Helical Water Chain Mediated Proton Conductivity in Homochiral Metal-Organic Frameworks with Unprecedented Zeolitic (unh) Topology

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ABSTRACT

Four new homochiral metal organic framework (MOF) isomers namely, [Zn(L-cl)(Cl)](H$_2$O) (1), [Zn(L-br)(Br)](H$_2$O) (2), [Zn(d-L-cl)(Cl)](H$_2$O) (3), and [Zn(d-L-br)(Br)](H$_2$O) (4) [L = 3-methyl-2-(pyridine-4-ylmethylamino) butanoic acid] have been synthesized by using a derivative of L-/D-valine, and Zn(CH$_3$COO)$_2$.2H$_2$O. A 3-periodic lattice with parallel 1D helical channel was formed along the crystallographic c-axis. Molecular rearrangements results in an unprecedented zeolitic unh-topology in
In each case, lattice water molecules weakly coordinated to halogen atoms form a secondary helical water chain inside the molecular helix. In MOFs 1 and 2, water escapes at ~40–80 °C but show reversible crystallization by readily re-absorbing moisture. In MOFs 1 and 2, frameworks are stable after solvent removal which is confirmed by a single-crystal to single-crystal (SC-SC) transformation. The MOFs 1 and 3 show high proton conductivity of $4.45 \times 10^{-5}$ and $4.42 \times 10^{-5}$ S cm$^{-1}$ respectively, while 2 and 4 shows zero proton conductivity.

INTRODUCTION

Research on Metal–organic frameworks (MOFs) has picked up researchers attention because of their diverse topological architectures and applications like gas sorption,$^1$ catalysis,$^2$ magnetism,$^3$ and electrical conductivity.$^4$ Proton (ion) conductivity in solid-state materials are important due to their application in transport dynamics, electrochemical devices, fuel cells and most importantly to understand the complex biological ion channels.$^5$ Design and synthesis of new proton conductors are enormously important for clean energy application where efficiency of proton exchange membrane based fuel cells could be greatly improved both for cost and performance aspect. As a key structural basis, these materials need proton carriers such as H$_3$O$^+$ or H$^+$ given by acid or OH groups and proton-conducting pathways composed of hydrogen-bond networks for proton conduction. It is well known that nafion has been extensively used as proton conductors in fuel cells in hydrous condition. However, nafion suffers a limitation of operating in high temperature. Owing to this importance, few deliberate
attempts have been made to design inorganic or organic proton conductors such as metal phosphate, oxalate, metal oxides, and organic polymers for their applications in fuel cells and sensors.

Application of MOFs in energy related domain like ion conduction has not been explored in literature as broadly as gas storage and separation. The crystallinity of MOFs can provide new breakthrough into the field of ion conducting system which is often absent in polymer based electrolytes because of the lack of long-range order. The main advantages of MOFs over other porous materials like activated carbon and zeolites, is their highly designable nature, by which not only the size and shape but the physical properties can also be tuned. In particular, the inner surface of MOFs can be tuned with respect to hydrophilicity and acidity via suitable links to control the proton-conduction. Still very limited work on the proton conductivity on MOFs has been reported where, either lattice backbone, addition of guest molecules like imidazole, and 1,2,4-triazole in anhydrous medium, or already present water chains and clusters inside the framework are facile for proton conduction. Kitagawa et.al and others have extensively studied the proton conductivity in various MOFs where coordinated water or guest molecules play a vital role in proton conduction. However, the role of halogen (especially the halogens coordinated to metals) in controlling proton conduction in MOFs has not been explored at all. Here we present a series of chiral MOFs 1-4 with an unprecedented zeolitic unh-topology which contains helical water chain inside the pores. MOFs 1 and 3, due to this helical water chain, exhibit a high proton conductivity of \( \sim 4.45 \times 10^{-5} \text{ S cm}^{-1} \) at ambient temperature while MOFs 2 and 4 show almost zero proton conductivity even though all the four MOFs adopts similar architecture. So far there has been no literature report of proton conduction in chiral MOFs with helical water chain. It is
noteworthy that 1D water chains has become a domain of interest because of their crucial role in the biological transport of protons, and ions.\textsuperscript{9} We have also provided evidence behind the proton conduction due to helical water chain by variable temperature proton conduction experiment and D\textsubscript{2}O exchange. Though many such helical water chains exist in synthetic complexes but there are only handful of reports where 1D water chain exists as default chain after MOF synthesis, because most of the cases high boiling solvents like DMF, DEF, DMA, and DMSO are used instead of water.\textsuperscript{10} These MOFs 1–4 are characterized by single crystal X-ray diffraction, thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), circular dichroism (CD), and hot stage microscopy. The mobility of the water molecule with respect to temperature has been monitored by in situ variable temperature powder X-ray diffraction (VT-PXRD) and single-crystal to single-crystal (SC-SC) transformation experiments. The ordered water molecules anchored by weak metal halogen atoms, facile for proton conduction, as confirmed by proton conductivity measurement coupled with deuterium exchange and solid state NMR experiments.

