distribution of the constituent elements within the film was systematically evaluated using energy-dispersive X-ray (EDX) spectroscopy. The resulting elemental mapping confirms the highly uniform dispersion of essential framework elements, namely zinc (Zn), carbon (C), and nitrogen (N), throughout the entire *a*ZIF-90 layer. This homogeneous distribution effectively eliminates the occurrence of localized phase separation or elemental agglomeration. Moreover, the intrinsic mesoporous framework remains clearly distinguishable within the Zn elemental map, further corroborating the morphological observations from SEM and STEM.

Furthermore, a specific region of elevated intensity is observed at the top edge of the C elemental map. It should be noted that this localized carbon concentration does not originate from the intrinsic MOF structure; rather, it corresponds to the protective carbon coating that was intentionally deposited to preserve the film surface during the focused ion beam (FIB) milling process for cross-sectional sample fabrication.

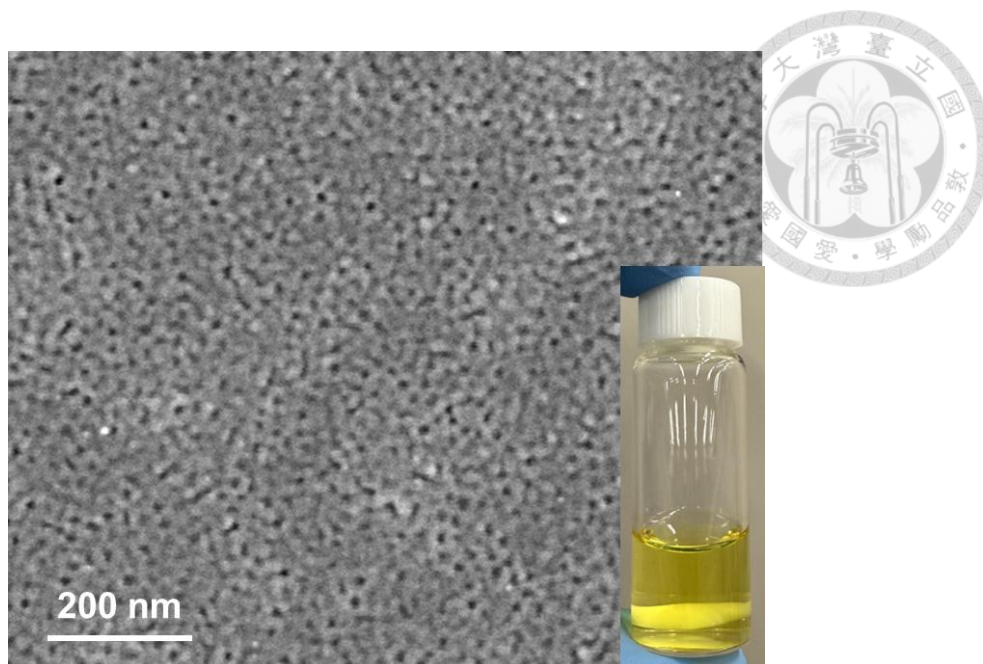


Figure 47 Surface morphology of the *a*ZIF-90 thin film observed by SEM; inset: photograph of the *a*ZIF-90 precursor solution. Reproduced with permission [107].

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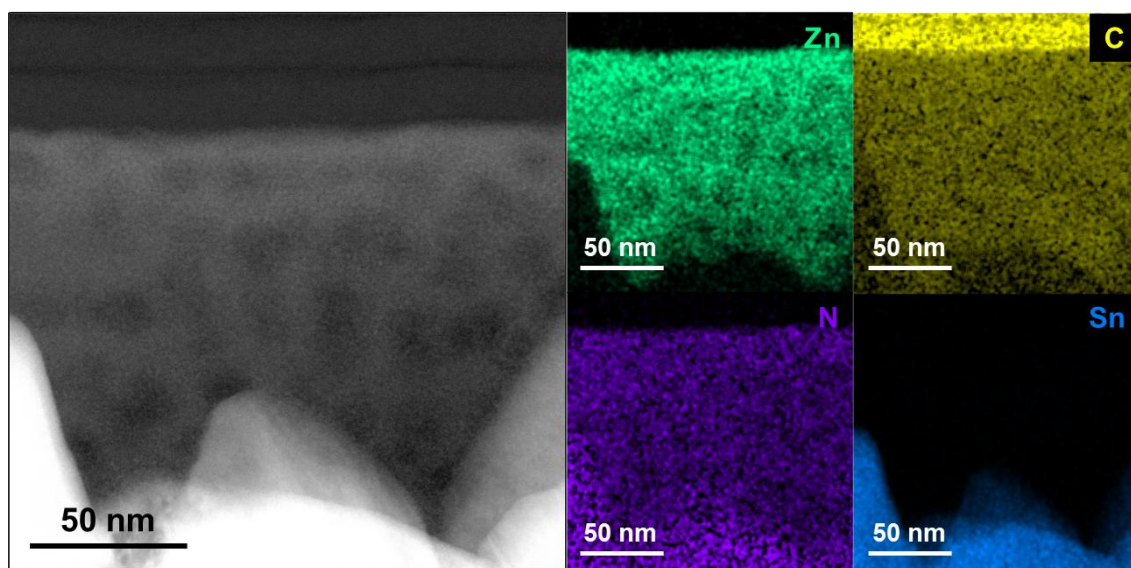


Figure 48 Cross-sectional HAADF-STEM characterization of the *a*ZIF-90 thin film: left, HAADF-STEM image; right, corresponding EDX elemental mapping. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

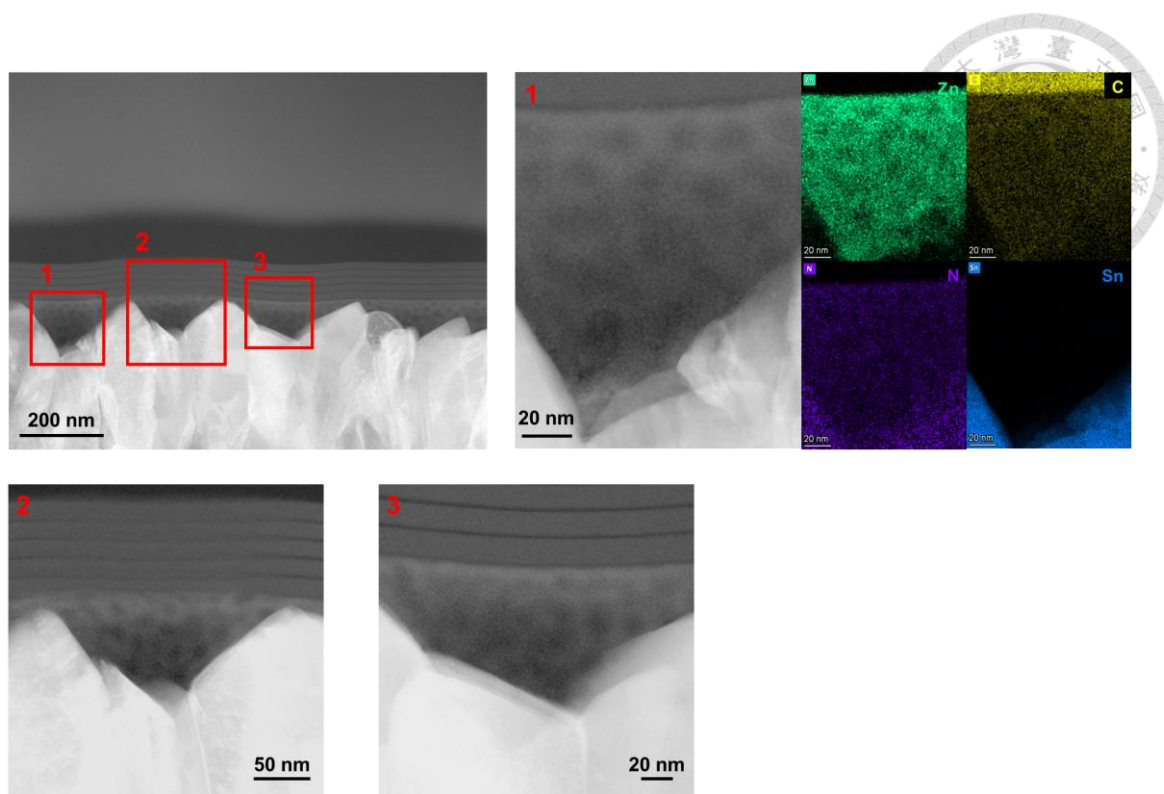


Figure 49 Cross-sectional HAADF-STEM images of the *a*ZIF-90 thin film with magnified views at selected regions labeled 1, 2, and 3, together with EDX elemental mapping of region 1. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

To meet the requirements for various bulk characterizations (including nitrogen adsorption-desorption, FTIR, XPS, NMR, and XAS), we synthesized powder forms of both amorphous and crystalline ZIF-90 (designated as *a*ZIF-90 and *c*ZIF-90 powder, respectively). Detailed synthetic protocols are provided in Chapter 4.3. SEM imaging indicates that the *a*ZIF-90 powder possesses a distinct, uniformly distributed mesoporous structure, which remains consistent regardless of whether drop-casting or spin-coating

was employed (**Figure 50**). In contrast, the *c*ZIF-90 powder exhibits a conventional rhombic dodecahedral morphology (**Figure 51**) [119].

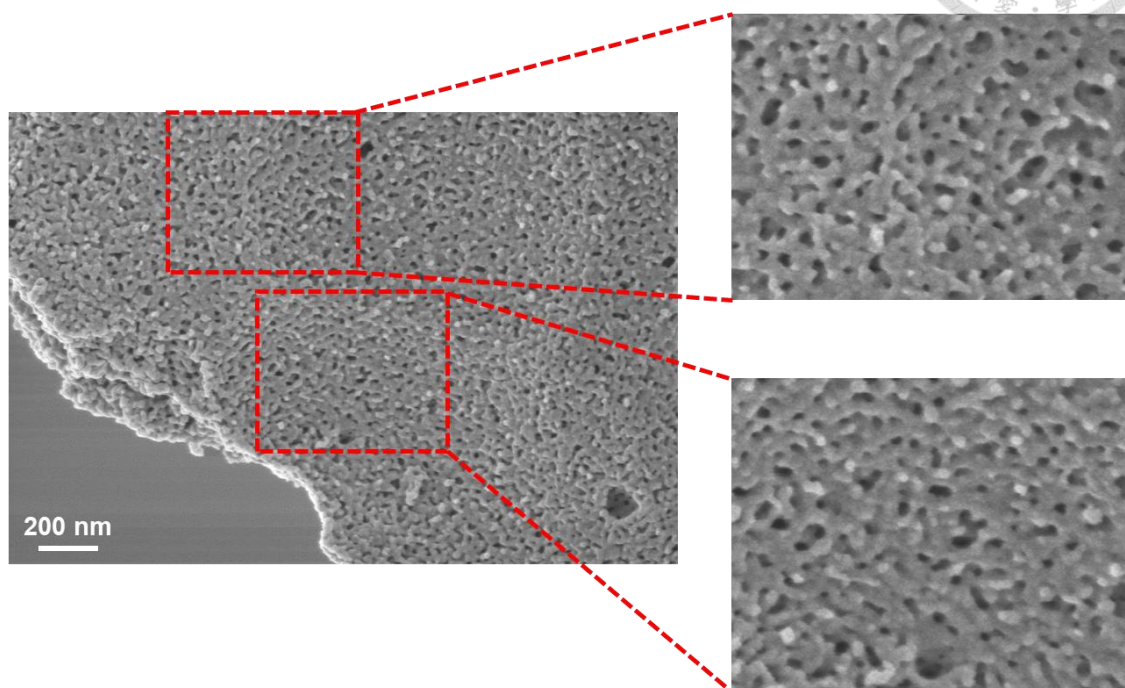


Figure 50 SEM morphologies of mesoporous ZIF-90 prepared by the drop-casting method. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

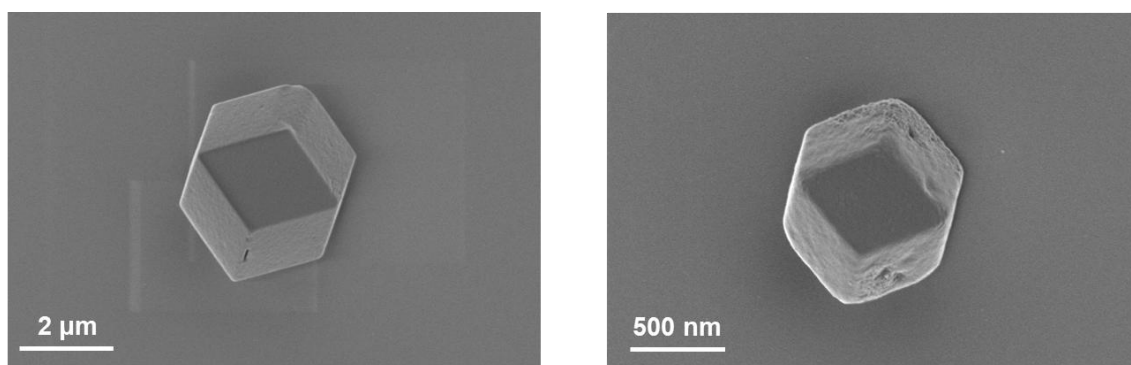
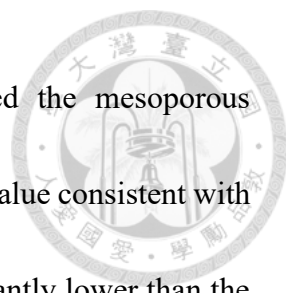


Figure 51 SEM morphologies of crystallized ZIF-90 prepared by the solvothermal synthesis method. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



Nitrogen adsorption-desorption measurements further verified the mesoporous nature of *a*ZIF-90, revealing a specific surface area of $170 \text{ m}^2 \cdot \text{g}^{-1}$, a value consistent with prior amorphous MOF literature (**Figure 52a**) [120]. This is significantly lower than the $1122 \text{ m}^2 \cdot \text{g}^{-1}$ observed for the crystalline counterpart (**Figure 53a**), a common phenomenon for amorphous MOFs due to the absence of a highly ordered microporous framework. To distinguish the hierarchical pore structure more rigorously, both BJH and NLDFT pore-size distribution analyses were performed, since the two models are applicable to different pore regimes. BJH analysis, derived from the Kelvin equation, is suitable mainly for mesopore evaluation but is not reliable for micropores because capillary condensation concepts are no longer valid at such small length scales [121]. By contrast, NLDFT is better suited for adsorption in confined nanopores and is therefore more appropriate for resolving microporous features [122]. Additionally, BJH analysis shows a mesopore distribution centered around 13 nm (**Figure 52b**, inset), corroborating our SEM and TEM findings. Meanwhile, NLDFT analysis confirms the presence of micropores ranging from 0.98 to 1.12 nm, closely matching the inherent 1.12 nm pore size of *c*ZIF-90 (**Figure 52b**, **Figure 53b**).

