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# MOFs as proton conductors – challenges and opportunities

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Padmini Ramaswamy, Norman E. Wong and George K. H. Shimizu\*

Proton conducting materials have garnered immense attention for their role as electrolytes in fuel cells. Metal Organic Frameworks (MOFs) and coordination polymers have recently been investigated as possible candidates for proton-conducting applications. Their crystallinity, chemically functionalizable pores and options for systematic structural variation are some of the factors that allow for the targeted design of better proton conductors operating over a wide variety of temperatures and/or humidity conditions. This review will examine selected examples from this nascent field, and will focus on the design and synthesis of proton conducting MOFs, their properties and conditions under which they operate.

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## Introduction

Advances in new materials for any targeted application require the ability to make progressive changes through an iterative cycle of design, execution and assessment. Metal–organic frameworks (MOFs), or coordination polymers (CPs) are a class of compounds which consist of metal clusters or nodes linked by organic moieties. MOFs are highly crystalline, which allows for ease in structural determination and tunability of components.

When one considers the design, the crystallinity and the systematic/modular variability of MOFs are key enablers. With respect to ion conduction, designing a better material offers several challenges. Ideally, a solid electrolyte would offer an insulating and robust support for facile transfer of a mobile ion in three dimensions. The solid would also have mechanical strength and the ability to be manufactured into a thin film with good interfacial compatibility with other device components. Translating the desired properties into the structure of an ion conductor, there are diverse possibilities. Some questions researchers may ponder include: are ordered or disordered solids preferred? (Mobility should be facilitated by a less efficiently packed solid, but crystallinity enables visualization and hence design.) To what extent can the mobility of components and crystallinity be reconciled? Is a rigid or flexible structure preferred? Are porous or dense structures preferred? (Pores could be loaded with additional ion carriers but, at the same time, open structures are generally less robust and could enable crossover of fuel in a cell.) A key observation is that many of the ideal features of an ion conducting material are potentially conflicting and there is a broad domain spanning from metal



Padmini Ramaswamy

Padmini Ramaswamy obtained her PhD degree in Solid State Chemistry from the Indian Institute of Science, Bangalore in 2011. She moved to Kyoto, Japan in 2012 to carry out postdoctoral research under the supervision of Prof. Susumu Kitagawa as part of the ERATO project. Since April 2013, she is working under the supervision of Prof. George Shimizu at the University of Calgary, researching phosphonatebased metal-organic frameworks for proton conductivity.



Norman E. Wong

Norman Wong obtained his BSc degree from the University of Calgary in 2010. He is currently in the 4th year of his postgraduate research, working towards a PhD degree in Chemistry under the supervision of Prof. George Shimizu. He is interested in developing novel sulfonate and phosphonate metal-organic frameworks for proton conducting applications.

Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4, Canada. E-mail: gshimizu@ucalgary.ca; Tel: +1 403 220 5347

oxides to macromolecular polymers that are candidate materials as proton conductors. MOF materials represent a true hybrid approach. A key point is that there is no single best electrolyte material from even an academic and certainly not a commercial perspective, and so there is ample opportunity for design of new proton conducting systems. In this regard, MOF materials offer both potential candidates and crystalline model compounds for better understanding of proton conduction in diverse structures.<sup>1–5</sup>

This review will focus on MOF proton conductors operating below 200 °C. This domain of proton conductors has primary interest as electrolytes for proton exchange membrane fuel cells, and so a specific overview of those challenges is presented along with a brief background on proton conducting mechanisms. Finally a survey of MOF proton conductors will be presented with a compilation of key structural features evaluating design strategies for good proton conducting materials and membranes.

## Proton exchange membrane fuel cells

Energy consumption globally is projected to increase by 56% by 2040 as a result of various factors such as rapid urbanization and population growth.<sup>6</sup> In response to this growing energy demand, several alternative energy technologies have been proposed, among which fuel cell technology has attracted considerable attention. Fuel cells are defined as electrochemical conversion devices which operate based on two components - a fuel component such as hydrogen, natural gas, methanol etc., and an oxidant such as oxygen, air or hydrogen peroxide.<sup>7</sup> An electrolyte serves to transfer charges between the positively charged cathode and the negatively charged anode. The first commercial use of fuel cells was in the Gemini and Apollo space programs, and since then they have emerged as a clean route for the efficient utilisation of a variety of energy sources. Several different fuel cell systems have been developed over the years, among which the polymer electrolyte membrane fuel cells (PEMFCs) are important. The US Department of Energy (DOE) has set certain guidelines for the development of fuel cell technology, the prominent targets being the development of a fuel cell system for portable power (<250 W) with an energy density of 900 W h L<sup>-1</sup> by 2015, and the development of a 60% peak-efficient, 5000 hour durable,



George K. H. Shimizu

George Shimizu completed his BSc and PhD at the Universities of Winnipeg and Windsor, respectively. He then undertook postdoctoral work at the University of Birmingham and the National Research Council of Canada. Presently, he is a Full Professor and his research concerns MOFs for clean energy applications including gas storage/separation and proton conduction.

direct hydrogen fuel cell power system for transportation at a cost of \$30/kW, by 2017.8 New electrolyte materials are critical for efficient operation and for achieving these targets. Among the requirements for a better electrolyte are: high proton conductivity ( $>10^{-2}$  S cm<sup>-1</sup>) to facilitate efficient transport of protons between electrodes; good thermal and chemical stability to preserve electrolyte integrity under fuel cell operating conditions (variable temperatures, humidity/hydrating environments, chemical resistance to by-product species like peroxides, etc.); act as a gas tight separator to prevent crossover of fuel gases; membrane (thin-film) processable; low cost; ease in high volume manufacturing; compatibility with other fuel cell components (bipolar plates, electrode materials, etc.). Polymers such as Nafion, polybenzimidazole (PBI) and sulfonated polyether-ether ketones (SPEEK) have been used widely as electrolytes in PEMFCs. In particular, Nafion, which consists of a perfluorinated polyethylene backbone upon which are grafted side chains with terminal sulfonic acid groups, has been the popular material of choice. The presence of acidic moieties in these polymers is known to generate hydrophilic domains in which proton conduction occurs. Proton conduction has been achieved in the order of  $10^{-1}$  to  $10^{-2}$  S cm<sup>-1</sup> at T < 85 °C with humidification. However, these polymeric materials suffer from several limitations. Active humidification is necessary for performance and adds complexity, while the potential for physical degradation from hydration/dehydration results in a loss of efficiency. In addition, there is also a need to power the humidifiers. Such a need also limits the use of Nafion in terms of operating temperatures which has several caveats: potential for CO poisoning of Pt catalysts at temperatures  $< 100 \,^{\circ}C$  (CO from steam reforming to produce H<sub>2</sub>), poorer reaction kinetics and potential for flooding of electrodes from condensing water at the catalyst/electrode interface.<sup>7</sup>

## Proton conduction mechanisms

Two general mechanisms relating to the transport of protons are known, namely the Grotthuss and the vehicular mechanisms. The Grotthuss or proton-hopping mechanism addresses the conduction of protons within a hydrogen-bonded network of water molecules. Protons are envisaged as forming H<sub>3</sub>O<sup>+</sup> species within a water cluster, with transfer occurring upon concurrent severing of hydrogen-bonds, transfer of the proton and subsequent rearrangement between nearby H<sub>2</sub>O molecules. In this manner, protons "hop" along their conduction pathway through protonation and deprotonation of water molecules. The vehicular mechanism involves transport of protons through self-diffusion of protogenic species, essentially as proton carriers. More detailed descriptions of these mechanisms can be found in work by Kreuer et al.9,10 Such processes have been identified primarily by activation energies obtained through ac impedance data. Given that hydrogen-bond cleavage requires an energy penalty in the range of 2–3 kcal  $mol^{-1}$  $(\sim 0.11 \text{ eV})$ ,<sup>14</sup> Grotthuss mechanism conduction processes generally involve activation energies  $(E_{act}) < 0.4$  eV. With the vehicular mechanism, transport of larger ionic species (with greater mass compared to H<sup>+</sup>) requires a larger energy contribution, and as such processes with  $E_{act} > 0.4$  eV generally refers to the latter mechanism.

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In Nafion, the industry standard polymer electrolyte for fuel cells, sulfonic acid side chains and water molecules give rise to conductivities on the order of  $10^{-1}$ – $10^{-2}$  S cm<sup>-1</sup>. Activation energies typically reside between 0.1–0.5 eV depending on hydration levels, likely resulting from a Grotthuss-like conduction mechanism.<sup>15</sup>

In general, ionic conductivity can be expressed as in eqn (1), where  $\sigma$  is ionic conductivity (units S cm<sup>-1</sup>), *n* represents the number of charge carriers, *e* represents the charge on the mobile ion,  $D_0$  is a constant which is related to the mechanism of ionic conductivity, *k* is the Boltzmann constant, *T* is the temperature in Kelvin,  $\Delta S_m$  is the motional entropy and  $E_a$  is the activation energy for ion transport.

$$\sigma = \frac{ne^2 D_{\rm o} \exp\left(\frac{\Delta S_{\rm m}}{k}\right)}{kT} \exp\left(\frac{-E_{\rm a}}{kT}\right) \to \sigma = \frac{\sigma_{\rm o}}{kT} \exp\left(\frac{-E_{\rm a}}{kT}\right) \quad (1)$$

With proton conductivity, the charge remains constant at +1 and mobility of protons is influenced by kinetic factors whereas the concentration of protons can be variable. Hence, the factors which would contribute to increased conductivity of protons in a MOF structure are an increase in the number of charge carriers, greater motional entropy, lower activation energy and a 3-dimensional conduction pathway.

Measurements are usually carried out on powdered samples in a pressed pellet form (Fig. 1(a)). This, while being a useful and convenient method to reveal the bulk proton conductivity



**Fig. 1** (a) A Nyquist plot; open symbols represent experimental data while the solid line corresponds to a proposed equivalent circuit (inset top left) to model the system. Inset bottom right: zoomed-in view of high frequency region,  $R_{\text{bulk}}$  obtained at 10 kHz;<sup>11</sup> (b) Arrhenius plot to determine activation energy for proton conduction;<sup>12</sup> (c) a conductivity *vs.* humidity cycling plot; linear correlation indicates water dependent proton conductivity.<sup>13</sup> Reproduced with permission from ref. 12, 13 and 14 for figures (a), (b) and (c). Copyright 2012 American Chemical Society ((c)).

behaviour of the compound under study, however fails to shed light on the anisotropic conduction phenomena. This information can be obtained from measurements on single crystals, where available. Information on the activation energy for proton transfer is essential to determine the mechanism by which protons are transported. This is obtained from Arrhenius plots, which are usually plotted with  $ln(\sigma T)$  as a function of inverse temperature (Fig. 1(b)). In addition to the above experiments. conductivity experiments making use of D<sub>2</sub>O in systems where water is crucial for performance, can confirm the role of water in the conduction process via the kinetic isotope effect. In waterassisted proton conduction, it is essential to have information on the water content in order to rationalise the conduction behaviour. This is typically provided by relative humidity (RH) cycling experiments, in which conductivity is measured under varying humidities, at constant temperature (Fig. 1(c)). Equilibration of microporous or ultramicroporous samples after changing relative humidity can take many hours (>20) and so making conductivity measurements at a given RH on a heating and cooling cycle is recommended. This also will ensure sample integrity.