**EXPERIMENTAL PROCEDURES**

*Materials and general methods.* All reagents were commercially available and used as received. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu K\textsubscript{α} radiation (\(\lambda = 1.5406 \text{ Å}\)), with a scan speed of 2° min\textsuperscript{−1} and a step size of 0.02° in 2\(\theta\). The Fourier transform (FT) IR spectra (KBr pellet) were taken on a PERKIN ELMER FT-IR SPECTRUM (Nicolet) spectrometer. Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25–800 °C on a SDT Q600 TG-DTA analyzer under N\textsubscript{2} atmosphere at a heating rate of 10 °C
min$^{-1}$. All low-pressure CO$_2$ adsorption experiments (up to 1 bar) were performed on a *Quantachrome Quadrasorb* automatic volumetric instrument. All low pressure water adsorption experiments (up to 1 bar) were performed on the BELSORP-max volumetric instrument. Leica M-80 optical microscope with hot stage and camera attachment was used for collecting photographs. Proton conductivity data were measured in a quasi-two-probe method, with a Solartron 1286 Electrochemical Interface with frequency response analyzer; Circular dichromism (CD) data were measured in JASCO J-851-150 L CD Spectropolarimeter. Solid state NMR (SSNMR) was taken in a Bruker 300 MHz NMR spectrometer and Ligand NMR data were taken in Bruker 200 MHz NMR spectrometer.

**Synthesis**

**N-(4-Pyridylmethyl)-L-valine.HCl (l-L$_{Cl}$):** The ligand N-(4-Pyridylmethyl)-L-valine.HCl (l-L$_{Cl}$) was prepared using a modified literature procedure$^{11}$. To an aqueous solution (10 mL) of L-Valine (2 g, 17 mmol) and Na$_2$CO$_3$ (0.91 g, 8.5 mmol), 4-pyridinecarboxaldehyde (1.82 g, 17 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and cooled in an ice bath. NaBH$_4$ (0.76 g, 20.4 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3N HCl was used to adjust the pH to 5-6. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL x 3), and the filtrate was evaporated to get white powder (2.9 g, 70% yield). IR (KBr, cm$^{-1}$): $\nu$ (OH), 3421; $\nu$ (as (CO$_2$)), 1562; $\nu$ (s (CO$_2$)), 1409. $^1$H NMR (D$_2$O, ppm): -CH$_3$ (1.21, d, 3H), -CH$_3$ (1.35, d, 3H), -CH (3.20, m, 1H), -HN-CH (3.65, m, 1H), -CH$_2$ (3.82, dd, 2H), py-H (7.34, d, 2H), py-H (8.38, d, 2H).

**N-(4-Pyridylmethyl)-L-valine.HBr (l-L$_{Br}$):** The ligand N-(4-Pyridylmethyl)-L-valine.HBr (l-L$_{Br}$) was prepared exactly as l-L$_{Cl}$ only HBr was used instead of HCl for pH adjustment. Yield, 3.4 g, 70%. IR
(KBr, cm\(^{-1}\)): \(\equiv_{\text{OH}}, 3420; \equiv_{\text{s}}(\text{CO}_2), 1560; \equiv_{\text{as}}(\text{CO}_2), 1411.\) \(^1\text{H}\) NMR (D\(_2\)O, ppm): -CH\(_3\) (1.20, d, 3H), -CH\(_3\) (1.33, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH\(_2\) (3.79, dd, 2H), py-H (7.34, d, 2H), py-H (8.37, d, 2H).

**N-(4-Pyridylmethyl)-D-valine.HCl \([d-L_{\text{Cl}}]\):** The ligand N-(4-Pyridylmethyl)-D-valine.HCl \([d-L_{\text{Cl}}]\) was prepared exactly as \((l-L_{\text{Cl}})\), only D-valine was used instead of L-valine. Yield, 3.1 g, 72% . IR (KBr, cm\(^{-1}\)): \(\equiv_{\text{OH}}, 3417; \equiv_{\text{as}}(\text{CO}_2), 1564; \equiv_{\text{s}}(\text{CO}_2), 1415.\) \(^1\text{H}\) NMR (D\(_2\)O, ppm): -CH\(_3\) (1.21, d, 3H), -CH\(_3\) (1.34, d, 3H), -CH (3.22, m, 1H), -HN-CH (3.65, m, 1H), -CH\(_2\) (3.78, dd, 2H), py-H (7.30, d, 2H), py-H (8.36, d, 2H).

