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Ion Conductivity and Transport by Porous Coordination Polymers and Metal–Organic Frameworks

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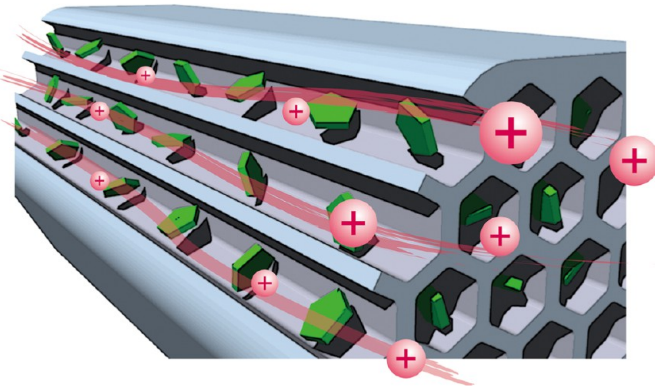

Ion conduction and transport in solids are both interesting and useful and are found in widely distinct materials, from those in battery-related technologies to those in biological systems. Scientists have approached the synthesis of ion-conductive compounds in a variety of ways, in the areas of organic and inorganic chemistry. Recently, based on their ion-conducting behavior, porous coordination polymers (PCPs) and metal–organic frameworks (MOFs) have been recognized for their easy design and the dynamic behavior of the ionic components in the structures. These PCP/MOFs consist of metal ions (or clusters) and organic ligands structured via coordination bonds. They could have highly concentrated mobile ions with dynamic behavior, and their characteristics have inspired the design of a new class of ion conductors and transporters.

In this Account, we describe the state-of-the-art of studies of ion conductivity by PCP/MOFs and nonporous coordination polymers (CPs) and offer future perspectives. PCP/MOF structures tend to have high hydrophilicity and guest-accessible voids, and scientists have reported many water-mediated proton (H^+) conductivities. Chemical modification of organic ligands can change the hydrated H^+ conductivity over a wide range. On the other hand, the designable structures also permit water-free (anhydrous) H^+ conductivity. The incorporation of protic guests such as imidazole and 1,2,4-triazole into the microchannels of PCP/MOFs promotes the dynamic motion of guest molecules, resulting in high H^+ conduction without water. Not only the host–guest systems, but the embedding of protic organic groups on CPs also results in inherent H^+ conductivity. We have observed high H^+ conductivities under anhydrous conditions and in the intermediate temperature region of organic and inorganic conductors. The keys to successful construction are highly mobile ionic species and appropriate intervals of ion-hopping sites in the structures. Lithium (Li^+) and other ions can also be transported. If we can optimize the crystal structures, this could offer further improvements in terms of both conductivity and the working temperature range.

Another useful characteristic of PCP/MOFs is their wide application to materials fabrication. We can easily prepare heterodomain crystal systems, such as core–shell or solid solution. Other anisotropic morphologies (thin film, nanocrystal, nanorod, etc.,) are also possible, with retention of the ion conductivity. The flexible nature also lets us design morphology-dependent ion-conduction behaviors that we cannot observe in the bulk state.

We propose (1) multivalent ion and anion conductions with the aid of redox activity and defects in structures, (2) control of ion transport behavior by applying external stimuli, (3) anomalous conductivity at the hetero-solid–solid interface, and (4) unidirectional ion transport as in the ion channels in membrane proteins. In the future, scientists may use coordination polymers not only to achieve higher conductivity but also to control ion behavior, which will open new avenues in solid-state ionics.

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1. Introduction

Solid compounds that exhibit ion conductivity or transport are interesting because of their fundamental synthetic challenges and potential applications.[1,2] Structural components (atoms, ions) in the solid state are easily condensed, and it is difficult to render them mobile; hence, we need to design an ion-hopping pathway for conductivity. Solid-state ion conductors are an important class of materials because they are useful in electrolytes in batteries and fuel cells, gas sensors, etc. (Figure 1A,B). Ion transportation behavior is also seen in biological systems, for example, in membrane proteins (Figure 1C). Various cations (K^+, Na^+, Ca^{2+}, etc.) move through the cell matrix. The integration of an artificial ion transporter into *in vivo* systems and control of the extra- and intracellular ion behavior is a great challenge in biomaterials chemistry.[3]

The mechanism of ion conduction in solids depends on the structures, regardless of whether crystalline or amorphous. Significant factors are concentration, mobility, and charge of conductive ions. Control of the spatial distribution and dynamic behavior of target ions in solids is then critical. Ion conductivity is also related to the working temperature because ions need to overcome the activation energy between the hopping sites in structures. In other words, control of the working temperature of ion conductivity is a challenge. Mostly, organic polymers exhibit ion conductivity below 200 °C and inorganic compounds (metal oxides, metal halides, etc.) above 400 °C (except for a few examples).[2,4] The discovery and development of a new class of solid ion conductors that work in the intermediate area between organic and inorganic compounds is significant for promoting the field of solid-state ionics and contributing to materials science in terms of applications.

2. PCPs and MOFs for Solid-State Ionics

Over the past two decades, porous coordination polymers (PCPs) and metal–organic frameworks (MOFs) have been highlighted as a family of crystalline solids.[5−10] They are constructed from metal ions and organic ligands via coordination bonds, and self-assembly reactions provide open structures. According to the terminology, PCP/MOF is classified as the coordination polymer (CP) with open frameworks