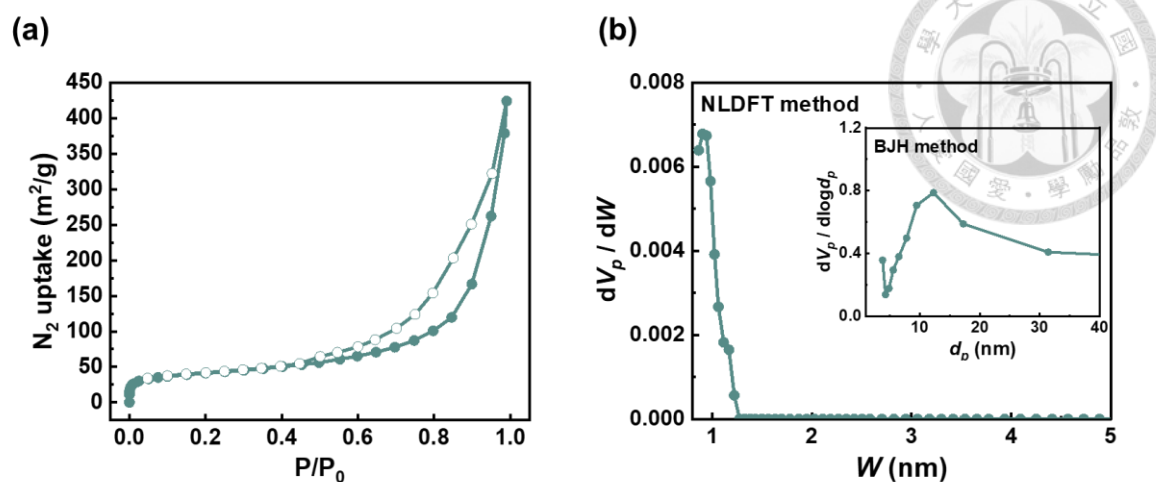


Figure 52 Porosity analysis of powdered *a*ZIF-90. (a) N₂ adsorption-desorption isotherm. (b) NLDFT-derived pore-size distribution, with the inset showing the corresponding BJH analysis. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

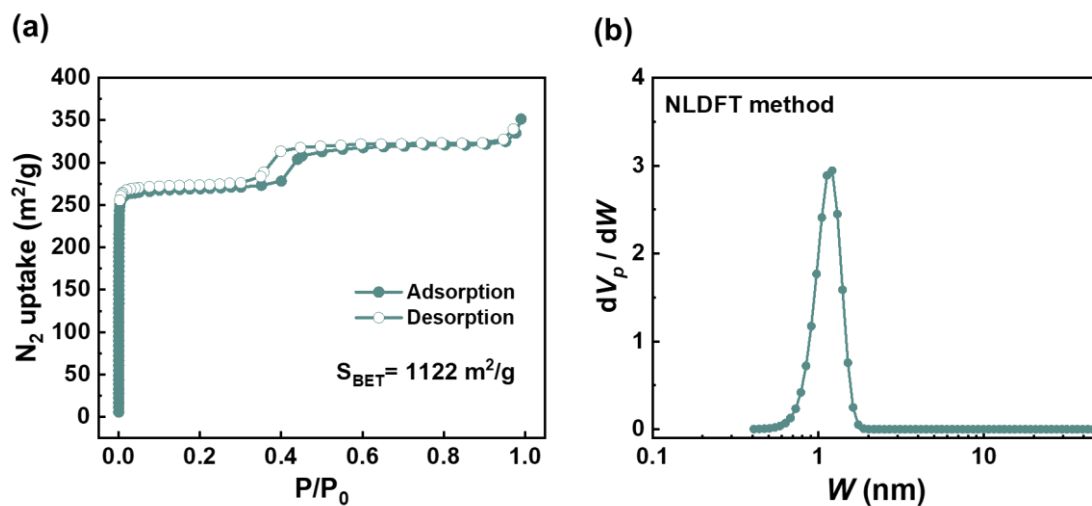


Figure 53 Porosity analysis of powdered *c*ZIF-90. (a) N₂ adsorption-desorption isotherm. (b) NLDFT-derived pore-size distribution, with the inset showing the corresponding BJH analysis. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



The reduced crystallinity of the *a*ZIF-90 powder was initially verified by wide-angle X-ray diffraction (XRD), which exhibited a noticeably broader diffraction peak compared to the sharp profile of the *c*ZIF-90 reference (**Figure 54**) [123]. Fourier-transform infrared (FTIR) spectroscopy was then used to confirm the structural integrity of the functional groups (**Figure 55**). The acquired spectra displayed characteristic absorption bands at 2800–2860 cm⁻¹ (aldehyde C—H stretching), 1676 cm⁻¹ (aldehyde C=O stretching), 956 and 789 cm⁻¹ (imidazole ring bending), as well as 533 cm⁻¹ (Zn—N oscillations between the metal node and organic linker). All these features align perfectly with standard *c*ZIF-90 signatures [124,125]. Importantly, FTIR also confirmed the complete removal of the PEO-*b*-PMMA soft template following the THF and MeOH washing steps, as evidenced by the disappearance of the PMMA ester C=O stretching band at 1725 cm⁻¹ (**Figure 56**).

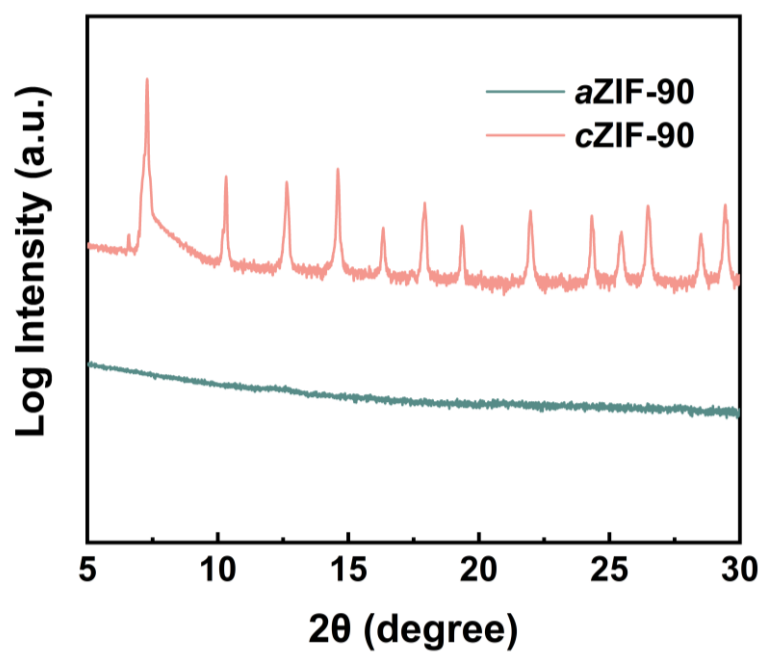


Figure 54 XRD pattern of *a*ZIF-90 and *c*ZIF-90. Reproduced with permission [107].

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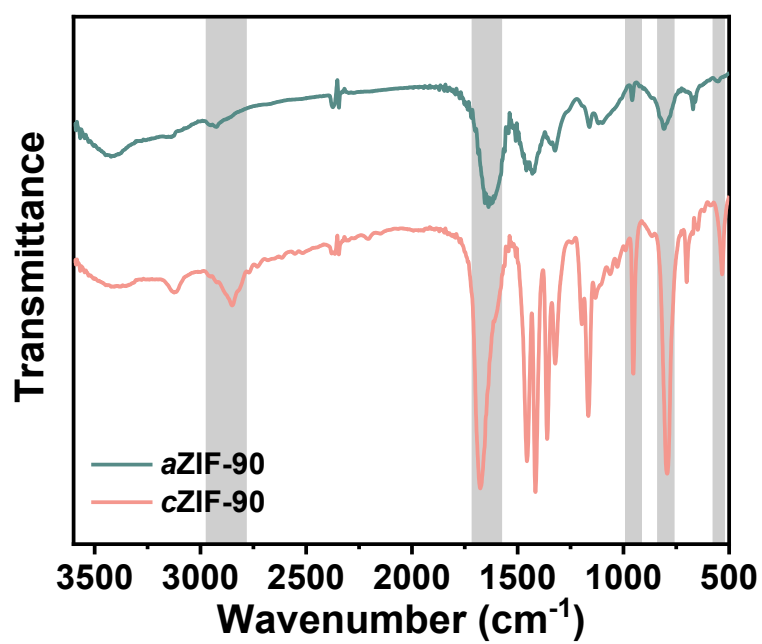


Figure 55 FTIR characterization of amorphous *a*ZIF-90 and crystalline *c*ZIF-90.

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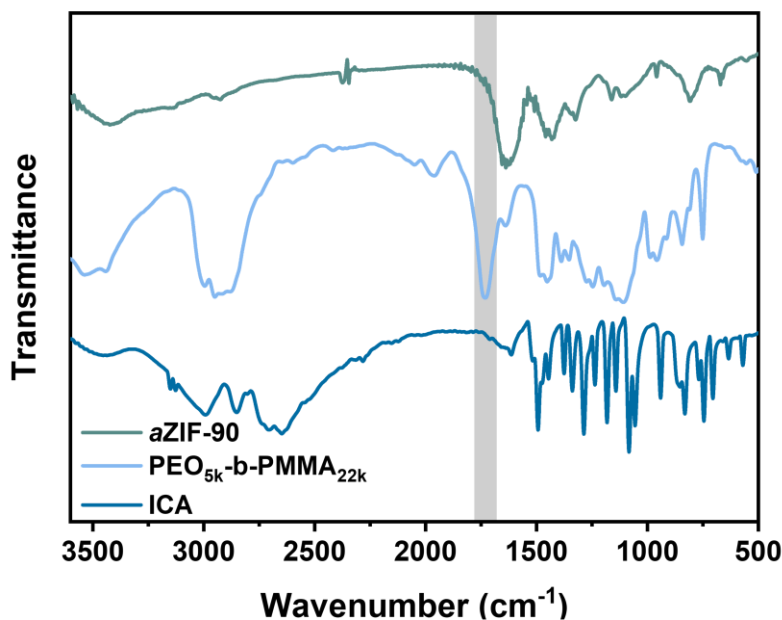
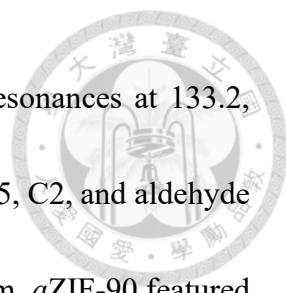


Figure 56 FTIR spectra of *a*ZIF-90, PEO-b-PMMA, and ICA. Reproduced with

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To elucidate the elemental bonding states, XPS measurements were performed and calibrated against the C—C/C=C peak at 284.6 eV, revealing distinct signals for Zn, C, N, and O (**Figure 57**). The high-resolution XPS data yielded binding energies for Zn 2p (1044.7 and 1021.6 eV), C 1s (284.6, 285.51, 286.5, and 288.16 eV), and N 1s (398.8 and 399.74 eV) (**Figure 57b-d**). These values exhibit strong agreement with those of crystalline ZIF-90 (**Figure 58**). Finally, local atomic structures were probed via ^{13}C solid-



state NMR (**Figure 59**). Both samples showed identical primary resonances at 133.2, 150.2, and 180.0 ppm, assigned respectively to the imidazolate C4/C5, C2, and aldehyde carbons [123]. While *c*ZIF-90 retained a trace THF signal at 70.0 ppm, *a*ZIF-90 featured a unique carbamate peak at 167.6 ppm. This specific signal likely stems from atmospheric CO₂ reacting with structural defect sites, which are inherently more abundant in amorphous architectures [126]. Ultimately, these characterizations demonstrate that *a*ZIF-90 and *c*ZIF-90 share a highly consistent chemical makeup, differing fundamentally only in their crystalline order and enhanced mesoporosity.

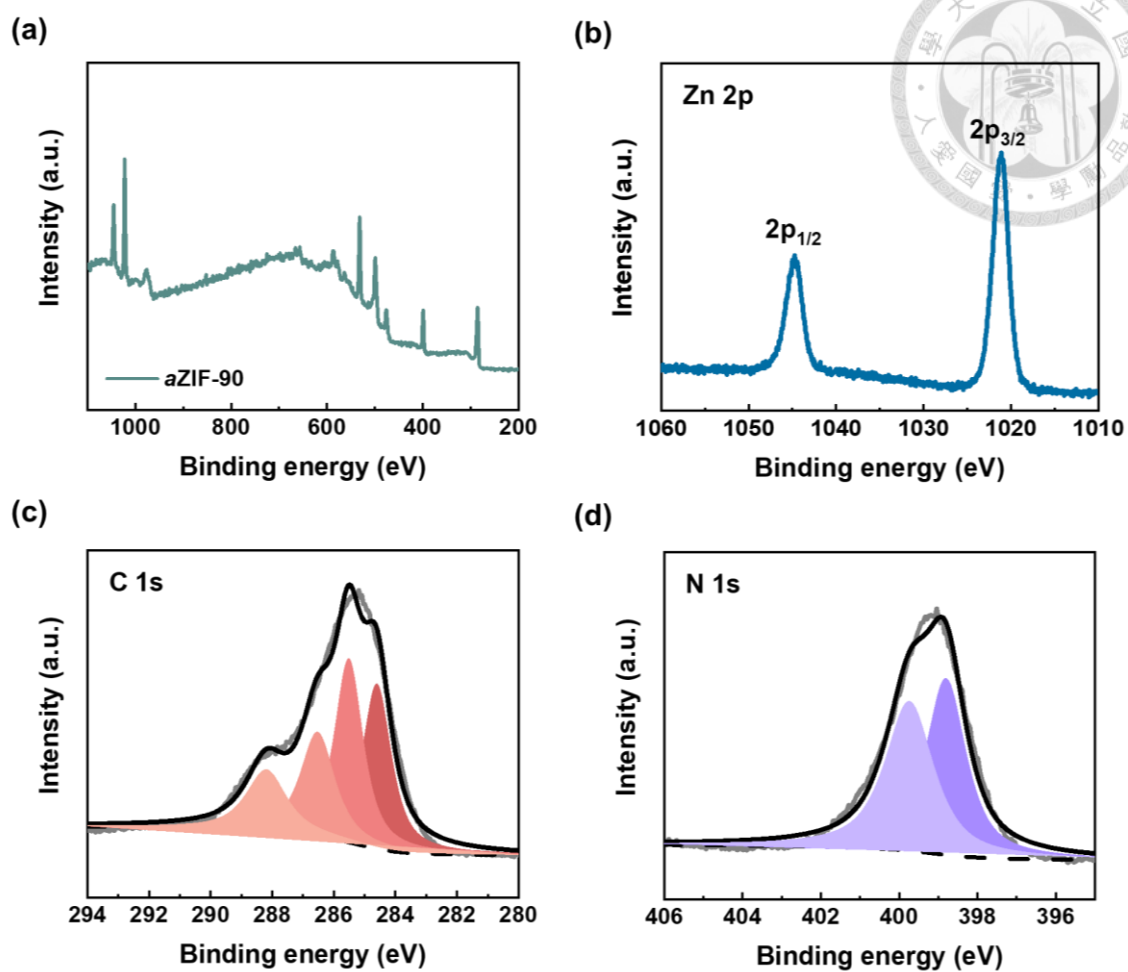


Figure 57 XPS analysis of *a*ZIF-90. (a) *a*ZIF-90 full XPS profile, (b) Zn 2p, (c) C 1s, and (d) N 1s profiles of *a*ZIF-90. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

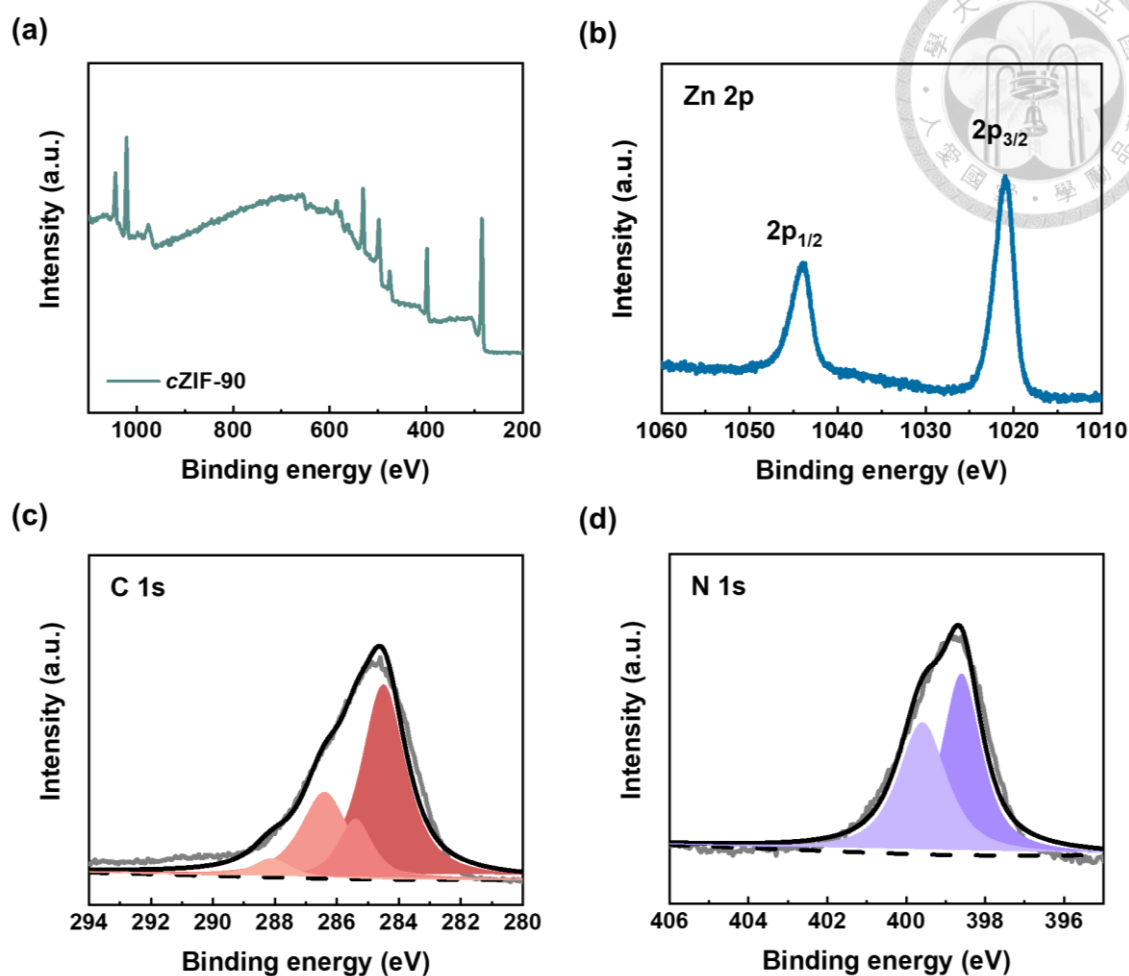


Figure 58 XPS analysis of *c*ZIF-90. (a) *c*ZIF-90 full XPS profile, (b) Zn 2p, (c) C 1s, and (d) N 1s profiles of *c*ZIF-90. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