**N-(4-Pyridylmethyl)-D-valine.HBr \([d-L_{\text{Br}}]\):** The ligand N-(4-Pyridylmethyl)-D-valine.HBr \([d-L_{\text{Br}}]\) was prepared exactly as \((l-L_{\text{Br}})\), only D-valine was used instead of L-valine. Yield, 3.6 g, 72% . IR (KBr, cm\(^{-1}\)): \(\equiv_{\text{OH}}, 3419; \equiv_{\text{as}}(\text{CO}_2), 1570; \equiv_{\text{s}}(\text{CO}_2), 1421.\) \(^1\text{H}\) NMR (D\(_2\)O, ppm): -CH\(_3\) (1.20, d, 3H), -CH\(_3\) (1.34, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.65, m, 1H), -CH\(_2\) (3.78, dd, 2H), py-H (7.35, d, 2H), py-H (8.37, d, 2H).

**[Zn\((l-L_{\text{Cl}})\)(Cl)](H\(_2\)O) \((1)\):** To an aqueous solution (2ml) of \((l-L_{\text{Cl}})\) (0.044 g, 0.2 mmol), Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5ml vial for 24 h at 90 °C to produce rod shaped transparent crystals (0.025 g, 75% yield). IR (KBr, cm\(^{-1}\)): \(\equiv_{\text{OH}}, 3421; \equiv_{\text{N-H}}, 2977; \equiv_{\text{as}}(\text{CO}_2), 1589; \equiv_{\text{s}}(\text{CO}_2), 1395.\) \(^{13}\text{C}\) NMR (D\(_2\)O, ppm): -CH\(_3\) (1.20, d, 3H), -CH\(_3\) (1.33, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH\(_2\) (3.79, dd, 2H), py-H (7.34, d, 2H), py-H (8.37, d, 2H).

**Elemental Analysis:** Calculated- C (40.51%), H (5.25%), N (8.59%); Found C (40.57%), H (5.21%), N (8.62%).

**[Zn\((l-L_{\text{Br}})\)(Br)](H\(_2\)O) \((2)\):** To an aqueous solution (2ml) of \((l-L_{\text{Br}})\) (0.044 g, 0.2 mmol), Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was
kept in a tightly capped 5ml vial for 24 h at 90 °C to produce rod shaped transparent crystals (0.026 g, 70% yield). IR (KBr, cm⁻¹):  = OH, 3427;  = N-H, 2974;  = as(CO₂), 1590;  = s(CO₂), 1394.  = C-N, 1623.
Elemental Analysis: Calculated- C (35.65%), H (4.62%), N (7.60%); Found C (35.68%), H (4.60%), N (7.63%).

[Zn(d-LCl)(Cl)](H₂O) (3): To an aqueous solution (2ml) of d-LCl (0.044 g, 0.2 mmol), Zn(CH₃COO)₂.2H₂O (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5ml vial for 24 h at 90 °C to produce rod shaped transparent crystals (0.023 g, 71% yield). IR (KBr, cm⁻¹):  = OH, 3420;  = N-H, 2975;  = as(CO₂), 1589;  = s(CO₂), 1397.  = C-N, 1627.
Elemental Analysis: Calculated- C (40.51%), H (5.25%), N (8.59%); Found C (40.54%), H (5.28%), N (8.57%).

[Zn(d-LBr)(Br)](H₂O) (4): To an aqueous solution (2ml) of d-LBr (0.044 g, 0.2 mmol), Zn(CH₃COO)₂.2H₂O (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5ml vial for 24 h at 90 °C to produce rod shaped transparent crystals (0.026 g, 72% yield). IR (KBr, cm⁻¹):  = OH, 3425;  = N-H, 2970;  = as(CO₂), 1592;  = s(CO₂), 1395.  = C-N, 1622.
Elemental Analysis: Calculated- C (35.65%), H (4.62%), N (7.60%); Found C (35.60%), H (4.64%), N (7.62%).

[Zn(l-LCl)(Cl)] (1→l): 1g sample of MOF 1 was evacuated at 150 °C for 12 h and further characterized by elemental analysis and TGA. Single crystal of 1→l suitable for X-ray diffraction was obtained by slow thermal heating at a rate of 6 K min⁻¹ and data collected at various interval of temperature (25-100 °C) and observed that at 80 °C we could able to achieve a evacuated framework of 1 with reasonable good data [(R₁) = 6.4%, weighted R (wR₂) = 14.7%, GOF = 1.005] below which water stay
at lattice as solvents and above which the framework remains intact but high thermal vibration observed in the atom sites results in high refinement parameters. Elemental Analysis: Calculated-C (42.84%), H (4.90%), N (9.0%); Found C (42.52%), H (4.74%), N (8.77%).

\[\text{Zn}(d-L_{\text{Br}})(\text{Br})\] (2→1): 1g sample of MOF 2 was evacuated at 150 °C for 12 h and further characterized by elemental analysis and TGA. Single crystal of 2→1 suitable for X-ray diffraction was obtained by slow thermal heating at a rate of 6 K min⁻¹ and data collected at various interval of temperature (25-100 °C) and observed that at 40 °C we could able to achieve a evacuated framework of 2 with reasonable good data [(R₁) = 5.7%, weighted R (wR₂) = 15.12%, GOF = 1.071] below which water stay at lattice as solvents and above which the framework remains intact but high thermal vibration observed in the atom sites results in high refinement parameters. Elemental Analysis: Calculated- C (37.44%), H (4.28%), N (7.94%); Found C (37.36%), H (4.21%), N (7.72%).

