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AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Switched Proton Conduction in Metal–Organic Frameworks

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Cite This: *JACS Au* 2022, 2, 1043–1053 Read Online

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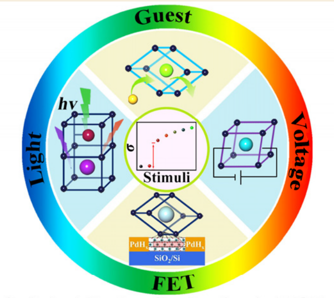
ABSTRACT: Stimuli-responsive materials can respond to external effects, and proton transport is widespread and plays a key role in living systems, making stimuli-responsive proton transport in artificial materials of particular interest to researchers due to its desirable application prospects. On the basis of the rapid growth of proton-conducting porous metal–organic frameworks (MOFs), switched proton-conducting MOFs have also begun to attract attention. MOFs have advantages in crystallinity, porosity, functionalization, and structural designability, and they can facilitate the fabrication of novel switchable proton conductors and promote an understanding of the comprehensive mechanisms. In this Perspective, we highlight the current progress in the rational design and fabrication of stimuli-responsive proton-conducting MOFs and their applications. The dynamic structural change of proton transfer pathways and the role of trigger molecules are discussed to elucidate the stimuli-responsive mechanisms. Subsequently, we also discuss the challenges and propose new research opportunities for further development.



Switched Proton Conduction in MOFs

KEYWORDS: *Metal–Organic Frameworks, Proton Conduction, Switch, Stimuli Responsive, Porous Materials*

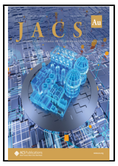
1. INTRODUCTION

From inspiration by the fact that all living organisms and soft matter are intrinsically responsive and adaptive upon external stimuli, the research on stimuli-responsive materials has elicited considerable interest in the interdisciplinary fields of materials science, chemistry, and others in the past few decades.[1−3] These so-called "smart materials" can adapt to various stimuli, such as electric field, solvent, light, heat, and stress, resulting in emerging applications in diverse fields such as biomedicine, biotechnologies, renewable energies, data storage, imaging and sensing, textiles, and smart coatings.[4−20] In particular, stimulus-induced proton (H^+) transport has aroused great attention,[21−24] stemming from the importance of proton transfer in living systems,[25−27] wherein electrical signals are communicated and processed via protonic currents.[28,29] The development of artificial stimuli-responsive proton conductors is intriguing not only in useful applications, such as drug delivery,[22,30,31] sensors,[32,33] memory,[34−36] and display devices,[37] but also in a better understanding of proton-transport paths.[34,38] The essential process to biomimic is to construct dynamic proton transport pathways with controllable stimulus triggers in response to different stimuli. However, progress has been relatively slow due to the lack of potential platforms for dynamic proton transport and a suitable matrix for the flexible and oriented functional sites as triggers.

As the largest type of crystalline porous materials, metal–organic frameworks (MOFs)/porous coordination polymers (PCPs) built from metal ions (clusters) and organic linkers by reticular chemistry have been deeply investigated over the last 20 years.[39−45] Since the first proton conductive MOF reported in 1979, $(HOC_2H_4)_2$dtoaCu,[46] continuous studies have been focused on improving the proton conduction of MOFs, accelerated by the potential application of conducting MOFs in proton exchange membrane fuel cells.[47−50] Despite the inherently poor proton conduction of MOFs, the strategy of loading protonic media molecules into pores to form hydrogen-bond networks acting as protonic transfer pathways has successfully induces a series of MOFs with high proton conductivity ($>10^{-3}$ S cm^{-1}) over a wide operating temperature.[51−57]

In comparison to traditional solid-state proton conductors, including solid acids,[58] ceramic oxides,[59−62] and polymers,[63,64] MOFs are qualified as candidates for stimuli-responsive materials because their high specific surface area, multifunctional pores, designable pore structures, and versatile framework topologies provide huge opportunities for realizing dynamic proton transport within the available spaces as well as loading different functional moieties onto backbones or inside pores working as triggers.[65−67] At the same time, the good crystallinity of MOFs allows an in-depth understanding of the dynamics of stimuli responsivity and the effect of triggers.[68−70] In recent years, proton-conducting MOFs with

Received: January 30, 2022
Revised: April 21, 2022
Accepted: April 21, 2022
Published: May 4, 2022