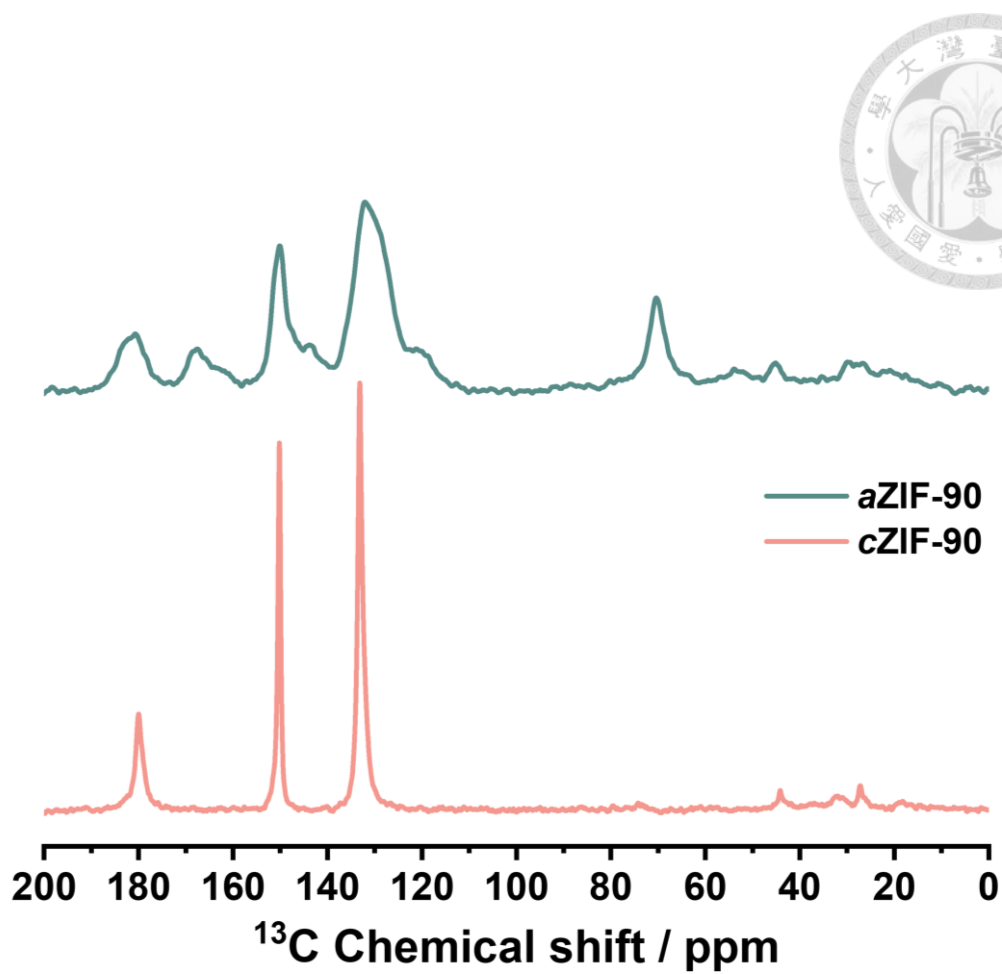


Figure 59 ^{13}C solid-state NMR spectra collected from *a*ZIF-90 and *c*ZIF-90 powder samples. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



The uniform and flat nature of the spin-coated *a*ZIF-90 film was highlighted by its surface average roughness (Ra) of only 0.522 nm within a 1 μm^2 scan window, as measured by AFM (**Figure 60a-c**). These AFM observations, along with depth profile analysis, clearly revealed an ordered mesoporous topography with pore sizes between 15 and 25 nm, corroborating the TEM, SEM, and BET findings. To gain deeper insights into the internal pore arrangement and sizing of the thin film, grazing-incidence small-angle X-ray scattering (GISAXS) was applied. The presence of spherical mesopores was deduced from the rounded diffraction features observed in the 2D GISAXS pattern (Figure 3a). Meanwhile, the domain spacing of this mesoporous framework was evidenced by a broad peak in the 1D in-plane line cut (Figure 3b). A Guinier analysis of the data provided a radius of gyration (Rg) of 18.35 nm for the pore domains (Figure 3c,d), a measurement that is in excellent agreement with the dimensions obtained from our other characterization techniques.

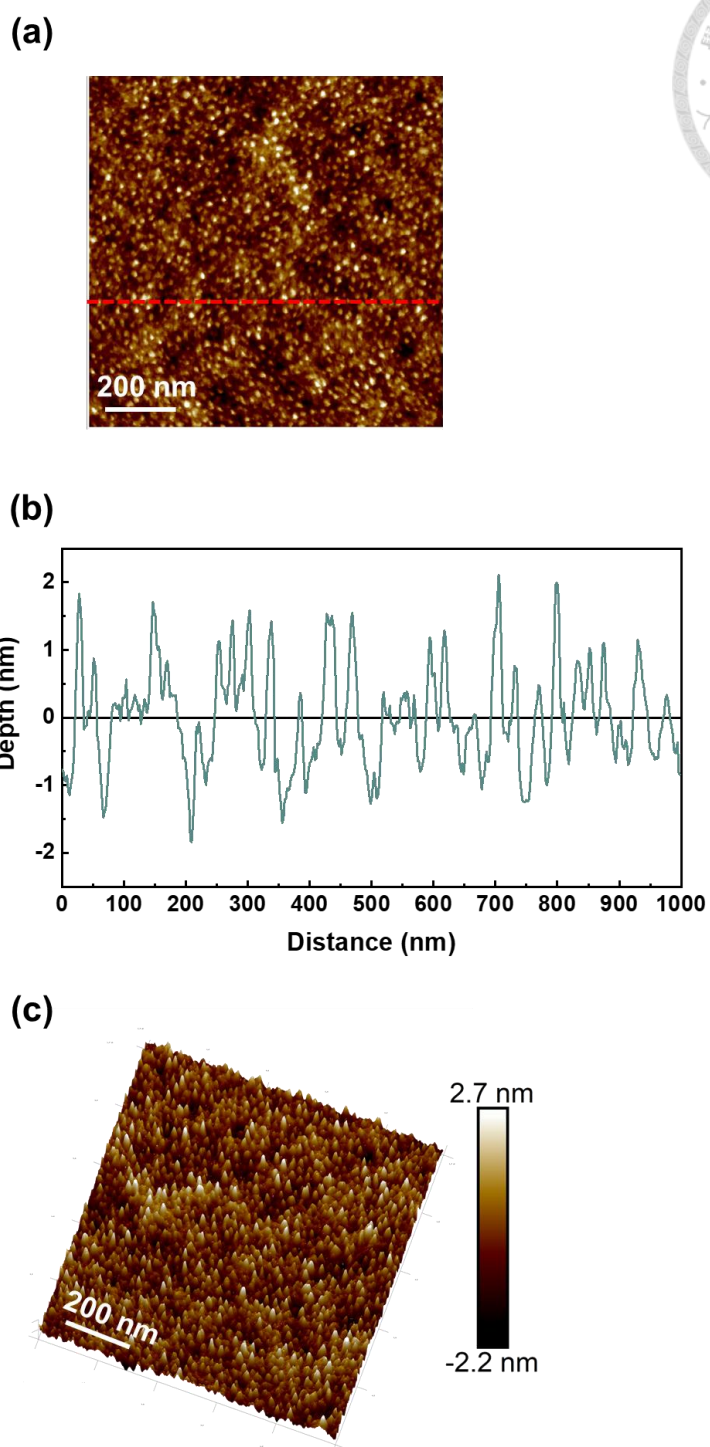


Figure 60 Topographical characterization of the *a*ZIF-90 thin film, showing (a) the 2D surface image, (b) the line-profile analysis along the red dashed cross-section, and (c) the reconstructed 3D surface morphology. Reproduced with permission [107]. Copyright

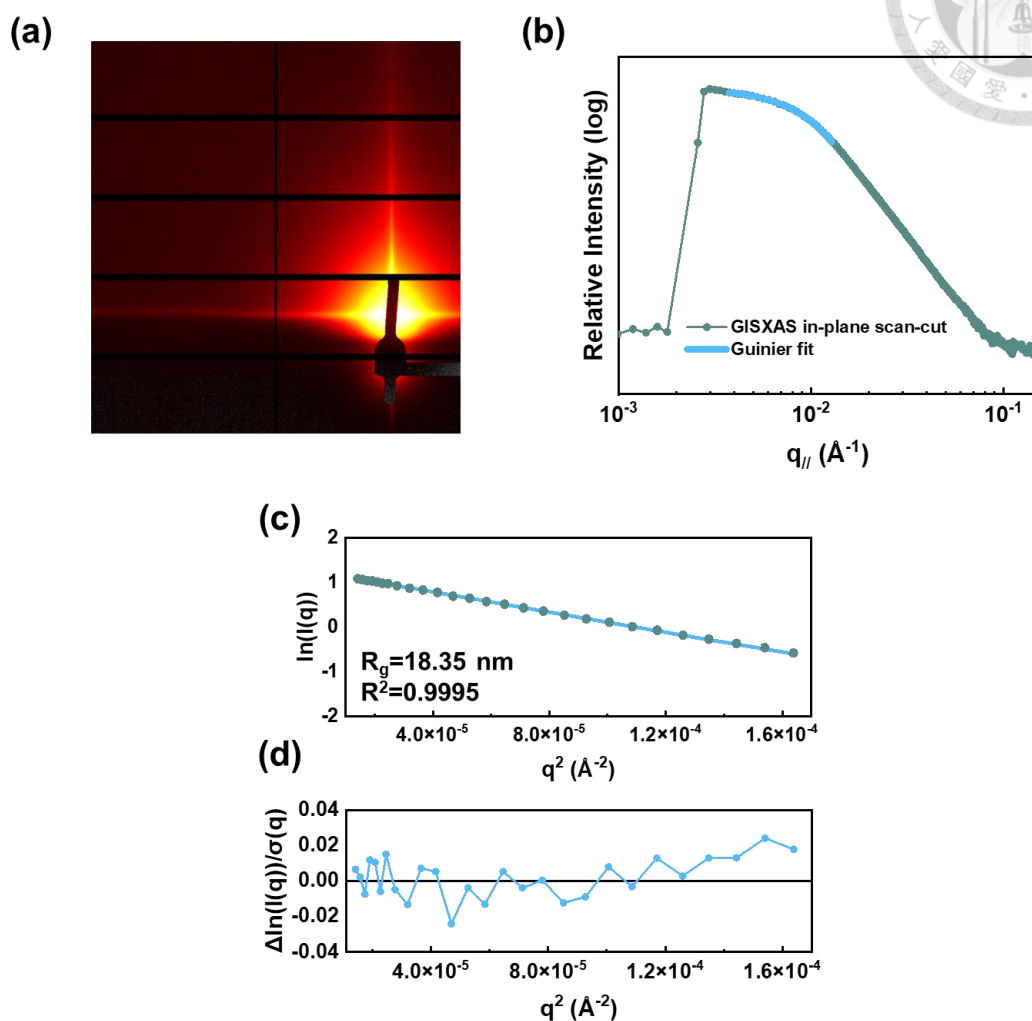


Figure 61 GISAXS measurements of *a*ZIF-90. (a) GISAXS 2D pattern of *a*ZIF-90 film, (b) 1D in-plane scan-cut of *a*ZIF-90 film following the Yoneda line. (blue) Guinier fit fitting line, (c) linear regression, and (d) Normalized residual of Guinier fit and 1D in-plane scan-cut of *a*ZIF-90 film. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



To gain deeper insights into the short-range atomic arrangements within amorphous MOFs, X-ray absorption spectroscopy (XAS) was utilized to systematically investigate their local coordination environments [127,128]. The comparative XAS profiles of the mesoporous *a*MOF (*a*ZIF-90 powder), its crystalline counterpart (*c*ZIF-90 powder), and a metallic zinc reference (Zn foil) are illustrated in **Figure 62a**. As depicted in the inset of **Figure 62a**, the X-ray absorption near-edge structure (XANES) region reveals that both the amorphous and crystalline ZIF-90 samples exhibit an absorption edge positioned at 9663 eV. In contrast, the reference Zn foil displays its absorption edge at a lower energy of approximately 9659 eV. This positive energy shift observed in the ZIF materials is a direct consequence of their differing electronic states and coordination bonding natures; specifically, the zinc atoms in the ZIF frameworks exist within coordination complexes, which feature a distinct electronic environment compared to the zero-valent state of metallic zinc.

Further structural details were extracted from the extended X-ray absorption fine structure (EXAFS) analysis. The Fourier-transformed EXAFS spectra, shown in **Figure 62b**, demonstrate that both the *a*ZIF-90 and *c*ZIF-90 powders share an identical primary peak located at a radial distance of 1.54 Å. This signal represents the first coordination



shell and corresponds to an actual Zn—N bond length of 1.94 Å. Conversely, the Zn foil spectrum features its main peak at 2.28 Å, which is indicative of the metallic Zn—Zn bond with a true length of 2.6 Å. It is important to note that the radial distances observed in these Fourier-transformed spectra consistently appear roughly 0.3 to 0.4 Å shorter than the crystallographically determined actual bond lengths. This discrepancy is a well-documented phenomenon arising from photoelectron phase shifts that occur during the mathematical Fourier transform process [129,130].

In addition, the k-space oscillations and wavelet transform profiles (**Figure 62c–f**) align well with these structural findings. The data show that the *a*ZIF-90 powder closely matches the *c*ZIF-90 powder, clearly differing from the Zn foil. From these spectroscopic results, it is evident that while the *a*ZIF-90 powder does not possess long-range crystalline periodicity, its local atomic coordination remains highly preserved, closely mirroring the structure of the crystalline *c*ZIF-90 [127].