**X-ray crystallography**

All single-crystal data were collected on a Bruker SMART APEX three-circle diffractometer equipped with a CCD area detector (Bruker Systems Inc.) and operated at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of the Zn-MOFs reported in the paper were mounted on nylon CryoLoops (Hampton Research) with Paratone-N (Hampton Research). Data were integrated using Bruker SAINT Software. Data were subsequently corrected for absorption by the program SADABS. Space group determinations and tests for merohedral twinning were carried out using XPREP. All cases, the highest possible space group was chosen. All structures were solved by direct methods and refined using the SHELXTL 97 software suite. Atoms were
located from iterative examination of difference F-maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times $U_{eq}$ of the attached C atoms. Hydrogen atoms attached to the lattice water molecules in 1-4 could not be located or fixed. Data were collected at 296(2) K for MOFs 1-4, 353(2) K for MOF 1-evac (1{-J}), and 313 (2) K for MOF 2-evac (2{-J}) reported in this paper. All structures were examined using the Addsym subroutine of PLATON\textsuperscript{12e} to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise (Figure S15). The Supporting Information contains a detailed data collection strategy and crystallographic data (Table S7 and S8) for the MOFs reported in this paper. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No.CCDC 831054–831059. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [fax: þ 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk].

RESULTS AND DISCUSSION

Synthesis and characterization: Chirality, helicity and porosity play important roles in chemistry and biology\textsuperscript{13} and it is a challenge to combine all the properties in a single domain. The construction of a helical MOF is considered as one fascinating structure as helical assemblies such as protein bundles and DNA are prevalent in biological systems and play key roles in molecular recognition, replication, and catalysis.\textsuperscript{14} Several approaches have been developed for constructing chiral MOFs with potential applications in the field of chiral synthesis, optical devices, sensory functions, modelling of biological
compounds etc. Multitopic linkers derived from natural amino acids, because of their biological functional properties and highly selective substrate-binding abilities, are an attractive choice as chiral building blocks for the preparation of aforementioned materials. Although Rosseinsky et al. reported diverse three dimensional MOFs using pure amino acids and 4,4-l-bipyridine based ancillary ligands, but chiral MOFs from amino acid derived links that possess 3-D architecture as well as porosity are rare. On the contrary amino acid derivatives (links that has been synthesized from amino acids) are good choice over pure natural amino acids as most of the latter prefer to chelate metal centers utilizing the amino and carboxylate groups to form mostly zero/one dimensional complexes. Recently Wu et al. have synthesized a similar serine derivative ligand which shows promising catalytic activity but resulting MOF adopts a 2D chain rather creating a 3D architecture. Based on the above facts it is evident that amino acid derivatives (naturally available and pure enantiomer) are good choice as chiral links for designing 3D homochiral MOFs after judicial choice with various promising application.