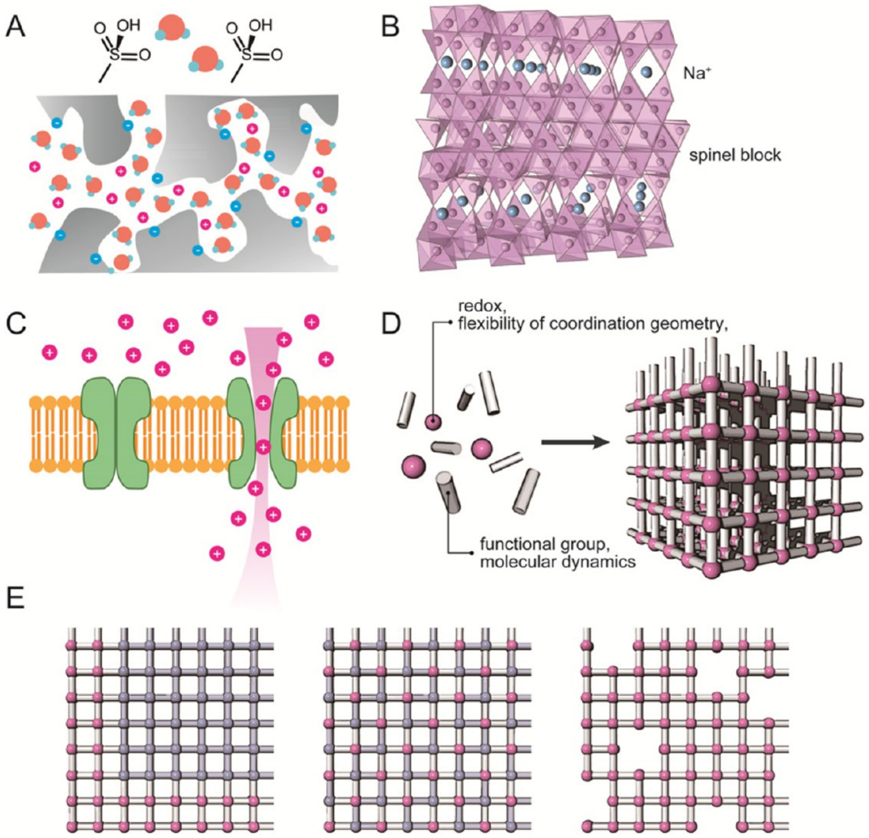

FIGURE 1. (A) Schematic representation of Nafion. (B) Crystal structure of β-alumina. (C) Membrane protein for ion transportation. (D) Schematic representation of PCP/MOF construction from metal ions (pink balls) and organic ligands (gray rods). (E) Schemes of phase separation, solid solution, and defect containing structures (from left to right) of PCP/MOFs.

TABLE 1. Ion Conductivity of Selected PCP/MOFs and CPs[a]

entry	compound[b]	conductive ion	conductivity, S cm^{-1}	conditions: temp, °C (RH, %)	ref
1	R_2dtoaCu (R = H, C_2H_4OH, C_3H_6OH, C_2H_5)	H^+	10^{-6}–10^{-5}	23–27 (75–100)	11, 16, 17
2	$(NH_4)_2$(adp)$[Zn_2(ox)_3]\cdot 3H_2O$	H^+	8×10^{-3}	25 (98)	18
3	M(dhbq)$\cdot nH_2O$ (M = Mg, Mn, Ni, Zn)	H^+	10^{-4}	25 (98)	19
4	Zn_3(btp)$(H_2O)_2\cdot 2H_2O$	H^+	3.5×10^{-5}	25 (98)	20
5	[Zn(*l*-L_{Cl})(Cl)]$(H_2O)_2$	H^+	4.45×10^{-5}	31 (98)	21
6	$(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$	H^+	1.1×10^{-3}	22 (96)	22
7	Fe(OH)(14bdc-$(COOH)_2$)	H^+	7×10^{-6}	25 (95)	23
8	[Al(OH)(14ndc)]$\supset$ImH	H^+	2.2×10^{-5}	120 (anhydrous)	24
9	[Al(OH)(14ndc)]$\supset$histamine	H^+	1.7×10^{-3}	150 (anhydrous)	25
10	$[Na_3$(2,4,6-trihydroxy-1,3,5- benzenetrisulfonate)]$\supset$0.45(124triH)	H^+	5×10^{-4}	150 (anhydrous)	26
11	$[Cr_3F(H_2O)_2O$(14bdc$)_3]\supset H_2SO_4$	H^+	1×10^{-2}	150 (0.13)	27
12	$[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$	H^+	2.6×10^{-4}	130 (anhydrous)	28
13	$Zn(H_2PO_4)_2$(124triH$)_2$	H^+	1.2×10^{-4}	150 (anhydrous)	29
14	Mg_2(dobdc)$\cdot 0.35LiO^iPr\cdot 0.25LiBF_4\cdot$EC$\cdot$DEC	Li^+	3.1×10^{-4}	27 (in Ar)	30
15	$[Co_2Na$(bptc$)_2]$(Emim$)_3$	$Emim^+$	2.63×10^{-5}	rt (N/A)	31
16	$V[Cr(CN)_6]_{2/3}\cdot 4.2H_2O$	H^+	2.6×10^{-3}	50 (100)	32
17	$[Cu_3$(btc$)_2]\cdot 3H_2O\supset$methanol	H^+	1.5×10^{-5}	rt (methanol vapor)	33
18	$(Mo_5P_2O_{23})$[Cu(phen)$(H_2O)]_3\cdot 5H_2O$	H^+	2.2×10^{-5}	28 (98)	34

[a] rt = room temperature, and these conductivities are measured by AC impedance spectroscopy with pelletized microcrystalline powder sample. [b] dtoa = dithiooxamide anion, adp = adipic acid, ox = oxalate, H_2(dhbq) = 2,5-dihydroxy-1,4-benzoquinone, btp = 1,3,5-benzenetriphosphonate, *l*-L_{Cl} = *N*-(4-pyridylmethyl)-L-valine·HCl, 14bdc = 1,4-benzenedicarboxylate, 14ndc = 1,4-naphthalenedicarboxylate, Im = imidazolate, 124tri = 1,2,4-triazolate, dobdc = 1,4-dioxido-2,5-benzenedicarboxylate, EC = ethylene carbonate, DEC = diethyl carbonate, bptc = 2,2′,4,4′-biphenyl tetracarboxylate, Emim = 1-ethyl-3-methyl imidazolium, btc = 1,3,5-benzenetricarboxylate, phen = 1,10-phenanthroline.

containing potential voids.[10] In this Account, we discuss both PCP/MOFs and nonporous CPs. They have a variety of properties, including the physical properties of magnetism and photoluminescence. Functions of gas storage, separation, and catalysis are also observed. Notwithstanding their usefulness, we could only find a few reports on their ion conductivity.[11,12]

The structural characteristics of PCP/MOFs are promising for the design of ion conductors. There are many reports on the ion conductivity by use of other porous compounds[13,14] and organic polymers.[15] Compared with these conventional materials, one unique characteristic of PCP/MOFs for ion conductivity is the coexistence of crystallinity and dynamics. As shown in Figure 1D, we could employ various features in the components for ion conductivity. Redox activity and multivalence state for metal ions and various functional groups and molecular dynamics for organic ligands are available. Consequently, phase separation type structure, solid–solution type structure, defect-tuning structure, and flexible structure are available (Figure 1E). These characteristics offer many opportunities to synthesize new types of ion conductors.

The ion conductivities of selected PCP/MOFs and CPs are reported in Table 1. We should note that not only the conducting behavior but other factors such as chemical stability, material fabrication, and feasibility of hybridization with other materials are also important for the application. In this Account, we review the relationship between ion conductivity and structure characteristics and propose future perspectives.

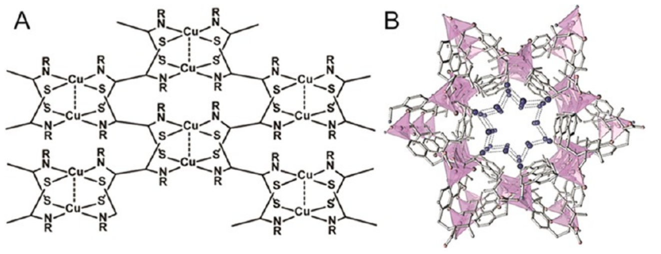

FIGURE 2. (A) Structure of R_2dtoaCu (R = H, C_2H_4OH, C_3H_6OH, C_2H_5; dtoa = dithiooxamide anion). (B) Crystal structure of [Zn(*l*-L_{Cl})(Cl)]$(H_2O)_2$ (*l*-L_{Cl} = *N*-(4-pyridylmethyl)-L-valine·HCl). Blue balls in the pore are water molecules.