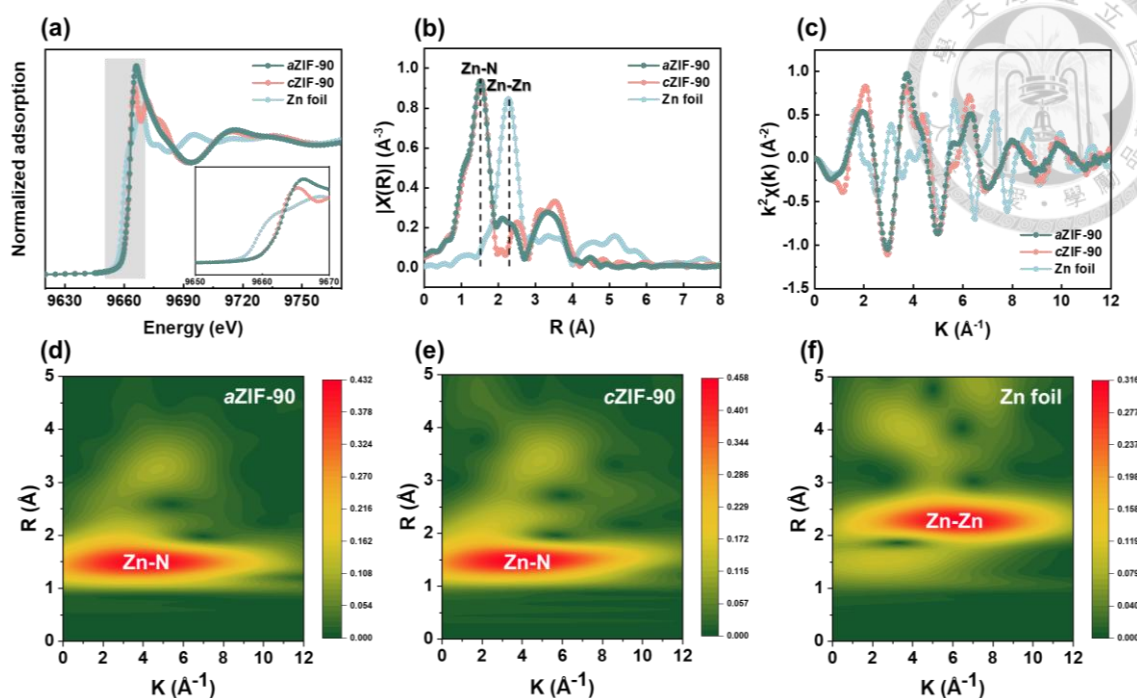


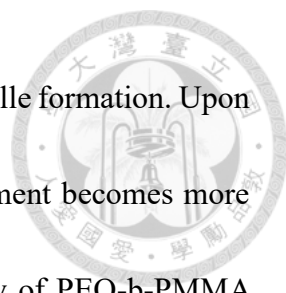
Figure 62 Zn K-edge X-ray absorption spectroscopic analysis of amorphous *a*ZIF-90 powder, crystalline *c*ZIF-90 powder, and Zn foil as the metallic reference. (a) Normalized XAS spectra, with the inset highlighting the X-ray absorption near-edge structure (XANES) region. (b) Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) spectra. (c) k^2 -weighted EXAFS oscillation curves in k -space. (d–f) Wavelet transform (WT) contour plots for (d) *a*ZIF-90 powder, (e) *c*ZIF-90 powder, and (f) Zn foil. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

6.1.2. Formation Mechanism of Continuous Mesoporous *a*MOF Films via Spin-Coating

The successful synthesis of mesoporous amorphous ZIF-90 relies on carefully balancing micellization, nucleation, and crystallization under appropriate synthetic conditions. In this section, we discuss how these competing processes were regulated to achieve a continuous mesoporous film while maintaining the amorphous state. From the perspectives of both kinetics and thermodynamics, this systematic analysis provides deeper insight into the formation mechanism of the mesoporous film and may offer useful guidance for extending this strategy to other types of metal–organic frameworks in future studies.

a. The selection of solvent types in the co-solvent system

In the initial stage of the soft-templating strategy for mesoporous MOF synthesis, the block copolymer must first be dissolved and then induced to self-assemble into micelles in solution. Because MeOH, water, and DMSO are selective solvents for PEO-*b*-PMMA but cannot fully dissolve the block copolymer on their own, THF was first used as the primary solvent to molecularly dissolve PEO-*b*-PMMA. These selective solvents were then individually introduced into the THF solution to create co-solvent environments that promote micellization. Although THF effectively dissolves PEO-*b*-



PMMA, it is a non-selective solvent and therefore does not favor micelle formation. Upon addition of MeOH, water, or DMSO into THF, the solvent environment becomes more selective toward the PEO block, thereby inducing the self-assembly of PEO-b-PMMA into micelles. Under these conditions, the solvophilic PEO chains preferentially extend into the surrounding medium to form the micellar shell, whereas the less-solvated PMMA segments aggregate inward to form the micellar core.

In the THF/MeOH co-solvent system (**Figure 63**), continuous mesoporous films were formed over a broad methanol composition range, specifically from 20 to 80 vol% MeOH. In contrast, when pure THF was used, the surface morphology became poorly defined, and no well-developed continuous mesoporous network could be identified. Notably, among all the compositions examined, the sample prepared with 20 vol% MeOH displayed the highest degree of pore ordering (**Figure 63b**). This result suggests that the incorporation of an appropriate amount of methanol is essential for establishing a solvent environment favorable for block-copolymer self-assembly. The absence of a continuous mesoporous architecture in pure THF, despite the addition of the block copolymer, indicates that simple polymer dissolution is not sufficient; rather, micelle formation is a prerequisite for directing the development of an ordered and continuous mesoporous framework.

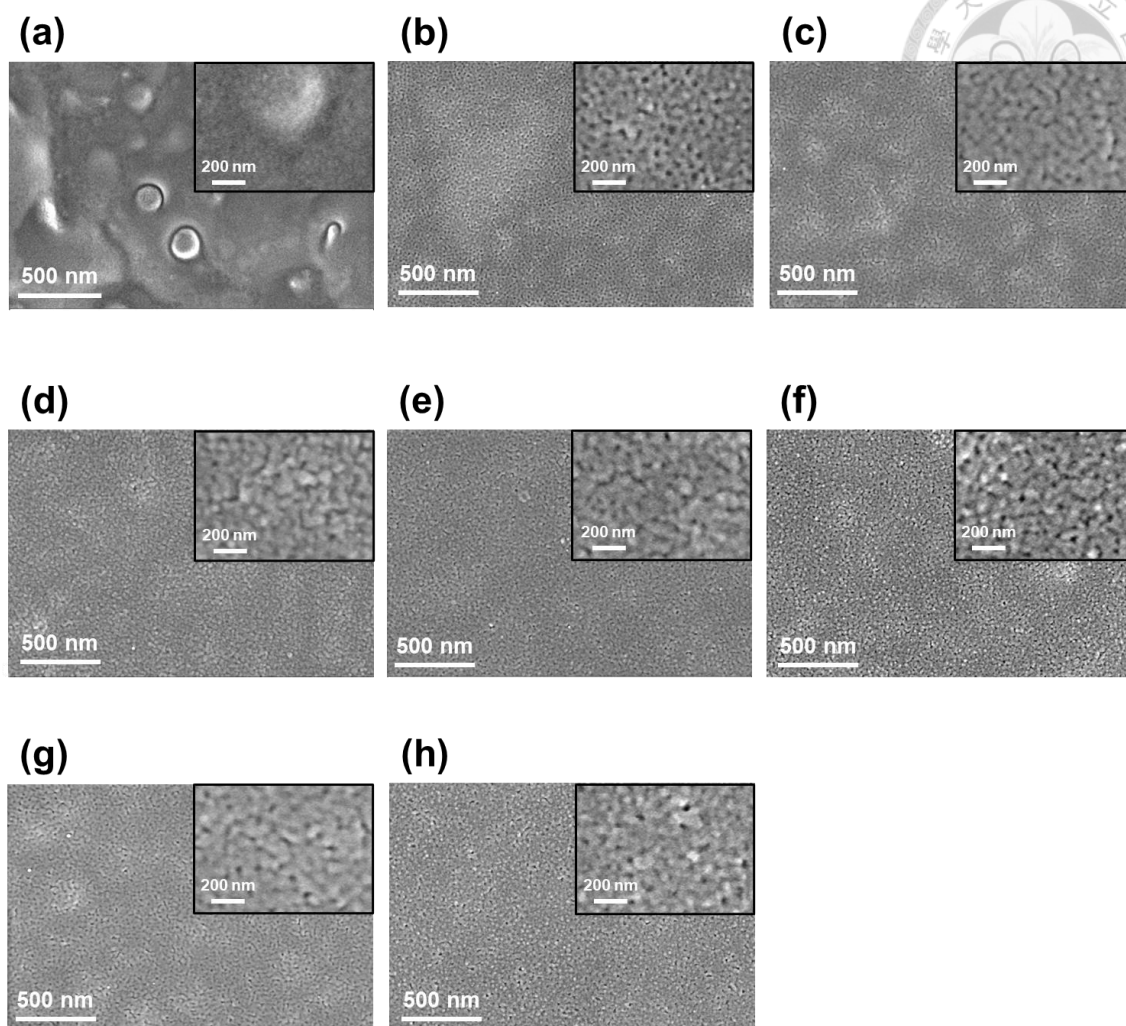
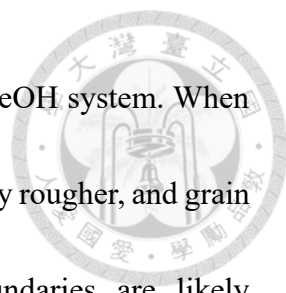


Figure 63 SEM morphologies of mesoporous *a*ZIF-90 film prepared with different amounts of methanol (MeOH) in THF/MeOH co-solvent systems. (a) 0, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, and (h) 80 vol% of methanol. Reproduced with permission [107].

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In the THF/water co-solvent system (**Figure 64**), continuous mesoporous structures were obtained only at relatively low water contents, namely 20 and 30 vol%, and their



spatial ordering was clearly poorer than that observed in the THF/MeOH system. When the water content exceeded 40 vol%, the film surface became markedly rougher, and grain boundaries appeared randomly across the substrate. These boundaries are likely associated with the underlying FTO surface, suggesting that the deposited layer became too thin and discontinuous to fully cover the substrate at higher water fractions. This poorer film quality is largely due to the fact that water-rich solvent systems are less suitable for spin-coating. Because water has a relatively high boiling point and evaporates more slowly than typical organic solvents, residual solvent can remain in the wet film for longer, which may hinder rapid solidification and promote morphological instability or roughening during spinning [131]. In addition, the relatively poor wettability of water on oxide substrates may further limit uniform spreading of the precursor solution during spin-coating, thereby contributing to film discontinuity and increased surface roughness [132]. Therefore, although water is effective in inducing micellization, water-rich conditions are not ideal for obtaining smooth and continuous mesoporous films by spin-coating.

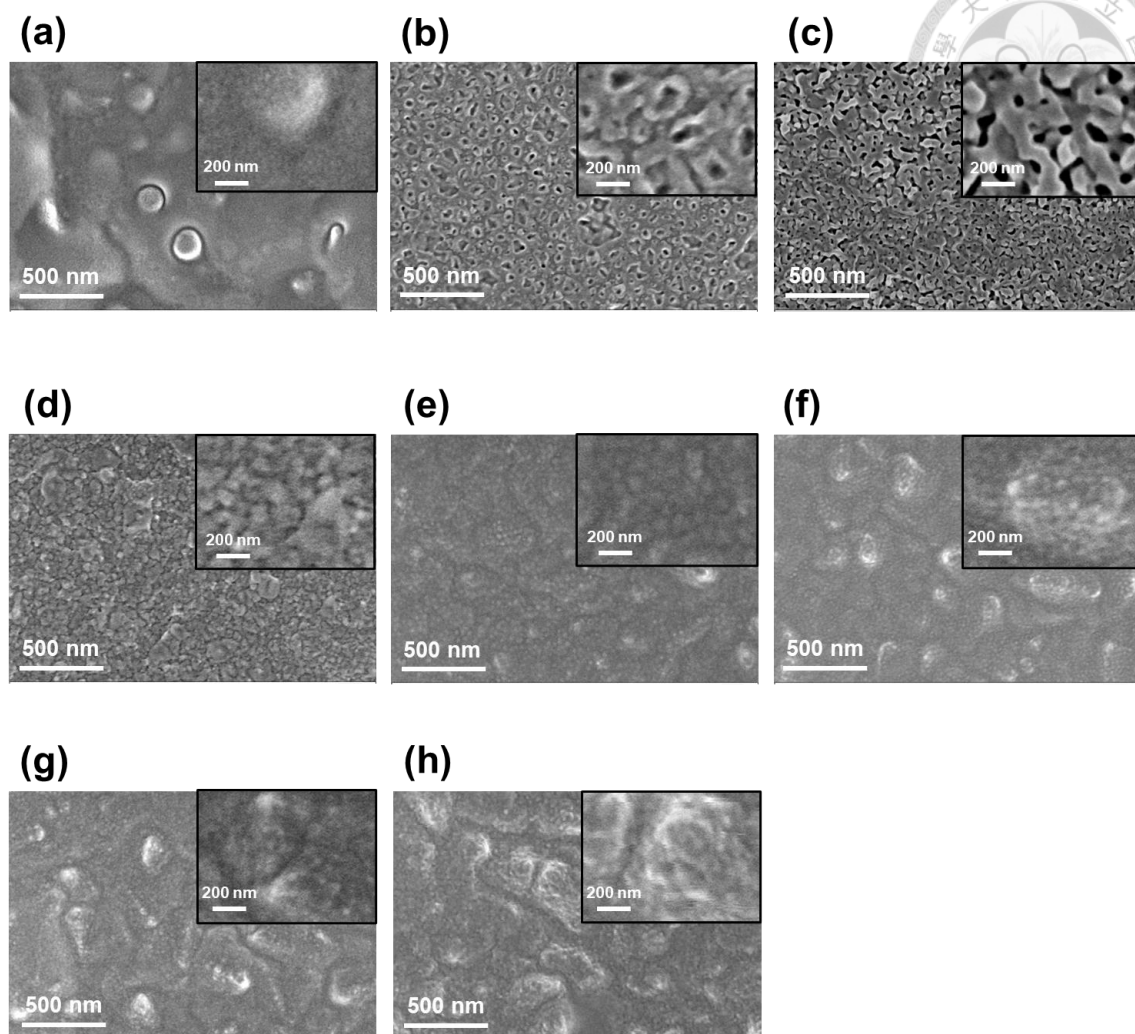
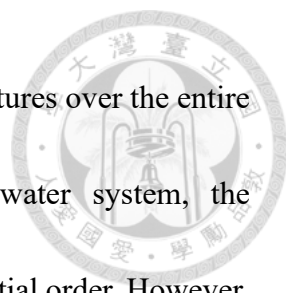


Figure 64 SEM morphologies of mesoporous *a*ZIF-90 film prepared with different amounts of water in THF/water co-solvent systems. (a) 0, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, and (h) 80 vol% of water. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



The THF/DMSO co-solvent system produced mesoporous structures over the entire range of blending ratios examined. Compared with the THF/water system, the mesoporous arrangement in THF/DMSO generally showed better spatial order. However, the resulting films still displayed evident surface irregularities, including large macropores and cracks (**Figure 65**). This behavior is most likely associated with the very low volatility of DMSO (boiling point = 189 °C), which makes it difficult for the solvent to fully evaporate within the 60s spin-coating process. As a result, part of the framework may remain in a partially dried state during film formation, leading to insufficient structural consolidation and, ultimately, a rougher and less uniform surface morphology.

In summary, among all the co-solvent systems examined above, THF/MeOH appears to be the most suitable for the preparation of mesoporous amorphous MOF films. Its advantage lies in the balance between providing an appropriate solvent environment for soft-template micellization and maintaining sufficient volatility for uniform film formation during spin-coating. Among the various THF/MeOH compositions, the film prepared with 20 vol% MeOH showed the highest degree of pore ordering. The underlying reason for this result will be discussed in the following section.