MOFs 1–4 reported in this paper were synthesized by mixing Zn(CH$_3$COO)$_2$.2H$_2$O and 3-methyl-2-(pyridine-4-ylmethylamino)butanoic acid (a valine derived link) (Figure 1a) using hydrothermal condition in water medium. Phase pure rod shape crystals were grown in the caped vial at 90 °C within 5-6 h. 1–4 were structural isomers with respect to either different anions (–Cl$^-$ or –Br$^-$) coordinated to metal atoms or enantiomers with respect to (–d or –l) ligand backbone. MOF 1 crystallizes in the P6$_3$ space group, which comprises of one Zn(II), one l-L$_{Cl}$ ligand and one lattice water molecule in the asymmetric unit. The Zn(II) center adopts a distorted square pyramidal geometry ($	au$ = 0.88) chelated by monodentate carboxylate [(Zn1–O2 2.170(3) Å)], and one amino functionality [(Zn1–N1 2.092(4) Å)] of first l-L$_{Cl}$ link. One pyridyl functionality and one carboxyl oxygen atom of the second l-L$_{Cl}$
ligand coordinates in the equatorial positions, and one free chlorine atom occupies the axial site (Figure 1b). Noticeably, the amine group is induced by the neighboring chiral carbon center into a homochiral unit to coordinate the zinc atom. As a result, the zinc atom acquires a third homochiral center associated with two homochiral centers. All adjacent zinc nodes are bridged, by pyridyl group to form a 6,1 helical chain with a pitch of 12 Å along the crystallographic c axis (Figure 1c). The two coordinated carboxylate oxygen stay opposite to each other along c axis through which additional molecules link to form the wall of the helical chain. Among the pyridyl rings along the helical chain, one set of pyridyl rings run in clockwise direction while other (linking two molecular chains) run anti clockwise to extend the lattice along the ab-plane. This result in a 3D supramolecular network containing close-packed 1D open channel along the c-axis filled with water molecules (Figure 2a). All pyridyl rings and isopropyl groups constitute the wall of the helical channel and provide a hydrophobic environment to it. This molecular arrangement result in a rare zeolitic unh-topology which has not been perceived so far in any synthetic means even though it is theoretically proposed in ZIFs.\textsuperscript{17} The unh topology has a vertex symbol 5.5.5.5\textsubscript{2}.12.12. (Figure 2b). We analyzed the complexity of the nets in terms of their natural tiling, where the set of edges and vertices of the tiles is the same as that of the net.\textsuperscript{18} MOF 1–4 have the transitivity value of 1221, which means that the tiling has one kind of vertices, two kinds of edges, two kinds of faces, and one kind of tiles. MOFs 1–4 comprise a uninodal nets having an isohedral kind of tile. The tile has two five-sided and two twelve-sided faces with face symbol 5\textsuperscript{2}.12\textsuperscript{2} (Figure 2b). Lattice water molecules weakly H-bonded to M–Cl atom [(O···Cl–M, 3.175(1) Å)] run along the helical channel (Figure 2c). As a result a secondary helical water chain surrounded by the molecular helix is formed. Weak (O–H···Cl–M) H-bonding may facilitate the water protons to become more acidic. It was found that helical orientation of water molecules are the structural basis by which the K\textsuperscript{+} ion and proton
transport occurs inside KcsA K$^+$ channel and in protein aquaporin-1 respectively.\textsuperscript{19} 1D water chains also play vital roles for stabilizing the native conformation of biopolymers, but such helical water chains are less reported in synthetic homochiral crystal hosts\textsuperscript{30} espsecially in MOFs, because for most of the high boiling solvents like DMF, DMA, DMSO, DEF are used for MOFs synthesis instead of water. Single-crystal X-ray diffraction analysis revealed that MOF 2, 3, and 4 are isomorphous to MOF 1 where (1, 2) and (3, 4) are isomers with respect to substituted halogen atoms like 1[L$_2$M–Cl] and 2 [L$_2$M–Br] but (1, 3) and (2, 4) are enantiomers. In 2 each Zn$^{11}$ cation has similar coordination environment except the axial position is occupied by Br-atom. The $\tau$ (trigonality factor) is almost same ($\tau = 0.89$) as that of 1. Lattice water molecules are weakly H-bonded and placed almost in equivalent position with respect to –Br atom show a helical arrangement similar to 1. For comparative purpose, we prepared enantiomer \textit{d}-L$_{Cl}$ analogue of 1. We obtained two enantiomorphic frameworks [Zn(\textit{d}-L$_{Cl}$)(Cl)](H$_2$O)] (3) and [Zn(\textit{d}-L$_{Br}$)(Br)](H$_2$O)] (4) based on self-assembly between \textit{d}-L$_{Cl}$ and \textit{d}-L$_{Br}$ with Zn(CH$_3$COO)$_2$·2H$_2$O under similar hydrothermal conditions. The CD measurements on bulk crystals of 1 and 3 show opposite Cotton effects at ~ 238 and 265 nm (Figure S22), indicating that (1, 3) and (2, 4) are enantiomers. Compound 3 and 4 have similar coordination environment to that of 1 and 2 except the resulting crystal structure adopts opposite handedness. 3 and 4 also contain one water molecule as lattice solvent having week H-bonding of 3.17 Å (O···M–Cl) and 3.16 Å (O···M–Br) respectively. Overall it has been confirmed that all the four isomers possess similar lattice arrangement (unh topology) and the helical water chain persists irrespective of the different halogen substitution or change in chirality of the ligand backbone.