### MOFs as proton conductors

Metal-organic frameworks are a class of hybrid inorganicorganic compounds consisting of networks formed by metal ions or metal clusters connected via organic ligands. These networks are often porous, and exhibit a wide range of properties and applications, including but not limited to gas storage,<sup>16-27</sup> separation,<sup>28-31</sup> magnetism,<sup>32-39</sup> catalysis,<sup>40-42</sup> photoluminescence,43-48 etc.49 Structural features of MOFs such as their crystallinity, a regular arrangement of voids, tailorable porosity, and dynamic behaviour are especially attractive for their use as proton conductors. In addition, new developments in synthetic methodologies offer greater control towards the construction of MOFs with hierarchical microstructures.<sup>50-56</sup> Recent studies on fabrication of MOFs in the form of mixed-matrix membranes,<sup>16,57-59</sup> thin films *etc.*,<sup>60,61</sup> has increased their viability for industrial applications. In literature, proton conduction in metal-organic frameworks has been reported in two distinct regimes - below 100 °C, under hydrated conditions, where hydrogen bonding and water/solvent molecules aid the transport of protons; and under anhydrous conditions, at temperatures above 100 °C. In the sections below, we describe in detail the structures and properties of these proton-conducting MOFs. Not covered here are examples of proton conduction in hybrid organic-inorganic systems such as the  $\alpha$ - and  $\gamma$ -layered metal(IV) phosphates and derivatives,<sup>62–68</sup> or other hybrid membranes.<sup>69–72</sup>

#### Proton conducting MOFs operating at T < 100 °C

Most proton-conducting MOFs reported hitherto in the literature operate under low-temperature conditions, and are aided by the presence of water molecules and hydrogen-bond networks (Table 1). The earliest report of a proton conducting coordination polymer was by Kanda *et al.*, who reported the conductivity of a series of two-dimensional N,N'-disubstituted dithiooxamido (dtoa)

Table 1 Key structural features and pu	erformance indicators for	proton conducting	g MOFs/CPs (listed approximately	chronologically t	y publication date)			
MOFs/coordination polymers	Framework dimensionality	Pore size	Prominent features	Pore guests	$\begin{array}{c} \text{Conductivity} \\ \text{(S cm}^{-1}) \end{array}$	Analysis conditions (temperature/humidity)	$E_{ m a}$ (eV) I	kef.
(HOC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> -dtoa-Cu	2-D layers		Water-mediated pathways	Lattice water,	$2.2 imes10^{-6}$	T = 27 °C, RH = 100%	0.16 7	3
H <sub>2</sub> dtoaCu	2-D	••• • •	Clusters of water molecules	OH <sup>-</sup> ions Lattice water	$10^{-6}$	T = 27 °C, 75% RH		4
p-POMUF-2(12)0.45	3D-noneycomb with 1D channels	A 60.6	Oxygen atoms from SO <sub>3</sub> groups line channels	1,2,4-1riazoie	$-01 \times c$	$D_{-} 0$ $C_{-} I$	0.34	-
{MH(prol) <sub>3</sub> }[M <sup>H</sup> Cr <sup>III</sup> (ox) <sub>3</sub> ] (M <sup>II</sup> = Mn <sup>II</sup> , Fe <sup>II</sup> , Co <sup>II</sup> )	2D oxalate-bridged layers	7.96 Å $ imes$ 9.16 Å	The hydrogen-bonded network formed by the bimetallic layer, {NH(prol) <sub>3</sub> } <sup>+</sup> ions, and water	{NH(prol) <sub>3</sub> } <sup>+</sup> ions, H <sub>2</sub> O molecules	$\sim 1  imes 10^{-4}$	T= 25 °C, 75% RH		80
$(NH_4)_2(adp)[Zn_2(ox)_3].3H_2O$	2D honeycomb layer with hydrophilic interlaver	$8.14~\textrm{\AA}\times9.16~\textrm{\AA}$	Adipic acid (protonated) resides in honeycomb voids and in the interlaver	Lattice water and NH4 <sup>+</sup> molecules	$8  imes 10^{-3}$	T = 25 °C, 98% RH	0.63	<u>ר</u>
Im@{Al( $\mu_2$ -OH)(1,4-ndc)} <sup>n</sup>	3D framework con-	8Å °	Included imidazole acts as	Imidazole	$2.2 imes 10^{-5}$	T=120 °C	0.6	8
ш.@үлцрг <sup>-</sup> Оц)(1,4- <sup>10</sup> цс) <i>jn</i> {Mn(DHBQ)(H <sub>2</sub> O) <sub>2</sub> }	1-D chain structure	¥ 0	protont transfer agent Coordinated water and oxygen atoms of DHBQ participate in bud accord booding	Lattice water	$4 \times 10^{-5}$	T = 25 °C, 98% RH	0.26	10
${\rm Fe}({\rm ox})({\rm H}_2{\rm O})_2$	1D chain	I	nyurogen ponuning water molecules coordinate axially to ferrous ions and form a 1D ordered array of water molecules	Lattice water	$1.3  imes 10^{-3}$	T = 25 °C, 98% RH	0.37	9
PCMOF-3	2D-layered structure		H-bond anchored array of H <sub>2</sub> O	Lattice water	$3.5 imes10^{-5}$	T = 25 °C, 98% RH	0.17 8	8
Co[Cr(CN) <sub>6</sub> ], <sub>13</sub> .zH,O	3D Prussian blue	$\sim$ 2 Å	in interlayer space Hvdrogen bonding network of	molecules Lattice water	$1.2  imes 10^{-3}$	T = 20 °C. 100% RH	0.22	Ħ
	analogues	1	zeolitic water		$1.7  imes 10^{-3}$	T = 35 °C, 100% RH		
V[Cr(CN) <sub>6</sub> ] <sub>2/3</sub> .2H <sub>2</sub> O	)	~2 Å			$1.6  imes 10^{-3} \ 2.6  imes 10^{-3}$	T = 20 °C, 100% RH T = 50 °C, 100% RH	$\begin{array}{l} 0.10 \ (T > 40 \ ^{\circ}\mathrm{C}) \ 0.19 \end{array}$	
ய்ன[viton)(ப	3D fromound on	Ŷ	Indudad histomina aats as	Uictomino	$1.7 < 10^{-3}$	- 150 °C	$(T < 40 \ ^{\circ}C)$	5
his@[Ai[Off](Juc]]n	taining 1D channels	A O	broton carrier		01 × 71	D 001 - 1	r c7.0	71
$Fe(OH)(bdc-(COOH)_2)(H_2O)$	3D frameworks with MIL-53 structure con- taining 1D channels	19.34 Å × 7.63 Å–17.47 Å × 12.18 Å	Functional group utilized to tune acidity of 1D channels	Lattice water	$2.0 imes10^{-6}$	T= 25 °C, 95% RH,	0.21	13
(NH4,)4[MnCr2(0x)6]3·4H2O	3D chiral (quartz-like) anionic network	5.23 Å (A channels) 7.52 Å (B channels)	Terminal oxalate ligands protrude into channels	Lattice water and NH <sub>4</sub> <sup>+</sup> ions	$1.1  imes 10^{-3}$	T = 22 °C, 96% RH	0.23 8	0
[Zn(tL <sub>cl</sub> )(Cl)](H <sub>2</sub> O) <sub>2</sub> [L = 3-methyl-2-(pyridin-4-ylmethyl- amino)butanoic acid]	3D supramolecular structure with 1D channels	14.52 Å	Continuous helical water chain inside pores	Lattice water	$3.13  imes 10^{-5}$	$T = 26  ^{\circ}\text{C},  98\%  \text{RH}$	0.34 8	 
$Gd_3(H_{0.75}^{0.75}O_3PCHOHCOO)_4 \cdot xH_2O$ (x = 15-16)	3D, with oval-shaped one-dimensional channels	11.07 Å $\times$ 14.77 Å	POH groups point inward into channel	Lattice water molecules	$3.2 imes 10^{-4}$	T = 21 °C, RH = 98%	0.23	14
MgH <sub>6</sub> ODTMP-6H <sub>2</sub> O	3D-pillared framework containing 2 types of 1-D channels	8.61 Å $\times$ 7.95 Å (along <i>a</i> -axis) 15.10 Å $\times$ 5.39 Å (along <i>b</i> -axis)	Phosphonate tetrahedral point into 1-D channel	Lattice water molecules	$1.6 imes10^{-3}$	T = 19 °C, RH = 100%	0.31	15
PCMOF-5	3D pillared layer	5.81 Å	Free phosphonic acid groups and water lining 1D pores	Lattice water molecules	$2.5 imes 10^{-3}$	T = 60.1 °C, 98% RH	0.16	.16