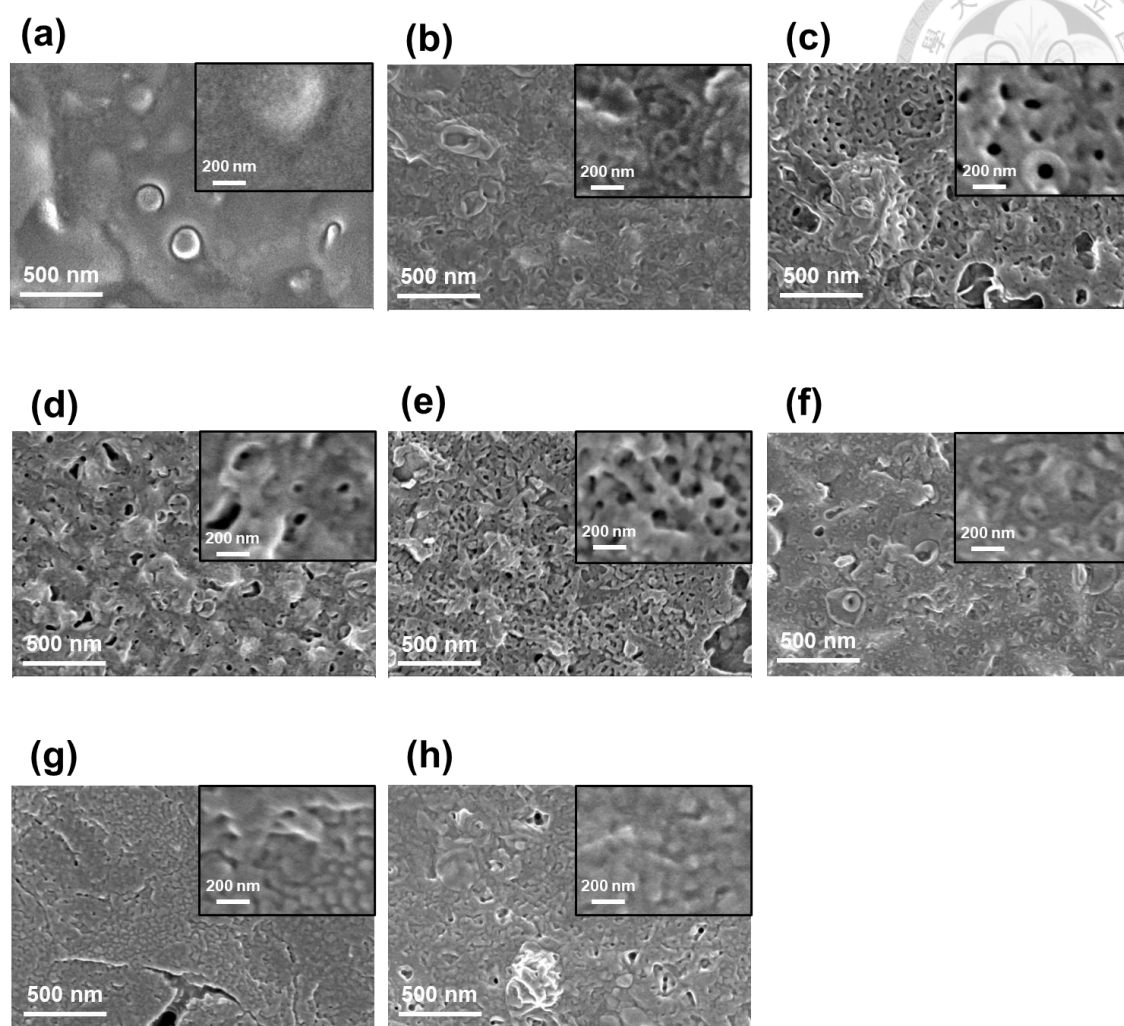


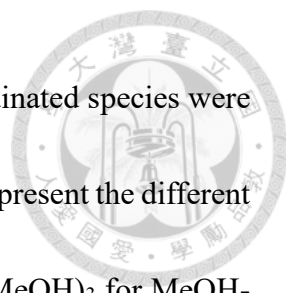
Figure 65 SEM morphologies of mesoporous *a*ZIF-90 film prepared with different amounts of DMSO in THF/DMSO co-solvent systems. (a) 0, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, and (h) 80 vol% of DMSO. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



b. The optimal ratio of the co-solvent system

Following the discussion in the previous section, the THF/MeOH cosolvent system appears to be the most suitable medium for preparing mesoporous amorphous ZIF-90 films. Mesoporous structures were observed across a wide composition range, from 20 to 80 vol% MeOH. Notably, the sample prepared with 20 vol% MeOH showed the highest spatial order among all compositions. To further understand why this method preserves the amorphous state rather than promoting crystallization, DFT calculations were carried out to probe the underlying mechanism.

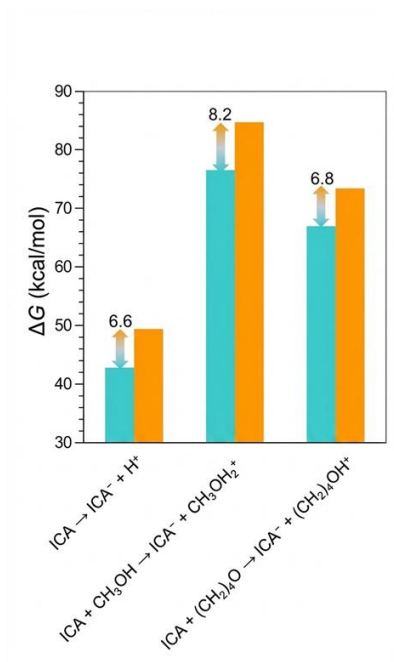
To gain mechanistic insight into the observed crystallization behavior, DFT calculations were performed to examine both the deprotonation of ICA ($\text{C}_4\text{H}_4\text{N}_2\text{O}$) and the subsequent ligand-exchange processes at Zn(II) centers (**Figure 66**). As shown in **Figure 66a**, the Gibbs free energies (ΔG) associated with ICA deprotonation, either through direct proton dissociation or through proton transfer to MeOH or THF, depend strongly on the solvent environment. In MeOH-rich media, the deprotonation of ICA is energetically more favorable, with free energies lower by approximately $6\text{--}8 \text{ kcal mol}^{-1}$ compared with those in THF-rich mixtures. This result suggests that MeOH-rich conditions promote the formation of ICA^- , thereby increasing the availability of the deprotonated ligand required for Zn–imidazolate bond formation.



The energetics of ligand exchange between ICA^- and Zn(II) -coordinated species were further evaluated, and the results are summarized in **Figure 66b**. To represent the different solvent environments, two cluster models were adopted: $\text{Zn(NO}_3)_2(\text{MeOH})_3$ for MeOH-rich conditions and $\text{Zn(NO}_3)_2(\text{THF})_2$ for THF-rich conditions. In both cases, coordination of ICA^- to Zn(II) is thermodynamically favorable and proceeds with a substantial decrease in free energy, allowing ICA^- to readily replace coordinated solvent molecules ($\Delta G \approx -31 \text{ kcal mol}^{-1}$ for MeOH; $-24 \text{ kcal mol}^{-1}$ for THF). In addition, ICA^- coordination also renders nitrate displacement favorable, with calculated free energies of approximately $-13 \text{ kcal mol}^{-1}$ in MeOH and -9 kcal mol^{-1} in THF. Overall, these calculations indicate that once ICA^- is formed, it can efficiently compete for Zn(II) coordination sites against both solvent molecules and nitrate anions, and that this process is more strongly favored in MeOH-rich environments.



(a)



(b)

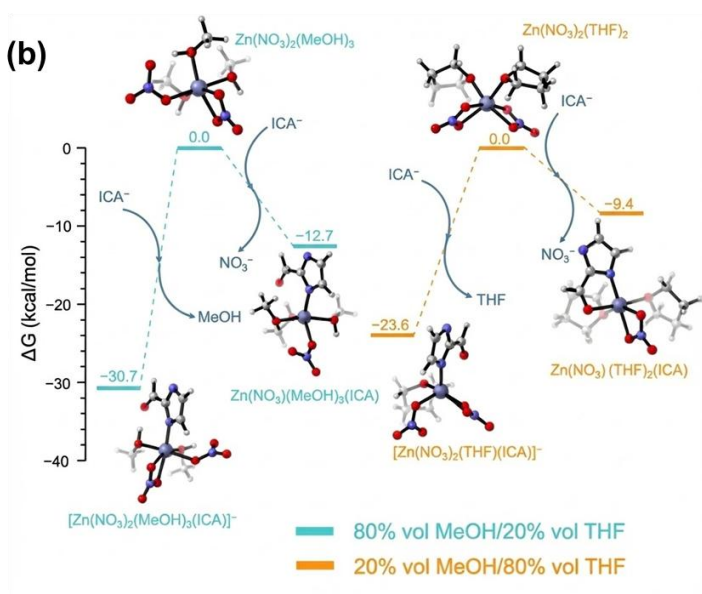


Figure 66 Theoretical comparison of reaction energetics in MeOH-rich and THF-rich media, with the corresponding profiles displayed in teal and orange, respectively. (a) Calculated deprotonation free energies of ICA. (b) Ligand-exchange reactions at Zn(II) clusters. Energy values are in kcal mol⁻¹. Zn, O, N, C, and H atoms are represented by

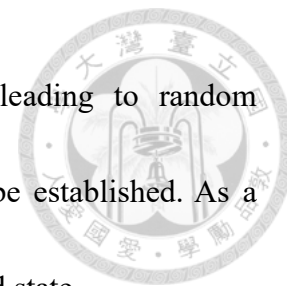
dark blue, red, bright blue, gray, and white spheres, respectively. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



Taken together, these calculations help explain the experimental trend in a more intuitive way. Under MeOH-rich conditions, ICA can be deprotonated more readily, and the resulting ICA^- also shows a stronger tendency to coordinate with Zn(II) . Such a combination is favorable for the rapid generation of Zn–imidazolate bonds and, consequently, for the formation of the tetrahedral Zn-imidazolate nodes that are essential for constructing the ZIF-90 framework. In other words, MeOH-rich environments provide a chemical situation that is more compatible with the ordered coordination process required for crystallization.

By contrast, in THF-rich conditions, the deprotonation of ICA becomes less favorable, meaning that the amount of reactive ICA^- available for framework construction is reduced. At the same time, the coordinated ligands around Zn(II) , especially nitrate species, are less easily displaced and therefore tend to remain associated with the metal centers for a longer period. During the rapid solvent evaporation involved in film formation, these partially occupied Zn sites may not reorganize efficiently into a well-defined crystalline network. Instead, the coordination process is more likely to proceed

in a less selective and more kinetically constrained manner, leading to random crosslinking and structural trapping before long-range order can be established. As a result, the framework is frozen into an amorphous yet interconnected state.



c. Optimal amount of reactant (linker)

Beyond identifying the optimal solvent environment for preparing mesoporous amorphous films, the amount of organic ligand is also a critical factor in maintaining the precursor network in an amorphous state during the rapid solvent evaporation process. To examine this effect, precursor solutions with different ICA amounts ranging from 40 to 100 mg were prepared in both THF-rich environments (20 vol% MeOH) and MeOH-rich environments (80 vol% MeOH).

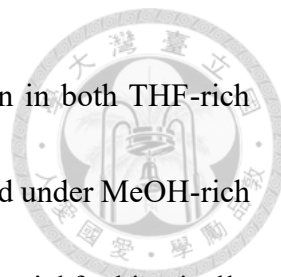
In the THF-rich environment (**Figure 67a, c, e, and g**), irregularly shaped pores can be observed to be randomly distributed throughout the films. However, these pores do not exhibit a well-defined or spatially ordered mesoporous arrangement. In addition, polyhedral particles are randomly located on the film surface, suggesting the partial formation of crystalline ZIF-90 domains. These observations indicate that increasing the ICA content does not improve the spatial ordering of mesopores under THF-rich conditions. Instead, the excessive amount of ICA may promote local coordination and nucleation events, eventually leading to the formation of crystalline ZIF-90 particles.

Therefore, although THF-rich environments are generally favorable for suppressing rapid crystallization, an overly high ICA concentration can still disturb the amorphous film-forming process and reduce the structural uniformity of the mesoporous network.

In contrast, in the MeOH-rich environment (**Figure 67b, d, f, and h**), all samples show continuous film-like morphologies, but no clear mesoporous structure can be identified. Moreover, abundant crystalline ZIF-90 particles are randomly distributed on the film surface. This result suggests that the increased ICA amount further facilitates the crystallization of ZIF-90 after precursor nucleation during the stirring process. Based on our previous DFT calculation, in MeOH-rich media, ICA deprotonation and coordination with Zn^{2+} are more favorable, which accelerates the formation of Zn–imidazolate linkages and promotes the growth of crystalline ZIF-90 domains. As crystallization proceeds, the initially formed mesostructured precursor network may be occupied, disrupted, or consumed by crystalline domains, resulting in the disappearance of observable mesoporosity. Therefore, the ligand concentration must be carefully controlled to balance precursor network formation, micelle-directed mesostructure development, and suppression of crystallization during rapid solvent evaporation.

Overall, these results demonstrate that the formation of mesoporous amorphous ZIF-90 films is governed not only by the solvent composition but also by the ligand

concentration. An excessive amount of ICA promotes crystallization in both THF-rich and MeOH-rich environments, although the effect is more pronounced under MeOH-rich conditions. Therefore, maintaining a relatively low ICA amount is essential for kinetically trapping the ZIF-90 precursor into an amorphous mesoporous film rather than allowing it to evolve into crystalline ZIF-90 particles.



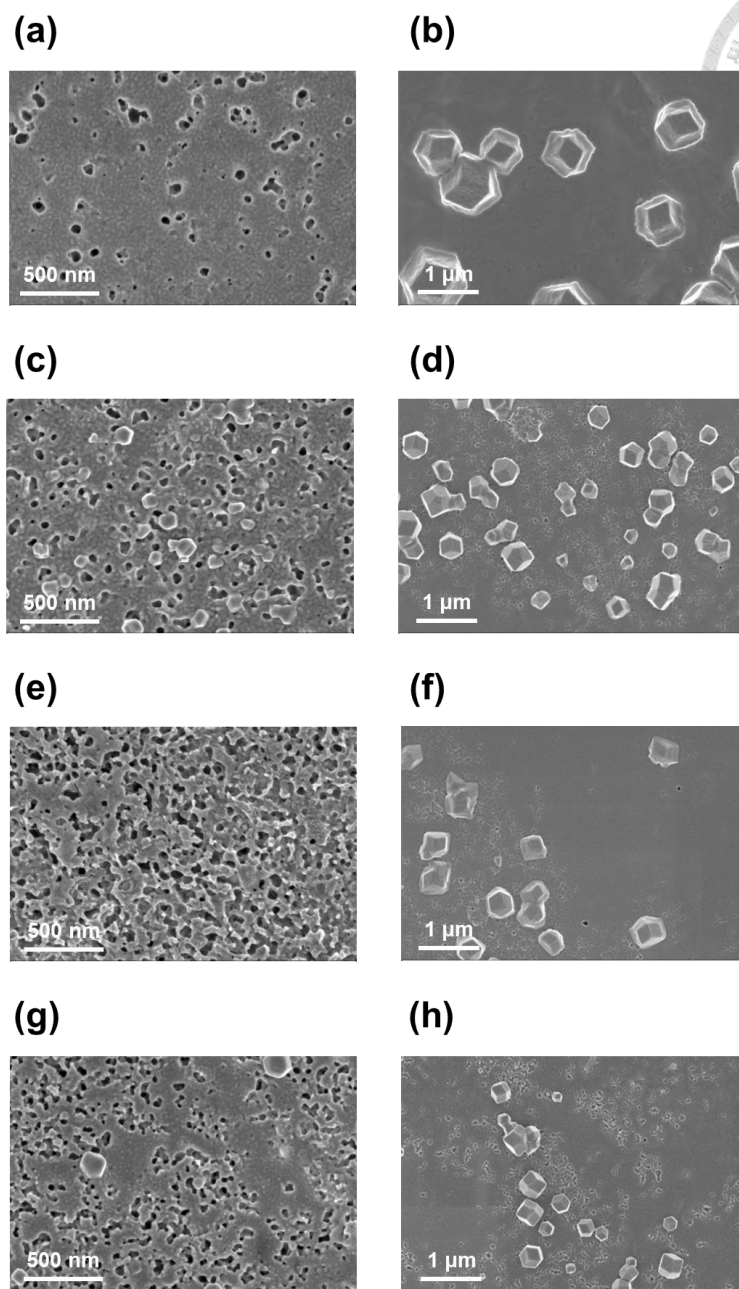


Figure 67 SEM images of mesoporous *a*ZIF-90 film synthesized with varying amounts of ICA (a, b) 40 mg, (c, d) 60 mg, (e, f) 80 mg, and (g, h) 100 mg in THF/MeOH co-solvent systems. Images (a, c, e, and g) correspond to 20 vol% MeOH, while (b, d, f, and h) correspond to 80 vol% MeOH. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



The above comparison is summarized in **Figure 68**. Overall, two key criteria should be satisfied for the successful formation of continuous mesoporous amorphous MOF films. First, the block copolymer must be effectively dissolved and subsequently induced to form micellar structures, thereby allowing it to function as a soft template for mesopore generation [133,134]. Second, the solvent system should possess sufficient volatility to promote rapid evaporation-driven film thinning. This process enables the homogeneous immobilization of reactants and facilitates the formation of a continuous thin-film architecture before significant crystallization occurs.

Based on these findings, the following section further extends this evaporation-induced self-assembly (EISA) from spin coating to spray coating. Compared with spin coating, spray coating is more suitable for large-area processing and offers better scalability, making it closer to practical and industrially relevant film fabrication.