The phase purity of the bulk materials were confirmed by powder X-ray diffraction (PXRD) experiments which are in well agreement with the simulated PXRD patterns (Figure S2-S5). Thermogravimetric analysis (TGA) performed on as-synthesized 1–4 revealed that these compounds have thermal stability upto ~270 °C (Figure S17). The TGA trace for as synthesized 1, 2, 3 and 4 showed a gradual weight-loss step of 6.0 % [1 H₂O in 1 and 3; calcd. 5.52%] and 5.10 % [1 H₂O in 2 and 4; calcd. 4.85%] at temperature range of 40–100 °C, corresponding to escape of guest water molecules from the pores (Figure S17). We note that the water molecules of 1 and 2 were released without damaging the frameworks, as evidenced by the coincidence of the PXRD patterns of 1 and 2 samples heated to and held at 150 °C in N₂ atmosphere with the PXRD patterns simulated from single-crystal structures. The above fact is also verified by in situ VT-PXRD of MOF 1 (Figure 3a and S18) and MOF 2 (Figure S19). All major peaks of experimental and simulated PXRDs are well matched, indicating the sample’s phase purity (Figure 3a). A combine heating and cooling in situ VT-PXRD experiment reveals that the frame work is stable and remain crystalline over a wide temperature range (heating from 25 to 200 °C and then cooling from 200 to 25 °C) and remain stable after solvent removal (solvent escapes ~100 °C, confirmed by TGA). Escape of water molecules from the crystals were also monitored by hot stage microscopy at different temperature intervals (25–270 °C). Pictures taken on hot stage microscope reveals that the trapped water molecules escape the lattice in between 60-120 °C as heating goes on and cracking appears on the crystal surface, but crystallinity remain intact up to 250 °C (Figure S23). This observation indicated that it is possible to achieve a solvent free framework after successful removal of solvent.
It is noteworthy that the water molecules adopt similar arrangements in all MOFs 1–4 reported in this paper except the handedness. The guest free framework of MOFs 1-4 reported in this paper show high affinity for water irrespective of different structural variation. It is worth mentioning that only a handful of Zn based MOFs reported in literature can withstand moisture. Upon exposure to moisture Zn-based MOFs undergo phase transformation which leads to decrease in gas sorption. Few well known MOFs like MOF-5 and MOF 177 shows this kind of behavior. Recently water stable methyl modified MOF-5 was successfully synthesized by incorporation methyl group in the parent ligand of MOF-5. To provide a further evidence of water affinity apart for crystallographic information, MOF 1 was extensively studied by various experiments. MOF 1 shows a reversible transformation in presence of water vapor. After evacuation at 150 °C for two days, the dehydrated polycrystalline sample of 1 (confirmed by PXRD, IR, and TGA) was exposed in a closed chamber saturated with water vapor. Single crystalline nature of MOF 1 comes back within 6-12 hrs (Figure 4a), which is confirmed by IR, TGA, and crystallography. FT-IR spectra of the evacuated MOF 1 sample collected at a time interval of one hour showed gradual increase in intensity water peaks after exposed to moisture (Figure 4c), which further confirms the high affinity of 1 for water. Water affinity of 1 and 2 were examined by water adsorption isotherm. MOF 1 and 2 showed 150 (12 wt %) and 75 cc/gm (6 wt %) water uptake respectively at RT and relative pressure (P/P₀) of 0.9 (Figure 3b). It is quite clear that MOF 2 has less water affinity compared to 1, though framework arrangement in MOF 1 and 2 are similar. CO₂ adsorption isotherm indicates quite less uptake (25 cc/g for 1, 20 cc/g for 2) than predicted on basis of X-ray crystallography and indicates low degree of interaction points inside the pore. (Figure S27)
Inspired by the above results we thought to establish the above fact by in situ variable temperature single crystal x-ray diffraction experiment (SCXRD). We performed this variable temperature SCXRD on MOF 1 and 2 at different temperature interval of like 25, 40, 50, 60, 70, 80, 90, 100 and 115 °C. Before data collection crystallinity of MOF suitable for single crystal diffraction was checked by taking snap shots and unit cell determination at that particular temperature which confirms that the sample’s crystallinity remain intact for suitable data collection (Figure S20 and S21). From TGA experiments it was found that the MOFs loose lattice water molecule during a temperature range of 60-100 °C. Taking clue from the above observations we anticipated that there is a possibility to achieve an evacuated framework via a single-crystal to single-crystal (SC-SC) transformation. After carefully solving the above collected data sets we found that 80 °C is the ideal temperature at which we could able to achieve stable and solvent free framework of 1 with reasonable good data [(R$_1$) = 6.4%, weighted R (wR$_2$) = 14.7%, GOF = 1.005] below which water stay at lattice as solvents and above which the framework remains intact but high thermal vibration observed in the atom sites results in high refinement parameters (Table SX). Similar experiment performed on MOF 2 (–Br analogue of MOF 1) reveals that we can achieve an evacuated framework at much lower temperature of 40 °C [(R$_1$) = 5.7%, weighted R (wR$_2$) = 15.12%, GOF = 1.071]. The above result attributed to the fact that the above MOFs have not only affinity for water but can perform SC-SC transformation and MOF 2 has a lower affinity towards water than MOF 1 (Figure 4d). It has been mentioned already that the structural arrangement of MOFs 1-4 are all similar except the handedness and halogen atoms in the framework [M–X (X= –Cl, –Br)]. It is well established that metal halides (M–X) have shown to be strong hydrogen bond acceptors, compared to organic halides (principally C–Cl and C–Br groups). The normalized distance function, R$_{HX}$, for D–H···X hydrogen bonds [(R$_{HX}$ = d(H···X)/...]}
(r_H + r_X) [R_{HX} value of 0.799 and 0.820 for O–H−l−l−l−lX−M (X= Cl, Br)] show a major of acceptor capabilities of halogens.\textsuperscript{23,24} It is anticipated that due to increase in polarity of the D–H bond, for a given halide ion, O–H donors can contribute stronger interaction than N–H donors. Similarly comparison of halide ion acceptors for a given donor are compared, interactions follow an order H−l−l−l−lF > H−l−l−l−lCl > H−l−l−l−lBr > H−l−l−l−lI. In the present scenario for MOFs 1 and 2, it is expected that O–H−l−l−l−lX–M interaction is stronger in 1 (X= Cl) than 2 (X=Br).

