

Proton Conduction in Zirconium-Based Metal–Organic Frameworks for Advanced Applications

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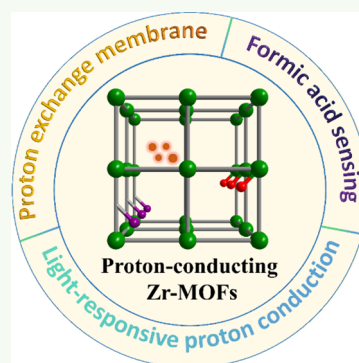
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ABSTRACT: Zirconium-based metal–organic frameworks (Zr-MOFs) have emerged as a promising class of crystalline porous materials, attracting significant interest in the field of proton conduction due to their exceptional chemical stability, structural flexibility, and functional tunability. Notably, proton-conducting Zr-MOFs show immense potential for diverse advanced technological applications. In this Spotlight on Applications paper, we provide an overview of proton-conducting Zr-MOFs and spotlight the recent progress of their utilization as proton exchange membranes in proton exchange membrane fuel cells (PEMFCs), light-responsive systems for proton pumps, and chemical sensors for formic acid detection. Furthermore, we also discussed the challenges, future prospects, and opportunities for promoting the application of proton-conducting Zr-MOFs.



KEYWORDS: Zr-MOFs, proton conduction, proton-exchange membrane, proton pumps, chemical sensor

1. INTRODUCTION

Proton conduction is a fundamental natural phenomenon, playing a critical role in various biochemical processes.^{1–5} Notable examples include proton transport across the inner mitochondrial membrane⁶ or chloroplast thylakoid membrane via ATP synthase,⁷ and the proton-pumping mechanism of bacteriorhodopsin in halobacteria.⁸ Beyond biological systems, solid-state proton-conducting materials have been developed to harness proton transport for numerous technological applications, such as fuel cells,^{9–11} sensors,^{12–14} electrolysis cells,¹⁵ and electrochromic displays.¹⁶ In these technologies, proton conductors function as solid electrolytes, selectively facilitating proton transport.

Conventional proton-conducting materials, including organic polymers,^{17,18} ceramic oxides,¹⁹ and solid acids,²⁰ have been extensively studied to elucidate their conduction mechanisms and optimize their performance for practical applications in electrochemical devices. Among them, Nafion is the most common and commercially available proton-conducting polymers. It consists of hydrophobic perfluorinated polyethylene backbones with pendant side chains terminating in hydrophilic sulfonic acid groups, conferring excellent structural integrity and hydrated proton conduction. Nafion exhibits proton conductivities of 10^{-1} – 10^{-2} S·cm⁻¹ at moderate temperatures (60–80 °C) and high relative humidity (98% RH).^{21–24} Despite their widespread use, Nafion faces significant limitations, including high production costs, environmentally hazardous manufacturing processes, and low

thermal stability.^{25,26} Its proton conductivity heavily depends on water molecules, which act as proton carriers, resulting in a sharp decline in conductivity at temperatures above 80 °C.^{27,28} Consequently, the search for alternative proton-conducting materials has gained significant attention from researchers in chemistry, physics, and materials science, driven by the growing demand for efficient and cost-effective solutions in electrochemical devices.

2. PROTON-CONDUCTING ZR-MOFS

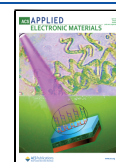
During the past decade, crystalline porous materials such as metal–organic frameworks (MOFs), covalent-organic frameworks (COFs), and hydrogen-bonded organic frameworks (HOFs) have been extensively studied for their potential as proton-conducting materials. Their well-defined crystalline structures enable direct observation of proton transport pathways and a deeper understanding of the associated mechanisms, shedding light on structure–function relationships. Among these, MOFs represent a versatile class of crystalline porous materials formed through the self-assembly

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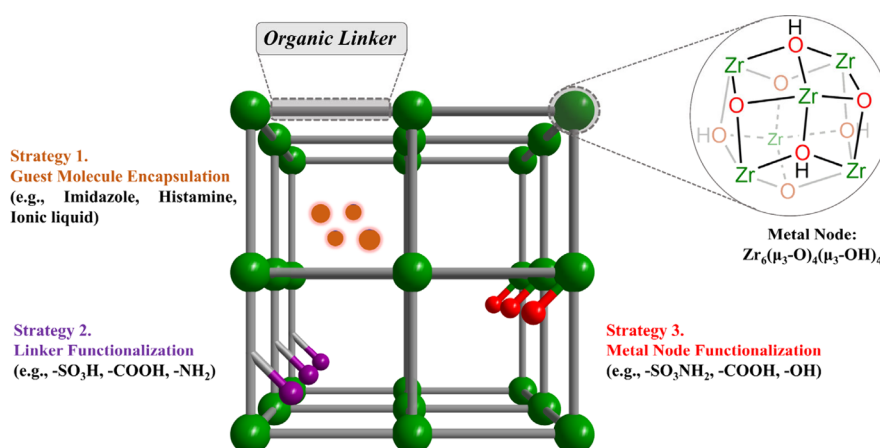


Figure 1. Schematic illustration of strategies for designing Zr-MOFs with proton conduction.