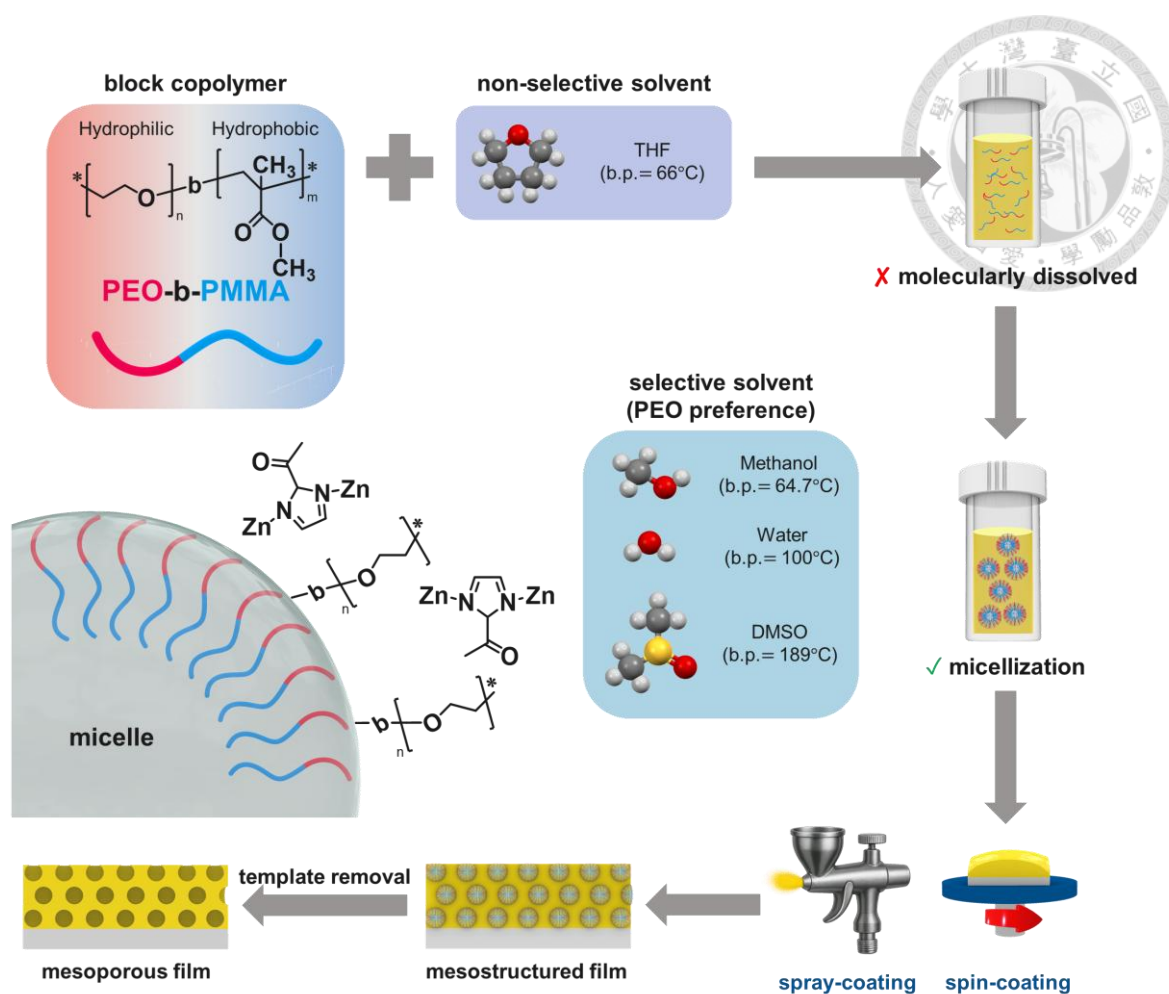


Figure 68 Illustration of the solvent-evaporation-assisted spin-coating strategy for fabricating mesoporous amorphous MOF thin films. Formation of the continuous mesoporous amorphous framework is governed by the choice of co-solvent system, which directs micelle assembly, and by the evaporation rate during spin coating. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.

6.2. Versatility of Fabrication



The successful preparation of mesoporous amorphous ZIF-90 films relies on a delicate balance between thermodynamic control and kinetic trapping. As discussed above, the solvent environment, ligand concentration, micelle formation, and evaporation rate must be carefully coordinated to suppress excessive crystallization while allowing the block copolymer micelles to direct the formation of mesoporous structures. Therefore, the precursor solution developed in this work is not merely optimized for a single coating process but is designed to create a suitable evaporation-induced assembly environment for amorphous mesoporous film formation.

To further examine the versatility and practical applicability of this precursor system, we extended the fabrication method from spin coating to spray coating. Spray coating is particularly attractive because it is more compatible with large-area deposition, scalable processing, and industrially relevant thin-film fabrication. Unlike spin coating, which is generally limited by substrate size and rotational coating conditions, spray coating allows the precursor solution to be deposited in a more flexible and continuous manner [135,136]. Therefore, successful film formation by spray coating would strongly support the generality of our solvent-evaporation-assisted strategy.

As shown in **Figure 69**, continuous mesoporous *a*ZIF-90 films were successfully

obtained on both FTO glass and Si wafer substrates. The formation of mesoporous structures on the Si wafer demonstrates that the precursor solution can generate uniform amorphous mesoporous films on relatively smooth substrates. More importantly, the successful deposition on FTO glass further highlights the robustness of this method, because FTO substrates possess an intrinsically rough and textured surface. In the *a*ZIF-90 film deposited on FTO, the observed polyhedral-like surface features are mainly attributed to the underlying roughness of the FTO substrate rather than the formation of large crystalline ZIF-90 particles. Despite this surface roughness, a continuous mesoporous film can still be formed, indicating that the precursor solution can adapt to non-ideal substrate morphologies while maintaining the desired mesoporous amorphous architecture.

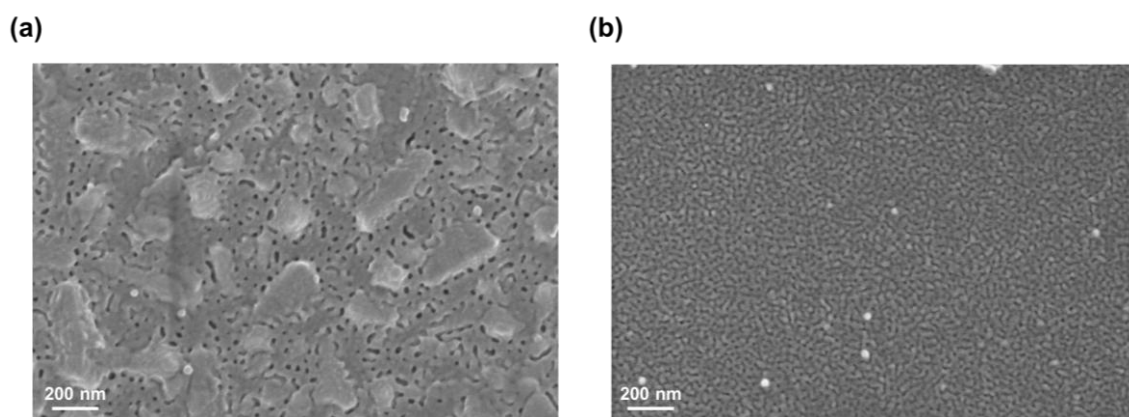


Figure 69 SEM morphologies of mesoporous *a*ZIF-90 film prepared through the spray coating method on different substrates (a) FTO glass; (b) Si wafer. The island morphologies shown in Figure S10a are from the tips of FTO substrates [137], not from

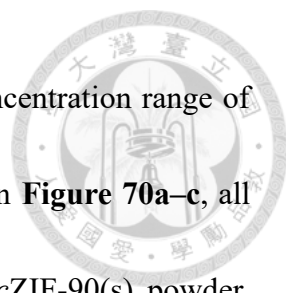
MOF crystals. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



These results demonstrate that the developed precursor solution is not restricted to spin coating, but can also be applied to spray coating for the fabrication of mesoporous amorphous ZIF-90 films. The successful extension to spray coating validates the rational design of the precursor solution and confirms that the evaporation-induced assembly mechanism can operate under different deposition conditions. More broadly, this versatility suggests that the present strategy has considerable potential for scalable and substrate-compatible fabrication of continuous mesoporous amorphous MOF thin films, which is essential for future practical applications in sensing, separation, catalysis, and other thin-film-based devices.

6.3. Application in Electrochemical Sensing

To further demonstrate the structural merits of the mesoporous amorphous ZIF-90 system, uric acid oxidation was selected as a model electrochemical reaction. For a more direct comparison between amorphous mesoporous and crystalline architectures, a size-reduced crystalline ZIF-90 sample with an average particle size of approximately 500 nm was additionally prepared and denoted as *c*ZIF-90(s) powder (**Figure 51**). The



electrochemical response toward uric acid was evaluated over a concentration range of 0–500 μM using differential pulse voltammetry (DPV). As shown in **Figure 70a–c**, all MOF samples, including *a*ZIF-90 powder, *c*ZIF-90 powder, and *c*ZIF-90(s) powder, exhibit negligible current response in the absence of uric acid, confirming that no obvious electrochemical reaction occurs without the target analyte. After the addition of 100 μM uric acid, a distinct oxidation peak appears, which is associated with the electrochemical oxidation of uric acid to allantoin [138-140]. Among the three samples, *a*ZIF-90 powder delivers the strongest current response, suggesting that its mesoporous amorphous architecture offers more accessible electroactive sites than the corresponding crystalline materials.

The quantitative sensing performance was further analyzed using calibration plots derived from the DPV responses. The calculated sensitivities of *a*ZIF-90 powder, *c*ZIF-90 powder, and *c*ZIF-90(s) powder are 0.064, 0.052, and 0.045 $\mu\text{A } \mu\text{M}^{-1}$, respectively, while their limits of detection are estimated to be 68, 85, and 76 μM , respectively (**Figure 70d**). The superior sensitivity of *a*ZIF-90 can be attributed to its interconnected mesoporous framework, which facilitates analyte diffusion and increases the accessibility of reactive sites [44,77,80]. In contrast, crystalline ZIF-90 particles suffer from less efficient mass transport. For larger *c*ZIF-90 crystallites, the long intraparticle diffusion

distance restricts the utilization of internal sites. Although *c*ZIF-90(s) possesses a smaller particle size and therefore shorter intraparticle diffusion pathways, the dense packing of small particles may introduce extended and tortuous interparticle diffusion channels within the electrode layer, thereby limiting the overall mass-transfer efficiency and reducing the calibration slope.

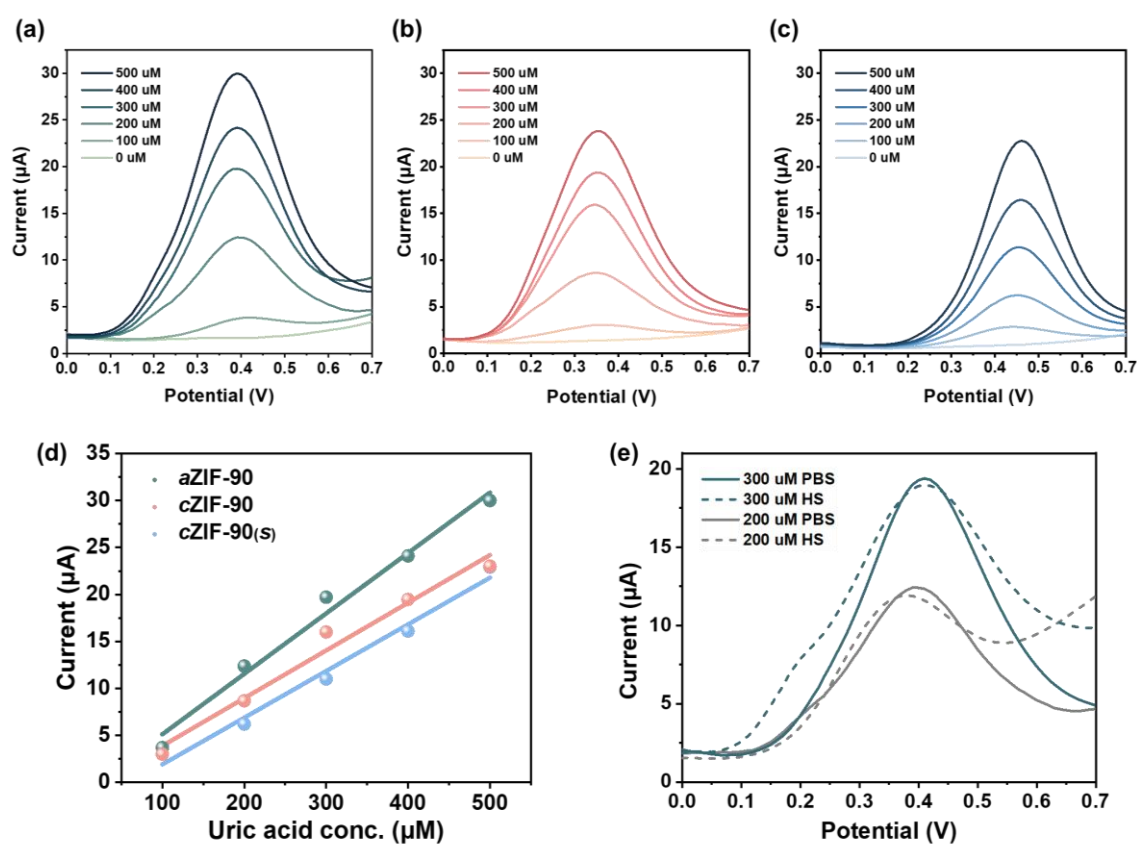


Figure 70 Uric acid sensor test of *a*ZIF-90 powder, *c*ZIF-90 powder, and *c*ZIF-90(s) powder. The differential pulse voltammetric (DPV) response of (a) *a*ZIF-90 powder, (b) *c*ZIF-90 powder, and (c) *c*ZIF-90(s) powder for uric acid. (d) Linear relationship of peak current with different uric acid concentrations. (e) Differential pulse voltammetric (DPV)

response of *a*ZIF-90 powder for uric acid in PBS (phosphate-buffered saline) and HS (human serum) solution. Reproduced with permission [107]. Copyright 2026, Wiley-VCH.



It is also worth noting that sensitivity and detection limit do not necessarily follow the same trend because they are governed by different factors. Sensitivity mainly reflects the overall current response per unit concentration, which is strongly related to the number of accessible active sites and the efficiency of mass transport under the tested concentration range. In contrast, the detection limit is more dependent on the signal-to-noise ratio at low analyte concentrations. Therefore, although *c*ZIF-90(s) shows a lower sensitivity than *c*ZIF-90, its larger external surface area may provide a slightly improved initial response at low uric acid concentrations, resulting in a marginally lower LoD. By comparison, *a*ZIF-90 combines abundant accessible sites with a continuous mesoporous diffusion network, leading to improved performance in both sensitivity and detection limit.

To further examine its applicability in a complex biological matrix, *a*ZIF-90 powder was also tested for uric acid detection in human serum. The recovery rates for 200 and 300 μ M uric acid were 95% and 98%, respectively, which are close to the ideal value of

100% and indicate acceptable accuracy in real-sample analysis. Although this sensing experiment is intended primarily as a proof-of-concept demonstration rather than a fully optimized analytical platform, the results clearly highlight the potential of mesoporous amorphous ZIF-90 as an efficient electrochemical sensing material.

6.4. Summary

In this chapter, a solvent evaporation-induced assembly strategy was developed for the fabrication of continuous mesoporous amorphous ZIF-90 thin films. Unlike conventional crystalline MOF films, which often form discrete particles or grain-boundary-rich layers during rapid crystallization, the present approach deliberately controls the balance between micelle assembly, precursor coordination, solvent evaporation, and crystallization kinetics. By using PEO-*b*-PMMA as a soft template and tuning the THF/MeOH co-solvent environment, continuous aZIF-90 films with uniformly distributed mesopores were successfully prepared through spin coating.

Structural characterization confirmed that the mesoporous architecture extends throughout the entire film rather than being limited to the surface. Cross-sectional STEM and elemental mapping demonstrated that the film is continuous, conformal, and chemically homogeneous, with a thickness of approximately 100 nm. XRD analysis verified the amorphous nature of the aZIF-90, while FTIR, XPS, solid-state NMR, and



XAS confirmed that the essential Zn–imidazolate coordination environment is retained despite the absence of long-range crystallinity. These results indicate that the amorphous state is not simply a structural deficiency, but a useful phase-engineering tool for suppressing uncontrolled crystallization and promoting continuous film formation.

The formation mechanism was further clarified by systematically changing the co-solvent composition and ligand concentration. The results showed that successful film formation requires two key conditions: effective micelle formation from the block copolymer template and sufficiently rapid solvent evaporation to immobilize the precursor network before excessive crystallization occurs. The method was also extended from spin coating to spray coating on both FTO glass and Si wafer substrates, demonstrating its versatility and potential scalability.

Finally, uric acid sensing was used as a proof-of-concept application to evaluate the structural advantages of the mesoporous amorphous architecture. Compared with crystalline ZIF-90 samples, *a*ZIF-90 exhibited higher sensitivity and a lower detection limit, mainly because its interconnected mesoporous network improves analyte diffusion and active-site accessibility. Overall, this chapter establishes solvent evaporation-induced soft-template assembly as an effective route for preparing continuous mesoporous amorphous MOF thin films.