The X-ray crystal structures of 1–4 established that these materials are amenable to proton conducting property owing to the helical 1D water chain in a confined hydrophobic and acidic environment. Stronger O–H−l−l−lCl–M interaction results in the increasing acidity of the water protons and subsequently becomes the major driving force of the proton conduction. The proton conductivities of two halogen isomers 1 and 3 were measured by a quasi-two-probe method, with a Solartron 1286 Electrochemical Interface with frequency response Analyser. The conductivities were determined from the semicircles in the Nyquist plots (Figure 6 and S29). The proton conductivities of 1 and 3 were 4.45 × 10\(^{-5}\), 4.42 × 10\(^{-5}\) S cm\(^{-1}\), respectively, at 304 K and 98% relative humidity (RH). This value was highly humidity-dependent and dropped to 1.49 × 10\(^{-5}\) S cm\(^{-1}\), 1.22 × 10\(^{-5}\)S cm\(^{-1}\) at 75%, and 60% RH respectively at 304 K (Figure S29). Surprisingly, 2 and 4 show almost zero proton conductivity. Before coming to any conclusion, the reproducibility was tested by measuring the aforementioned proton conduction 4–5 times on different batch of samples. Each experiment revealed similar result. From the above result it is evident that the interior of the cavity with respect to different halogen substituent is responsible for differential proton conductivity and the –Cl atom having more electronegativity (as compared to –Br) making H-bonded water molecule more acidic for available
proton source. The present results also supported by less water adsorption property shown by MOF 2 (75 cc/gm) compared to MOF 1 (150 cc/gm) as discussed previously. To prove the role of water molecules, we synthesized 1-D$_2$O [Zn(I-L$_{cl}$)(Cl)(D$_2$O)], taking D$_2$O as solvent of synthesis. 1-D$_2$O was studied further by IR and solid state $^2$H SSNMR (Figure 4c) which confirmed the D$_2$O incorporation in 1-D$_2$O and its structural similarity to MOF 1. Impedance studies on the deuterated sample in a H$_2$ atmosphere humidified (98%) with D$_2$O, gave a conductivity value of $1.33 \times 10^{-5}$ Scm$^{-1}$. The lower value is expected due to the heavier isotopic substitution. Proton conductivity measurements performed at different temperature shows gradual increase in proton conductivity value from $3.13 \times 10^{-5}$ to $4.45 \times 10^{-5}$ Scm$^{-1}$ as temperature increases from 299 K to 304K, respectively (Figure 6b). At higher temperature, above 40 °C the proton conductivity decreases due to partial dehydration as indicated by TGA plot and the $^2$H SSNMR data had indicated mobile protons/deuterons even at 25 °C. Similar property was also observed by a previously reported MOF by Shimizu et al.$^{6b}$ The activation energy (Ea) for the proton transfer derived from the bulk conductivity of 1 and 3 were 0.34, and 0.36 eV, respectively, as determined from least-squares fits of the slopes. Compared with proton conductors in hydrated medium having this mechanism, MOF 1 show high Ea value than Nafion (Ea 0.22 eV)$^{25b}$, but comparable with Zr(HPO$_4$)$_2$ (0.33)$^{25c}$ and HUO$_2$PO$_4$$_{4H_2}O$ (Ea 0.32 eV). This low Ea observed in 1 indicates that the ordered helical water chain (observed crystallographically) function to transport protons via a Grotthuss hopping mechanism as opposed to the more Ea value observed for vehicular transfer mechanism. Proton conductivity value of MOF 1 is quite high as compared to MIL-53 based MOFs ($\sim 10^{-6}$–$10^{-9}$ studied by Kitagawa et al. at 25 °C, 95 % RH), and comparable to a zinc-phosphonate MOF(1.33×10 $^{-5}$ S cm$^{-1}$ at 25 °C, 98 % RH) by Shimizu et al.$^{6b}$ but, possess a lower value.
as compared to a ferrous oxalate dehydrate\(^6\) (1.3 x 10\(^{-3}\) S cm\(^{-1}\) at 25 °C, 98 % RH) under similar condition (Table S9).