Table 1. Summary of Zr-MOF-Based Proton Conductors

MOFs	Conditions	σ (S cm ⁻¹)	Ref
UiO-66	30 °C, 97% RH	7.54×10^{-6}	63
UiO-66-NH ₂	30 °C, 97% RH	1.4×10^{-5}	63
UiO-66-SO ₃ H	30 °C, 97% RH	3.4×10^{-3}	63
UiO-66-2COOH	30 °C, 97% RH	1.0×10^{-3}	63
UiO-66(SH) ₂	80 °C, 90% RH	2.25×10^{-5}	64
UiO-66(SO ₃ H) ₂	80 °C, 90% RH	8.4×10^{-2}	64
UiO-66-defects	65 °C, 95% RH	6.93×10^{-3}	65
UiO-66-AS	80 °C, 98% RH	1.7×10^{-4}	66
IM-UiO-66-AS	80 °C, 98% RH	1.54×10^{-1}	66
PSM 1	80 °C, 95% RH	1.64×10^{-1}	42
PSM 2	80 °C, 95% RH	4.66×10^{-3}	42
Im@UiO-67	120 °C	1.44×10^{-3}	67
IL@UiO-67	200 °C	1.67×10^{-3}	68
MOF-801	25 °C, 98% RH	1.88×10^{-3}	69
MIP-202(Zr)	90 °C, 95% RH	1.1×10^{-2}	70
MOF-802	15 °C, 98% RH	1.05×10^{-2}	71
Im@MOF-802-S	15 °C, 98% RH	1.58×10^{-2}	71
MOF-808	42 °C, 99% RH	7.58×10^{-3}	72
Im@MOF-808	65 °C, 98% RH	3.45×10^{-2}	38
IL@UiO-66	70 °C, 98% RH	1.42×10^{-1}	73
IL@MOF-808	70 °C, 98% RH	7.01×10^{-1}	73
MOF-808-IL	60 °C, 100% RH	1.28×10^{-1}	74
(Me ₂ NH ₂) ₄ [Zr ₆ (SO ₄) ₆ (μ ₃ -O) ₃ (HTHAM) ₃ (CH ₃ O) ₄](DMF)·H ₂ O	70 °C, 98% RH	1.71×10^{-1}	75
[Zr ₁₈ (SO ₄) ₁₃ (O/OH/H ₂ O) ₅₆].xH ₂ O	70 °C, 98% RH	2.01×10^{-2}	75
Zr ₇₀ (SO ₄) ₅₈ (O/OH) ₁₄₆ .x(H ₂ O)·Mg(H ₂ O) ₆]	70 °C, 98% RH	3.73×10^{-2}	75
60-UiO-66-1.8	100 °C, 98% RH	3×10^{-2}	76
DUT-67(Zr)	100 °C, 98% RH	2.98×10^{-3}	77
ZrP-3	90 °C, 95% RH	1.91×10^{-2}	78
VNU-17	70 °C, 98% RH	6.65×10^{-6}	79
HIm ₁₁ CVNU-17	70 °C, 85% RH	5.93×10^{-3}	79
VNU-23	70 °C, 90% RH	2.5×10^{-5}	80
His _{8.2} CVNU-23	95 °C, 85% RH	1.79×10^{-2}	80
Zr ₆ O ₄ (OH) ₈ L _{4.2} .xH ₂ O	65 °C, 95% RH	1.93×10^{-3}	58
AcOH@Zr ₆ O ₄ (OH) ₈ L ₄ .xH ₂ O	65 °C, 95% RH	2.4×10^{-3}	58
SA@Zr ₆ O ₄ (OH) ₈ L ₄ .xH ₂ O	65 °C, 95% RH	5.62×10^{-3}	58
H ₂ SO ₄ @Zr ₆ O ₄ (OH) ₈ L _{3.8} .xH ₂ O	65 °C, 95% RH	3.46×10^{-3}	58
MOF-808-IMDC	80 °C, 98% RH	1.11×10^{-2}	81
10HSA@MOF-808-(bSA) ₂	85 °C, 98% RH	2.47×10^{-1}	82
MOF-808-4SA-150	60 °C, 95% RH	7.89×10^{-2}	83
LiCl@UiO-66-F ₂ (SO ₃ H) ₂	90 °C, 90% RH	2.86	84

of metal ions or clusters with organic linkers. Their exceptional structural characteristics, including high crystallinity, porosity,

and tunable functionality, make them promising candidates for proton conduction.^{29–35} The pores and channels of MOFs can

encapsulate guest proton carriers to enhance proton transport.³⁶ Alternatively, functionalizing the pore surfaces with specific groups can significantly boost proton conductivity.^{37,38} The proton transfer process in MOFs is generally recognized to follow two primary mechanisms: the Grotthuss mechanism and the vehicle mechanism.^{39–41} The Grotthuss mechanism involves a rapid proton-hopping process within an extended hydrogen-bonding network formed within the framework of MOFs, enabling efficient proton transport. In contrast, the vehicle mechanism relies on the diffusion of protonic species through the channels or pores of the MOFs. Notably, some MOF-based proton conductors achieved proton conductivities comparable to commercial Nafion.^{42,43} Despite these advantages, MOFs face significant challenges, particularly their limited chemical stability under high humidity or acidic conditions.^{44,45}