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Table 1 (continued)								
MOFs/coordination polymers	Framework dimensionality	Pore size	Prominent features	Pore guests	Conductivity (S cm <sup>-1</sup> )	Analysis conditions (temperature/humidity)	$E_{ m a}$ (eV)	Ref.
La(H <sub>5</sub> DTMP) 7H <sub>2</sub> O	3D pillared frame- work with small 1D channels	$6.67~{ m \AA} imes12.50~{ m \AA}$	1D channels filled with water	Lattice water	$8  imes 10^{-3}$	T = 24 °C, 98% RH	0.25	117
Sr-SBBA	2D layered structure hydrogen bonds to form 3D supramole-	I	Sulfone group in backbone facilitate H-bonding	Lattice water	$4.4  imes 10^{-5}$	T= 25 °C, 98% RH	0.56	82
Ca-BTC-H <sub>2</sub> O	cutat succut e 3D framework con- taining 1D channels	$5.95 \ \mathring{\mathrm{A}} \times 8.01 \ \mathring{\mathrm{A}}$	Coordinated H <sub>2</sub> O molecules and COOH oxygen form hydrogen-bonded water array in channels	Lattice water	$1.2 imes10^{-4}$	$T=25~^{\circ}\mathrm{C},~98\%~\mathrm{RH}$	0.18	118
H <sub>2</sub> O-HKUST-1	3D framework containing open metal sites	10 Å	$H_2O$ coordinated to $Cu^{II}$ sites	Solvent MeOH	$1.5  imes 10^{-5}$	$T=25^{\circ}\mathrm{C},$ MeOH vapour	I	87
$[\{(Zn_{0,25})_{69}(NO_3)\}Zn_6(L)_{12}(H_2O)_{29}-(DMF)_{69}(NO_3)_2]_n$	2-D sheets inter- penetrate (3-fold) forming 1-D channels	13.13 Å $\times$ 17.96 Å (along <i>a</i> -axis) 22.56 Å $\times$ 15.57 Å (along <i>b</i> -axis)	Imidazolium groups line channel walls	DMF and water molecules	$2.3  imes 10^{-3}$	T = ambient, 95% RH	0.22	13
$[Zn_2(2,5-DOTP)]_n$ -His	3D honeycomb structure containing 1D micronores	11 Å	Pores are lined with hista- mine, which is grafted onto the metal sites	Histamine	$4.3  imes 10^{-9}$	T = 146 °C, N <sub>2</sub> atmosphere		119
Cd-5TIA and In-5TIA metal-organic nanotubes (MONTs)	3D structure containing 1D nanochannels	7.85 Å (Cd) 8.23 Å (In)	Triazole moiety provides a proton conduction pathway	Dimethyl ammonium cations	$3.61 \times 10^{-3}$ (Ca) $5.35 \times 10^{-5}$ (In)	T=28 °C, 98% RH	0.163 (Ca) 0.137 (In)	120
{NMe <sub>3</sub> (CH <sub>2</sub> COOH)}[FeCr(ox) <sub>3</sub> ]·3H <sub>2</sub> O	2D layer with NMe <sub>3</sub> groups occupying the interlaver spaces		Water mediated, alkyl groups tune hydrophilicity	Lattice water	$8  imes 10^{-5}$	T=25 °C, 65% RH	I	121
{NEt <sub>3</sub> (CH <sub>2</sub> COOH)}[MnCr( $\infty$ ) <sub>3</sub> ]-2H <sub>2</sub> O	2D layer with NEt <sub>3</sub> groups occupying the interlaver spaces				$2 imes 10^{-4}$	T=25 °C, 80% RH	I	
H <sub>2</sub> SO <sub>4</sub> @MIL-101	3D ,	12 Å (smaller channels) 14.5 Å × 16 Å (larger channels)	Impregnation of inorganic acids inside pores of Cr-MIL-101	$H_2SO_4$	$egin{array}{l} 4.0  imes 10^{-2} \ 6.0  imes 10^{-2} \ 1.0  imes 10^{-2} \end{array}$	T = 23 °C, 20% RH T = 80 °C, 20% RH T = 150 °C 0.13% RH	~ 0.42 	66
$H_3PO_4$ (a) MIL-101		2		$H_3PO_4$	$egin{array}{cccc} 2.5 imes10^{-4}\ 3 imes10^{-3} \end{array}$	T = 23 °C, 20% RH T = 150 °C, 0.13% RH	$\sim 0.42$ 0.25	
$[\operatorname{Zn}(\operatorname{H}_2\operatorname{PO}_4)_2(\operatorname{TzH})_2]_n$	2D	l	Phosphate and triazole groups		$egin{array}{c} 1.2  imes 10^{-4} \ \sigma_{\parallel} = 1.1  imes 10^{-4} \ \sigma_{\parallel} = 2.0  imes 10^{-6} \end{array}$	$T = 150 \circ C$ $T = 130 \circ C$ (single	0.6	100
$[Zn(HPO_4)(H_2PO_4)_2]$ (ImH <sub>2</sub> ) <sub>2</sub>	1D chains templated by imidazolium cations	Ι	Phosphate groups and proto- nated imidazole molecules	Protonated imi- dazole cations	$2.5 imes 10^{-4}$	$T = 130 ^{\circ}\mathrm{C}$	0.47	101
$ \begin{array}{l} Zr(L)_2X_2H_2\cdot 5H_2O\\ (L=cyclohexyl-N,N',N',N'-diamino-tetraphosphonate, X=H, Na^+, NH_4^+ \end{array} $	<ul><li>3D open-framework, inorganic units bridged</li><li>by cyclohexyl into "brickwall-like"</li></ul>	$12 \ \text{\AA} \times 5 \ \text{\AA}$	Polar 1D channels, with eight PO <sub>3</sub> tetrahedra per channel	Water molecules along with included cations where available	$\begin{array}{c} 5.4 \times 10^{-5} \\ (X=H) \\ 1 \times 10^{-4} \\ (bulk \sigma_b, X=H) \end{array}$	T= 80 °C, 95% RH	$0.23 \left( \sigma_{\mathrm{b}}  ight)$	122
[Mo <sub>5</sub> P <sub>2</sub> O <sub>23</sub> ] [Cu(phen)(H <sub>2</sub> O)] <sub>3</sub> ·5H <sub>2</sub> O (Cu <sub>3</sub> Mo <sub>5</sub> P <sub>2</sub> , Phen = phenanthroline)	3D network built from POM and Cu unit chains that are then $\pi - \pi$ stacked	6.2 Å	1D parallel water chain resides within with H-bonding to OH and POM units	Lattice, uncoor- dinated water	$2.2  imes 10^{-5}$	T = 28 °C, 98% RH	0.232	123

Table 1 (continued)								
MOFs/coordination polymers	Framework dimensionality	Pore size	Prominent features	Pore guests	Conductivity (S cm <sup>-1</sup> )	Analysis conditions (temperature/humidity)	$E_{ m a}~({ m eV})$	Ref.
$M[(HO_3PCH_2)_N(H) - CH_2C_6H_4CH_2N(H) - CH_2C_6H_4CH_2N(H) - CH_2C_6H_4CH_2N(H) - CH_2C_6H_4CH_2N(H) - CH_2C_6H_2N(H) - CH_2N(H) - CH_2C_6H_2N(H) - CH_2N(H$	3D pillared framework with 1D channels	11.44 Å $\times$ 12.73 Å	POH oxygen point towards the interior of the channels	Lattice water	$\begin{array}{c} 1.39 \times 10^{-4} \ \mathrm{(Zn)} \\ 9.75 \times 10^{-5} \ \mathrm{(Mg)} \end{array}$	T = 41 °C, 98% RH	$\sim 0.50 \ (Mg)$	124
(Un2FO3H)2(In2O)2]·2H2O PCMOF2 <sup>1</sup> /2	3D honeycomb with 1D	) 5.65 Å	Oxygen atoms from SO <sub>3</sub> <sup>-</sup> ,	Lattice water	$2.1 \times 10^{-2}$	T = 85 °C, 90% RH,	0.21	06
[Cu(bpdc)(H <sub>2</sub> O)] <sub>n</sub>	channels 1D [Cu(bpdc)(H <sub>2</sub> O)] <sub>n</sub> chains connected supramolecularly by	I	PO <sub>3</sub> groups inte channels Coordinated water molecules exhibiting strong hydrogen bonding in the framework	molecules	$1.55 imes10^{-4}$	T = 100 °C, 98% RH		85
{H[Cu(Hbpdc)(H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> [PM <sub>12</sub> O <sub>40</sub> ]. $nH_2O$ }, M = Mo and W $n = 7.5-8$	nyarrogen bonds to form a 2D structure 3D poly-POM-MOFs built upfrom [Cu(bpdc)[(H <sub>2</sub> O)] <sub>n</sub> <sup>n+</sup> and poly-Keggin-anion chains forming 1D	10.94 Å	Hydrophilic channels with water	Lattice water	$1.25 \times 10^{-3}$ (Mo), $1.56 \times 10^{-3}$ (W)		1.02	
Cu-DSOA	channels 3D structure containing two types of hydrophilic	; 9.61 Å	Pores lined with uncoordinated O atoms of SO <sub>3</sub> groups	Lattice water/ hydronium ions	$1.9 imes10^{-3}$	T = 85 °C, 98% RH,	1.04	125
In-IA-2D-1	channels 2D layer	8.95 Å $ imes$ 9.69 Å	Proton carriers (dimethyl ammonium cations) occupy	[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup> and water	$3.4  imes 10^{-3}$	T= 27 °C, 98% RH	0.61	81
In-IA-2D-2		$\begin{array}{c} 10.41 \ \text{\AA} \times \\ 10.05 \ \text{\AA} \end{array}$	voius	[[CH <sub>3</sub> ] <sub>2</sub> NH <sub>2</sub> ] <sup>+</sup> and DMF	$1.59  imes 10^{-5}$	T = 120 °C	0.48	
	2D layers with {NEt <sub>3</sub> (CH <sub>2</sub> COOH)} groups residing in the	I	Water mediated conductivity, hydrophilicity tuned by R groups	molecules Lattice water	$1 \times 10^{-7}$ (R = Et, Bu)	$T = 25 ^{\circ}\text{C}$ , 65% RH (Et) 85% RH (Bu)		79
$[\mathrm{Zn}_3(\mathrm{H}_2\mathrm{PO}_4)_6](\mathrm{Hbim})$	Intertayer voids Neutral 1D zinc phos- phate chains templated by neutral	۱	Phosphate groups and free benzimidazole molecules	Benzimidazole molecules	$1.3  imes 10^{-3}$	$T = 120 \ ^{\circ}\mathrm{C}$	0.5	126
ZrF[H <sub>3</sub> (O <sub>3</sub> PCH <sub>2</sub> NHCH <sub>2</sub> COO) <sub>2</sub> ]	benzimidazole 1D chains connected <i>via</i> hydrogen bonds in	I	Hydrogen bonding between carboxylic acid groups on	I	$\sim 1  imes 10^{-3}$	T= 140 °C, 95% RH	I	127
Zr <sub>3</sub> H <sub>8</sub> [(O <sub>3</sub> PCH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> COO] <sub>4</sub> ·2H <sub>2</sub> O	2D layered structure from two types of chains of ZrO <sub>6</sub> octa- hedra and PO <sub>3</sub>	I	Hydrogen bunding network in interlayer between carboxylic acid, intercalated water and PO <sub>3</sub> groups	Intercalated water molecules	$\sim 1  imes 10^{-3}$		0.1	
Zr[(O <sub>3</sub> PCH <sub>2</sub> )(HO <sub>3</sub> PCH <sub>2</sub> )NHCH <sub>2</sub> - COOH] <sub>2</sub> ·2H <sub>2</sub> O	tertaneura 3D structure from chains of ZrO <sub>6</sub> and PO <sub>3</sub> polyhedra, connected	13.79 Å $\times$ 9.04 Å	Hydrogen bonding within pores between carboxylic acid, pore water and protonated N	Water molecules	$\sim 10^{-4}$		I	
[H <sub>3</sub> O][Mn <sub>3</sub> - (μ <sub>3</sub> -OH)(SDBA) <sub>3</sub> (H <sub>2</sub> O)][(DMF) <sub>5</sub> (H <sub>2</sub> SDBA = 4,4'-sulfonyldibenzoic acid)	by giypnosine Mn clusters connected by SDBA <sup>2-</sup> into 2D layers, cross-linked further into 3D struc- ture with 1D channels	15.76 Å × 13.39 Å	Water (hydronium) mediated	H <sub>3</sub> O <sup>+</sup> ions, DMF and lattice water	$3 \times 10^{-4}$	$T = 34  ^{\circ}\mathrm{C},  98\%  \mathrm{RH}$	0.93	128