2.1. Water-Mediated Proton Conductivity.

Proton (H^+) conductivity is important for the performance of solid electrolyte in fuel cells. Nafion is a well-known organic polymer because it has high H^+ conductivity and chemical stability under humid conditions.[35,36] Here, the combination of both hydrophobic and hydrophilic pores is key to attaining high H^+ conductivity. To synthesize H^+-conducting PCP/MOFs under humid conditions, the framework should retain a large number of water molecules, and the accommodated water should have high mobility. The series of compounds R_2dtoaCu (R = H, C_2H_4OH, C_3H_6OH, C_2H_5; dtoa = dithiooxamide anion, Figure 2A) have 2-D layer-type structures (entry 1). They exhibit H^+ conductivity on the order of 10^{-5}–10^{-6} S cm^{-1} at room temperature and high relative humidity (RH).[11,16,17,37] The H^+ conductivities depend on the ligands. Oxalate-based compounds (entry 2)[18,38,39] and the 1-D chain structure Mn(dhbq)$\cdot nH_2O$ (H_2(dhbq) = 2,5-dihydroxy-1,4-benzoquinone, entry 3)[19] are further examples of the water-mediated system.

$Zn_3(btp)(H_2O)_2 \cdot 2H_2O$ (btp = 1,3,5-benzenetriphosphonate) also forms a 2-D layered structure (entry 4).[20] The well-ordered chains of free water molecules in the interlayer form a proton-hopping path, as supported by solid-state ^{2}H NMR (all sites of H^+ (D^+) are exchanging, even at −20 °C). There have been many reports on H^+ conductivity with metal phosphates.[40,41] The tetrahedral coordination geometry of the $-PO_4$ group is a suitable building block for the construction of H^+ conductive PCP/MOFs. H^+ conductivities in the homochiral porous frameworks have been reported (entry 5 and 6).[21,22] In $[Zn(l\text{-}L_{Cl})(Cl)](H_2O)_2$ ($l\text{-}L_{Cl}$ = *N*-(4-pyridylmethyl)-L-valine·HCl),[21] the 1-D pores contain lattice water molecules, which form a helical chain with a pitch of 12 Å (Figure 2B).

Grafting of substituent groups is also a route to achieving high hydrophilicity.[42] The systematic incorporation of substituent groups in M(OH)(14bdc) (M = Al, Fe; 14bdc = 1,4-benzenedicarboxylate) and the dependency on the grafted groups for H^+ conductivity under humid conditions has been reported (entry 7).[23] The pK_a values of meta-substituted terephthalate linkers ($-NH_2$, −H, −OH, and −COOH) are related to the observed H^+ conductivity. Immobilization of the sulfonic acid group ($-SO_3H$) in a porous framework has also been studied.[43] When 50% of the terephthalate of Al(OH)(14bdc) is replaced with the 2-SO_3H-terephthalate, H^+ conductivity $>10^{-3}$ S cm^{-1} was observed under humid conditions. Construction of ligand−base solid solutions and the postsynthesis modification are useful approaches to stabilize the highly acidic groups in the frameworks.[44,45] Decoration of acidic groups into the pore surface is the main strategy for achieving hydrous H^+ conductivity.

2.2. Anhydrous Proton Conductivity by Enhanced Dynamics of Guests in Pores. When H^+ conductivity without water support is considered, different approaches apply. The development of an anhydrous H^+ conductor in an intermediate temperature region (100−400 °C) is important in a wide area of materials chemistry.[4] Because water cannot be used as a proton carrier, the synthesis of an anhydrous H^+ conductor is much more difficult. Some anhydrous H^+ conductors have been studied, and the advantages of CP-based compounds are the high designability to control the conductive temperature and water stability. One approach is the utilization of protic organic molecules, to be accommodated in the porous framework. The restricted and regular micropores of PCP/MOFs do not allow the isotropic motion of guests; only anisotropic motion is feasible.[46] The comparable sizes of pore diameters and guests enable the enhancement of the mobility of guest molecules and ions; H^+ conductivity without water can be achieved by accumulating protic organic molecules in the pores.

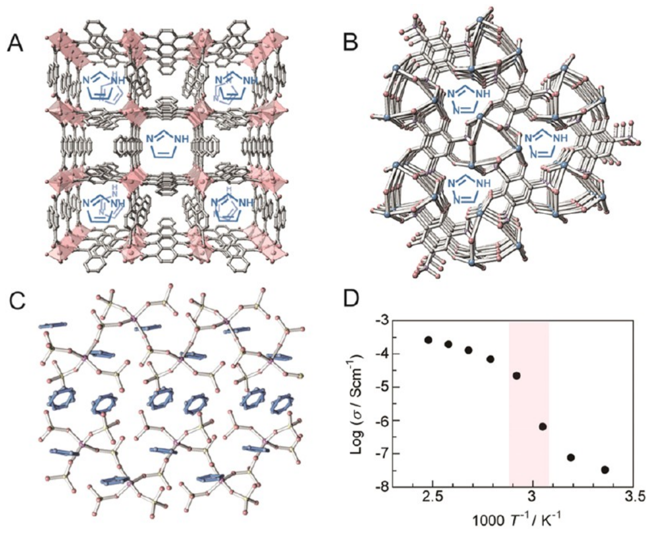

FIGURE 3. (A) Structure of Al(OH)(14ndc) (14ndc = 1,4-naphthalenedicarboxylate) with guest imidazole. (B) Structure of $[Na_3(2,4,6\text{-trihydroxy-1,3,5-benzenetrisulfonate})]$ with guest 1,2,4-triazole. (C) Crystal structure of $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$, where the disordering protonated imidazole (ImH_2) is shown in blue, and (D) its Arrhenius plot under anhydrous conditions. The highlighted area represents the phase transition.

One-dimensional pores of Al(OH)(14ndc) (14ndc = 1,4-naphthalenedicarboxylate), with a diameter of 1 nm, accommodate imidazole, as shown in Figure 3A.[24] The straight pores with relatively flat potential provoke an anisotropic alignment of imidazole and afford high mobility. The highly rotational imidazole in the pores provides anhydrous H^+ conductivity of 2.2×10^{-5} S cm^{-1} at 120 °C (entry 8). Conductivity occurs via the Grotthuss mechanism, determined by the activation energy. The high concentration and dynamics of imidazole in the porous framework is the origin of the successful anhydrous conductivity. If we employ larger pore sizes, the accommodated imidazoles aggregate with each other to form hydrogen bonds, even in the pores, resulting in low H^+ conductivity. Optimization of the size and shape of the pores and protic guest molecules is important for obtaining high conductivity. Instead of using imidazole, accommodation of histamine into Al(OH)(14ndc) improves the anhydrous conductivity (1.7×10^{-3} S cm^{-1} at 150 °C, entry 9).[25] Histamine contains three H^+ hopping sites in the structure, and various isomers are available. This composite is regarded as a "superionic" conductor, based on the conventional criteria.[13] The confinement effect of restricted spaces in PCP/MOFs, which also could change the ion conduction from diffusion limited to concentration of hopping sites limited, is promising to achieve even higher conductivity or suitability for use in an even higher temperature range.