Among all MOFs, zirconium-based MOFs (Zr-MOFs) have garnered considerable attention due to their exceptional stability.^{46–49} These materials feature $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ clusters connected by multitopic carboxylate linkers.^{50,51} Their superior chemical stability across a broad pH range and remarkable thermal robustness stem from the strong Zr(IV)–O coordination bonds within the clusters and between the nodes and carboxylate linkers.⁵¹ Over the past decade, Zr-MOFs have been extensively explored in applications such as catalysis, molecular adsorption and separation, fluorescence sensing, drug delivery, and as porous carriers.^{52–57} Additionally, both experimental and computational studies have demonstrated that the –OH groups on the $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ clusters in Zr-MOFs possess low pK_a values,⁵⁸ allowing them to ionize readily and generate protons as charge carriers. This intrinsic property significantly enhances proton conductivity, making Zr-MOFs highly attractive for real-world applications in proton-conducting materials. As a result, Zr-MOFs have garnered considerable research interest in the field of proton conduction,^{59–62} with ongoing efforts focused on optimizing their structural design and functionalization to further improve their performance in practical applications. To enhance the proton conductivity of Zr-MOFs, researchers have employed three primary strategies (Figure 1): (1) Guest Encapsulation: Incorporating guest molecules like imidazole, histamine, or ionic liquids as proton carriers within the Zr-MOF pores. (2) Linker Functionalization: Integrating acidic functional groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$, or $-\text{NH}_2$ into the Zr-MOF framework via linker modification. (3) Node Functionalization: Functionalizing $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ clusters with moieties such as formate, sulfamate, or hydroxyl groups introduced during synthesis or post-synthetic treatment. These approaches have led to the development of numerous Zr-MOF-based proton conductors with impressive performance. A summary of representative examples is provided in Table 1, showing their potential for advancing proton-conducting materials.

3. APPLICATIONS

3.1. Proton-Exchange Membrane Based on Zr-MOFs.

Proton exchange membrane fuel cells (PEMFCs) are advanced electrochemical devices that efficiently convert chemical energy into electrical energy with minimal environmental impact.^{85–87} Their development is crucial for addressing global energy and environmental challenges. As the demand for clean, sustainable energy sources increases, PEMFCs stand out for their high energy conversion efficiency, zero pollutant emissions, and

versatility across diverse applications.^{88,89} Central to PEMFC technology is the proton exchange membrane—the design and synthesis of a high-performance proton exchange membrane is critical to achieving optimal performance of PEMFCs.^{90–93} To this date, Zr-MOFs have been extensively exploited for proton conduction,^{94–96} however, Zr-MOFs are typically synthesized in powder form, which presents significant challenges for their direct application as proton exchange membranes in PEMFCs due to their poor processability.^{97,98} Unlike conventional polymeric proton conductors, which can be readily fabricated into flexible and mechanically stable membranes, Zr-MOF powders lack the inherent mechanical integrity required for standalone membrane formation. As a result, they are not directly suitable for application in PEMFCs. The poor processability of Zr-MOFs in their powdered form remains a major barrier to their practical use in these fuel cell systems.^{17,99} To solve this problem, Zr-MOF powders have been fabricated into composite membranes, which is considered a significant step toward their practical application in electrochemical devices.^{66,69,100–104}

In 2017, we pioneered using MOF-808 for proton conduction, presenting the first example of proton-exchange membranes derived from this material.⁷² MOF-808, a Zr-MOF composed of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes connected by benzene tricarboxylate (BTC) linkers, forms a three-dimensional porous framework (Figure 2a). Under high relative humidity (98% RH), MOF-808 exhibited excellent room-temperature proton conductivity of $2.14 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, increasing to $7.58 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 315 K. This performance is attributed to the ionization of terminal –COOH groups, which generate protons that migrate through hydrogen-bonding networks formed by adsorbed water molecules, –COOH,

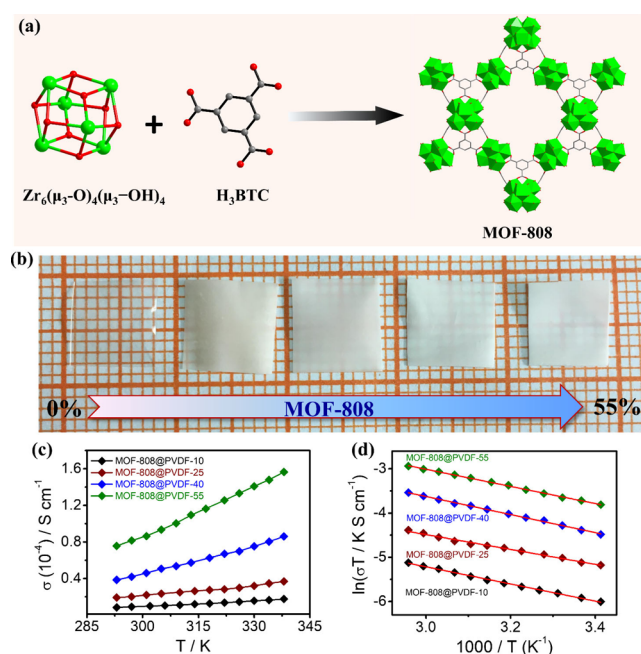


Figure 2. (a) Schematic illustrating the construction of MOF-808. (b) Optical images of the pure PVDF membrane and MOF-808@PVDF composite membranes. Reprinted with permission from ref 72. Copyright 2017 American Chemical Society. (c) Temperature-dependent proton conductivity and (d) the corresponding Arrhenius plots for MOF-808@PVDF composite membranes. Reprinted with permission from ref 72. Copyright 2017 American Chemical Society.