Table 1 (continued)								
MOFs/coordination polymers	Framework dimensionality	Pore size	Prominent features	Pore guests	Conductivity (S cm <sup>-1</sup> )	Analysis conditions (temperature/humidity)	$E_{ m a}$ (eV)	Ref.
$[H_3O]_2[Mn_7(\mu_3-OH)_4(SDBA)_6(H_2O)_4]^-$	$6.42~\textrm{\AA}\times15.65~\textrm{\AA}$	$3.44 \times 10^{-4}$	1.16					
$\{[(Me_2)_2(DM1)_3] \\ [[(Me_2NH_2)_3(SO_4)]_2[Zn_2(0X)_3]\}_n \\ [(Ne_2 overlate)]$	3D supramolecular structure build un by	13.31 Å × 12 50 Å	Hydrogen bonding between sulfate and dimethyl ammo-	Dimethyl	$4.2 imes 10^{-2}$	T = ambient, 98% RH	I	102
	[Zn <sub>2</sub> (ox) <sub>3</sub> ] <sup>2</sup> -layers interpenetrated with cationic		nium ions	cations, sulfate anions	$1 imes 10^{-4}$	$T = 150 ^{\circ}$ C, N <sub>2</sub> atmosphere	0.13	
[Zn(5-sipH)(bpy)]:DMF·2H <sub>2</sub> O (5-sipH <sub>3</sub> = 5-sulfo-isophthalic acid bpy = 4,4'-bipyridine DMF = dimethyl formamide)	[[Me_2NH2]SO4] <sup>-</sup> net 2D layers by coordination of Zn and by chains to 5-sipH moieties. Stacking of layers form 1-D	$5.6 \rm{\AA} \times 7.1 \rm{\AA}$	Channels lined with proto- nated sulfonic acid moiety	DMF and water molecules	$3.9  imes 10^{-4}$	<i>T</i> = 25 °C, 60% RH	I	129
[Zn(H <sub>2</sub> O)(5-sipH)(bpe) <sub>0.5</sub> ]-DMF (bpe = 1,2-di(4-pyridyl)ethylene)	1D chain ladder structure, stacking of which forms 1-D channels	$10.4~\mathrm{\AA}\times3.1~\mathrm{\AA}$	1D channels lined with sulfonic acid moieties, coordinated water (1 ner Zn atom)	I	$3.4  imes 10^{-8}$			
[Zn <sub>3</sub> (5-sip) <sub>2</sub> (5-sipH)(bpy)]·(DMF)· 2(DMA) (DMA = dimethvl ammonium)	3D structure with 1D channels	$3.4~\mathrm{\AA}  imes 4.2~\mathrm{\AA}$	Two deprotonated 5-sipH and one unprotonated 5-sipH <sub>3</sub>	Dimethyl ammonium and DMF	$8.7 imes10^{-5}$			
[[CH3,2NH2]-[Zn3,Na2(cpida)3]. 2.5DMF [H3cpida = N-{4- carboxrohenv]]iminodiacetic acid]	3D pillar-layer structure with 1D honeycomb channels	10.6 Å	1D channels are hydro- phobic, lined with benzene and methylene moieties	[NH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> and absorbed water molecules	$2.1 imes10^{-6}$	T = 95 °C, ~97% RH	0.81	130
Cu-bpdo- <i>p</i> -sulfonatocalix[4]arene´	2D layers forming a three-dimensional supramolecular architecture through C-H···π and C-H···Ο interactions	12.23 Å × 11.99 Å	Sulfonate groups, -OH groups and water molecules, which participate in hydrogen bonding	Calixarene	$5.42 \times 10^{-7}$	T= 25 °C, 95% RH	0.39	131
[LnL(H <sub>2</sub> O) <sub>3</sub> ].2H <sub>2</sub> O (L = <i>N</i> -phenyl- <i>N'</i> -phenylbicyclo- [2,2,2]-oct-7-ene-2,3,5,6-tetra- carboxdiimide tetracarboxylic acid, 1.n = F.1 Dv)	3-D double chain structure where chains are crosslinked by Ln–O	10.5 Å	Free carboxylates lining 1D channel with water	Uncoordinated pore water	$1.6  imes 10^{-5}$ (Eu) $1.33  imes 10^{-5}$ (Dy)	T= 75 °C, 97% RH	0.91 0.87	132
$[H_2L^{(1)}(MF)(NO_3)] \cdot [DMF]_3 \cdot (H_2O)_8 \\ [H_2L^+CI^- = 1,3-bis-(4-carboxyphenyl)-imidazolium chloride)$	2-D puckered sheets interpenetrate in 3-fold fashion, 3-D structure forms from parallel catenation of 3 such interpenetrated networks	11.09 Å × 10.63 Å	Free water and DMF mole- cules reside within 1D channels with aligned imidazolium	Pore water, DMF	$1.3  imes 10^{-5}$	T= 25 °C, 98% RH	I	133
CaPiPhtA-NH <sub>3</sub>	3D structure with 1D channels filled with water molecules and guest NH <sub>3</sub> groups	1	Hydrogen bonded pathway between the lattice water molecules and NH <sub>3</sub> guests	Lattice water, NH <sub>3</sub>	$6.6  imes 10^{-3}$	T= 24 °C, 98% RH	0.4	134

copper(II) complexes.<sup>73,74</sup> This was followed by a report of the conductivity of hydrogen-doped  $(HOC_2H_4)_2$ dtoaCu by Kitagawa *et al.*<sup>75</sup> This 2D compound exhibited a proton conductivity value of 2.2 × 10<sup>-6</sup> S cm<sup>-1</sup> at a temperature of 27 °C and 100% RH. This value was highly humidity dependent, and dropped to 2.6 × 10<sup>-9</sup> S cm<sup>-1</sup> at 45% RH. The conductivity was attributed to H<sub>3</sub>O<sup>+</sup> ions, which are generated at ~100% RH by a reaction between water and hydrogen at the NH bonds of the polymer. Although the value of conductivity for this polymer was not very high, it paved the way for further studies on proton conductivity in MOFs.

Kitagawa *et al.* also studied the proton conductivity of several oxalate-based MOFs. Among these,  $Fe(ox) \cdot 2H_2O$  (ox = oxalate), is noteworthy.<sup>76</sup> In this compound, Fe(II) and oxalate ions are connected to form 1D-chains wherein Fe is coordinated equatorially to oxalate anions, with the remaining axial coordination sites occupied by water molecules. Given the formation of 1-D arrays of water molecules, the proton conductivity was analyzed.  $Fe(ox) \cdot 2H_2O$  exhibits a conductivity of  $1.3 \times 10^{-3}$  S cm<sup>-1</sup> at 25 °C and 98% RH. As a result of the relatively high conductivity and activation energy (0.37 eV),  $Fe(ox) \cdot 2H_2O$  was deemed a superprotonic conductor at ambient temperatures. Herein was an early example of a proton conducting MOF, where a regular array of water molecules can enable conduction of protons.

Another oxalate-based network,  $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$ , (adp = adipic acid) was investigated by the same group.<sup>77</sup> Three rational design strategies were utilized to incorporate proton carriers into this MOF: using protonated counterions, functionalizing the framework with acidic groups and filling the pore spaces with acidic molecules. An anionic, layered framework was formed by  $[Zn_2(ox)_3]^{2-}$ , and  $NH_4^+$  counterions were present for charge balance (Fig. 2(a)). The inner pore spaces were then filled with adipic acid and water for an overall formula of  $(NH_4)_2(adp)[Zn_2(ox)_3] \cdot 3H_2O$ .  $Zn^{2+}$  ions and oxalate moieties coordinate to form 2-D honeycomb layers along the bc-plane, forming 1-D pores of size 8.44 Å  $\times$  9.16 Å perpendicular to the plane (Fig. 2(b)). Within these pores, adipic acid,  $NH_4^+$  ions, water molecules and framework oxalates form 2-D hydrogenbonding networks. Proton conductivity of  $8 \times 10^{-3}$  S cm<sup>-1</sup> was achieved at 25 °C and 85% RH, with activation energy of 0.63 eV. Additionally, the conductivity was highly humidity dependent; at 85% the trihydrate is obtained. However, lowering the humidity to 70% results in a dihydrate which exhibits a conductivity value of 6  $\times$  10<sup>-6</sup> S cm<sup>-1</sup>. This PCMOF demonstrated high proton conductivity through incorporation of acidic moieties by rational design of the framework structure.

Bimetallic complexes bridged by oxalate anions were investigated by Okawa *et al.*<sup>78</sup> The coordination polymer,  $\{NH(prol)_3\}[M^{II}Cr^{III}(ox)_3]$ (prol = tri(3-hydroxylpropyl)ammonium,  $M^{II} = Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ) generated a bimetallic, 2-D honeycomb layer with pores measuring 7.96 Å × 9.16 Å, wherein oxalate groups bridge the two metals in alternating fashion (analogous to the previously reported  $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$ ). The pore spaces were modified using an ammonium counter-ion, tri(3-hydroxylpropyl)ammonium, to charge balance as well as to form hydrophilic layers of hydroxyl groups for proton conduction (Fig. 3). The hydroxyl groups of



Fig. 2 (a) The honeycomb layer structure of  $(NH_4)_2(adp)[Zn_2(ox)_3]\cdot 3H_2O$ , containing adipic acid groups in the inter-layer spaces; (b) perspective view along the *b*-axis. Zn green, O red, C gray.

the ammonium cations form hydrogen bonds with pore water, and in combination with the bulkiness, also distort the bimetallic layer. Water adsorption isotherms of the CPs reveal a continuous increase with RH until a saturation point upon which the compounds decompose (~70% RH for  $M^{II} = Mn^{2+}$ , ~75% for Fe<sup>2+</sup> and ~80% for Co<sup>2+</sup>). At 40% RH, two water molecules reside in the interlayer spaces for the Mn complex while one resides in both Fe and Co complexes. At RH > 40%, water content increases to 5 molecules in Mn and Fe complexes, while for the Co complex it reaches up to 5 only at ~80% RH. As a result of the increased water content, proton conductivities of the complexes are highly dependent on humidity levels. At 40% RH, proton conductivity ranged from  $1.2 \times 10^{-10}$  to  $4.4 \times 10^{-10}$  S cm<sup>-1</sup>, and then increased to  $1 \times 10^{-4}$  S cm<sup>-1</sup> at 75% RH.

Of significance, these CPs were the first to demonstrate both ferromagnetism and proton conductivity within a single material ( $T_{\rm C} = 5-10$  K). Proton conductivity arose due to hydrogen bonding within interlayer spaces between a hydrophilic ammonium counterion and water molecules. The tri(3-hydroxylpropyl)ammonium cations in the above compound can be substituted with trialkyl (carboxymethyl) ammonium ions, to yield bimetallic oxalates of the formula, {NR<sub>3</sub>(CH<sub>2</sub>COOH)}[M<sub>a</sub><sup>II</sup>M<sub>b</sub><sup>III</sup>(ox)<sub>3</sub>].<sup>79</sup> The cationic groups reside in the inter-layer spaces. The inter-layer hydrophilicity is tuned by the hydrophilicity of the cations, thereby affecting the water adsorption, and hence the proton conduction. The {NEt<sub>3</sub>(CH<sub>2</sub>COOH)}<sup>+</sup> groups are more hydrophilic than the {NBu<sub>3</sub>(CH<sub>2</sub>COOH)}<sup>+</sup> groups, and hence the Et-MOFs exhibit a higher conductivity than the Bu-MOFs, with conductivity





#### (b)

**Fig. 3** (a) View of  $\{NH(prol)_3\}[MnCr(ox)_3]\cdot 2H_2O$  along *a*-axis; (b) view of the bimetallic layer and cations in the *ab*-plane. Cr teal, Mn dark green, O red, C gray, N dark blue.

values reaching  $\sim 1 \times 10^{-7}$  S cm<sup>-1</sup> at 65% RH. Again, of particular interest are the R-FeFe MOFs, which exhibit both proton conductivity and Néel N-type ferrimagnetic ordering with  $T_{\rm C}$  of 42–44 K.