**Conclusion**

In conclusion, we have synthesized four new homochiral Zn-MOFs 1-4 using amino acid derived links. These MOFs adopt 3D periodic architecture with 1D helical water chains irrespective of type of halogen atom substitution or enantiomeric difference. All four MOFs 1-4 show an unprecedented zeolitic (unh) topology which is not perceived so far by any synthetic means. Lattice water molecules are weakly coordinated to halogen atoms and form a secondary helical water chain inside the molecular helix. In MOFs 1 and 2, water escapes at ~40–100 °C but show reversible crystallization by readily re-absorbing moisture which is also confirmed by the single-crystal to single-crystal (SC-SC) transformation. The hydrophobic environment of the 1D channel along with weak H-bonding with halogen atoms provide a facile path way for proton conduction in humid conditions. This is the first example in which proton conductivity has been observed in chiral MOFs having helical water chains confined in hydrophobic and acidic environment controlled by metal bound halogen atoms. Stronger O–H\(\cdots\)Cl–M interaction results in the increasing acidity of the water protons and subsequently becomes the major driving force of the proton conduction in MOF 1 than 2. The role of water chain in proton conduction has been further confirmed by D\(_2\)O exchanged experiments. Ion conduction in MOF has been reported in only a handful of cases. These results will provide good roadmap towards tuning and precise control of the proton conductivity and consequently enable us to develop useful domain both for solid electrolytes and biological perspective.
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Figure 1. (a) Schematic representation of the links with mirror isomers (l-\(L_X\)) and (d-\(L_X\)) in the form of different salts, where \(X= \text{Cl}^-\), \(\text{Br}^-\) are shown in green. (b) Ball and stick model of asymmetric unit of MOFs with mirror isomers showing a five coordinated zinc centre (pink ball). (c) Space fill model of two enantiomers of MOF 1 and 3. Opposite helicity is shown as a blue curved arrow. [Color Code: gray-C, green-Cl, red-O, blue-N, Pink-Zn, white-H]
Figure 2. (a) Polyhedral representation of MOF 1 lattice viewing down c-axis. Pink polyhedra represent zinc centers and lattice water molecules are shown as red balls. (b) Tiling figure of MOF 1 showing zeolitic unh-topology along c-axis. The tiling represents one kind of vertices, two kinds of edges, two kinds of faces and one
kind of tile. (c) Mirror isomers of helical water chain surrounded by molecular helix (outer helix). The molecular helix (outer helix) shown as pink balls connected via gray bonds and helical water chain (inner helix) as red balls connected via blue rods.
Figure 3. (a) In situ variable temperature PXRD of MOF 1 at both heating (25–200 °C) and cooling (200–25 °C) condition. This VT-PXRD experiment shows the framework is stable and remains crystalline over a wide range of temperature and after solvent removal. (b) Water adsorption isotherm of MOF 1 and MOF 2 showing 150 cc/gm and 75 cc/gm of adsorption respectively at RT and relative pressure.
Figure 4. (a) Photographs of MOF 1 before and after evacuation at 150 °C, followed by rehydration showing reappearance of single crystallinity. (b) Reversible crystal transformation of MOF 1 confirmed by in situ single crystal X-ray diffraction showing MOF framework with/without solvent (water) as ball stick model along c-axis. Crystallinity of the MOF 1 remains intact and suitable for data collection over the temperature as shown by crystal pictures taken during data collection. (c) Appearance and disappearance of water peaks in IR spectra of as-synthesized, evacuated and rehydrated MOF 1 confirms the reversible transformation. Solid state NMR spectra of MOF 1-D$_2$O (D$_2$O exchanged sample of MOF 1) is shown at inset. (d) Thermal desolvation and in situ VT single crystal experiment of evacuated MOF 1 and 2 achieved at 80 and 40 °C respectively confirms that MOF 2 has lower water holding capacity than MOF 1.

Figure 6. (a) Proton conductivity data comparison of MOF 1 and 1-D$_2$O (inset) at 98 % relative humidity (RH) showing decreasing proton conductivity value after D$_2$O substitution. (b) Temperature dependent in proton conductivity value of MOF 1 at different temperature. (c) Proton conductivity of MOF 2 at 98 % RH showing
zero proton conduction as compared to MOF 1 under similar condition. (d) Arrhenius plots of proton conductivity of MOF 1.
A series of Zn-based homochiral MOFs were synthesized in hydrothermal condition in water using valine derivative and Zn(CH$_3$COO)$_2$.2H$_2$O. The MOFs show an unprecedented zeolitic ( unh) topology which was predicted in theory but not perceived experimentally yet. The MOFs have high affinity towards water and show reversible crystal transformation in water. The MOFs show proton conductivity at humidified condition and halogen atoms have a great impact on proton conduction.