As a protic organic guest, 1,2,4-triazole was also used (entry 10).[26] In this case, components of the porous framework (Na^+ and 2,4,6-trihydroxy-1,3,5-benzenetrisulfonate) and 1,2,4-triazole were mixed simultaneously to yield the framework with the formula $[Na_3$(2,4,6-trihydroxy-1,3,5-benzenetrisulfonate)$]\supset x$(1,2,4-triazole) ($x = 0-0.60$, Figure 3B). The 1,2,4-triazole is incorporated during the construction of the framework. The compound $x = 0.45$ gives an anhydrous H^+ conductivity of 5×10^{-4} S cm^{-1} at 150 °C. The fabrication of a membrane–electrode assembly (MEA) was also demonstrated. A pelletized sample was used to measure the open circuit voltage (OCV). A high voltage (1.18 V) at 100 °C was observed.

In terms of hybridization with protic precursors, a high surface area porous framework $Cr_3F(H_2O)_2O(14bdc)_3$ (MIL-101) and $CsHSO_4$ or H_2SO_4/H_3PO_4 hybrids have been reported (entry 11).[27,47] $CsHSO_4$ is a family of solid acids and shows phase transition to a high proton-conducting phase at ca. 140 °C, with H^+ conductivity on the order of 10^{-2} S cm^{-1}. The phase transition behavior depends on the amount of hybridized $CsHSO_4$ into MIL-101. In the case of H_2SO_4-impregnated MIL-101 hybrids, 1×10^{-2} S cm^{-1} at 150 °C and RH = 0.13% was recorded. The conductivity is high enough to consider application.

Anhydrous H^+ conductivity can be attained not only by a combination of neutral host framework and guest molecules, but also in ionic CP crystals. $[Zn(HPO_4)(H_2PO_4)_2](ImH_2)_2$ (Im = imidazolate) is an ionic crystal containing the anionic 1-D chain structure $[Zn(HPO_4)(H_2PO_4)_2]^{2-}$, with Zn^{2+} and phosphate groups, and protonated imidazole (ImH_2) as a countercation (Figure 3C, entry 12).[28] The interchain spaces of the CP afford packed alignments of ImH_2, and the ionic crystal system exhibits H^+ conductivity. The H^+ conductivity is 2.6×10^{-4} S cm^{-1} at 130 °C. The temperature dependency of the H^+ conductivity is not a simple Arrhenius-type plot; there is a nonlinear jump in the profile (Figure 3D). This is attributed to the dynamic reorientation of ImH_2 species in the ionic crystal, and the sudden rotational motion of ImH_2 at 70 °C contributes the nonlinear increase in H^+ conductivity. The entropy change of the phase transition is 6.6 J mol^{-1} K^{-1} and the compound is regarded as a plastic crystal. Plastic crystals have been widely studied in the areas of inorganic and organic compounds.[48,49] This work illustrates the potential of coordination-network-based ionic plastic crystals for the design of various ion conductors.

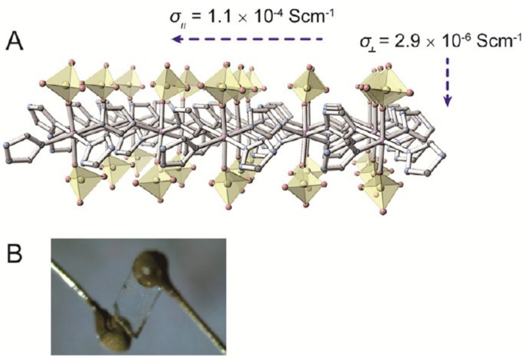

FIGURE 4. (A) Crystal structure of 2-D layer of $Zn(H_2PO_4)_2(124triH)_2$ (124tri = 1,2,4-triazolate). H_2PO_4 groups are shown as polyhedra. H^+ hopping occurs on the layers. (B) Image of a single crystal with gold electrolyte for anisotropic conductivity measurement.

Ion-conductive mobile groups can be introduced not as guests but in the structure of CPs. Each mobile group could be spatially isolated in frameworks, and then free rotation or vibration is feasible.[50] The distance of each ion-hopping site must be optimized by suitable coordination bonds; too short distances give strong interaction, long distance gives little opportunity for frequent hopping, and both cases have negligible ion conductivity.

There is one example of CP-based inherent H^+ conductivity.[29] The compound $Zn(H_2PO_4)_2(124triH)_2$ (124tri = 1,2,4-triazolate) is composed of Zn^{2+}, 1,2,4-triazole, and phosphoric acid, all of which are connected by coordination bonds (Figure 4A, entry 13). It is a 2-D layered structure on which orthophosphates are aligned with ideal intervals for H^+ hopping because of the 1,2,4-triazole linkage. Each phosphate is rotationally free, and there are H-bonded inter- and intralayers. The anhydrous H^+ conductivity is 1.2×10^{-4} S cm^{-1} at 150 °C. The anisotropy of conductivity was confirmed by single crystal anisotropic conductivity measurement (Figure 4B). The conductivity along the parallel direction to the 2-D layer is much higher than that in the vertical direction. The H^+ hopping is promoted by rotation of phosphate ligands, determined by solid-state NMR. Various dynamic motions in the crystalline lattice, such as rotation, vibration, sliding, and expansion, could be applied to the intrinsic ion hopping. To improve the thermal stability, optimization of the combination of multivalent metal ions and ligands to have stronger interaction and higher ionicity in the crystal is the key. Furthermore, introducing defects will be interesting for the improvement of ion conductivity. Defect control is important to tune the occupancy and mobility of the conductive ions.

2.3. Other Types of Ion Conductivity. Besides H^+ transfer, other types of ion transfer should be possible.

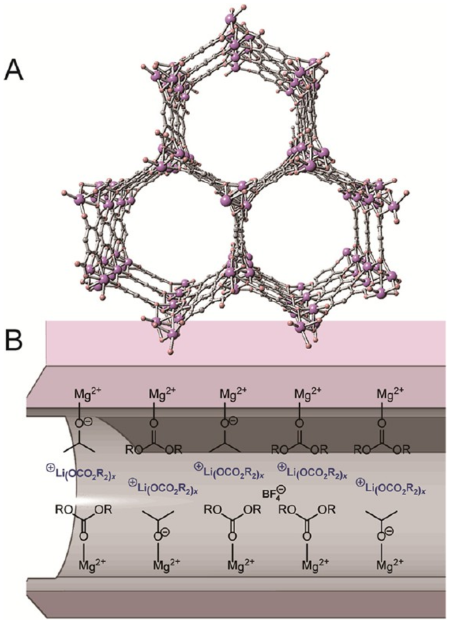

FIGURE 5. (A) Crystal structure of Mg_2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate). Mauve balls represent unsaturated Mg^{2+} sites. (B) Scheme of its modification (R = $-CH_2-CH_2-$ or $-CH_2-CH_3$).