https://doi.org/10.1021/jacsau.2c00069
JACS Au 2022, 2, 1043−1053

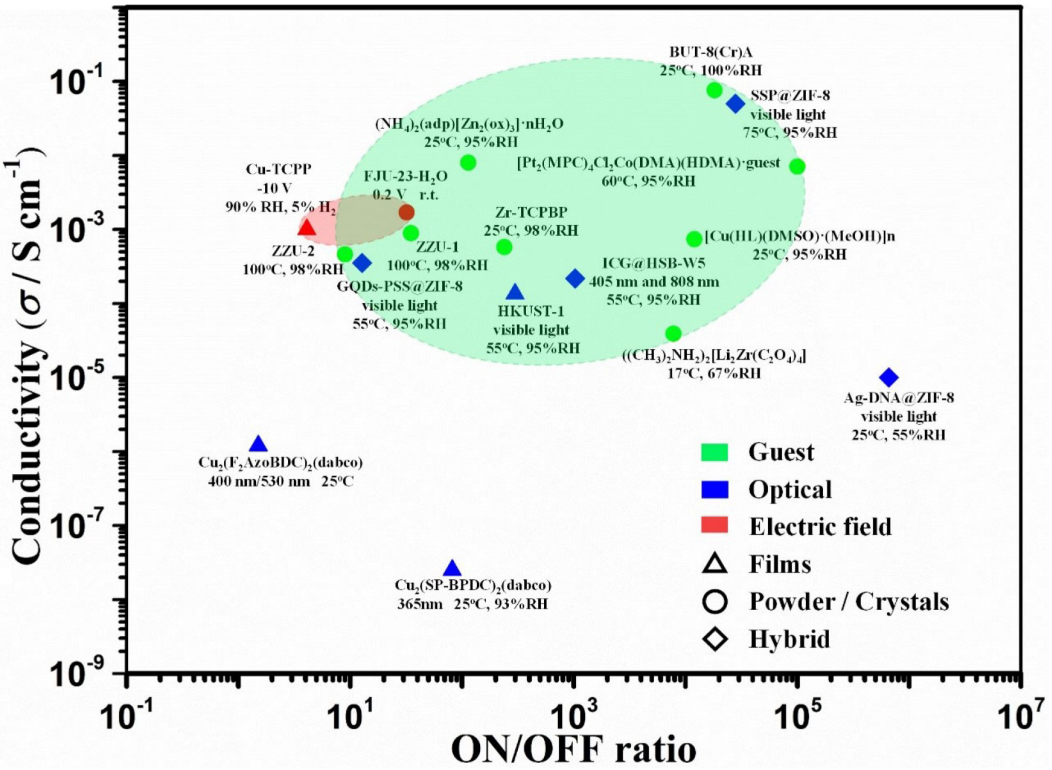


Figure 1. Comparison of proton conductivities and ON/OFF ratios of MOFs upon different stimuli.

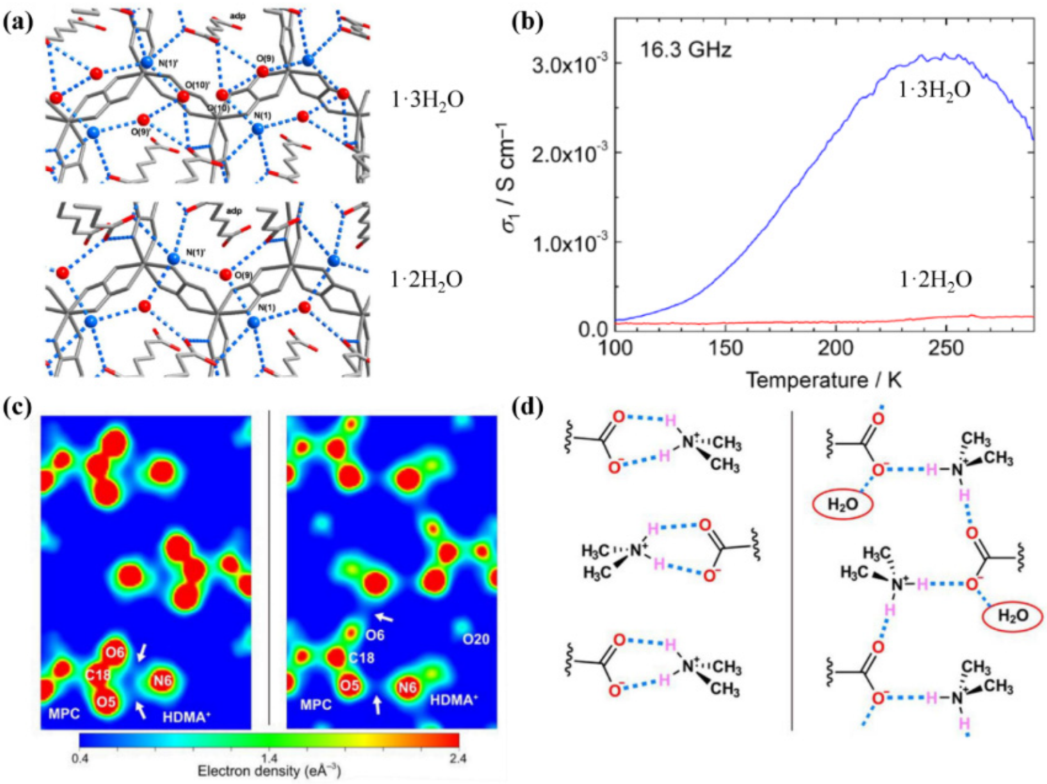


Figure 2. (a) Hydrogen-bonded frameworks in **1**·3H$_2$O (a) and **1**·2H$_2$O. (b) Temperature dependence of proton conductivity in a hydrated sample of **1**·3H$_2$O and a dehydrated sample of **1**·2H$_2$O. Permission from the American Chemical Society, copyright 2014. (c) Two-dimensional MEM charge density views sliced in the (400) plane. White arrows indicate potential hydrogen bonds. (d) Diagrammatic sketch of **1A** (left) and **1H** (right) in Pt$_2$(MPC)$_4$Cl$_2$Co(DMA)(HDMA)·guest.[88] Reused under Creative Commons CC BY-NC-ND 4.0 (visit https://creativecommons.org/licenses/by-nc-nd/4.0/). Copyright 2022 The Authors.