A three-dimensional chiral bimetallic oxalate with quartz structure,  $(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$ , was reported by Train, Verdaguer *et al.*<sup>80</sup> The oxalate anions bridge Mn and Cr cations to form helices along the *c*-axis, forming two types of 1-D channels; hexagonal A channels with 5.23 Å diameter, and triangular B channels with a diameter of 7.52 Å (Fig. 4). The inner surface of A channels are lined with terminal oxalates, with half the unit coordinated to Cr, forming a hydrophilic surface filled with guest water molecules. Water also exists in the B channels but is very disordered. Proton conductivity at 23 °C and 96% RH was  $1.1 \times 10^{-3}$  S cm<sup>-1</sup>, which increased with temperature to  $1.7 \times 10^{-3}$  S cm<sup>-1</sup> at 40 °C. The low activation energy of 0.23 eV and high conductivity were attributed to the hydrogen bonded species within the A channels.

Proton conductivity in other carboxylate-based MOFs has also been reported. Banerjee *et al.* reported the conductivity of two isomeric indium isophthalate-based MOFs, In-IA-2D-1 and In-IA-2D-2.<sup>81</sup> The structures contain tetrahedral In(m) secondary



(a)



Fig. 4 (a) View of the bimetallic oxalate structure,  $(NH_4)_4[MnCr_2(ox)_6]$ -4H<sub>2</sub>O, along the *c*-axis, showing the presence of two types of channels. Cr polyhedra are in green, Mn polyhedra are in purple; (b) view of the quartz-like assembly of the MnCr<sub>4</sub> tetrahedra along the *c*-axis.

building units (SBUs), which are connected to each other via isophthalic acid linkers to form a 1D coordination network, which are bridged via additional isophthalic acid moieties to form a 2D layer structure. The layers consist of rectangular channels of size 8.95 Å imes 9.69 Å (In-IA-2D-1) and 10.41 Å imes10.05 Å (In-IA-2D-2).  $H_2O$  and  $[(CH_3)_2NH_2]^+$  cations are present as guests in In-IA-2D-1, whereas In-IA-2D-2 contains  $[(CH_3)_2NH_2]^+$  cations and DMF molecules inside the framework (Fig. 5). At 27 °C and 98% RH, In-IA-2D-1 showed a conductivity of 3.4  $\times$  10  $^{-3}$  S cm  $^{-1}$  , while In-IA-2D-2 showed a conductivity of  $4.2 \times 10^{-4}$  S cm<sup>-1</sup>. This difference was attributed to the presence of bulky DMF molecules in the latter, which restricted the accessibility of water molecules to  $[(CH_3)_2NH_2]^+$  cations. However, unlike In-IA-2D-1, In-IA-2D-2 showed a conductivity of  $1.18 \times 10^{-5}$  S cm<sup>-1</sup> at high temperatures (90 °C) under anhydrous conditions due to the presence of the [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations and high boiling DMF solvent molecules.

Conductivity studies have been reported in MOFs which contain the carboxylate moiety in conjunction with an additional functional group. The alkali metal SBBAs (SBBA = 4,4'-sulfobisbenzoic acid) reported by Banerjee *et al.*, in which the SBBA ligand contains both the sulfone and carboxylate groups, belong to this category.<sup>82</sup> In Ca-SBBA, two octahedrally-coordinated Ca centres are linked





(a)

Fig. 5 (a) Assembly of isophthalic acid and  $[In(COO)_4]^{-}SBU$  resulting in two isomeric MOFs: In-IA-2D-1 (left), containing H<sub>2</sub>O and  $[(CH_3)_2NH_2]^{+}$  guests, and In-IA-2D-2 (right), containing  $[(CH_3)_2NH_2]^{+}$  and DMF molecules as guests; (b) a single layer in In-IA-2D-1 (left) and In-IA-2D-2 (right). In<sup>III</sup> teal, O red, C gray, N dark blue.

*via*  $\mu_2$  carboxylate oxygen to form one-dimensional chains, which are further interconnected to form a 2D layer structure. The layers are arranged in supramolecular-fashion through C-H···O interactions to yield a three-dimensional architecture. DMF molecules are coordinated to the Ca centres in the axial positions, and are also present as free guests in the inter-layer spaces. In the crystal structure of Sr-SBBA, pentanuclear metal clusters are present, which are linked through carboxylate groups of the SBBA ligand to give rise to three different SBUs containing either ten-coordinated SrO<sub>10</sub> or eight-coordinated SrO<sub>8</sub> polyhedra. The clusters are connected to neighboring clusters via the SBBA ligands to form the 2D architecture. DMF molecules coordinate to the central Sr(II) atoms in two of the SBUs. The proton conductivity values are modest; Ca-SBBA was measured as  $8.58 \times 10^{-6}$  S cm<sup>-1</sup>, whereas Sr-SBBA showed a higher proton conductivity of  $4.4 \times 10^{-5}$  S cm<sup>-1</sup>, at 25 °C and 98% RH. The activation energy values for Sr-SBBA and Ca-SBBA were 0.56 eV and 0.23 eV respectively. The higher value of proton conductivity in Sr-SBBA was due to a high carrier concentration, originating from the combination of metal clusters and solvent molecules. Ba-SBBA did not exhibit any conductivity due to phase change and loss of crystallinity upon humidification.

Fig. 6 (a)  $Zn_BO$  cluster connected to six metallomacrocycles; (b) spacefilling diagram along the *a*-axis, showing the alignment of acidic methylene groups of the imidazolium moieties. Reproduced with permission from ref. 13. Copyright 2012 American Chemical Society.

Sen et al. reported a MOF based on a ligand with both the carboxylate and imidazolium functionalities.<sup>13</sup> The compound,  $[{(Zn_{0.25})_8(O)}Zn_6(L)_{12}(H_2O)_{29}(DMF)_{69}(NO_3)_2]_n {H_2L = 1,3-bis(4$ carboxyphenyl)imidazolium}, possesses a three-dimensional structure and has a unique Zn<sub>8</sub>O cluster. The extended structure consists of a 48-membered metallomacrocycle (Fig. 6(a)), and six such macrocycles are connected through a ligand molecule to the Zn<sub>8</sub>O cluster to form an extended 2D sheet structure. These 2D sheets exhibit 6,3-connected, 3-fold interpenetration and propagate in all directions to give rise to a 3D structure with rectangular channels along the *a* and *b* axes, measuring 13.13 Å × 17.96 Å and 22.56 Å × 15.57 Å, respectively (Fig. 6(b)). Of particular interest is the fact that the methylene groups of the imidazolium moieties are aligned inside the channels, which contain solvent water and DMF along with nitrate anions to balance the charge. Proton conductivity studies on this compound showed that the conductivity increases with humidity and reaches a maximum value of  $2.3 \times 10^{-3}$  S cm<sup>-1</sup> at 25 °C and 95% RH. This was correlated with the water adsorption experiments, which showed plateau regions at two, five and eight water molecules per formula unit. The proton conductivity of the MOF up to the tetrahydrate state was low. However, upon hydration with the fifth water molecule, the conductivity was enhanced significantly, showing that the degree of hydration played an important role in the proton conduction. The activation energy was determined to be 0.22 eV, thereby suggesting

that the water molecules in the channels take part in a Grotthusstype conduction of protons originating from the imidazolium groups.

Proton conductivity studies were recently carried out on homochiral MOFs by Sahoo *et al.*<sup>83</sup> Enantiomeric MOFs,  $[Zn(L-L_{Cl})(Cl)](H_2O)_2$  and  $[Zn(D-L_{Cl})(Cl)](H_2O)_2$  (L = 3-methyl-2-(pyridin-4-yl-methylamino)-butanoic acid) were synthesized using L-/D-valine derivatives respectively, and possessed the zeolitic unh topology (Fig. 7(a) and (b)). 1D continuous helical water chains are present inside the pores of both the MOFs (Fig. 7(c)).



**Fig. 7** (a) Polyhedral representation of the homochiral MOF viewed along the *c*-axis. Zn polyhedral are in blue, while lattice water molecules are shown in red; (b) space filling model of the two enantiomers of chiral MOF showing opposite helicity; (c) mirror images of helical water chains in the two enantiomers, surrounded by the molecular helices. Water molecules are shown in red.

The diameter of the pore measures approximately 14.5 Å. The proton conductivities of both the MOFs were similar – 4.45 imes $10^{-5}$  and  $4.42 \times 10^{-5}$  S cm<sup>-1</sup>, respectively, still at 31 °C and 98% RH, with activation energies of 0.34 and 0.36 eV. This value dropped to  $1.49 \times 10^{-5}$  and  $1.22 \times 10^{-5}$  S cm<sup>-1</sup> at 75% and 60% RH, respectively, at 31 °C. The conductivity was attributed to the presence of continuous helical water chains, in which  $D_{O \cdots O}$  is 3.234(3) Å.  $[Zn(L-L_{Cl})(Cl)(D_2O)]$ , which was synthesized using D<sub>2</sub>O as solvent of synthesis, showed a lower conductivity of  $1.33 \times 10^{-5}$  S cm<sup>-1</sup> in a H<sub>2</sub> atmosphere humidified with D<sub>2</sub>O (98%).  $[Zn(D-L_{Br})(Br)](H_2O)_2$  and  $[Zn(D-L_{Br})(Br)](H_2O)_2$ , although structurally similar to the chloride analogues, did not exhibit any conductivity, thereby showing that the electronegativity of the halogen atom which is hydrogen-bonded to the water in the channels also plays an important role in determining the conduction pathway.

Recently, the conductivity of compounds containing both the carboxylate moiety and polyoxometalate anions has been examined.<sup>84,85</sup> Polyoxometalates (POMs), especially of the Keggin type, have been used in a variety of electrochemical applications such as solid state electrochromic devices, electrochemical fuel cells, as electrolytes for capacitors etc.<sup>86</sup> Wei et al. used Keggin anions of the type  $[PM_{12}O_{40}]^{3-}$ , along with 2,2'-bipyridyl-3,3'dicarboxylic acid (H<sub>2</sub>bpdc), to synthesize two poly-POM-MOF composites,  $\{H[Cu(Hbpdc)(H_2O)_2]_2[PM_{12}O_{40}] \cdot nH_2O\}_n, (M = W, Mo).^{85}$ In the composites,  $[Cu(Hbpdc)(H_2O)_2]^{2+}$ ,  $[PM_{12}O_{40}]^{3-}$ , protons and water molecules assemble together to form three-dimensional structures with 1D hydrophilic channels of diameter 10.94(2) Å, along the *a*-axis. In these channels, a continuous water phase is stabilized by hydrogen bonding between the oxygen atoms of Hbpdc<sup>-</sup> ligands, polyanion oxygen and coordinated water molecules. Proton conductivity studies at 25 °C and 98% RH showed poor conductivities of  $\sim 3.0 \times 10^{-7}$  S cm<sup>-1</sup> for both compounds, with an activation energy of  $\sim 1.02$  eV. However, with increasing temperature, the conductivities of both the compounds also increased to 1.25  $\times$   $10^{-3}~S~cm^{-1}$  (Mo) and 1.56  $\times$   $10^{-3}~S~cm^{-1}$ (W), at 100 °C and 98% RH. This study showed for the first time that MOF-POM composites can be used to increase the stability and conductivity of inorganic-organic hybrid materials.