and μ_3 -OH groups. To enhance processability, we developed a series of composite membranes by incorporating MOF-808 microparticles into a poly(vinylidene fluoride) (PVDF) matrix. PVDF was selected for its excellent chemical and thermal stability, mechanical strength, and ease of membrane fabrication. MOF-808 particles were embedded into the PVDF matrix using a slurry casting method to create mixed-matrix membranes (MOF-808@PVDF-X, where X represents the mass percentage of MOF-808) (Figure 2b). These composite membranes combined the mechanical flexibility and durability of PVDF with the high proton conductivity of MOF-808. Proton conductivity tests revealed that the conductivity increased with both temperature and MOF-808 content. Among the samples, MOF-808@PVDF-55 demonstrated the highest performance, achieving proton conductivities of $7.55 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 293 K and $1.56 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 338 K (Figure 2c and 2d), making it suitable for PEMFC applications.

We further examined the proton-conducting properties of MOF-801, another Zr-MOF composed of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes and fumarate linkers (Figure 3a).⁶⁹ MOF-801

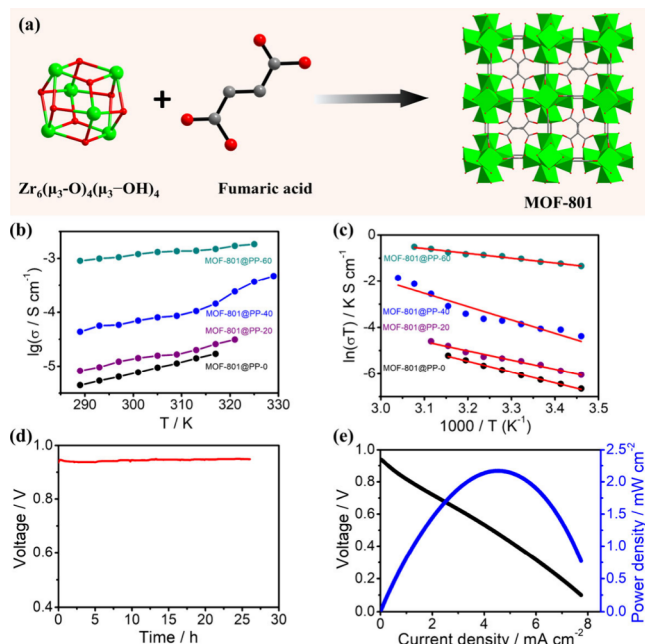


Figure 3. (a) Schematic illustrating the construction of MOF-801. (b) Temperature-dependent proton conductivity and (c) the corresponding Arrhenius plots for MOF-801@PP composite membranes. Reprinted with permission from ref 69. Copyright 2018 American Chemical Society. (d) The plot of open-circuit voltage versus time. (e) Polarization and power density curves of PEMFC prototype fabricated with MOF-801@PP-60 at 303 K and 100% RH. Reprinted with permission from ref 69. Copyright 2018 American Chemical Society.

exhibited excellent proton conductivity, reaching $1.19 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 289 K and 98% RH, which increased further at higher temperatures, achieving $4.16 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 334 K. The material also demonstrated exceptional chemical and water stability, retaining its structural integrity after exposure to boiling water, hydrochloric acid, and sodium hydroxide solutions. Building on these properties, we fabricated mixed-matrix membranes by combining MOF-801 microcrystals with a blend of poly(vinylpyrrolidone) (PVP) and PVDF. PVP, a

hydrophilic polymer, enhances the water-assisted proton transport within the composite membrane. Among these membranes, MOF-801@PP-60, with a 60% mass fraction of MOF-801, showed the highest proton conductivity of $1.84 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 325 K and 98% RH (Figure 3b and 3c). When integrated into a PEMFC prototype, MOF-801@PP-60 delivered an open-circuit voltage of 0.95 V, a maximum power density of $2.2 \text{ mW}\cdot\text{cm}^{-2}$ at $4.53 \text{ mA}\cdot\text{cm}^{-2}$, and demonstrated long-term stability (Figure 3d and 3e). These findings highlight the potential of Zr-MOFs as high-performance proton conductors for PEMFCs, providing new opportunities to advance clean energy technologies.