7. Conclusions

This dissertation investigated the phase engineering and structural design of porous framework thin films, with the aim of transforming MOF- and COF-based materials from conventional powder forms into continuous functional thin-film and membrane architectures. Two representative systems were developed to demonstrate how film continuity, pore structure, interfacial design, and framework phase state can be used to regulate transport-related performance.

In the first part, a heterogeneous MOF-on-COF membrane was constructed as a crystalline bilayered framework platform for ion transport and osmotic energy harvesting. A free-standing COF membrane was used as a continuous porous substrate, and a UiO-66-NH₂ MOF layer was selectively grown on one side of the COF membrane. This asymmetric design successfully combined the sub-nanometer ion-sieving ability of the MOF layer with the continuous transport pathways of the COF layer. The opposite surface charges and different pore dimensions of the two framework layers generated an ionic diode-like membrane structure, which enhanced directional ion transport and improved osmotic power generation compared with the single-layer COF membrane. Further ion-type-dependent studies demonstrated that both cations and anions strongly influence power generation behavior, confirming that ion transport in the MOF-on-COF membrane

is governed by hydrated ion size, pore confinement, surface charge, and interfacial asymmetry. This study highlights crystalline hetero-interface engineering as an effective structural design strategy for framework-based ion-selective membranes.

In the second part, a solvent evaporation-induced assembly strategy was developed to prepare continuous mesoporous amorphous ZIF-90 thin films. By controlling the co-solvent environment, block-copolymer micelle formation, ligand concentration, and rapid solvent evaporation, the crystallization of ZIF-90 was deliberately suppressed while mesoporous structures were introduced into the amorphous framework. The resulting *a*ZIF-90 films exhibited continuous morphology, accessible mesoporosity, and retained Zn–imidazolate coordination despite the absence of long-range crystallinity. This result demonstrates that the amorphous phase can be used as a useful phase-engineering tool rather than being regarded as a structural disadvantage. The mesoporous amorphous architecture further improved mass transport and active-site accessibility, as demonstrated by enhanced uric acid sensing performance compared with crystalline ZIF-90 samples.

Overall, these two studies show that the performance of porous framework thin films is determined not only by framework composition, but also by how the framework is organized across multiple length scales. Through crystalline hetero-interface design and amorphous mesoporous film formation, this dissertation provides new insights into the

development of continuous porous framework thin films for ion transport, energy harvesting, and electrochemical sensing applications.





8. Challenges and Future Perspectives

8.1. Framework-Based Membranes for Ion Transport and Osmotic Energy

Harvesting: The Interface Issue

Although the MOF-on-COF membrane developed in this dissertation demonstrates high ion selectivity and promising osmotic power generation performance, the interfacial issue between two different framework materials remains an important challenge. In the present design, the MOF layer provides well-defined sub-nanometer windows for ion sieving, while the COF membrane offers continuous transport channels and mechanical integrity. However, MOFs and COFs are intrinsically different materials, with different bonding chemistry, crystallization behavior, pore structures, surface charge distributions, and mechanical properties. Therefore, even when a continuous bilayered structure is successfully fabricated, the interface between the MOF and COF layers may still introduce additional ion-transport resistance. This interfacial resistance may partially limit ion flux, disturb local ion concentration distribution, or reduce the efficiency of directional ion migration across the membrane.

To further improve framework-based membranes for osmotic energy harvesting, one possible direction is to construct heterostructures from two-dimensional MOFs and two-dimensional COFs. In the current system, a three-dimensional MOF layer is grown on a



COF membrane, which may cause structural incompatibility at the interface because of the difference in framework geometry and growth mode. Replacing the 3D MOF layer with a 2D MOF layer-by-layer structure could provide a more compatible interface with 2D COF membranes. Such a design may reduce interfacial mismatch, improve contact between the two framework layers, and create a more continuous ion-transport pathway. Moreover, the layered nature of 2D MOFs and COFs may allow better control over thickness, orientation, and charge distribution, which are all important parameters for ionic diode behavior and osmotic power generation.

Another promising direction is to apply the amorphous MOF thin-film concept developed in the second part of this dissertation to ion-transport membranes. The mesoporous amorphous ZIF-90 film demonstrates that a continuous porous framework film can be constructed without obvious crystalline grain boundaries. This feature is highly attractive for osmotic energy harvesting because grain-boundary-free films may reduce discontinuous transport barriers and provide more uniform ion pathways. More importantly, a micropore–mesopore hierarchical architecture could offer complementary functions: micropores may contribute to ion selectivity through size confinement, while mesopores may act as ion-buffering and transport domains to enhance ion flux. In this sense, mesoporous amorphous MOF films may provide a new platform for balancing ion

selectivity and ion permeability.

The main challenge for this direction is the generalization of the solvent evaporation-induced amorphous MOF film strategy to other MOF systems. For example, extending this approach from ZIF-90 to more ion-transport-relevant MOFs, such as UiO-66-NH₂. However, different MOFs have different coordination chemistry, nucleation kinetics, crystallization tendencies, and solvent compatibility. Therefore, the key future task is to understand how to control precursor coordination, micelle assembly, solvent evaporation, and crystallization suppression for each specific MOF system. If this challenge can be addressed, continuous mesoporous amorphous MOF films may become an important next-generation membrane platform for high-performance ion transport and osmotic energy harvesting.

8.2. Broaden this methodology to different kinds of MOFs

Based on these results, we further considered extending the solvent-evaporation-induced fabrication strategy (spin coating) to other types of MOFs. As a preliminary exploration, we recently attempted to prepare ZIF-8, Co-ZIF-90, and ZIF-67 films under similar processing conditions. As shown in **Figure 71**, neither ZIF-8 nor ZIF-67 formed a continuous thin film comparable to that of *a*ZIF-90. Instead, nanosheets or nanosheet-

assembled microspheres were observed, indicating that the current precursor formulation and evaporation conditions are not directly transferable to these systems.

Interestingly, among the tested MOFs, only Co-ZIF-90 prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ produced a relatively continuous film with randomly distributed pores. This result suggests that the ligand structure, metal source, coordination kinetics, solvent environment, and crystallization tendency all play important roles in determining whether a continuous mesoporous amorphous MOF film can be obtained. Therefore, although the present solvent-evaporation-induced strategy shows promising potential beyond Zn-based ZIF-90, the balance between precursor stabilization, micelle-directed assembly, nucleation, and crystallization must be individually optimized for each MOF system.

This requirement represents one of the major challenges in further extending this method to a broader range of mesoporous amorphous MOF films. Unlike conventional particle synthesis, where crystallization is often desirable, the fabrication of continuous amorphous mesoporous MOF films requires precise kinetic control to suppress uncontrolled crystal growth while preserving film continuity and mesostructural organization. Therefore, the generalization of this approach to other MOF systems remains non-trivial and will require system-specific optimization of both coordination chemistry and evaporation-induced assembly conditions.

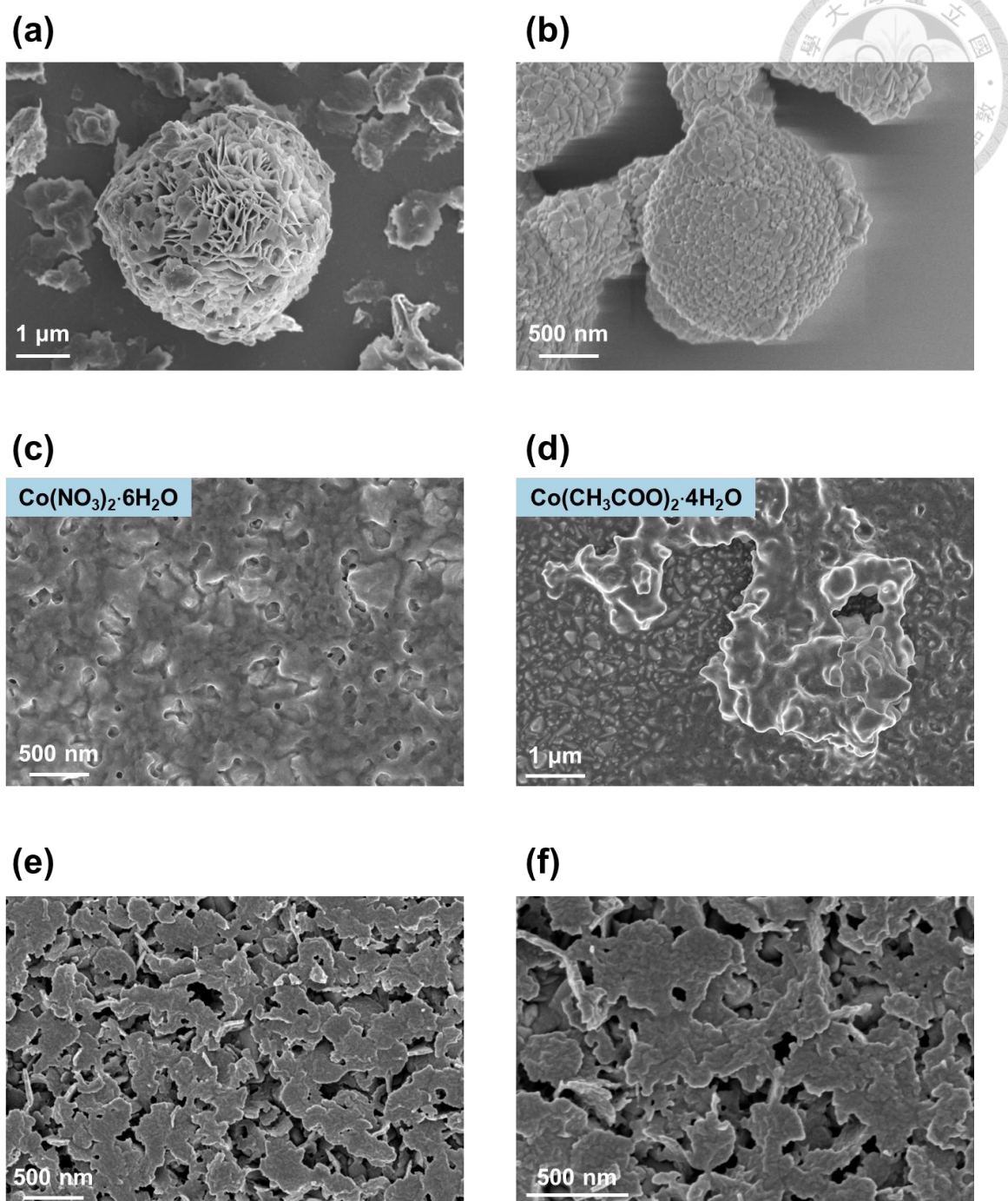


Figure 71 SEM images of (a, b) ZIF-8, (c, d) Co-ZIF-90 and (e, f) ZIF-67 by using spin coating method. (c) sample is using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as precursor, (d) sample is using $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as precursor.



9. Appendix

9.1. Computational Analysis of ICA Deprotonation and Zn(II)-Centered Ligand-

Exchange Processes

All DFT calculations were carried out with the Orca 6.0 program package [141]. Geometry optimizations were done at the B3LYP-D3(BJ)/def2-TZVP level of theory, using the RIJCOSX approximation with the def2/J auxiliary basis set and TightSCF convergence criteria [142-147]. Frequency calculations were performed to verify the nature of the optimized structures and to obtain the harmonic free energy corrections. Single-point calculations were then performed at the ω B97M-V/def2-TZVPD level of theory [148]. Solvation effects were included using the SMD solvation model with the solvent-accessible surface (SAS) [149]. Two solvents were considered: THF ($\epsilon = 7.25$) and MeOH ($\epsilon = 32.63$). A correction of 1.89 kcal/mol was applied to convert solvation free energies from the 1 atm to the 1 M standard state. To estimate the reaction Gibbs free energy ΔG in mixed solvents of MeOH and THF, we used a linear interpolation approach:

$$\Delta G_{\text{mix}} \approx x_{\text{MeOH}} \Delta G_{\text{MeOH}} + (1 - x_{\text{MeOH}}) \Delta G_{\text{THF}}$$

where x_{MeOH} is the mole fraction of MeOH, ΔG_{MeOH} and ΔG_{THF} are the reaction Gibbs free energies in pure MeOH and THF, respectively. For a mixed solvent of 80 vol% MeOH and 20 vol% THF, $x_{\text{MeOH}} \approx 0.890$. For the 20 vol% MeOH and 80 vol% THF solvent, $x_{\text{MeOH}} \approx 0.334$. The solvation Gibbs free energies of proton in MeOH and THF are taken from the work of Marković et al. (−1071.9 and −1047.6 kcal/mol, respectively) [150]. Raw data and relative free energies are provided in Tables S1-S6.

Table S1. Raw energies (in au) used for the calculations of ICA deprotonation free

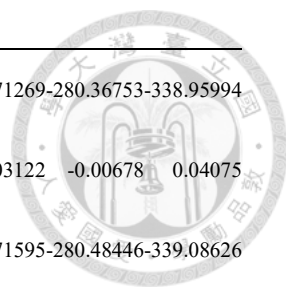
energies. Structures were optimized and free-energy corrections (1 M standard state) were obtained at the B3LYP-D3(BJ)/def2-TZVP level, while single-point energies in solvent (MeOH and THF) were evaluated with ω B97M-V/def2-TZVPD using the SMD model.

	ICA	ICA ⁻	CH ₃ OH	CH ₃ OH ₂ ⁺	(CH ₂) ₄ O	(CH ₂) ₄ OH ⁺	H ⁺
E_{B3LYP}	-339.51533	-338.95994	-115.71269	-116.01160	-232.41218	-232.73745	
Free energy							
correction	0.05436	0.04075	0.03122	0.04361	0.09155	0.10387	
$E_{\omega\text{B97M-V}}(\text{MeOH})$	-339.57432	-339.08626	-115.71595	-116.08347	-232.43165	-232.81401	
$E_{\omega\text{B97M-V}}(\text{THF})$	-339.58015	-339.08244	-115.71806	-116.07168	-232.43359	-232.80604	
$G_{\omega\text{B97M-V}}(\text{MeOH})$	-339.51996	-339.04551	-115.68473	-116.03986	-232.34010	-232.71014	-0.40827 ^a
$G_{\omega\text{B97M-V}}(\text{THF})$	-339.52579	-339.04169	-115.68684	-116.02807	-232.34203	-232.70217	-0.39901 ^a

^a The values were calculated based on solvation Gibbs free energies of proton in MeOH and THF, taken from the work of Marković et al. (−1071.9 and −1047.6 kcal/mol, respectively) [150].

Table S2. Raw energies (in au) used for the calculations of free energies of ion exchange (model 1). Structures were optimized and free-energy corrections (1 M standard state) were obtained at the B3LYP-D3(BJ)/def2-TZVP level, while single-point energies in solvent (MeOH and THF) were evaluated with ω B97M-V/def2-TZVPD using the SMD model.

Zn(NO ₃) ₂ (MeOH) ₃	[Zn(NO ₃) ₂ (MeOH) ₂ (ICA)] ⁻	Zn(NO ₃)(MeOH) ₃ (ICA)	MeOH	NO ₃ ⁻	ICA ⁻
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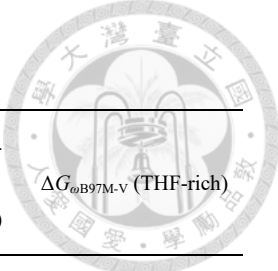
E_{B3LYP}	-2687.22229	-2910.54378	-2745.84145-115.71269-280.36753-338.95994
Free energy correction	0.14664	0.16126	0.19874 0.03122 -0.00678 0.04075
$E_{\omega\text{B97M-V}}(\text{MeOH})$	-2687.30461	-2910.72863	-2745.93183-115.71595-280.48446-339.08626
$E_{\omega\text{B97M-V}}(\text{THF})$	-2687.31859	-2910.73923	-2745.94494-115.71806-280.47642-339.08244
$G_{\omega\text{B97M-V}}(\text{MeOH})$	-2687.15797	-2910.56737	-2745.73309-115.68473-280.49124-339.04551
$G_{\omega\text{B97M-V}}(\text{THF})$	-2687.17194	-2910.57797	-2745.74620-115.68684-280.48320-339.04169

Table S3. Raw energies (in au) used for the calculations of free energies of ion exchange (model 2). Structures were optimized, and free-energy corrections (1 M standard state) were obtained at the B3LYP-D3(BJ)/def2-TZVP level, while single-point energies in solvent (MeOH and THF) were evaluated with $\omega\text{B97M-V}/\text{def2-TZVPD}$ using the SMD model.