Hupp et al. recently adopted another approach in which conductivity was altered by changing the solvent molecules coordinated to the central metal atom.<sup>87</sup> HKUST-1, possessing a three-dimensional structure which consists of Cu<sup>II</sup> paddlewheel nodes and 1,3,5-benzenetricarboxylate (BTC) linkers, was chosen as the compound for the study. This compound contains a 3D channel with a pore size of 10 Å and has high thermal and aqueous stability. In the as-synthesized HKUST-1, CuII ions, bearing an open-coordination site, were coordinated to  $\sim 60\%$  H<sub>2</sub>O molecules and  $\sim 40\%$  EtOH molecules. These solvent molecules were then completely replaced by H2O, EtOH, MeOH and MeCN molecules, as confirmed by NMR and PXRD. Conductivity studies carried out on the modified compounds under MeOH vapour revealed that H<sub>2</sub>O-HKUST-1 exhibited a conductivity of  $1.5 \times 10^{-5}$  S cm<sup>-1</sup>, which is  $\sim$  75 times larger than those of EtOH-HKUST-1 and MeCN-HKUST-1, and is ~90 times larger than that of bulk MeOH. As the MeOH vapour fills the pores, the H<sub>2</sub>O molecules

coordinated to the central  $Cu^{II}$  ions act as proton donors, leading to an increase in the  $CH_3OH_2^+$  carrier concentration and an increase in the conductivity. However, under *n*-hexane, the same compound (H<sub>2</sub>O-HKUST-1) exhibited a conductivity which was more than 5 orders of magnitude below that obtained under MeOH. This study provided a new strategy to achieve control over the conductivity of a framework compound.

Apart from carboxylates, proton conductivity studies have also been carried out on a number of phosphonate-based frameworks. The phosphonate group possesses three oxygen atoms, so one can envisage the formation of multidimensional frameworks given the number of coordination modes possible. MOFs constructed with phosphonates could benefit from free oxygen atoms acting as H-bond acceptors for proton conductivity or the presence of hydrogen phosphonate groups within the framework. Taylor et al. reported a proton conducting metal phosphonate framework consisting of Zn<sup>2+</sup> ions and 1,3,5-benzenetriphosphonic acid (H<sub>6</sub>L) to yield a compound of formula, Zn<sub>3</sub>(L)(H<sub>2</sub>O)<sub>2</sub>·2H<sub>2</sub>O (PCMOF-3).<sup>88</sup> The coordination of Zn ions to L results in a layered structure wherein the metal ions cross-link L into a layer along the bc plane. A hydrophilic interlayer arises from well ordered, uncoordinated water molecules which are anchored via hydrogen bonding to Zn, coordinated water molecules (two per ion), as well as phosphonate oxygen atoms. With oxygen atom distances of 2.698(2)-2.895(2) Å within the interlayer, as well as an extremely low activation energy of 0.17 eV, PCMOF-3 demonstrated Grotthuss mediated proton conductivity of  $3.5 \times 10^{-5}$  S cm<sup>-1</sup> at 25 °C and 98% RH.

Taylor et al. further reported a proton conducting metal phosphonate MOF which exhibited good humidity stability and proton conductivity over 10<sup>-3</sup> S cm<sup>-1</sup>. PCMOF-5 was synthesized by combining La(HSO<sub>4</sub>)<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> with 1,2,4,5-tetrakisphosphonomethylbenzene  $(L^{8-})$  to form  $[La(H_5L)(H_2O)_4]$  (PCMOF-5), a 3-D framework (Fig. 8(a)).<sup>89</sup> The use of a flexible, tetrapodal ligand allowed formation of a 3-D structure with narrow 1-D channels of diameter 5.81 Å. Proton conductivity of 2.5  $\times$   $10^{-3}\,S\,cm^{-1}$  at 60  $^\circ C$  and 98% RH was achieved as a result of the formation of one-dimensional acidic channels along the a-axis (Fig. 8(b)). Uncoordinated, diprotic phosphonic acid groups lined these channels with monodentate hydrogen phosphonate (one each per formula unit) and uncoordinated water to form a facile proton conduction pathway. The low  $E_a$  of 0.16 eV suggested an efficient Grotthuss mechanism proton conductivity. To assess humidity stability, PCMOF-5 was boiled in water for 1 week with no significant loss in crystallinity (by powder XRD), in mass, or in terms of performance (conductivity), suggesting a highly robust material. PCMOF-5 demonstrated good proton conductivity, but more importantly was an example of a boiling water stable PCMOF. Additionally this MOF was also the first reported 3-D metal phosphonate containing free phosphonic acid pendants.

Kim *et al.* presented a material designated PCMOF-2.5 as a hybrid of two previously reported PCMOFs;<sup>90</sup>  $\beta$ -PCMOF-2 by Hurd *et al.*<sup>91</sup> and PCMOF-3 by Taylor *et al.*<sup>88</sup> Herein, the ligands 2,4,6-trihydroxy-1,3,5-benzene trisulfonate (L1) from  $\beta$ -PCMOF-2 was combined withbenzene-1,3,5-triphosphonate (L2) from PCMOF-3



**Fig. 8** (a) Polyhedral representation of the structure of PCMOF-5 viewed along the *a*-axis. Free phosphonic acid groups and lattice water molecules occupy the pores. La polyhedra are shown in brown. P pink, O red, C black; (b) view of the one-dimensional hydrogen-bonded array formed between free phosphonic acid groups and lattice water molecules, along the *a*-axis. La blue, P pink, O red, C gray.

into a structure which forms 1-D channels and1-D columns of ligands that are then cross-linked with Na ions into 3-dimensions. β-PCMOF-2 demonstrated anhydrous proton conductivity at 150 °C by loading 1,2,4-triazole as a proton carrier (to replace water) within the 5.6 Å 1-D channels. Despite various loadings, between 0.3-0.6 per formula unit, conductivity did not exceed 5  $\times$  10<sup>-4</sup> S cm<sup>-1</sup> at the highest loading. Herein, the limiting factor was hypothesized as the number of available protons within the structure. Thus, increasing the ion concentration should raise the conductivity. In building PCMOF-2.5, L2 was chosen as it shared similar size, a hydrophobic core, polar periphery and  $C_3$  symmetry with L1; therefore substitution of ligands should not perturb the structure. Secondly, for charge balance with the sulfonates, the phosphonates within L2 would need to be monoprotonated giving additional protons, which could contribute to conduction. Thus the 1-D channels of PCMOF-2.5 were lined with hydrogen phosphonate and sulfonate groups to form proton conduction pathways, efficiently conducting protons at 2.1  $\times$   $10^{-2}~S~cm^{-1}$  at 85  $^\circ C$  and 90% RH. PCMOF-2.5 was isostructural to β-PCMOF-2 by powder XRD patterns performed after combining Na<sub>3</sub>L1 and Na<sub>3</sub>H<sub>3</sub>L2. Notably, the mixed ligand system could only be prepared through a solid state synthetic route first achieved in situ during the impedance measurements. PCMOF-2.5 demonstrated the use of isomorphous replacement of deprotonated organosulfonates with

organohydrogenphosphonates with common size and shape, yielding the first PCMOF with proton conductivity over  $10^{-2}$  S cm<sup>-1</sup>.

#### Proton conducting MOFs operating at $T \ge 100$ °C

As discussed above, most reported PCMOFs operate in the lowtemperature, hydrated regime. However, it is important to explore the proton-conducting properties of MOFs under hightemperature, anhydrous conditions, especially as an alternative to Nafion, which undergoes dehydration above 80  $^{\circ}$ C.

There are several strategies to improve the performance of a conductor at high temperatures, one of which is to load carrier molecules such as organic heterocycles like imidazole or 1,2,4triazole into the channels of a MOF. Imidazolium ( $pK_a$ : 6.9) and pyrazolium  $(pK_a: 2.6)^{92}$  have been proposed as proton transfer agents due to their fast proton transfer behaviour and amphiprotic nature, analogous to that of water.93-96 The additional advantage of higher melting points also enables proton conduction at T >100 °C. 1,2,4-Triazole was also investigated as a protogenic group<sup>97</sup> and has also been utilized (along with 1,2,3-triazole) to enhance intermediate temperature conductivity of polymeric conductors. 1,2,4-Triazolium was suitable given the greater electrochemical stability under fuel cell conditions in addition to lower  $pK_{a1}$ compared to imidazolium (2.2 vs. 6.9).97 Hurd et al. reported a sulfonate metal-organic framework Na<sub>3</sub>(2,4,6-trihydroxy-1,3,5benzenetrisulfonate) (β-PCMOF2).<sup>91</sup>

The structure is made up of hexagonal sheets of trihydroxybenzenetrisulfonate molecules which are cross-linked *via* Na atoms to form a three-dimensional honeycomb structure with one-dimensional channels of diameter 5.65(2)-5.91(2) Å (Fig. 9). These channels are lined with oxygen atoms from the sulfonate groups. The hydrated framework exhibited a conductivity of  $5.0 \times 10^{-6}$  S cm<sup>-1</sup>, which dropped to below  $10^{-8}$  S cm<sup>-1</sup> above 70 °C due to dehydration. However, when 1,2,4-triazole(Tz) was introduced into the channels of the framework, the conductivity at 150 °C increased to  $2 \times 10^{-4}$  S cm<sup>-1</sup>,  $5 \times 10^{-4}$  S cm<sup>-1</sup>, and  $4 \times 10^{-4}$  S cm<sup>-1</sup>, at triazole loadings of 0.3, 0.45 and 0.6 respectively, at 150 °C. The activation energies changed with the triazole loadings. Additionally, a membrane-electrode assembly (MEA) was constructed using β-PCMOF2(Tz)<sub>0.45</sub> as the electrolyte, and electromotive force was measured under H<sub>2</sub>/air



**Fig. 9** View of a single layer in PCMOF-2 along the *c*-axis, showing the open, 18-membered channels. Guest triazole molecules are shown in blue. Na green, C gray, O red, S yellow.

atmospheres. An open circuit voltage of 1.18 V was obtained, which was stable for 72 h at 100  $^\circ$ C, thereby showing for the first time that PCMOFs could potentially be used in fuel cells.