3.2. Light-Responsive Proton Conduction of Zr-MOFs. Biological proton pumps are integral membrane proteins that transport protons across membranes, creating a concentration gradient essential for various physiological processes.^{105,106} Inspired by these natural systems, artificial stimuli-responsive proton-conducting materials have been developed to replicate their functionality.^{107–109} These materials hold promise for applications in biomimetic processes such as ATP synthesis and power generation, as well as in bioelectronics and smart devices.^{109–113} With growing interest in MOFs for proton conduction, stimuli-responsive proton-conducting MOFs have emerged as a focal point of research.³⁸ In 2017, Kitagawa et al. introduced the first optically switchable proton-conducting MOF by incorporating the photoacid molecule pyranine into melted $[\text{Zn}(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2](\text{ImH}_2)_2$.¹¹⁴ Subsequent efforts proposed grafting photoactive groups, such as azobenzene and spiropyran, onto MOF linkers to create light-responsive proton-conducting materials. Despite the versatility of Zr-MOFs as proton conductors, their light-responsive applications have received limited attention.

Recently, we demonstrated the first example of light-responsive proton conduction in Zr-MOFs.¹¹⁵ Using a solvent-assisted ligand incorporation method, we substituted terminal formates on the $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes of MOF-808 with photoactive azobenzene-4,4'-dicarboxylic acid (AZOA), yielding MOF-808-AZOA (Figure 4a). The trans–cis isomerization of AZOA in MOF-808-AZOA is triggered by 365 nm UV light irradiation. As illustrated in Figure 4b, exposure to UV light causes the absorption peak at 340 nm, corresponding to the π – π^* transition, to weaken rapidly within 50 s, while the absorption peak at 450 nm, associated with the n – π^* transition, intensifies and undergoes a blue shift. In the absence of irradiation, AZOA predominantly exists in its trans-isomer form, and MOF-808-AZOA exhibits an ohmic resistance of approximately 15 k Ω . Under UV light, the trans–cis isomerization of AZOA leads to a significant increase in resistance, reaching an enhancement of about 200 times after 100 s, indicating a pronounced change in the proton conductivity of MOF-808-AZOA. When UV light is turned off, the AZOA gradually reverts to its trans-isomer state, accompanied by a decrease in resistance. Within 8 min, the resistance returns to its original value. During repeated cycles of UV light “ON” and “OFF”, MOF-808-AZOA demonstrates highly reversible and durable switchable resistance behavior (Figure 4c).

The isomerism of the AZOA ligand plays a crucial role in modulating the light-responsive proton conduction properties of Zr-MOFs. Structural simulations showed a clear difference in proton conductivity between the trans- and cis-configurations of AZOA. In the trans-configuration, the hydrogen

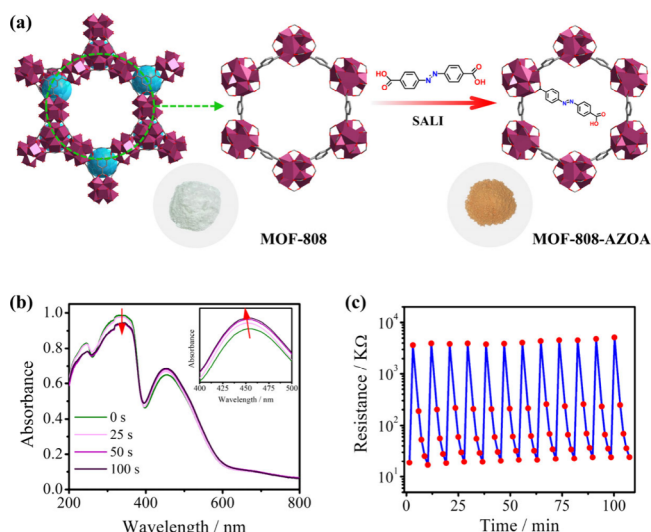


Figure 4. (a) Schematic illustration of the preparation of MOF-808-AZOA via solvent-assisted ligand incorporation (SALI). The inset shows the optical photographs of MOF-808 and MOF-808-AZOA. Reprinted with permission from ref 115. Copyright 2024 American Chemical Society. (b) Cycling impedance response of MOF-808-AZOA with and without 365 nm UV light irradiation. Reprinted with permission from ref 115. Copyright 2024 American Chemical Society. (c) Switchable resistance of MOF-808-AZOA with and without 365 nm UV light irradiation. Reprinted with permission from ref 115. Copyright 2024 American Chemical Society.

atom of the $-\text{COOH}$ group and the oxygen atom of the terminal formates are 3.51 Å apart (Figure 5a). This distance

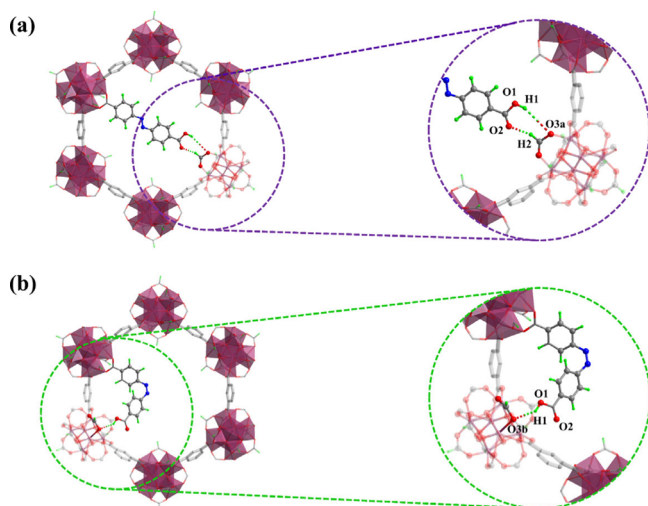


Figure 5. Molecular simulations on a single large pore structure of MOF-808 bearing an AZOA group in either the trans- (a) or cis- (b) configuration. The atoms are colored in plum (Zr), gray (C), red (O), blue (N), and green (H). Reprinted with permission from ref 115. Copyright 2024 American Chemical Society.