The lithium ion (Li^+) is also a highly attractive target for solid-state lithium conductors because of their application in secondary batteries. Mg_2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate) has 1-D honeycomb-type pores with a diameter of 1.4 nm, and the pore interior possesses unsaturated Mg^{2+} metal centers (Figure 5A, entry 14).[30] The metal centers can bind the anions, and the leaving cation (in this case, Li^+ complex) is relatively free to run along the pores. As shown in Figure 5B, the stepwise procedures with LiO^{i}Pr and $LiBF_4$ in ethylene carbonate/diethyl carbonate solution give selective binding of alkoxide anions and leave Li^+ complexes inside the pores as mobile species. The observed Li^+ conductivity is 3.1×10^{-4} S cm^{-1} at 27 °C. This work demonstrates that non-H^+ conductivities can be achieved by employing structure modification techniques.

On the other hand, the ionothermal synthesis of PCP/MOFs has been developed.[51] In many cases, countercations are occluded into the cavities. Such a structure is potentially useful for preparing ion conductors. An example is $[Co_2Na(bptc)_2](Emim)_3$ (bptc = 2,2′,4,4′-biphenyl tetracarboxylate, Emim = 1-ethyl-3-methyl imidazolium, entry 15), containing Emim as countercation.[31] The countercations exhibit conductivity (2.63×10^{-5} S cm^{-1}) at room temperature.

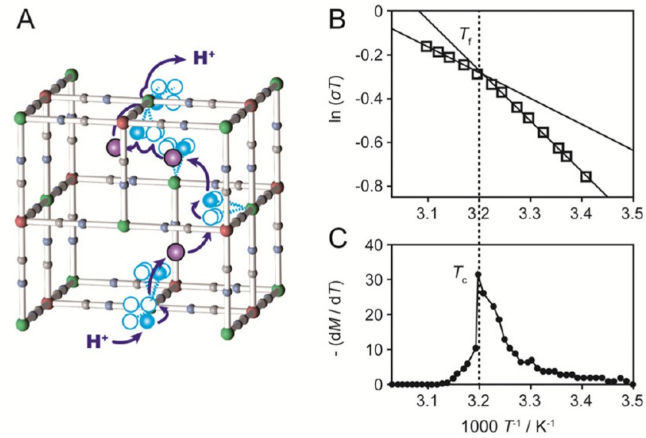

FIGURE 6. (A) Schematic illustration of the crystal structure of $V^{II}[Cr^{III}(CN)_6]_{2/3} \cdot zH_2O$ and possible pathway of the H^+ transfer through hydrogen bonds between ligand water and zeolitic water molecules. (B) Plot of H^+ conductivity at 100% RH. (C) Plot of the derivative of the magnetization, $-(dM/dT)$, vs T^{-1}.

2.4. Multifunctionality with Ionics. Magnetism and gas adsorption have been studied intensively in the area of PCP/MOFs, and the idea of the coupling of ionics and these properties is of interest. A Prussian blue analogous compound $V^{II}[Cr^{III}(CN)_6]_{2/3} \cdot zH_2O$ was demonstrated as having the potential of multifunctionality of magnetism and ionics (Figure 6A, entry 16).[32] The compound exhibits H^+ conductivity of 1.6×10^{-3} S cm^{-1} under RH = 100% through hydrogen bonds between ligand water and zeolitic water molecules in the structure. It shows an interference effect between magnetic ordering and H^+ conductivity (Figure 6B,C), which is due to the distortion of the 3-D hydrogen-bonding network by magnetostriction below T_C (40 °C). This is a meaningful example of the cooperative behavior of physical properties.

A H^+ conductivity change attributed to different solvents in the pores has been reported.[33] Conductivities of $[Cu_3(btc)_2] \cdot 3X$ (btc = 1,3,5-benzenetricarboxylate; X = H_2O, MeOH, EtOH, MeCN; entry 17) under methanol atmosphere were investigated. The framework possesses coordinatively unsaturated Cu^{2+} sites and different solvents (X) are bound to the sites, resulting in variable H^+ conductivity. In the case of H_2O, the highly acidic proton of coordinated H_2O is generated, and it enhances H^+ hopping through pore-filling methanol.

3. Morphology Control

It is important to understand and be able to manipulate the interface of ion-conductive solids to overcome serious problems (the junction of conductive materials and others). Mismatch at the interface, such as the electrolyte and electrode, significantly increases the resistance of the system, resulting in poor performance of devices. The synthesis of nanocrystals of PCP/MOFs using surfactant, modulator, and microwaves has been reported.[52] Thin films are tailored by several techniques, such as the Langmuir–Blodgett method and a layer-by-layer

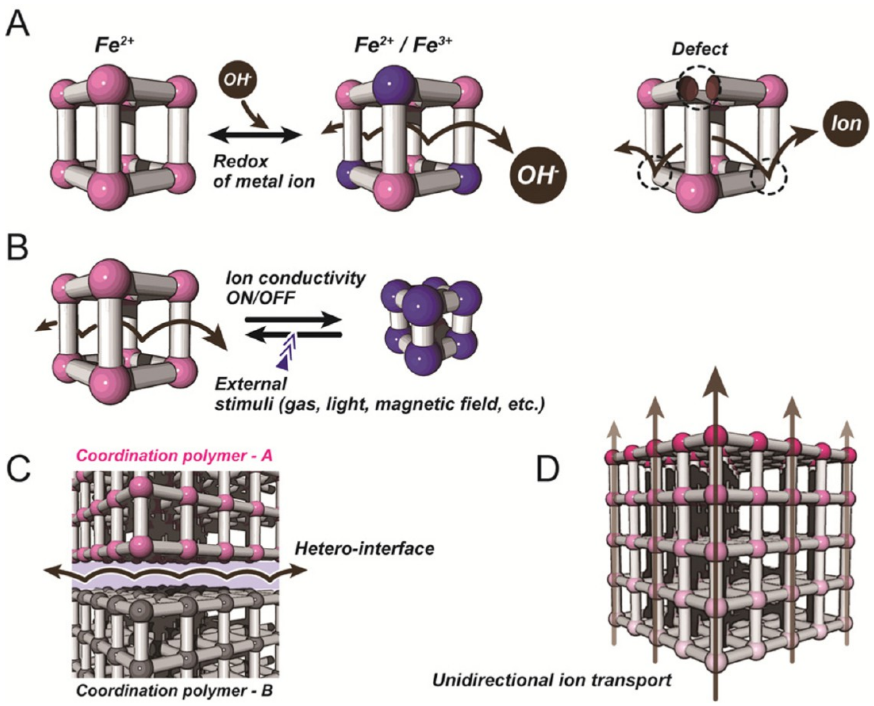

FIGURE 7. Schematic illustrations of some future ideas. (A) Conductivity of various ions by use of redox properties or defects. (B) Control of ion conductivity by applying external stimuli. (C) Development of ionics in the heterointerfaces. (D) Unidirectional ion transportation from one side to the other side of crystals.

procedure.[53,54] We could even fabricate solid−solution-type[55,56] or phase-separated-type crystals,[57,58] both of which possess distinct crystal domains in one crystal particle. These developments provide a wide variety of options to overcome interfacial issues in ionics. Construction of PCP/MOFs and CPs always takes place under equilibrium conditions between the metal and ligand precursors, and the coordination bond is more labile than the covalent bond and ionic bond. Control of the kinetics of framework construction could provide crystals with various morphologies. The space charge of the solid interfaces has a crucial effect on the conductivity, as represented by the field of nanoionics.[59] The tuning of size and interfacial properties of crystals would offer great opportunity for hybridization with other materials and attaining unique conductivity.