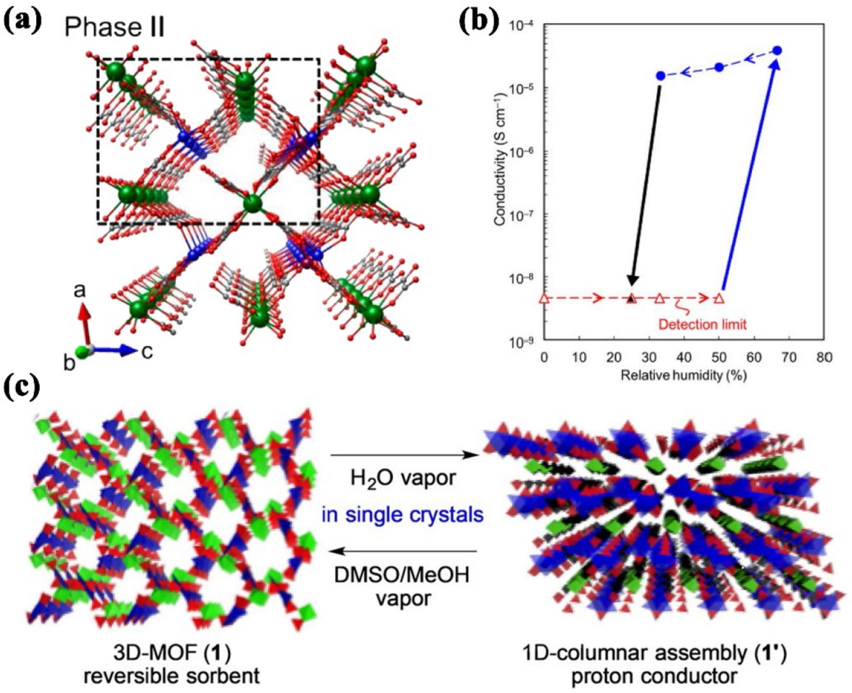


Figure 3. (a) Topotactic hydration of phase II in $((CH_3)_2NH_2)_2[Li_2Zr(C_2O_4)_4]$. (b) Humidity dependence of proton conductivity in $((CH_3)_2NH_2)_2[Li_2Zr(C_2O_4)_4]$ measured through single-crystal impedance at a temperature of 17 °C. The arrows display the relative humidity direction change(0%−67%−25%). Permission from the American Chemical Society, copyright 2015. (c) Reversible formation for the 3D MOF $[Cu(HL)(DMSO)\cdot(MeOH)]$ (left) and 1D $H_3L\cdot 0.5[Cu_2(OH)_4\cdot 6H_2O]\cdot 4H_2O$ (right). Permission from Wiley-VCH, copyright 2020.

switching behaviors have received more and more attention, which exhibit potential applications in smart devices, resistive switching devices, and field-effect transistors.[34,71,72] On the basis of the rapid growth of proton-conducting MOFs, studies on the switched proton conduction of MOFs have also entered the initial stage and a few examples have been reported. Nevertheless, it still remains a great challenge to design and synthesize MOFs with good stimulus responsiveness, i.e., high stimulus conductivity, fast response, high ON/OFF ratio, stable cycling capability, as well as understand the dynamics of proton transfer and the role of triggers.

In this Perspective, we highlight the progress in the design and fabrication of stimuli-responsive proton-conducting MOFs and their applications. We classify the switching behaviors by the different stimulus resources, including a guest, light, voltage, and electric field transistor (Figure 1). Considering that the proton transfer pathways fabricated by H-bonded networks play a crucial role in proton migration, we discuss the dynamic structural changes of the proton transfer pathways and the role of triggering molecules to clarify the stimuli-responsive mechanism. Challenges and new research opportunities for further development are also proposed. The loading of guest molecules, acting as media in MOF proton conductors, is a common strategy to improve the proton conductivities of MOFs,[73−78] which will not be discussed in this Perspective.

2. GUEST-CONTROLLING SWITCHABLE PROTON CONDUCTIVITY IN METAL−ORGANIC FRAMEWORKS

In terms of porous materials, guest molecules can not only work as media to tune the concentration of protons as well as to construct proton transport pathway, but also play an important role in the phase transformation of frameworks,[79,80] which thus can be used as triggers for switching proton conductivity. Guest adsorption/desorption, a one-step reaction, and guest exchange are the three main methods to capture guests as triggers into MOFs. In comparison to other media used in MOF proton conductors, such as nonvolatile acids (H_3PO_4,[53] H_2SO_4,[81,82] and CF_3SO_3H[83]) and heterocycles (histamine,[84] imidazole,[85] and triazole[86]), water molecule is the most suitable trigger because it has strong donor−acceptor ability and is easy to control remotely.

2.1. Guest-Induced Transformations of Hydrogen-Bonding Networks in Unchanged Frameworks

Since many MOFs can maintain backbone structures even in a humid environment, water molecules have been selected as triggers in some stable MOFs for a deep understanding of the reversible proton transfer pathways in pores. The first example of the MOF $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot nH_2O$ ($\mathbf{1}\cdot n H_2O$; adp = adipic acid, ox = oxalate, n = 0, 2, 3) was reported by Sadakiyo and Kitagawa in 2014,[87] which exhibited a reversible structural transformation from a dihydrate ($\mathbf{1}\cdot 2H_2O$) to a trihydrate ($\mathbf{1}\cdot 3H_2O$) phase during water adsorption/desorption processes. A negligible proton conduction was observed in the anhydrous MOF with a value of about 10^{-12} S cm^{-1} at room temperature. The proton conducting performance was increased from nearly 10^{-5} S cm^{-1} ($\mathbf{1}\cdot 2H_2O$) to about 10^{-3} S cm^{-1} ($\mathbf{1}\cdot 3H_2O$) under the conditions of 25 °C and 95% RH, which depends on the rearrangement of the hydrogen-bonded network, formed by H_2O molecules, ammonium ions, and carboxyl groups, under different humidity conditions (Figure 2a). It has been further confirmed by microwave conductivity measurements that the performance is triggered through water molecules (Figure 2b).