exceeds the combined van der Waals radii, preventing direct interaction between these groups. This separation also allows the hydrogen atom to ionize and transfer protons with the help of guest water molecules, promoting high proton conductivity. In contrast, the UV-induced cis-configuration brings the hydrogen and oxygen atoms into closer proximity (2.33 Å, Figure 5b), forming strong charge-assisted hydrogen bonds.

These bonds restrict the dissociation of the hydrogen atom from the $-\text{COOH}$ group, suppressing proton conduction of the MOF. Therefore, the isomerization from the trans- to the cis-configuration of the AZOA ligand directly affects the proton conduction of the MOF. The trans-configuration allows proton dissociation and transfer, while the cis-configuration forms restrictive hydrogen bonds that impede proton movement. This example highlights the crucial role of ligand isomerism in tuning proton conductivity, offering potential for light-responsive applications where proton conduction can be controlled by switching ligand configurations.

Notably, by functionalizing the cluster nodes of MOF-808, the resulting MOF-808-AZOA exhibits a significantly shorter response time and a higher ON/OFF ratio in light-responsive proton conduction compared to MOFs functionalized through organic linkers, such as $\text{Cu}_2(\text{F}_2\text{AzoBDC})_2(\text{dabco})^{111}$ and $\text{Cu}_2(\text{SP-BPDC})_2(\text{dabco})^{116}$. Furthermore, while MOF films incorporating photoactive species have demonstrated outstanding light-responsive proton conduction, their fabrication has been limited to Zn- or Cu-based MOFs due to the constraints imposed by the metal-hydroxide nanostrand confinement process.^{117–119} In this context, the Zr-MOF cluster-node functionalization strategy introduced in our study presents a promising alternative. This approach not only could expand the applicability of light-responsive proton conduction to a broader range of MOFs but also could enhance their photoswitchable performance, overcoming the limitations of previously reported methods. However, the field is still in its early stages, facing challenges in achieving fast response times and high ON/OFF ratios. Developing effective strategies to expand the range of light-responsive proton-conducting Zr-MOFs and improve their performance represents a critical direction for future research.

3.3. Formic Acid Sensing of Proton-Conducting Zr-MOFs. Formic acid, a widely used organic compound in medicine, pesticides, rubber, and tannery industries, poses significant health and safety risks due to its high volatility and strong corrosivity.^{120–124} The ease with which formic acid transitions into its gaseous form can lead to the corrosion of production equipment and pipelines, creating potential hazards in industrial environments.^{125–128} Furthermore, human exposure to formic acid vapor can cause severe health issues, including dermatosis, bronchitis, chemical pneumonitis, and even fatality in extreme cases.^{124,129,130} Consequently, the development of highly efficient sensors for formic acid vapor detection is of paramount importance, enabling effective air quality monitoring and timely detection of leaks to ensure both environmental and occupational safety.^{120,131–134} MOFs have garnered significant attention as ideal sensing materials in electrochemical sensors due to their exceptional porosity, large surface area, and structural tunability/diversity.^{135–140} These properties have enabled the detection of various gas molecules using MOFs, including ammonia,¹⁴¹ nitrogen monoxide,¹⁴² hydrogen sulfide,¹⁴³ and formaldehyde.¹⁴⁴ However, the development of MOF-based sensors for formic acid detection remains a significant challenge, primarily due to the chemical instability of most MOFs upon exposure to formic acid.^{145,146} This instability leads to the collapse of their highly ordered crystal structures,¹³⁴ rendering them ineffective for such applications.

For the first time, we reported using crystalline thin films of proton-conducting Zr-MOFs for formic acid detection. MOF-802 was chosen for this application due to its intrinsic proton

conduction and exceptional chemical stability.¹⁴⁶ MOF-802, comprising $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ cluster nodes and 1H-pyrazole-3,5-dicarboxylate (PZDC) linkers, maintains stability under harsh conditions, including in boiling water and acidic or basic aqueous environments. A crystalline thin film of MOF-802 was synthesized on a glass substrate using a solvothermal method, resulting in a densely packed and uniform structure. An interdigitated electrode was fabricated on the film to construct a custom sensor, which demonstrated excellent impedance response to formic acid (Figure 6a). The response-