	$\text{Zn}(\text{NO}_3)_2(\text{THF})_2$	$[\text{Zn}(\text{NO}_3)_2(\text{THF})(\text{ICA})]^-$	$\text{Zn}(\text{NO}_3)(\text{THF})_2(\text{ICA})$	THF	NO_3^-	ICA^-
E_{B3LYP}	-2804.89966	-2911.50243	-2863.51005	-232.41218	-280.36753	-338.95994
Free energy correction	0.22326	0.17253	0.27582	0.09155	-0.00678	0.04075
$E_{\omega\text{B97M-V}}(\text{MeOH})$	-2805.01400	-2911.70531	-2863.64100	-232.43165	-280.48446	-339.08626
$E_{\omega\text{B97M-V}}(\text{THF})$	-2805.02700	-2911.71404	-2863.65053	-232.43359	-280.47642	-339.08244
$G_{\omega\text{B97M-V}}(\text{MeOH})$	-2804.79074	-2911.53278	-2863.36517	-232.34010	-280.49124	-339.04551
$G_{\omega\text{B97M-V}}(\text{THF})$	-2804.80373	-2911.54151	-2863.37471	-232.34203	-280.48320	-339.04169

Table S4. Deprotonation free energies (in kcal/mol) of ICA in pure MeOH; pure THF; 80 vol% MeOH and 20 vol% THF (MeOH-rich); 20 vol% MeOH and 80 vol% THF (THF-

rich)



	$\Delta G_{\omega B97M-V}$ (pure MeOH)	$\Delta G_{\omega B97M-V}$ (pure THF)	$\Delta G_{\omega B97M-V}$ (MeOH-rich)	$\Delta G_{\omega B97M-V}$ (THF-rich)
ICA $\rightarrow$ ICA $^-$ + H $^+$	41.5	53.4	42.8	49.4
ICA + CH $_3$ OH $\rightarrow$ ICA $^-$ + CH $_3$ OH $_2^+$	74.9	89.7	76.5	84.7
ICA + (CH $_2$) $_4$ O $\rightarrow$ ICA $^-$ + (CH $_2$) $_4$ OH $^+$	65.5	77.8	66.9	73.7

Table S5. Gibbs free energies (in kcal/mol) of ion exchange in pure MeOH; pure THF; 80 vol% MeOH and 20 vol% THF (MeOH-rich)

	$\Delta G_{\omega B97M-V}$ (pure MeOH)	$\Delta G_{\omega B97M-V}$ (pure THF)	$\Delta G_{\omega B97M-V}$ (MeOH-rich)
R1	-30.5	-32.1	-30.7
R2	-13.1	-9.9	-12.7
R1: Zn(NO $_3$) $_2$ (MeOH) $_3$ + ICA $^-$ $\rightarrow$ [Zn(NO $_3$) $_2$ (MeOH) $_2$ (ICA)] $^-$ + MeOH			
R2: Zn(NO $_3$) $_2$ (MeOH) $_3$ + ICA $^-$ $\rightarrow$ [Zn(NO $_3$)(MeOH) $_3$ (ICA)] + NO $_3^-$			

Table S6. Gibbs free energies (in kcal/mol) of ion exchange in pure MeOH; pure THF; 20 vol% MeOH and 80 vol% THF (THF-rich)

	$\Delta G_{\omega B97M-V}$ (pure MeOH)	$\Delta G_{\omega B97M-V}$ (pure THF)	$\Delta G_{\omega B97M-V}$ (MeOH-rich)
R3	-23.0	-23.9	-23.6
R4	-12.7	-7.8	-9.4
R3: Zn(NO $_3$) $_2$ (THF) $_2$ + ICA $^-$ $\rightarrow$ [Zn(NO $_3$) $_2$ (THF)(ICA)] $^-$ + THF			
R4: Zn(NO $_3$) $_2$ (THF) $_2$ + ICA $^-$ $\rightarrow$ [Zn(NO $_3$)(THF) $_2$ (ICA)] + NO $_3^-$			



Cartesian coordinates

ICA⁻

O	1.159668	0.087052	-0.693423
N	2.446606	2.599689	0.366719
N	4.056521	1.152675	1.134069
C	2.877280	1.313257	0.462584
C	3.400322	3.289405	1.009475
C	4.387447	2.405009	1.479965
C	2.212246	0.152759	-0.068377
H	3.354834	4.367358	1.114028
H	5.289825	2.629872	2.035904
H	2.784289	-0.776803	0.153788

ICA

O	1.162689	0.237989	-0.673463
N	2.502462	2.516104	0.389261
N	4.086923	1.168133	1.153701
C	2.943512	1.229159	0.491257
C	3.411108	3.308337	1.017881
C	4.386627	2.451394	1.485277
C	2.210833	0.108105	-0.074634
H	1.651712	2.790377	-0.075854
H	3.301337	4.376797	1.083481
H	5.276504	2.704767	2.037424
H	2.687304	-0.874223	0.085009

CH₃OH

C	-0.000000	0.120103	0.342398
O	-0.000001	0.202986	-1.076447
H	0.891288	-0.388440	0.727114
H	-0.891288	-0.388440	0.727115
H	0.000000	1.142831	0.717382
H	0.000001	-0.689041	-1.437556



CH₃OH₂⁺

C 0.008193 0.133768 0.460319
O 0.118175 0.236127 -1.052196
H 0.846437 -0.489990 0.750917
H -0.957545 -0.300080 0.700015
H 0.122313 1.154168 0.809483
H 0.124237 -0.621216 -1.519679
H -0.520179 0.847511 -1.466990

(CH₂)₄O

O 1.221495 -0.000553 -0.000150
C -1.019817 -0.732957 -0.220648
C -1.019143 0.733783 0.220642
C 0.400305 -1.165080 0.139652
C 0.401283 1.164703 -0.139706
H -1.781502 -1.334945 0.274934
H -1.177468 -0.803809 -1.299428
H -1.780417 1.336370 -0.274870
H -1.177009 0.804771 1.299387
H 0.453211 -1.522387 1.175116
H 0.791278 -1.947482 -0.513918
H 0.454388 1.522092 -1.175129
H 0.792997 1.946693 0.513917

(CH₂)₄OH⁺

O 1.197169 -0.000465 -0.000123
C -1.000022 -0.736318 -0.224932
C -0.999470 0.737114 0.224896
C 0.371856 -1.255014 0.151039
C 0.372832 1.254750 -0.151094
H -1.778170 -1.310401 0.274834
H -1.153404 -0.814342 -1.301298
H -1.777154 1.311823 -0.274861
H -1.152606 0.815268 1.301287
H 0.471555 -1.555289 1.191010



H 0.799854 -1.988756 -0.525430
H 0.472740 1.555051 -1.191037
H 0.801449 1.988083 0.525426
H 2.165770 -0.000805 0.000083

NO₃⁻

N -0.019605 0.059735 0.000012
O -0.248019 -1.175978 -0.000024
O 1.164819 0.479768 -0.000001
O -0.975491 0.875439 0.000005

Zn(NO₃)₂(MeOH)₃

Zn -4.184234 -2.580459 1.142089
O -2.404507 -2.032272 2.001944
O -1.103591 -2.424625 0.271474
O -5.634434 -2.061941 2.679536
O -6.150963 -3.572339 4.168903
N -5.535793 -3.240775 3.190977
N -1.255596 -1.925866 1.421389
O -4.741673 -4.028734 2.569985
O -0.359629 -1.344310 1.989073
C -3.315046 0.334283 0.199247
O -4.441439 -0.494194 0.560769
H -2.651133 0.476865 1.050820
H -3.670500 1.295422 -0.172869
H -2.782122 -0.189158 -0.590038
H -4.869826 -0.125263 1.344421
C -3.328039 -5.042499 -0.353052
O -3.282771 -3.606475 -0.393921
H -2.814207 -5.448158 -1.225034
H -4.374707 -5.337417 -0.373246
H -2.867030 -5.421601 0.560311
H -2.347620 -3.270316 -0.252549
C -6.181944 -2.478288 -1.361657
O -6.034017 -2.928433 -0.006040
H -6.175975 -1.388564 -1.413261

H	-7.103547	-2.873457	-1.791123
H	-5.326867	-2.868008	-1.907075
H	-6.750828	-2.586044	0.542197

[Zn(NO₃)₂(MeOH)₂(ICA)]⁻

Zn	-4.478648	-1.928668	0.912962
O	-2.676120	-1.989942	2.169696
O	-1.190453	-1.842909	0.566361
O	-5.634755	-1.879821	2.720052
O	-6.343116	-3.671450	3.737802
N	-5.727683	-3.145726	2.829148
N	-1.495574	-1.695708	1.785565
O	-5.142531	-3.824542	1.925254
O	-0.676251	-1.283746	2.592885
C	-3.054971	-4.400138	-0.232151
O	-3.256688	-3.010275	-0.491926
H	-2.294785	-4.800000	-0.909050
H	-3.996628	-4.916819	-0.402895
H	-2.752143	-4.566893	0.803246
H	-2.412119	-2.540547	-0.225692
C	-6.508024	-3.453678	-0.926452
O	-6.163040	-2.196482	-0.359691
H	-7.494243	-3.398393	-1.397172
H	-6.532545	-4.185249	-0.121515
H	-5.772216	-3.763346	-1.673976
H	-5.973819	-1.545712	-1.095914
O	-5.561088	-0.497878	-2.216422
N	-4.193878	0.044212	0.460613
N	-3.862449	2.098321	-0.455220
C	-4.348346	0.849348	-0.639724
C	-3.591374	0.833864	1.368022
C	-3.395615	2.094301	0.798310
C	-4.964684	0.533854	-1.885184
H	-3.319294	0.465252	2.343743
H	-2.937535	2.962466	1.247788
H	-4.879762	1.360020	-2.608614





Zn(NO₃)(MeOH)₃(ICA)

Zn	-3.535020	-2.288969	1.037200
O	-1.927344	-1.418823	0.160029
O	-0.508222	-3.096755	0.088717
N	-0.725807	-1.877161	-0.070660
O	0.123008	-1.095521	-0.431117
C	-5.030220	0.507845	1.514929
O	-3.748768	-0.131174	1.476982
H	-5.535433	0.433662	0.550740
H	-4.925131	1.552969	1.809793
H	-5.614442	-0.018787	2.266311
H	-3.148827	0.306917	0.859330
C	-3.012266	-5.394650	1.178651
O	-2.858087	-4.204472	0.398351
H	-2.483715	-6.221114	0.701772
H	-4.074607	-5.623291	1.216921
H	-2.639381	-5.255091	2.195237
H	-1.901628	-3.987489	0.254043
C	-4.877077	-2.667507	-1.653209
O	-5.082963	-2.255846	-0.293176
H	-5.821217	-2.614348	-2.196059
H	-4.475009	-3.680154	-1.694855
H	-4.162542	-1.978773	-2.099425
H	-5.698663	-2.892406	0.176969
O	-6.449222	-3.895735	1.159543
N	-4.202508	-2.782823	2.837113
N	-5.342468	-3.723413	4.553388
C	-5.295203	-3.517371	3.223608
C	-3.547116	-2.521856	3.985731
C	-4.257198	-3.105556	5.036232
C	-6.327328	-4.032742	2.382552
H	-2.634476	-1.947190	4.003643
H	-4.019531	-3.093259	6.088387
H	-7.076385	-4.616009	2.936645

Zn(NO₃)₂(THF)₂

Zn	3.686339	0.376588	1.769588
O	3.395097	1.582935	3.455411
O	1.701945	0.562884	2.581876
O	3.688194	-1.205906	0.400957
O	4.223901	-1.591770	2.458770
N	4.066236	-2.066301	1.284681
N	2.126664	1.352097	3.490783
O	4.268331	-3.220746	1.009114
O	1.405499	1.859659	4.310418
O	5.709109	0.987853	1.639333
C	6.568764	0.714729	2.772973
C	7.358399	-0.542470	2.394931
C	7.247411	-0.620095	0.850561
C	6.475106	0.640233	0.463488
H	5.931836	0.604216	3.646327
H	7.219763	1.581966	2.910749
H	8.392253	-0.466032	2.729364
H	6.916831	-1.424228	2.853030
H	8.221275	-0.650066	0.363506
H	6.700539	-1.511653	0.548853
H	5.774080	0.508343	-0.355974
H	7.144536	1.476334	0.241289
O	3.276730	1.763380	0.223712
C	2.070228	1.566788	-0.553562
C	1.043974	2.542313	0.030596
C	1.896323	3.597232	0.782122
C	3.341587	3.178412	0.512931
H	1.796579	0.518422	-0.471598
H	2.307084	1.795668	-1.595904
H	0.439383	2.988016	-0.758201
H	0.380177	2.029070	0.721985
H	1.709031	4.611099	0.430912
H	1.682922	3.572485	1.849211
H	4.014603	3.308425	1.355915
H	3.755144	3.680898	-0.366240





[Zn(NO₃)₂(THF)(ICA)]⁻

Zn	4.256854	0.535664	1.553537
O	4.051810	1.723859	3.181770
O	1.938074	1.208340	3.074295
O	2.946070	-0.906368	0.943123
O	4.012772	-1.453285	2.737884
N	3.141653	-1.766346	1.888821
N	2.848656	1.789564	3.678997
O	2.508712	-2.802971	1.921081
O	2.680263	2.437920	4.703055
O	3.427594	1.966258	0.125957
C	2.550944	1.444113	-0.892204
C	1.159458	1.673704	-0.318811
C	1.306032	3.001570	0.458709
C	2.830394	3.196913	0.574922
H	2.820706	0.408071	-1.058952
H	2.717141	2.017143	-1.812266
H	0.394761	1.719148	-1.095324
H	0.918804	0.861544	0.365031
H	0.854154	3.837107	-0.078928
H	0.843424	2.931197	1.440186
H	3.183803	3.382094	1.584350
H	3.182859	4.000382	-0.080273
O	5.208084	-0.190825	-1.307787
N	6.209421	0.693347	1.280865
N	8.261971	0.683791	0.332032
C	6.948819	0.458952	0.161352
C	7.106080	1.088210	2.210102
C	8.365769	1.079053	1.616948
C	6.392377	0.019385	-1.090251
H	6.801477	1.351030	3.210344
H	9.314362	1.337225	2.063733
H	7.152866	-0.119411	-1.882732

Zn(NO₃)(THF)₂(ICA)

Zn	3.589244	0.522341	2.160598
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O	3.746844	-1.163313	0.875008
O	4.154191	-1.386531	2.983515
N	4.098886	-1.939850	1.833489
O	4.376414	-3.100949	1.654025
O	5.704835	1.027242	1.856375
C	6.632764	0.630185	2.887789
C	7.345002	-0.615576	2.349180
C	7.115678	-0.557632	0.817299
C	6.357034	0.751770	0.599650
H	6.060656	0.453538	3.794799
H	7.330238	1.457276	3.053772
H	8.402829	-0.601712	2.609021
H	6.906183	-1.517568	2.769866
H	8.049958	-0.570745	0.257055
H	6.516009	-1.402976	0.485821
H	5.584335	0.700757	-0.161613
H	7.035036	1.582895	0.380208
O	3.204817	1.698710	0.398731
C	2.044715	1.363106	-0.398517
C	0.988650	2.428418	-0.066115
C	1.773465	3.537945	0.676942
C	3.232768	3.135793	0.492945
H	1.755000	0.349844	-0.137816
H	2.340940	1.397644	-1.450022
H	0.518940	2.802561	-0.975095
H	0.207631	2.013364	0.567248
H	1.574258	4.531872	0.278162
H	1.521738	3.545206	1.736348
H	3.880299	3.398914	1.324744
H	3.652328	3.532249	-0.437304
O	1.415708	0.275404	2.519568
N	1.796784	2.853385	4.984409
N	3.327721	1.890984	3.611326
C	2.031143	1.929161	4.038442
C	2.993091	3.431693	5.171164
C	3.946041	2.841413	4.327232



C	1.091907	1.047813	3.438224
H	3.140698	4.229171	5.883097
H	4.997137	3.055901	4.216581
H	0.057836	1.073158	3.801670





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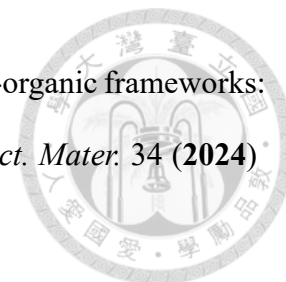
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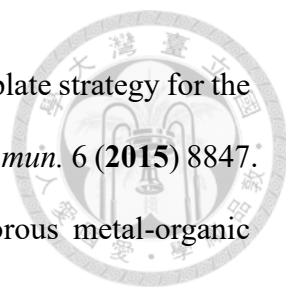
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