More recently, Otsubo and Kitagawa[88] reported the Pt dimer $Pt_2(MPC)_4Cl_2Co(DMA)(HDMA)\cdot$guest (DMA = dimethylamine, H_2MPC = 6-mercaptopyridine-3-carboxylic

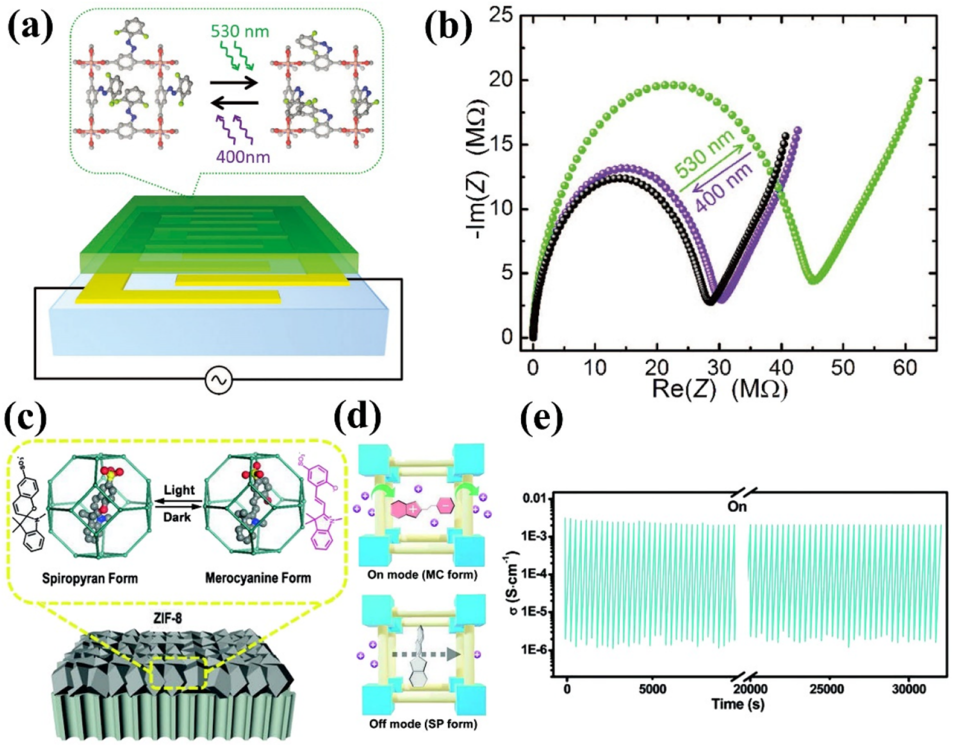


Figure 4. Photoswitchable guest@$Cu_2(F_2AzoBDC)_2(dabco)$ films: (a) illustration of films on an electrode substrate; (b) Nyquist plot for triazole@$Cu_2(F_2AzoBDC)_2(dabco)$. Color code: *trans* for the pristine sample (black circles), violet-light-stimulated sample (purple circles), and *cis* for the green-light-stimulated sample (green circles). Permission from Wiley-VCH, copyright 2018. Photoswitchable SSP@ZIF-8 films: (c) illustration of films on an electrode substrate; (d) side-group photoisomerization related switching proton conduction occurring in the dark (top) and upon visible light (bottom); (e) reversible proton conduction with the light ON/OFF. Permission from Wiley-VCH, copyright 2020.

acid), which reached a record proton conduction performance (2.2×10^{-2} S cm^{-1}) along the [010] direction under the conditions of 95% RH and 60 °C. Inspiringly, they used MEM charge density maps to successfully visualize different manners of H-bonding paths. As shown in Figure 2c, as the guest $HDMA^+$ is trapped by one carboxyl group in a pore, the hydrogen-bonding chain in dehydrated MOF is discontinuous, leading to the "off" state. Upon hydration, the framework backbones are almost the same, but the guest H_2O molecules have a significant effect on the position of $HDMA^+$ cations in the pore. The relocated $HDMA^+$ cations connect to the neighboring carboxyl groups to form a successive proton conduction network ("on" state) (Figure 2c,d), resulting in an ultrahigh on−off ratio of 10^5.

In addition to water molecules, the response to pH environment or solvent vapors is also attractive due to the potential of these materials for sensors. For examples, Gao et al. reported the pH-responsive MOF Zr-TCPBP, in which the proton conductivity and fluorescence characteristics of Zr-TCPBP simultaneously changed when the pH was changed. These changes are due to pH-changed cooperative protonation of the pyridyl sites.[89] Li's group observed the proton-conducting response to formic acid vapor in two 3D isostructural Ln(III) MOFs, ZZU-1 and ZZU-2.[90] They can distinguish formic acid vapor from other organic small-molecule vapors such as methanol, ethanol, acetone, toluene, acetic acid, etc. It may be concluded that only formic acid can form hydrogen bonds with H_2O and imidazole, ascribed to the large polarity (in comparison with hydrocarbons, alcohols, or ketones) and small volume (in comparison with acetic acid) of formic acid.