4. Perspectives for Ion Conductivity in PCP/MOFs

We have constructed a wide variety of structures from metal ions (or metal clusters) and organic ligands via the bottom-up approach. Control of mesoscale structures involving the crystal domain distribution, crystal surface, and morphology are feasible. These structural characteristics could manifest in the synthesis of unique ion conductors, which is otherwise not feasible with the conventional materials platform. Some future perspectives that we propose are illustrated in Figure 7.

4.1. Conductivity of Various Ion Species (Figure 7A). Currently, H^+ is observed predominantly for conductivity. We could design various ion conductors, such as multivalence cations and anions (OH^-, etc.) by tuning the electrostatic interactions in the frameworks. OH^- conductors are promising for alkaline fuel cells, but only a few classes of such compounds have been reported.[60] Some PCP/MOFs exhibit the ability of ion exchange and redox activity based on the specific metal ions (Fe^{2+}/Fe^{3+}, Cr^{2+}/Cr^{3+}, etc.). These structural features might contribute to the various ions being mobile in the structures.

4.2. Integration of Multifunctionality and the Control of Ion Conductivity by External Stimuli (Figure 7B). The mutual interplay of ionics and other physical/chemical properties would be a distinct feature in the family of ionic compounds. Gas adsorption/separation properties, followed by dynamic structure transformation,[50] magnetism (such as spin-crossover),[61] photoluminescence, and heterogeneous catalysis are candidate functions for integration. Multifunctional ion-conductive PCP/MOFs give switchable behavior with applied external stimuli, such as gas adsorption, light irradiation, and an electric field. Likewise, with yttria-stabilized ZrO_2, which has a conductivity that responds to a certain concentration of O_2 gas at high temperature, a monitoring system of gas sensors that function at lower temperature might be possible. The artificial switching systems of resistivity in solids by external stimuli are of great interest for future electric devices.

4.3. Development of Interfaces (Figure 7C). The ion conductivity of solid interfaces often shows unique behavior that is not observed in the bulk structure, as was briefly mentioned. The behavior is often described as "nanoionics", and the modification of a solid interface and junction of heterodomains is significant for conductivity enhancement.[59] Development of 2-D chemistry of PCP/MOFs and CPs is essential to access this area. Crystals with heterodomains, such as a solid solution/core−shell, and epitaxial growth of crystalline thin films on various substrates, would contribute to elucidating the unique ionic functions in solid interfaces.

4.4. Unidirectional Ion Transportation (Figure 7D). If we could design the gradient of ion-hopping potentials in a crystal structure, we could expect to have unidirectional ion transportation. A system would have unidirectionality for ion diffusion if one side of the crystal structure has an easier ion hopping path and the other side has a restricted structure for ion hopping. Possible approaches are the hierarchical stacking of crystals by growth of different crystal domains, postsynthetic modification, and using a solid solution of ligand or metal ions to provide the gradient chemical conversion from the outside to the inside of crystals. The control of unidirectionality of ions offers much potential. For instance, there are several reports on the creation of artificial ion channels by discrete metal complexes in lipid membranes.[3,62] These models ideally demand the unidirectional ion pumping response to the ion concentrations of extra- and intracellular regions.

These proposed perspectives serve as examples of many design possibilities of ion-conductive PCP/MOFs and CPs. There are already many solid conductors available in the wide areas of chemistry, and much research is currently underway. In our efforts to achieve improved materials for battery and fuel cells, we consider it significant to have higher ion conductivity, sufficient thermal/chemical stability, and flexibility. Simultaneously, it is important to consider fundamental interest in designing the mobile ion species in crystalline solids. The control of the behavior of ions with regulated crystal structures would offer further opportunities for the potential uses of ionic devices and biocompatible systems. We believe that advances made in the structural chemistry of PCP/MOFs and CPs will contribute to creating a new class of solid ion conductors.

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FOOTNOTES

The authors declare no competing financial interest.

REFERENCES

1 West, A. R. *Solid State Chemistry and its Applications*; John Wiley & Sons: Chichester, U.K., 1984.

2 Kudo, T.; Fueki, K. *Solid State Ionics*; Wiley-VCH Verlag GmbH: Weinheim, Germany, 1990.

3 Sakai, N.; Matile, S. Metal-Organic Scaffolds: Heavy-Metal Approaches to Synthetic Ion Channels and Pores. *Angew. Chem., Int. Ed.* **2008**, *47*, 9603–9607.

4 Kreuer, K. D. Proton Conductivity: Materials and Applications. *Chem. Mater.* **1996**, *8*, 610–641.

5 Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. Synthetic Strategies, Structure Patterns, and Emerging Properties in the Chemistry of Modular Porous Solids. *Acc. Chem. Res.* **1998**, *31*, 474–484.

6 Cheetham, A. K.; Férey, G.; Loiseau, T. Open-Framework Inorganic Materials. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268–3292.

7 Moulton, B.; Zaworotko, M. J. From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids. *Chem. Rev.* **2001**, *101*, 1629–1658.

8 Kitagawa, S.; Kitaura, R.; Noro, S. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.

9 Long, J. R.; Yaghi, O. M. The Pervasive Chemistry of Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214and references therein.

10 For the compound terminology, please see: Batten, S. R.; Champness, N. R.; Chen, X. M.; Garcia-Martinez, J.; Kitagawa, S.; Ohrstrom, L.; O'Keeffe, M.; Suh, M. P.; Reedijk, J. Coordination Polymers, Metal-Organic Frameworks and the Need for Terminology Guidelines. *CrystEngComm* **2012**, *14*, 3001–3004.

11 Kitagawa, H.; Nagao, Y.; Fujishima, M.; Ikeda, R.; Kanda, S. Highly Proton-Conductive Copper Coordination Polymer, H_2dtoaCu (H_2dtoa = Dithiooxamide Anion). *Inorg. Chem. Commun.* **2003**, *6*, 346–348.

12 Yoon, M.; Suh, K.; Natarajan, S.; Kim, K. Proton Conduction in Metal-Organic Frameworks and Related Modularly Built Porous Solids. *Angew. Chem., Int. Ed.* **2013**, *52*, 2688–2700.