Another study was carried out by Bureekaew et al., wherein imidazole (Im) was used as the guest proton carrier; this was loaded into two Al-based frameworks - [Al(µ2-OH)(1,4-ndc)]n (ndc – naphthalenedicarboxylate) and  $[Al(\mu_2-OH)(1,4-bdc)]_n$  (bdc – benzenedicarboxylate).98 Both frameworks contained corner-shared chains of  $AlO_4(\mu_2-OH)_2$  connected via the dicarboxylate ligand, resulting in a 3D framework containing 1D channels (Fig. 10). In the ndc framework, two types of hydrophobic microchannels were present, while in the bdc-framework, only diamond-shaped hydrophilic channels were observed. Both compounds contained pores of size 8 Å. Im@{Al( $\mu_2$ -OH)(1,4-ndc)}<sub>n</sub> and Im@{Al( $\mu_2$ -OH)(1,4-bdc)}<sub>n</sub> were prepared by loading 0.6Im/Al ion and 1.3Im/Al ion in the ndc and bdc frameworks, respectively. Im@ $\{Al(\mu_2-OH)(1,4-ndc)\}_n$ exhibited a conductivity of  $5.5 \times 10^{-8}$  S cm<sup>-1</sup> at room temperature, which increased to  $2.2 \times 10^{-5}$  S cm<sup>-1</sup> at 120 °C. On the other hand, despite having double the imidazole content compared to the ndc framework, Im@ $\{Al(\mu_2-OH)(1,4-bdc)\}_n$  exhibited a conductivity of 10<sup>-10</sup> S cm<sup>-1</sup> at room temperature, which increased to  $1.0 \times 10^{-7}$  S cm<sup>-1</sup> at 120 °C. This difference was attributed to the interactions of imidazole with the channel surfaces - the presence of non-polar channels in the ndc



**Fig. 10** Three-dimensional structures of (a) Al-ndc and (b) Al-bdc frameworks. Brown cubes represent guest imidazole molecules. Al green, O red, C gray.

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framework allows the polar imidazole to pass through freely, while the polar channels in the bdc framework interact strongly with the imidazole, thereby diminishing its mobility. This study proved that proton carriers can be matched with the appropriate MOF, thus taking advantage of the tunability of MOFs.

In line with the theme of loading guests into frameworks to improve conductivity is the study on inclusion of inorganic acids into MIL-101 hosts (MIL-Materials Institute Lavoisier) by Ponomareva et al.99 The MIL-101 structure is made up of inorganic trimers consisting of three octahedrally-coordinated Cr atoms, which are linked through 1,4-benzenedicarboxylate (terephthalate) anions to form a supertetrahedron (ST).<sup>27</sup> The vertices of the ST are occupied by the trimers, while the organic linkers occupy the edges. These STs are further connected with each other to yield a cubic, three-dimensional framework consisting of two types of mesoporous cages, which are occupied by solvent molecules. The smaller cages possess pentagonal windows with a free opening of 12 Å, while the larger cages contain both pentagonal and hexagonal windows with free apertures measuring 14.5 Å  $\times$ 16 Å. Cr<sup>III</sup> terephthalate frameworks with the MIL-101 structure were mixed with aqueous solutions of H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>. Upon drying at elevated temperatures, solid products H2SO4@MIL-101 and H<sub>3</sub>PO<sub>4</sub>@MIL-101 were obtained. Elemental analysis indicated that 50 H<sub>2</sub>SO<sub>4</sub> and 42 H<sub>3</sub>PO<sub>4</sub> molecules were incorporated per MIL-101 nanocage, respectively, and PXRD patterns showed that the host structures remained intact after the encapsulation of acids in the pores. The compounds, H<sub>2</sub>SO<sub>4</sub>@MIL-101 and H<sub>3</sub>PO<sub>4</sub>@MIL-101, showed conductivities of  $4.0 \times 10^{-2}$  S cm<sup>-1</sup> and  $2.5 \times 10^{-4}$  S cm<sup>-1</sup>, respectively, at low temperatures (  $\sim$  30 and 56  $^{\circ}$ C) and 20% RH, with an activation energy of  $\sim 0.42$  eV. The conductivities changed to  $1 \times 10^{-2}~\text{S cm}^{-1}$  and  $3 \times 10^{-3}~\text{S cm}^{-1}$  at 150  $^\circ\text{C}$  and 0.13% RH. Since  $K_a(H_2SO_4) > K_a(H_3PO_4)$ , higher conductivity was observed for the framework impregnated with sulfuric acid. The conductivities of the solid materials obtained by this approach are comparable to that of Nafion.

Another strategy to obtain anhydrous proton conductivity is to synthesize compounds which exhibit intrinsic proton conductivity. This was first demonstrated by Kitagawa and co-workers, who synthesized a two-dimensional zinc phosphate polymer with formula  $[Zn(H_2PO_4)_2(TzH)_2]_n$ .<sup>100</sup> Octahedrally-coordinated  $Zn^{2+}$ ions are connected to orthophosphate moieties and bridging triazole molecules, to give rise to two-dimensional layers, which are stacked along the c-axis. Significant inter-layer hydrogen bonding is present between axially coordinated phosphate groups of two different layers. Proton conductivity measurements on pellets at 150  $^\circ C$  resulted in a value of 1.2  $\times$   $10^{-4}~S~cm^{-1}$  and an activation energy of 0.6 eV. In addition, proton conductivity measurements were also performed on a single crystal of dimensions 0.55 mm  $\times$  0.25 mm  $\times$  0.06 mm. The in-plane and out-of-plane conductivities were measured to be 1.1  $\times$  10  $^{-4}$  S cm  $^{-1}$  and 2.9  $\times$  $10^{-6}$  S cm<sup>-1</sup> at 130 °C, thereby indicating that the compound conducts protons anisotropically.

Similar studies were carried out by the same group on another zinc phosphate coordination polymer,  $[Zn(HPO_4)(H_2PO_4)_2]$ - $(ImH_2)_2$ .<sup>101</sup> The compound consists of tetrahedrally coordinated Zn<sup>2+</sup> ions and two types of orthophosphates, which form



(b)

Fig. 11 (a) View of negatively charged one-dimensional chains of  $[Zn(HPO_4)(H_2PO_4)_2]^{2-}$  interleaved by protonated imidazolium cations. Zn blue, P pink, O red, C gray; (b) overall crystal structure of  $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$ . Imidazole is shown in blue, while the network is shown in gray.

one-dimensional chains bearing the formula,  $[Zn(HPO_4)(H_2PO_4)_2]^{2-1}$ (Fig. 11(a)), which is a highly acidic unit. Two crystallographically independent protonated imidazole molecules are located in the inter-chain space to result in an ionic crystal system (Fig. 11(b)). Multiple hydrogen bonds between protonated imidazolium cations and the orthophosphates are present. The ambient temperature conductivity of the compound was  $3.3 \times 10^{-8}$  S cm<sup>-1</sup>, which increased sharply at around 55 °C, and reached a value of  $2.6 \times 10^{-4}$  S cm<sup>-1</sup> at 130 °C, at which temperature it remained constant for 12 h. As the variable-temperature XRD revealed that the structure remained unchanged in this temperature region, the observed conductivity was assigned to the local motion of the imidazolium cations. The sudden increase in conductivity at 55 °C suggested that the compound behaved like a plastic crystal. This was further corroborated by DSC measurements, which showed an entropy change of 6.6 J mol  $^{-1}$  K  $^{-1}$  at 70  $^\circ C.$ Additionally, DC measurements proved unequivocally that the conduction was due to the local dynamic motion of protonated imidazolium cations.

While most MOFs reported in the literature operate either in the hydrated low-temperature region or in the anhydrous, high-temperature region, there are few reports of MOFs which can bridge this gap and exhibit conductivity in both regimes. Ghosh *et al.* recently reported an oxalate-based MOF,  $\{[(Me_2NH_2)_3-(SO_4)]_2[Zn_2(ox)_3]\}_n$ , which acts as a conductor in both the hydrated and anhydrous regimes.<sup>102</sup> The oxalate-based framework consists





**Fig. 12** (a) View of the tris-chelated  $[Zn_2(ox)_3]^{2-}$  subunit possessing  $D_3$  symmetry; (b) crystal structure of  $\{[(Me_2NH_2)_3(SO_4)]_2[Zn_2(ox)_3]\}_n$ , with DMA cations and disordered sulphate anions in pores; (c) view of the 3D supramolecular net,  $[(Me_2NH_2)_3(SO_4)]_n^+$ . Zn green, O red, N blue, C gray, S yellow, H white.

of an anionic framework interpenetrated with a cationic net. The anionic framework,  $[Zn_2(ox)_3]^{2-}$ , is built from zinc cations bound to oxalate units (Fig. 12(a)). In the three-dimensional channels of the oxalate network (diameter 11.12 Å) reside dimethyl ammonium (DMA) cations and sulphate anions (Fig. 12(b)), which are bound to each other by electrostatic interactions to form ionic nodes of formula,  $[(Me_2NH)_6SO_4]^{4+}$ . Several such cationic nodes are connected to form a supramolecular net,  $[(Me_2NH_2)_3(SO_4)]_n^+$  (Fig. 12(c)). Extensive hydrogen bonding exists between the

DMA cations and sulphate anions. The MOF exhibits a conductivity of  $1.0 \times 10^{-4}$  S cm<sup>-1</sup> at 150 °C under anhydrous conditions, with an activation energy of 0.129 eV, indicating that the protons are transported *via* Grotthuss mechanism. Under humid conditions (98% RH), the conductivity value reaches a maximum of  $4.2 \times 10^{-2}$  S cm<sup>-1</sup> at 25 °C, which is the highest value reported hitherto for a MOF.

#### PCMOF films or composites

Most studies on the proton conducting properties of MOFs have been carried out on either bulk samples pressed into pellets, or on single crystals. However, an important challenge remaining within the utilization of PCMOFs as electrolyte materials is addressing the fabrication of membranes from these crystalline materials. Some early efforts in thin-film formation have yielded promising results.<sup>4</sup> For example, Kitagawa, Kanaizuka et al. reported the layer-by-layer growth of highly crystalline surface coordination polymers (SCPs) with three dithiooxamides.<sup>103</sup> Bradshaw et al. recently reviewed efforts and methods in fabrication of MOF composite materials including thin-films for devices,60 while Jeong et al. recently reported the method of rapid thermal deposition (RTD), wherein a support substrate is soaked with a MOF precursor solution, followed by rapid heating at elevated temperatures to induce crystallization.<sup>61</sup> In addition to work on thin-films constructed from parent MOF structures, a new class of composites known as mixed-matrix membranes (MMM) has also been investigated where a flexible polymer matrix is embedded with a filler (such as MOFs) which impart some or all of its inherent properties. In the light of these developments, a few reports have recently emerged on the proton conduction properties of MOFs in these forms.

Xu et al. reported the proton conduction behavior in a highly oriented crystalline MOF nanofilm. 5,10,15,20-Tetrakis(4carboxyphenyl)porphyrin (TCPP) was used to synthesize a twodimensional Cu-TCPP nanosheet.<sup>104</sup> The nanosheet is made up of TCPP units bound to Cu centres, which are further connected to Cu<sub>2</sub>(COO)<sub>4</sub> paddle-wheels to form a three-dimensional structure, with one-dimensional channels along the c-axis. This nanosheet, containing dangling carboxyl groups, was then deposited onto a pre-fabricated Au/Cr electrode on a SiO<sub>2</sub>/Si wafer using the modular assembly method, to form a thin film between the electrodes (Fig. 13). Synchrotron grazing incidence XRD (GIXRD) patterns revealed in-plane hk0 peaks and out-of-plane 001 peaks, confirming that the *ab* plane of the MOF nanosheet lies parallel to the SiO<sub>2</sub>/Si substrate. AC impedance measurements at 25  $^{\circ}\mathrm{C}$  and 40% RH revealed a conductivity of 3.2  $\times$  $10^{-8}$  S cm<sup>-1</sup>, which increased rapidly by three orders of magnitude to  $6.2 \times 10^{-5}$  S cm<sup>-1</sup> at 90% RH, before reaching a value of 3.9  $\times$  10<sup>-3</sup> S cm<sup>-1</sup> at 98% RH. GIXRD patterns showed that the MOF nanofilm remains unaltered in humid conditions. Further, an analysis of the conductivity versus adsorbed water/TCPP unit showed that 4 mol of water is adsorbed by 1 mol TCPP unit when the humidity is increased from 40 to 90%, resulting in a jump by 3.5 orders of magnitude in the conductivity. Dangling carboxylic acid groups on the surface of the nanosheet adsorb water and act as Lewis acids, thereby functioning as effective proton donors. Beyond 90% RH, capillary condensation



**Fig. 13** (a) Figure representing the MOF nanofilm used for electrical measurement. Figures (b) and (c) represent the modelled crystal structures of the MOF nanofilm. Reproduced with permission from ref. 104. Copyright 2013 American Chemical Society.

takes place in the pores, resulting in an adsorption of 34 moles of water per TCPP unit. This study represented the first report of the electrical properties of a MOF nanofilm.