2.2. Guest-Induced Phase Transformations of Dynamic Frameworks

A single-crystal to single-crystal (SC-SC) transformation is always attractive in crystalline materials.[32,91,92] However, the switch of proton conduction in guest-induced SC-SC in MOFs has rarely been investigated, due to the lack of reversible frameworks as suitable platforms as well as the difficulty in realizing reversible proton transfer pathways with the change in framework structures.

Tominaka and Cheetham[91] reported the dense anhydrous MOF $((CH_3)_2NH_2)_2[Li_2Zr(C_2O_4)_4]$ (Figure 3a), phase-transforming to another dense phase structure, II, and further to the crystalline phase III upon exposure to humidity. Associated with an SC-SC transformation in phases II and III, a reversible response of proton conductivity of about 4 orders of magnitude (from $<10^{-9}$ to 3.9×10^{-5} S cm^{-1}) was observed at 17 °C (Figure 3b). It has been confirmed that the H_2O molecules coordinated to Li ions in the first step of the transformation are considered as proton sources, while the absorbed water molecules in the second step are proton carriers. Undoubtedly, the guest water molecules are triggers not only for the SC-SC transformation but also for the proton-conducting switch. Another interesting SC-SC transformation was observed in $[Cu(HL)(DMSO)\cdot(MeOH)]_n$ (H_3L = triphosphaazatriangulene) reported by Nakatsuka and co-workers.[92] As shown in Figure 3c, the high humidity induced a transformation from a 3D MOF into a 1D-columnar assembled framework, followed by an apparent proton-conducting switch from 5.9×10^{-8} S cm^{-1} at 55% RH to 7.4×10^{-4} S cm^{-1} at 96% RH. DMSO/MeOH vapor realized the reverse process. The authors claimed that the switching behaviors mainly arise from the robust interactions between guest molecules and hosting MOF.

MOFs with stable and structurally flexible frameworks have "self-adaption" capability and usually present a phase transformation upon a change in the guest, which facilitates the modification of pore structures and the proton transfer pathway.[93,94] Li and Chen[95] reported a unique proton-conducting switching behavior in a self-adapted MOF (BUT-8(Cr)A) with high-density sulfonic acid ($-SO_3H$) sites on channel surfaces. The humidity-dependent structural transformation of the framework ensures smooth proton conduction pathways under different humidity conditions. BUT-8(Cr)A exhibited an ultrahigh proton conduction of 1.27×10^{-1} S cm^{-1} at 100% relative humidity and 80 °C and kept a moderate conductivity over a wide range of temperature and RH. At 25 °C, an increase in the relative humidity from 11% to 100% led to an obvious proton conducting switch from 4.19×10^{-6} to 7.61×10^{-2} S cm^{-1}, with a high ON/OFF ratio of 10^4. Thus, designing stimuli-responsive MOFs that can self-adapt their structures under different humidity conditions is a promising pathway to efficiently tune hydrogen-bonding networks to ensure a high responsivity of proton conductivity.

3. LIGHT-INDUCED SWITCHING OF PROTON CONDUCTIVITY IN MOFS

A light-responsive MOF switch is particularly attractive, not only because light is a fast, typically nondestructive, and clean energy source, but also because it is convenient to control remotely.[96] Accordingly, the method of photoactive species grafted onto the skeleton or introduced into the pores has been widely studied in this direction.

Photoswitchable molecules, also referred as photochromic dyes (e.g., spiropyrans and azobenzenes), which can be isomerized between two different metastable forms upon irradiation with two different wavelengths,[97,98] are the most popular research species and have been successfully introduced into various materials.[38,99−101] The structural changes in photoswitchable molecules, including conjugation, dipole moment, and bond angle, will substantially affect the properties of materials. In previous work, it has been a common practice to incorporate photoresponsive triggers onto the framework backbones or into the pores.

Pioneering work reported by the Heinke group[38] initiated research on light-induced switching in MOF proton conductors through introducing an organic ligand with photoswitchable azobenzene (Azo) side groups onto the surface-mounted MOF. In this work, a reversible photoinduced *trans*−*cis* photoisomerization reaction in a $Cu_2(F_2AzoBDC)_2(dabco)$ film was observed (Figure 4a). Upon irradiation at 400 and 530 nm, the *cis*-Azo in a butanediol-loaded film exhibited a conductivity of 6.1×10^{-8} S cm^{-1}, while the *trans*-Azo in the film slightly improved the conductivity (9.0×10^{-8} S cm^{-1}). A similar switch between 7.9×10^{-7} (*cis*) and 1.2×10^{-6} S cm^{-1} (*trans*) was also realized in a 1,2,3-triazole-loaded film (Figure 4b). The *trans*−*cis* switch can be well maintained even after several cycles. It is notable that the hydrogen-bond networks between the Azo group and guest molecules are essential to the switch, as confirmed by the fact that a photoisomerization-related switch does not occur in the guest-molecule-free MOF. Moreover, calculations using MOPAC2016 with the semi-empirical PM6-D3H4 method and experimental infrared spectroscopy both showed that the H-bonding interaction between the guest molecule and the *cis* framework is stronger than that for the *trans* framework, leading to a decreased mobility and proton conductivity. More recently, this group synthesized a SURMOF (Cu_2(e-BPDC)$_2$(dabco)) film with spiropyran (SP) embedded onto linkers by postsynthetic modifications.[100] Due to the different dipole moment changes of the photoswitchable components, an ON/OFF ratio of 20 in ethanol@SP-SURMOF was higher than the value of 1.5 in the previously reported butanediol@Azo-SURMOF.[38] Moreover, the SP/MC photoisomerization in H_2O@SP-SURMOF led to a decreasing conductivity with an ON/OFF ratio of 82, mainly because the strong H-bonding interaction between water molecules and MC-SURMOF disturbs the proton transfer paths. The photoswitched proton conductivity can be reversed multiple times.