13 Colomban, P. *Proton Conductors: Solids, Membranes and Gels—Materials and Devices*; Cambridge University Press: Cambridge, U.K., 1992.

14 Nischwitz, P.; Amels, P.; Fetting, F. Studies on the Ionic-Conductivity of Zeolitic Solids. *Solid State Ionics* **1994**, *73*, 105–118.

15 Javaid Naidi, S. M.; Matsuura, T.: *Polymer Membranes for Fuel Cells*; Springer: New York, 2009.

16 Nagao, Y.; Fujishima, M.; Ikeda, R.; Kanda, S.; Kitagawa, H. Highly Proton-Conductive Copper Coordination Polymers. *Synth. Met.* **2003**, *133*, 431–432.

17 Nagao, Y.; Ikeda, R.; Iijima, K.; Kubo, T.; Nakasuji, K.; Kitagawa, H. A New Proton-Conductive Copper Coordination Polymer, $(HOC_3H_6)_2$dtoaCu (dtoa = dithiooxamide). *Synth. Met.* **2003**, *135−136*, 283–284.

18 Sadakiyo, M.; Yamada, T.; Kitagawa, H. Rational Designs for Highly Proton-Conductive Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2009**, *131*, 9906–9907.

19 Yamada, T.; Morikawa, S.; Kitagawa, H. Structures and Proton Conductivity of One-Dimensional M(dhbq)•nH_2O (M = Mg, Mn, Co, Ni, and Zn, H_2(dhbq)=2,5-Dihydroxy-1,4-benzoquinone) Promoted by Connected Hydrogen-Bond Networks with Absorbed Water. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 42–48.

20 Taylor, J. M.; Mah, R. K.; Moudrakovski, I. L.; Ratcliffe, C. I.; Vaidhyanathan, R.; Shimizu, G. K. H. Facile Proton Conduction via Ordered Water Molecules in a Phosphonate Metal−Organic Framework. *J. Am. Chem. Soc.* **2010**, *132*, 14055–14057.

21 Sahoo, S. C.; Kundu, T.; Banerjee, R. Helical Water Chain Mediated Proton Conductivity in Homochiral Metal-Organic Frameworks with Unprecedented Zeolitic unh-Topology. *J. Am. Chem. Soc.* **2011**, *133*, 17950–17958.

22 Pardo, E.; Train, C.; Gontard, G.; Boubekeur, K.; Fabelo, O.; Liu, H.; Dkhil, B.; Lloret, F.; Nakagawa, K.; Tokoro, H.; Ohkoshi, S.; Verdaguer, M. High Proton Conduction in a Chiral Ferromagnetic Metal-Organic Quartz-Like Framework. *J. Am. Chem. Soc.* **2011**, *133*, 15328–15331.

23 Shigematsu, A.; Yamada, T.; Kitagawa, H. Wide Control of Proton Conductivity in Porous Coordination Polymers. *J. Am. Chem. Soc.* **2011**, *133*, 2034–2036.

24 Bureekaew, S.; Horike, S.; Higuchi, M.; Mizuno, M.; Kawamura, T.; Tanaka, D.; Yanai, N.; Kitagawa, S. One-Dimensional Imidazole Aggregate in Aluminium Porous Coordination Polymers with High Proton Conductivity. *Nat. Mater.* **2009**, *8*, 831–836.

25 Umeyama, D.; Horike, S.; Inukai, M.; Hijikata, Y.; Kitagawa, S. Confinement of Mobile Histamine in Coordination Nanochannels for Fast Proton Transfer. *Angew. Chem., Int. Ed.* **2011**, *50*, 11706–11709.

26 Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. Anhydrous Proton Conduction at 150 Degrees C in a Crystalline Metal-Organic Framework. *Nat. Chem.* **2009**, *1*, 705–710.

27 Ponomareva, V. G.; Kovalenko, K. A.; Chupakhin, A. P.; Dybtsev, D. N.; Shutova, E. S.; Fedin, V. P. Imparting High Proton Conductivity to a Metal-Organic Framework Material by Controlled Acid Impregnation. *J. Am. Chem. Soc.* **2012**, *134*, 15640–15643.

28 Horike, S.; Umeyama, D.; Inukai, M.; Itakura, T.; Kitagawa, S. Coordination-Network-Based Ionic Plastic Crystal for Anhydrous Proton Conductivity. *J. Am. Chem. Soc.* **2012**, *134*, 7612–7615.

29 Umeyama, D.; Horike, S.; Inukai, M.; Itakura, T.; Kitagawa, S. Inherent Proton Conduction in 2-D Coordination Framework. *J. Am. Chem. Soc.* **2012**, *134*, 12780–12785.

30 Wiers, B. M.; Foo, M. L.; Balsara, N. P.; Long, J. R. A Solid Lithium Electrolyte via Addition of Lithium Isopropoxide to a Metal-Organic Framework with Open Metal Sites. *J. Am. Chem. Soc.* **2011**, *133*, 14522–14525.

31 Chen, W. X.; Xu, H. R.; Zhuang, G. L.; Long, L. S.; Huang, R. B.; Zheng, L. S. Temperature-Dependent Conductivity of $Emim^+$ ($Emim^+$ = 1-Ethyl-3-methyl Imidazolium) Confined in Channels of a Metal-Organic Framework. *Chem. Commun.* **2011**, *47*, 11933–11935.

32 Ohkoshi, S.; Nakagawa, K.; Tomono, K.; Imoto, K.; Tsunobuchi, Y.; Tokoro, H. High Proton Conductivity in Prussian Blue Analogues and the Interference Effect by Magnetic Ordering. *J. Am. Chem. Soc.* **2010**, *132*, 6620–6621.

33 Jeong, N. C.; Samanta, B.; Lee, C. Y.; Farha, O. K.; Hupp, J. T. Coordination-Chemistry Control of Proton Conductivity in the Iconic Metal-Organic Framework Material HKUST-1. *J. Am. Chem. Soc.* **2012**, *134*, 51–54.

34 Dey, C.; Kundu, T.; Banerjee, R. Reversible Phase Transformation in Proton Conducting Strandberg-type POM Based Metal Organic Material. *Chem. Commun.* **2012**, *48*, 266–268.

35 Mauritz, K. A.; Moore, R. B. State of Understanding of Nafion. *Chem. Rev.* **2004**, *104*, 4535–4585.

36 Lucid, J.; Meloni, S.; MacKernan, D.; Spohr, E.; Ciccotti, G. Probing the Structures of Hydrated Nafion in Different Morphologies Using Temperature-Accelerated Molecular Dynamics Simulations. *J. Phys. Chem. C* **2013**, *117*, 774–782.

37 Nagao, Y.; Kubo, T.; Nakasuji, K.; Ikeda, R.; Kojima, T.; Kitagawa, H. Preparation and Proton Transport Property of N,N′- Diethyldithiooxamidatocopper Coordination Polymer. *Synth. Met.* **2005**, *154*, 89–92.