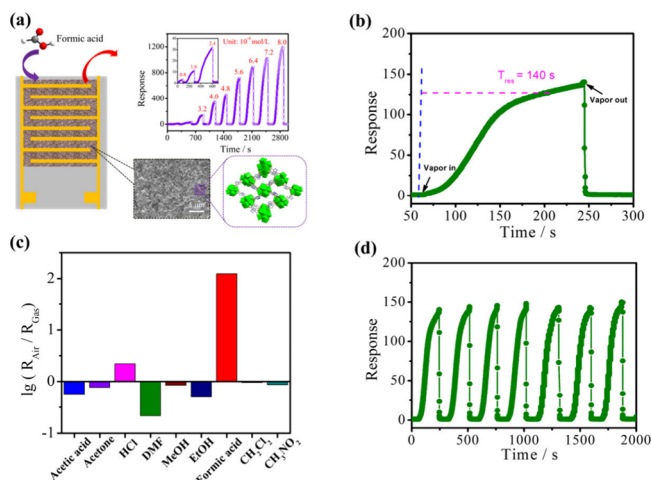


Figure 6. (a) Schematic illustration of MOF-802 thin film sensor for formic acid sensing. Reprinted with permission from ref 146. Copyright 2021 American Chemical Society. (b) Response–recovery time curve of MOF-802 thin film sensor toward 3.2×10^{-4} mol/L formic acid vapor. Reprinted with permission from ref 146. Copyright 2021 American Chemical Society. (c) Response of MOF-802 thin film sensor upon exposure to different chemical vapors. Reprinted with permission from ref 146. Copyright 2021 American Chemical Society. (d) Reproducibility cycles of MOF-802 thin film sensor toward 3.2×10^{-4} mol/L formic acid vapor. Reprinted with permission from ref 146. Copyright 2021 American Chemical Society.

recovery curve of the sensor for formic acid vapor at concentrations ranging from 8.0×10^{-5} to 8.0×10^{-4} mol/L shows a stepwise increase in response value with concentration. At 3.2×10^{-4} mol/L, the sensor exhibited a high response value of ~ 138 , a short response time of ~ 140 s, and achieved 90% of the maximum response (Figure 6b).

In MOF-802, besides the proton sources from $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes, two accessible Zr sites in each node are occupied by $-\text{COOH}$ groups derived from formic acid used during synthesis. These $-\text{COOH}$ groups also contribute to proton conduction. Upon exposure to formic acid vapor, molecules first adsorb onto the MOF-802 thin-film surface, then gradually permeate into the crystal channels. Permeation is slower than surface adsorption, as indicated by the rapid decrease in response after vapor removal. Thus, impedance changes mainly result from surface modifications. Adsorbed formic acid molecules promote proton transfer by forming hydrogen-bonding networks among their $-\text{COOH}$ groups, the pyrazole nitrogen atoms of PZDC linkers, the $-\text{OH}$ groups of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes, and adsorbed water molecules. Higher vapor concentrations could increase adsorption, raising proton concentration and forming denser, more continuous hydrogen-bonding networks, significantly improving proton conductivity.

It is worth noting that MOF-802 thin-film sensors utilize different mechanisms from conventional metal-oxide semiconductor sensors for formic acid detection. While the latter relies on resistance changes due to shifts in the semiconductor's energy gap upon formic acid adsorption,^{120,147} MOF-802 detects formic acid via its changes in proton conductivity. The sensing mechanism of the MOF-802 thin-film sensor also differs fundamentally from that of compacted pellets or interdigital electrodes composed of powdered crystalline MOFs used for chemical vapor detection. In MOF powder-based sensors, the response primarily stems from variations in grain-boundary resistance caused by the loose contact between crystalline grains. Several factors, such as the fabrication process of compacted pellets or interdigital electrodes and the size of crystalline grains, can significantly influence grain-boundary resistance. As a result, this type of impedance sensor often suffers from lower long-term stability, durability, and reproducibility.

On the other hand, the sensor based on MOF-802 demonstrated excellent repeatability, as evidenced by highly consistent response–recovery curves across test cycles and minimal degradation in response value and time during successive tests (Figure 6d). Furthermore, after four months of storage under ambient conditions, the sensor maintained its performance, confirming its long-term stability and reproducibility. In addition, the MOF-802-based sensor exhibited high selectivity for formic acid detection. As illustrated in Figure 6c, the sensor showed a slight response to HCl vapor, which was substantially lower than that for formic acid. In addition, the sensor showed negligible or opposite responses to other chemical vapors, including AcOH, MeOH, EtOH, Me_2CO , DMF, MeNO_2 , and CH_2Cl_2 , demonstrating its exceptional specificity for formic acid.

The potential of proton-conducting Zr-MOFs for highly efficient formic acid detection was further validated in our later study featuring MOF-801.¹⁴⁸ This Zr-MOF, composed of $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ nodes and fumarate linkers, exhibits intrinsic proton conductivity and excellent chemical stability. The structural differences between MOF-801 and MOF-802 have a significant impact on their sensing performance for formic acid detection. MOF-801 possesses a more intricate pore architecture, featuring one octahedral cavity with a diameter of 7.4 Å and two crystallographically distinct tetrahedral cavities measuring 5.6 Å and 4.8 Å in diameter, respectively. This hierarchical pore structure results in a highly porous framework with a larger internal surface area, providing more active sites for molecular interactions and adsorption. In contrast, MOF-802 has a simpler pore structure, comprising only a single type of cavity with a uniform diameter of 5.6 Å, which inherently limits its porosity and available surface area for analyte adsorption. Due to its superior porosity and increased adsorption capacity, MOF-801 demonstrates significantly better sensing performance than MOF-802. The MOF-801 thin-film sensor exhibited outstanding sensitivity, selectivity, and durability for formic acid detection (Figures 7b and 7d), achieving a response magnitude of approximately 871 (Figure 7c), which was roughly six times higher than that of the MOF-802 thin-film sensor. This substantial difference can be attributed to the larger surface area of MOF-801 and more efficient molecular confinement, which facilitates stronger interactions with formic acid molecules. The hierarchical pore structure of MOF-801 may also enhance the diffusion and retention of formic acid analytes, further improving the