On the other hand, the strategy of embedding photoswitchable molecules as guests into the pores of MOFs has also been investigated. The hydrogen-bonding network in the pores was changed through a structural transformation of the photoswitchable molecules, reducing the conductivity. Recently, Peng, Liang, Chen et al.[101] fabricated SSP@ZIF-8 (SSP = sulfonated spiropyran) hybrid membranes with SSP inside the channel through a one-step reaction (Figure 4c). At 75 °C and 95% RH, the SSP@ZIF-8−10% membrane exhibited an interesting switch in proton conductivity from 0.05 ± 0.01 S cm^{-1} in the dark state to $(1.8 \pm 0.2) \times 10^{-6}$ S cm^{-1} in the light state, giving the highest ON/OFF value of 2.8×10^4 for photoswitchable MOFs. The good performance of photostimuli response mainly arises from the high conversion of photoisomerization (71.4%) and greatly different properties between the MC and SP forms. In the dark, an open state was achieved because of the hydrophilic and charged MC form, in which the successive hydrogen-bonding interactions among sulfonate, phenol groups and water molecules contributed to the enhanced conductivity. In contrast, the decreasing proton conduction of the membrane upon exposure to visible light is ascribed to the disruption of the H-bonding pathway by the hydrophobic and neutral SP form (Figure 4d). As shown in Figure 4e, the photoswitchable proton conduction of the SSP@ZIF-8−10% film can be repeated over 100 cycles under the conditions of 55 °C and 95% RH, with a stable ON/OFF ratio of 1200.

In addition, it is desirable to explore examples with a wider range of photosensitive moieties rather than photoswitchable molecules.[102] In this context, Peng's group reported some MOF switches based on photoactive species, such as graphene quantum dots (GQDs)[103] and indocyanine green (ICG),[104] or based on a photothermal framework without introduction of any photoswitchable molecules or components.[105] Interestingly, three photocontrolled basic logic gates (NOT, NAND and NOR) with flexible thresholds can be simply realized by introducing ICG into the membrane of HSB-W5.[104] This group recently comodified a ZIF-8 membrane by single-strand DNA (Ag-DNA@ZIF-8) and sliver nanoparticles. Due to the advantage of the unique properties of localized surface plasmon resonances for silver, the surrounding Ag-NPs were heated when illuminated, and some H_2O molecules escaped from the hydrogen-bonding network, thereby changing the proton conductivity.[106]

4. ELECTRIC-FIELD-RESPONSIVE PROTON CONDUCTIVITY IN MOFS

The stimulation response of some MOF materials to an electric field, such as the formation of conducting filaments,[107]

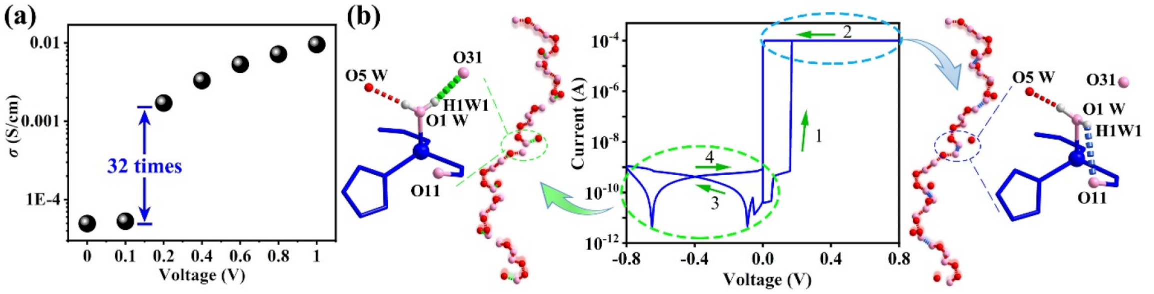


Figure 5. Electric field response in FJU-23-H_2O: (a) 32-fold improvement in proton conduction under an ac voltage of ∼0.2 V at 294 K; (b) switched proton transfer paths in FJU-23-H_2O.

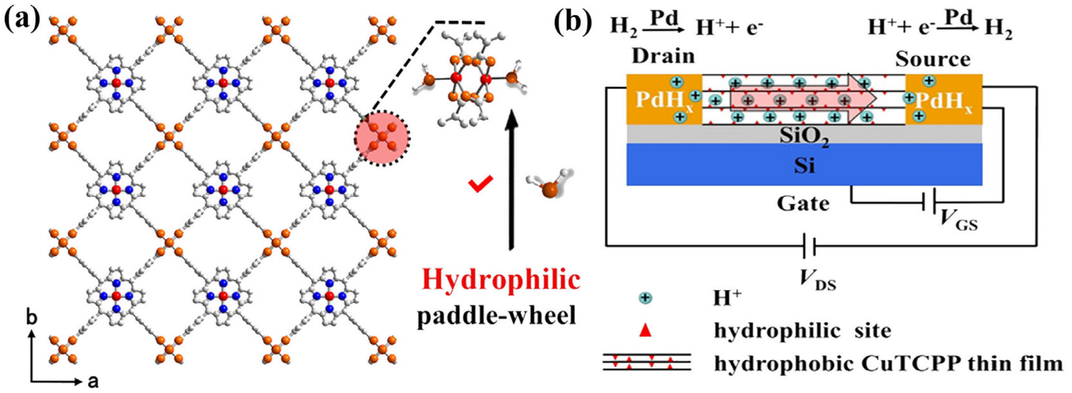


Figure 6. Cu-TCPP-based H^+-FET: (a) crystal structure; (b) schematic diagram of the working mechanism. Permission from Wiley-VCH, copyright 2021.