38 Yamada, T.; Sadakiyo, M.; Kitagawa, H. High Proton Conductivity of One-Dimensional Ferrous Oxalate Dihydrate. *J. Am. Chem. Soc.* **2009**, *131*, 3144–3145.

39 Sadakiyo, M.; Okawa, H.; Shigematsu, A.; Ohba, M.; Yamada, T.; Kitagawa, H. Promotion of Low-Humidity Proton Conduction by Controlling Hydrophilicity in Layered Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2012**, *134*, 5472–5475.

40 Alberti, G.; Casciola, M.; Costantino, U.; Vivani, R. Layered and Pillared Metal(IV) Phosphates and Phosphonates. *Adv. Mater.* **1996**, *8*, 291–303.

41 Jin, Y. C.; Shen, Y. B.; Hibino, T. Proton Conduction in Metal Pyrophosphates (MP_2O_7) at Intermediate Temperatures. *J. Mater. Chem.* **2010**, *20*, 6214–6217.

42 Laberty-Robert, C.; Valle, K.; Pereira, F.; Sanchez, C. Design and Properties of Functional Hybrid Organic-Inorganic Membranes for Fuel Cells. *Chem. Soc. Rev.* **2011**, *40*, 961–1005.

43 Goesten, M. G.; Juan-Alcañiz, J.; Ramos-Fernandez, E. V.; Sai Sankar Gupta, K. B.; Stavitski, E.; van Bekkum, H.; Gascon, J.; Kapteijn, F. Sulfation of Metal−Organic Frameworks: Opportunities for Acid Catalysis and Proton Conductivity. *J. Catal.* **2011**, *281*, 177–187.

44 Foo, M. L.; Horike, S.; Fukushima, T.; Hijikata, Y.; Kubota, Y.; Takata, M.; Kitagawa, S. Ligand-Based Solid Solution Approach to Stabilisation of Sulphonic Acid Groups in Porous Coordination Polymer $Zr_6O_4(OH)_4(BDC)_6$ (UiO-66). *Dalton Trans.* **2012**, *41*, 13791–13794.

45 Horike, S.; Kamitsubo, Y.; Inukai, M.; Fukushima, T.; Umeyama, D.; Itakura, T.; Kitagawa, S. Post-synthesis Modification of a Porous Coordination Polymer by LiCl To Enhance H^+ Transport. *J. Am. Chem. Soc.* **2013**, *135*, 4612–4615.

46 Uemura, T.; Horike, S.; Kitagawa, K.; Mizuno, M.; Endo, K.; Bracco, S.; Comotti, A.; Sozzani, P.; Nagaoka, M.; Kitagawa, S. Conformation and Molecular Dynamics of Single Polystyrene Chain Confined in Coordination Nanospace. *J. Am. Chem. Soc.* **2008**, *130*, 6781–6788.

47 Ponomareva, V. G.; Kovalenko, K. A.; Chupakhin, A. P.; Shutova, E. S.; Fedin, V. P. $CsHSO_4$-Proton Conduction in a Crystalline Metal-Organic Framework. *Solid State Ionics* **2012**, *225*, 420–423.

48 Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. Solid Acids As Fuel Cell Electrolytes. *Nature* **2001**, *410*, 910–913.

49 MacFarlane, D. R.; Forsyth, M. Plastic Crystal Electrolyte Materials: New Perspectives on Solid State Ionics. *Adv. Mater.* **2001**, *13*, 957–966.

50 Horike, S.; Shimomura, S.; Kitagawa, S. Soft Porous Crystals. *Nat. Chem.* **2009**, *1*, 695–704.

51 Parnham, E. R.; Morris, R. E. Ionothermal Synthesis of Zeolites, Metal-Organic Frameworks, And Inorganic-Organic Hybrids. *Acc. Chem. Res.* **2007**, *40*, 1005–1013.

52 Tsuruoka, T.; Furukawa, S.; Takashima, Y.; Yoshida, K.; Isoda, S.; Kitagawa, S. Nanoporous Nanorods Fabricated by Coordination Modulation and Oriented Attachment Growth. *Angew. Chem., Int. Ed.* **2009**, *48*, 4739–4743.

53 Makiura, R.; Motoyama, S.; Umemura, Y.; Yamanaka, H.; Sakata, O.; Kitagawa, H. Surface Nano-architecture of a Metal-Organic Framework. *Nat. Mater.* **2010**, *9*, 565–571.

54 Betard, A.; Fischer, R. A. Metal−Organic Framework Thin Films: From Fundamentals to Applications. *Chem. Rev.* **2012**, *112*, 1055–1083.

55 Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towne, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. Multiple Functional Groups of Varying Ratios in Metal-Organic Frameworks. *Science* **2010**, *327*, 846–850.

56 Fukushima, T.; Horike, S.; Inubushi, Y.; Nakagawa, K.; Kubota, Y.; Takata, M.; Kitagawa, S. Solid Solutions of Soft Porous Coordination Polymers: Fine-Tuning of Gas Adsorption Properties. *Angew. Chem., Int. Ed.* **2010**, *49*, 4820–4824.

57 Furukawa, S.; Hirai, K.; Nakagawa, K.; Takashima, Y.; Matsuda, R.; Tsuruoka, T.; Kondo, M.; Haruki, R.; Tanaka, D.; Sakamoto, H.; Shimomura, S.; Sakata, O.; Kitagawa, S. Heterogeneously Hybridized Porous Coordination Polymer Crystals: Fabrication of Hetero-metallic Core-Shell Single Crystals with an in-Plane Rotational Epitaxial Relationship. *Angew. Chem., Int. Ed.* **2009**, *48*, 1766–1770.

58 Fukushima, T.; Horike, S.; Kobayashi, H.; Tsujimoto, M.; Isoda, S.; Foo, M. L.; Kubota, Y.; Takata, M.; Kitagawa, S. Modular Design of Domain Assembly in Porous Coordination Polymer Crystals via Reactivity-Directed Crystallization Process. *J. Am. Chem. Soc.* **2012**, *134*, 13341–13347.

59 Maier, J. Nanoionics: Ionic Charge Carriers in Small Systems. *Phys. Chem. Chem. Phys.* **2009**, *11*, 3011–3022.

60 Pan, J.; Chen, C.; Zhuang, L.; Lu, J. Designing Advanced Alkaline Polymer Electrolytes for Fuel Cell Applications. *Acc. Chem. Res.* **2011**, *45*, 473–481.

61 Ohba, M.; Yoneda, K.; Agusti, G.; Munoz, M. C.; Gaspar, A. B.; Real, J. A.; Yamasaki, M.; Ando, H.; Nakao, Y.; Sakaki, S.; Kitagawa, S. Bidirectional Chemo-switching of Spin State in a Microporous Framework. *Angew. Chem., Int. Ed.* **2009**, *48*, 4767–4771.

62 Jung, M.; Kim, H.; Baek, K.; Kim, K. Synthetic Ion Channel Based on Metal-Organic Polyhedra. *Angew. Chem., Int. Ed.* **2008**, *47*, 5755–5757.