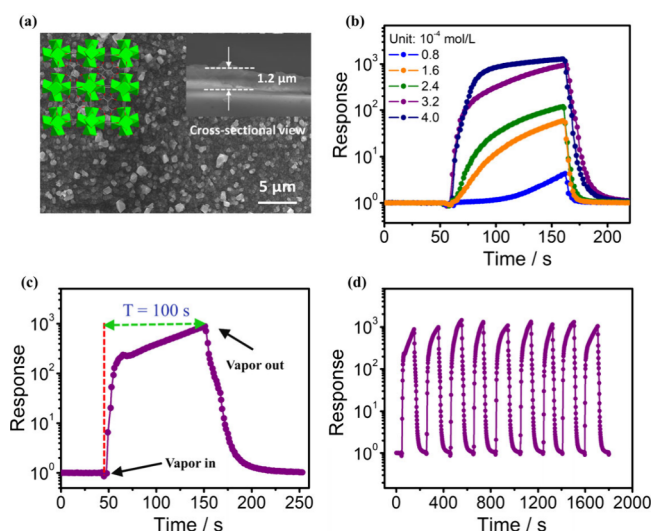


Figure 7. (a) SEM images of MOF-801 thin films. Reprinted with permission from ref 148. Copyright 2023 Elsevier. (b) Response of MOF-801 thin film sensor to formic acid with different concentrations. Reprinted with permission from ref 148. Copyright 2023 Elsevier. (c) Response–recovery time curve and (d) reproducibility cycles of MOF-801 thin film sensor to formic acid with a concentration of 3.2×10^{-4} mol/L. Reprinted with permission from ref 148. Copyright 2023 Elsevier.

sensor's response and stability. These findings highlight the crucial role of MOF topology in optimizing chemical sensing performance. Overall, these studies demonstrate the potential of proton-conducting Zr-MOF thin films as effective sensing materials for formic acid detection, offering promising opportunities for environmental and industrial applications.

4. CONCLUSIONS AND OUTLOOK

In conclusion, zirconium-based metal–organic frameworks (Zr-MOFs) have emerged as a promising platform for developing next-generation proton-conducting materials due to their exceptional chemical stability, structural versatility, and functional tunability. Through strategies such as node functionalization, guest encapsulation, and linker modification, the proton conductivity of Zr-MOFs has been significantly enhanced, achieving levels comparable to commercial materials like Nafion. More importantly, proton-conducting Zr-MOFs hold great promise for various advanced applications, including use as proton exchange membranes in PEMFCs, stimuli-responsive proton conduction for proton pumps, and chemical sensors for gas detection.

Despite the significant progress made in this field, several challenges must be addressed to unlock the full potential of proton-conducting Zr-MOFs in practical applications. (i) Most Zr-MOFs are synthesized via solvothermal reactions, which are time-consuming and environmentally unfriendly due to their reliance on organic solvents. Hydrothermal conditions usually require high temperatures and pressures, complicating scalable production. Developing convenient, low-cost, and environmentally sustainable synthesis methods is crucial for facilitating the practical application of Zr-MOFs. (ii) Zr-MOFs are typically produced in powder form, which limits their direct application as proton exchange membranes in PEMFCs due to their poor processability. A viable solution involves combining Zr-MOFs with polymeric binders to create composite membranes. The compatibility between Zr-MOFs and

polymers significantly impacts the membranes' proton conductivity and mechanical properties. This issue may be addressed through surface modification of Zr-MOFs with organic functional groups to enhance interfacial compatibility. (iii) Research on stimuli-responsive proton conduction in Zr-MOFs remains in its infancy and warrants greater attention. Incorporating diverse functional groups into Zr-MOFs could improve performance, while exploring additional external stimuli could expand the range of applications. These efforts could open new avenues for the development of multifunctional proton-conducting materials. (iv) Compared to bulk pellets or composite membranes, Zr-MOF thin films offer significant advantages, including reduced crystal defects and an increased density of binding sites, making them ideal for chemical gas sensing. Reliable techniques for fabricating high-quality Zr-MOF thin films are needed to advance this application. Additionally, computational and theoretical studies can provide deeper insights into the sensing mechanisms of proton-conducting Zr-MOFs, particularly their interaction with specific analyte molecules.

Addressing these challenges will not only enhance the performance of proton-conducting Zr-MOFs but also broaden their scope of applications, paving the way for their integration into real-world technologies. Continued interdisciplinary research combining material synthesis, computational modeling, and device engineering is essential for advancing Zr-MOFs-based proton-conducting materials and their impactful contributions across diverse technological domains.

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Notes

The authors declare no competing financial interest.

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