Zhu et al. integrated MOF crystals into a polymer matrix, and studied the conductivity of these composite MMMs under various conditions.<sup>105</sup> A chiral two-dimensional MOF, {[Ca(D-Hpmpc)- $(H_2O)_2$  2HO<sub>0.5</sub>, was synthesized from D-1-(phosphonomethyl)piperidine-3-carboxylic acid. Ca centres are connected via phosphonate oxygens to form 1D inorganic chains, which are further linked by carboxylic acid groups from the Hpmpc<sup>2-</sup> ligand molecules, to form a two-dimensional chiral layered architecture (Fig. 14(a)). A one-dimensional O-H···O hydrogen bonded chain is formed between the oxygen atoms of the coordinated water molecules, and the carboxylate oxygen atoms (Fig. 14(b)). Submicrorods of the Ca MOF (length: 3-4 µm, diameter: 0.3-0.4 µm) were then embedded into PVP polymer matrix via spin-coating method. Loading rates of the submicrorods were varied from 3 wt% (MOF-PVP-3) to about 50 wt% (MOF-PVP-50). Conductivity measurements on the MOF-PVP



Fig. 14 (a) Two-dimensional layer of the chiral Ca MOF; (b) view of the one-dimensional hydrogen-bonding  $(O-H\cdots O)$  chain between coordinated water molecules and carboxylate oxygens. Ca green, P pink, O red, N blue, C dark gray, H light gray.

composites at 53% RH and 333 K indicated that the conductivity increases with loading amounts; MOF–PVP-3 exhibited a conductivity of 4.8 × 10<sup>-7</sup> S cm<sup>-1</sup>, while MOF–PVP-50 showed a jump in conductivity of about three orders in magnitude to  $3.2 \times 10^{-4}$  S cm<sup>-1</sup>, with activation energy of 0.65 eV. It is notable that the MOF–PVP-50 also exhibits a higher conductivity ( $2.8 \times 10^{-5}$  S cm<sup>-1</sup>, 25 °C, 53% RH) than the pure submicrorods ( $6.9 \times 10^{-6}$  S cm<sup>-1</sup>) and pure PVP ( $1.4 \times 10^{-8}$  S cm<sup>-1</sup>) under similar conditions. Water adsorption experiments indicated that under about 95% RH, the maximum water vapor uptakes of PVP, MOF–PVP-50 and MOF are 1315, 761, and 25 cm<sup>3</sup> g<sup>-1</sup> (STP), corresponding to 105 wt%, 61 wt% and 2 wt%, respectively. These experiments showed that the proton conductivity of the composite membrane was influenced by the amount of the MOF filler, and the water sorption ability of PVP matrix.

Xu et al. reported the fabrication and characterization of a mixed matrix membrane (MMM) with high proton conductivity by combining a sulfonated polymer, poly(2,6dimethyl-1,4-phenylene oxide) (SPPO) with Fe-MIL-101-NH2 or  $[Fe_3(O)(BDC-NH_2)_3(OH)(H_2O)_2] \cdot nH_2O$  (where BDC-NH<sub>2</sub> = 2-aminoterephthalate).<sup>106</sup> The parent SPPO polymer incorporates Fe-MIL-101-NH<sub>2</sub> via the Hinsberg reaction, wherein a sulfonyl chloride reacts with an amine to form a sulfonamide salt. This was observed by FTIR wherein the -SO<sub>2</sub>Cl band disappeared and a new band at 1170  $\text{cm}^{-1}$  appeared from the sulphonamide linkage. SEM images of Fe-MIL-101-NH<sub>2</sub> revealed octahedral crystal morphology, which was then observed in the SEM images of the MMM, confirming the presence of the MOF in the polymer membrane (with further proof by XRD). Proton conductivity of the MMM reached a maximum of  $1 \times 10^{-1}$  S cm<sup>-1</sup> at room temperature and 98% RH with 6% MOF loading and with increasing temperature, conductivity increased to a maximum of 2.5  $\times$  10  $^{-1}$  S cm  $^{-1}$  at 90  $^{\circ}C$  and 98% RH.

#### Insights from other porous systems

Recently, proton conductivity studies have been carried out on a number of purely organic crystalline systems. These compounds often have multiple, strong hydrogen bonds and also possess a high degree of supramolecular order and have no relation to MOFs. However, they can still provide insight into proton conductivity through study of these supramolecular assemblies. Klapper, Müllen et al. studied a series of phosphonic acid containing small molecules,107 of note was hexakis(p-phosphonatophenyl)benzene (p-6PA-HPB) (Fig. 15).<sup>108</sup> Molecules of p-6PA-HPB were pi-stacked on top of each other with a distance of 0.6 nm. These stacks then self-assemble into 3D columns, with an inter-columnar distance of 1.4 nm, as shown by two-dimensional wide angle X-ray scattering (WAXS) experiments. Water adsorption isotherms indicated a pronounced hysteresis, showing that water molecules are immobilised in the crystal. p-6PA-HPB exhibited a conductivity of  $2.5 \times 10^{-2}$  S cm<sup>-1</sup> at room temperature and 95% RH. More importantly, the conductivity remained constant  $(3.2 \times 10^{-3} \text{ S cm}^{-1})$  with increasing temperature, in contrast to Nafion 117, and other industrially relevant polymers. In fact, above 160 °C, p-6PA-HPB showed proton conductivity higher than that of Nafion 117. This study showed the importance of



Fig. 15 Structure of hexakis (p-phosphonatophenyl) benzene (p-6PA-HPB).

supramolecular organisation in controlling proton conduction. It was found that materials that can assemble into columns, with a continuous acidic phase on the external surface of these columns, as in the structure of *p*-6PA-HPB, are highly conducive for conducting protons. In addition, the degree of crystallinity of the material was significant; likely with respect to the ordering (and thus arrangement) of proton conduction pathways throughout the material.

Kim et al. carried out conductivity studies on another family of organic solids, the cucurbit[n]uril.<sup>109</sup> Cucurbit[6]uril (CB[6]), was recrystallised from HCl and H<sub>2</sub>SO<sub>4</sub> solutions to give CB[6]·1.1HCl·11.3H<sub>2</sub>O and CB[6]·1.2H<sub>2</sub>SO<sub>4</sub>·6.4H<sub>2</sub>O, respectively, which have honeycomb-like structures with one-dimensional channels. The channels are filled with water and acid molecules, and exhibit heavy H-bonding. The HCl and H<sub>2</sub>SO<sub>4</sub> compounds exhibited conductivities of 1.1  $\times$   $10^{-3}$  and 1.3  $\times$   $10^{-3}~S~cm^{-1}$  at 25 °C and 98% RH, with activation energy values indicative of the Grotthus mechanism. Conductivity studies on single crystals indicated a highly anisotropic behaviour, with values of 2.4  $\times$  10<sup>-2</sup> S cm<sup>-1</sup> and 4.3  $\times$  10<sup>-2</sup> S cm<sup>-1</sup> along the *c*-axis, and  $7.1 \times 10^{-5}$  S cm<sup>-1</sup> and  $5.0 \times 10^{-6}$  S cm<sup>-1</sup> perpendicular to the *c*-axis, for the two compounds respectively. This study also demonstrated the use of H-bonded organic solids in proton conduction as well as tuning the proton conductivity of porous organic materials.

## Conclusions and future prospects

The examples surveyed have covered a range of different approaches to making better proton conducting MOFs, not just compositionally but philosophically. Two aspects of making a better proton conductor are to actually synthesize a promising material and another is to prepare or model a compound that gives insights into how to make such a material even though this latter material may not have commercial value. The systems presented have spanned a range of structures with different components, dimensionalities, pore structures, chemical functionalities and included proton carriers. As far as the question, "What is the best proton conducting MOF?" – there is no definitive answer. First of all, proton conduction below 100  $^{\circ}$ C in the presence of water and proton conduction above 100  $^{\circ}$ C under anhydrous conditions are different problems and will

require different materials. That said, some features are common to examples with high proton conductivity such as: incorporation of acidic groups; spatial alignment of protic sites to define an efficient proton transfer pathway; facile mobility of carriers; good match of  $pK_a$ 's in the pathway (a poor match in  $pK_a$  would mean relatively basic sites in the transfer pathway resulting in proton sinks). To attain higher operating temperatures (over 100 °C), loading guests (protic molecules or ions that are less volatile than water) into the pores of MOFs shows good promise. Merging these features with a robust structure has been achieved *via* a MOF approach with many more examples to come. Key proof of concept studies incorporating proton conducting MOFs or coordination polymers into membrane electrode assemblies have also been presented. While not approaching an industrial level of testing, these studies are critical for forward progress of this field.

Beyond the generation of a commercial fuel cell membrane, PCMOFs offer better insight towards materials design and understanding proton conduction phenomena. PCMOFs offer the ability to place proton transfer groups in an ordered matrix. In many cases, beyond the structural determination of the material (dimensionality, pore structures) visualization of the actual proton transfer pathway including volatile carriers can be achieved offering a valuable starting point for design and modelling of better systems.

At the outset of research on PCMOFs, there were certain key hurdles identified including, but not limited to, adequately high levels of conductivity (> $10^{-2}$  S cm<sup>-1</sup>), water stability, mechanical strength, and processability. There are now multiple examples of PCMOFs that conduct protons over 10<sup>-2</sup> S cm<sup>-1</sup> with every reason to believe even higher levels are attainable. Examples of water stable PCMOFs have been presented but more broadly, highly water stable MOFs for all applications are increasingly being reported. With the modular nature of MOF syntheses, these can offer additional scaffolds for modification for proton conducting applications. Mechanical strength and processability have not been addressed to a significant extent; these are not issues unique to the problem of proton conduction but to MOFs in general. With the range of potential structures and composite materials possible, it is difficult to believe that these are insurmountable challenges. At a fundamental level, these problems offer opportunities for creative design of new materials that bridge inorganic solid state and macromolecular organic domains. From a more applied perspective, progress will necessitate incorporation of leading candidates into engineered systems and another tier of testing as for any new membrane candidates. With the scope of accessible materials, continued progress in the field of PCMOFs is expected.

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