ferroelectric transitioned,[108] the migration of metal ions,[109,110] and oxidation/reduction processes at the insulator/electrode interface,[111] gives MOFs potential as memories, in which the carriers are usually metal ions or electrons. An electric-field-responsive proton conductor is desirable, because its largest electromigration can reduce the driving voltage required and the mass of a proton is larger than that of an electron to reduce the quantum tunneling effect.

Our group synthesized FJU-23-H_2O with a unique switchable H-bonding path in the channel of MOF along the *c* direction,[34] resulting in an electric-field-responsive switch in proton conduction in the *c* direction of the single crystal. As shown in Figure 5a, the MOF had a proton conductivity of 4.95×10^{-5} S cm^{-1} at the first stage. A sudden jump of conductivity to 1.70×10^{-3} S cm^{-1} appeared when the voltage was 0.2 V, resulting in a 32-fold increase in proton conduction. This MOF has proven to have an outstanding voltage-switchable conductivity with a low set voltage of ∼0.2 V and an ultrahigh ON/OFF ratio of $\sim 10^5$. Furthermore, the ultrahigh rectification ratio of $\sim 10^5$ provides the potential for applications in resistive random-access memories.

It needs to be mentioned that not only guests and external stimuli but also lattice water molecules are essential for the emergence and the change of proton conductivity. Thanks to the stable H-bonding paths in the MOF, an SCXRD analysis (Figure 5b) clarified that the voltage-switchable H-bonding interactions between the guest water molecules and the framework contribute to the switching proton conductivity in FJU-23-H_2O. The O1w atom from lattice water not only is essential for conductivity but also actually works as a trigger atom to reversibly modulate the proton transfer of a MOF conductor by a voltage stimulus, which has been further confirmed by a change in the difference Fourier maps with the hydrogen atoms riding on O1w.

5. PROTON FIELD-EFFECT TRANSISTORS IN MOFS

Proton conduction is a basic phenomenon in biosystems, such as the oxidative phosphorylation of mitochondria and bacteriorhodopsin and so on. It is significantly important to understand the working mechanisms in these biosystems. Monitoring and controlling proton transfer processes by an artificial device is an ideal method in combination with biological systems. Therefore, proton field-effect transistors (H^+-FETs), as a candidate device that can connect traditional electronics and biological systems, will still be a research hot spot in the future.[72,112−114]

Li and Xu[71] proved for the first time that MOFs are high-performance active-layer materials that can be used for bionic protonic field-effect transistors (H^+-FETs). Cu-TCPP was constructed into a two-dimensional gap nanocrystalline film with hydrophobic properties and abundant hydrophilic water points, which was used as a novel active-layer material of H^+-FET nanochannels with proton transport (Figure 6). The resultant device could physically and reversibly regulate the proton transfer through a change in the voltage on its gate electrode. In comparison to the typical H^+-FET made from maleic chitosan, reflectin, and a porous organic polymer, Cu-TCPP gave a higher proton mobility of up to 9.5×10^{-3} cm^2 V^{-1} s^{-1} and the highest ON/OFF ratio (about 4.1) among the reported H^+-FETs within the range of 10 V. More interestingly, the authors presented an electric-field-riven switching mechanism in the Cu-TCPP-based H^+-FET. Upon a negative gate voltage, positive charges would be induced onto the MOF active layer due to dielectric capacitive coupling,

Table 1. Switched Proton Conductions in MOFs

stimulus type	sample	sample type	proton conductivity (S cm^{-1})	ON/OFF ratio	activation energy (eV)	exptl conditions	responsive conditions	ref
optical	$Cu_2(F_2AzoBDC)_2(dabco)$	film	1.20×10^{-6}	1.51[a]		25 °C	530 or 400 nm	38
optical	$H_2O@Cu_2(SP\text{-}BPDC)_2(dabco)$	film	2.50×10^{-8}	82		25 °C, 93% RH	365 nm UV light or not	100
optical	SSP@ZIF-8	film	0.05	2.80×10^{4}	1.09	75 °C, 95% RH	in the dark or visible light	101
optical	Ag-DNA@ZIF-8	film	$\sim 10^{-5}$[b]	6.6×10^{5}	0.38	25 °C, 55% RH	in the dark or visible light	106
optical	ICG@HSB-W5	film	2.18×10^{-4}	1.03×10^{3}	0.48	55 °C, 95% RH	808 and 405 nm lights or in the dark	104
optical	HKUST-1	film	1.35×10^{-4}	299	0.33	55 °C, 95% RH	in the dark or visible light	105
optical	GQDs-PSS@ZIF-8	film	3.53×10^{-4}	12.8	0.83	55 °C, 95% RH	in the dark or visible light	103
electric field	$FJU\text{-}23\text{-}H_2O$	Single crystal	1.7×10^{-3}	32	0.42	room environment	dc voltage of 0.2 V	34
field effect transistors	Cu-TCPP	film	10^{-3}	4.1	0.28	90% RH and 5% H_2	−10 V	71
guest	$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot nH_2O$	powder	8×10^{-3}	114[a]		25 °C, 95% RH	water vapor	87
guest	$((CH_3)_2NH_2)_2[Li_2Zr(C_2O_4)_4]$	Single crystal	3.9×10^{-5}	7.8×10^{3}[a]	0.64	17 °C, 67% RH	humid environment	91
guest	BUT-8(Cr)A	powder	7.61×10^{-2}	1.82×10^{4}[a]	0.11	25 °C, 100% RH	humid environment	95
guest	ZZU-1	powder	8.9×10^{-4}	~35[b]	1.37	100 °C, 98% RH	formic acid vapor	90
guest	ZZU-2	powder	4.63×10^{-4}	~9[b]	1.65	100 °C, 98% RH	formic acid vapor	90
guest	$[Cu(HL)(DMSO)\cdot(MeOH)]_n$	powder	7.4×10^{-4}	1.2×10^{4}[a]	0.52	25 °C, 95% RH	H_2O vapor or DMSO/MeOH vapor	92
guest	$[Pt_2(MPC)_4Cl_2Co(DMA)(HDMA)\cdot guest$	powder	7.1×10^{-3}	10^{5}	0.4	60 °C, 95% RH	dimethylammonium cation ($HDMA^+$) and H_2O	88
guest	Zr-TCPBP	powder	5.8×10^{-4}	240	0.17	25 °C, 98% RH	HCl, different pH	89

[a] calculated. [b] Taken from the figures of the papers.

causing additional protons to be injected into the active layer via PdH_x contacts to increase conductivity. In contrast, a proton would be repelled from the active layer when a positive gate voltage is applied, reducing the proton conductivity of the H^+-FET (Figure 6b). This work shows a powerful strategy to design materials that nearly mimic the structure and performance of biological systems. The field-effect transistors based on proton-conductive MOFs provide a new idea for the regulation of proton transport and design of materials.

6. CONCLUSION AND PERSPECTIVE

The purpose of this Perspective has been to highlight recent advances in the challenging field of switched proton conduction in MOFs and their huge potential in different applications, which have never been summarized before. Due to the substantial progress in proton-conducting MOFs in the past decade, the effective strategies for controlling proton conductivity have laid a good foundation for the facile engineering of reversible proton transfer pathways. Through the modification of guest molecules, backbones, pore structures, and functional sites, switched proton-conducting behaviors stimulated by a guest, light, voltage, and electric field transistor have been developed in MOFs. The specific response characteristics, electrical conductivities, and switching ratios of representative materials are summarized in Table 1.

On the other hand, some important issues remain to be explored. (i) A judicious strategy for the comprehensive improvement of switching with high responsivity, high conductivity, quick response, high endurance, and high stability is challenging. The guest-induced switches show high ON/OFF ratios but are limited by relatively poor durabilities and slow response times. Guest species other than water molecules are expected to be the triggers. Due to the quick and enduring responsivity as well as wide applications in optoelectronic/electronic devices, photoinduced and electric-field-induced switching behaviors in MOFs are intriguingly attractive but are hampered by relatively low ON/OFF ratio and proton conductivities. In addition, some important issues such as response time, durability, and solution processability should be discussed for the further consideration of applications. (ii) Although lattice water molecules are essential for the emergence of proton conductivity and the triggering of a switchable response in many cases, it is a pity that lattice water molecules are difficult to clearly locate after stimuli due in part to the lack of crystallinity, let alone in the form of a film or powder. Thus, a new MOF platform with well-located lattice water molecules is needed to deeply investigate the relationship between internal and external environments in the channels. (iii) The investigation of proton transfer is always difficult, particularly in responsive MOFs with subtle and dynamic changes. Further in-depth studies of the dynamic proton transfer pathways are needed to elucidate the response mechanism and be used to guide the design and synthesis of new stimuli-responsive materials. Thus, it is desirable to develop *in situ* monitors during the reversible process. In particular, the mechanism of photoinduced switching behaviors is ambiguous because most examples have been investigated in the morphology of a thin film. (iv) With inspiration of the unique porous features of MOF materials, stimuli-responsive MOF proton conductors may have expanded applications to remote-controllable chemical sensors, proton-conducting field-effect transistors, and switchable devices interfaced with biological systems, and so on. Research on these materials will contribute to the development of a new generation of proton-conduction-controllable smart devices. (v) With the general trend of multifunctional development of materials, multistimuli-responsive proton-conducting MOFs will have a broader application space and will be one of the future development directions. It has been proved in a polymer system that multistimuli response can be achieved by incorporating a combination of two or more chemical, physical, or biological stimuli-responsive components. On consideration of the good assembly of organic and inorganic species in a single framework, a fundamental investigation into the MOFs in response to multiple stimuli and their utilization in a variety of practical applications are highly desirable and challenging.

In short, MOFs provide a new platform to address the challenges of stimuli-induced proton transfer with application possibilities beyond our imagination.

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Notes

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ACKNOWLEDGMENTS

This research work was financially supported by the National Natural Science Foundation of China (21805039, 21673039, 21573042, 21975044, and 21971028) and the Fujian Provincial Department of Science and Technology (2019L3004, 2018J07001 and 2019H6012).

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