Supporting Information

Moisture-Triggered Proton Conductive Switch in Metal-Organic Frameworks: Role of Coordinating Solvents

Hong Kyu Lee, ‡^a Yasaswini Oruganti, ‡^b Jonghyeon Lee, ‡^c Seunghee Han,^d Jihan Kim,^d Dohyun Moon, *^e Min Kim, *^c Dae-Woon Lim*^b and Hoi Ri Moon*^f

^{*a*} Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea.

^b Department of Chemistry and Medical Chemistry, Yonsei University, Wonju, Gangwondo 26493, Republic of Korea. E-mail: limdaewoon@yonsei.ac.kr

^c Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea. E-mail: minkim@chungbuk.ac.kr

^d Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and

Technology (KAIST), Daejeon 34141, Republic of Korea. E-mail: jihankim@kaist.ac.kr

^e Beamline Department, Pohang Accelerator Laboratory, Pohang, Gyeongbuk 37673, Republic of Korea. Email: dmoon@postech.ac.kr

^f Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Republic of Korea.

E-mail: hoirimoon@ewha.ac.kr

‡ These authors contributed equally to this work.

Experimental Section

Materials and characterization.

All chemicals and solvents were of reagent grade and were used as received without further purification. $Zn(NO_3)_2 \cdot 6H_2O$ were bought from Sigma-Aldrich, *N*,*N*-diethylformamide (DEF) from TCI, and dichloromethane from Dae Jung. 9H-Fluorene-2,7-dicarboxylic acid (H₂FDC) was synthesized following procedures outlined in previous literature.



Scheme. S1 Process of synthesis of H₂FDC (3, H₂FDC)



Scheme. S2 Synthesis of fluorene-2,7-dicarboxylic acid (2, FDCN)

Synthesis of *9H***-fluorene-2,7-dicarbonitriledicarboxylate (FDCN) (2).**^{S1} 2,7-dibromofluorene (1, 2.9 g, 9.0 mmol), copper(I) cyanide (2.0 g, 22 mmol), and *N*-methylpyrrolidine (NMP, 7 mL) were placed in the pressure tube. The mixed solution was agitated at 180 °C for 2 days. After cooling the solution to room temperature, the residue was poured into aqueous solution of iron(III) chloride hexahydrate (7.3 g, 27 mmol), and 2 M HCl (13 mL), stirred at 70 °C for 1 h to decompose the complex. The residue was extracted 3 times with chloroform after hot stirring, and further extraction was conducted three times with chloroform to obtain the remaining

residue. The residues were combined, washed with brine, dried with magnesium sulfate, and organic solvents were removed. The desired white solids (7, 0.83 g, 43% yield) was obtained by column chromatography (Dichloromethane (DCM):*n*-Hexane (*n*-Hex)=1:1). *9H*-fluorene-2,7-dicarbonitriledicarboxylate (**2**): ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 0.7 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 4.04 (s, 2H); ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 144.35, 144.28, 131.67, 129.10, 121.70, 119.14, 111.80, 36.85.



Scheme. S3 Synthesis of fluorene-2,7-dicarboxylic acid (2, FDCN)

Synthesis of 9*H*-fluorene-2,7-dicarboxylic acid (H₂FDC, 3). 100 mg (0.47 mmol) of 2 was placed in a microwave reactor vial (10 mL size). 2 mL of 9 M H₂SO₄ solution and 3 mL of anhydrous tetrahydrofuran (THF) was added to the vial. The mixture was stirred at 110 °C for 8 hours using the microwave reactor. After the microwave reaction, the mixture was allowed to cool to room temperature. The solid was obtained by filtration and washed with distilled water and acetone. The final product, **3**, was obtained as a gray-colored solid (115 mg, 97% yield). *9H*-fluorene-2,7-dicarboxylic acid (C):¹H NMR (DMSO-*d*₆, 500 MHz, ppm) δ 12.91 (br, 1H), 8.19 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 8.02 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.08 (s, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz, ppm) δ 167.48, 144.44, 144.29, 129.94, 128.50, 126.30, 120.96, 36.48.

Synthesis of Zn₅FDC-DEF. Zn(NO₃)_{2□}6H₂O (0.150 g, 0.5 mmol) was dissolved in 1 mL of DEF in a vial.

 H_2 FDC (0.025 g, 0.1 mmol) was dissolved in 2 mL of DEF in a vial. The ligand solution was stirred on a hot plate. To Zn nitrate solution, ligand solution was added and heated at 85 °C oven for 48 h. After cooling to room temperature, the mother liquor was decanted, and the colourless rod crystals were washed with fresh DEF and dichloromethane. Anal Cald for $Zn_5C_{70}H_{56}N_2O_{20}$ (Zn₅FDC-DEF): C, 53.48; H, 3.59; O, 20.35; N, 1.78.; Found: C, 53.54; H, 3.40; O, 20.23; N, 1,60.

Synthesis of Zn_8FDC . $Zn(NO_3)_{2\square}6H_2O$ (0.180 g, 0.6 mmol) and H_2FDC (0.050 g, 0.2 mmol) were dissolved in 10 mL of DEF in a glass jar. The glass jar was placed at 100 °C oven. After 24 h, the hot mother liquor was decanted, and the large colorless cubic crystals (mixture of Zn_8FDC and Zn_7FDC) were immersed in fresh DEF for three days to convert into Zn_8FDC .

Structural Transformation Zn_8FDC to Zn_5FDC -DCM. Zn_8FDC crystals were exchanged with fresh DCM three times a day for a week. As a result, Zn_8FDC underwent a transformation into the Zn_5FDC -DCM. Anal Clad for $Zn_5C_{60.80}H_{35.60}O_{18}Cl_{1.60}$ (Zn_5FDC -DCM): C, 50.76; H, 2.49; O, 20.06.; Found: C, 49.84; H 2.46; O, 20.99.

Characterization methods

Fourier-transform (FT)-NMR spectra were performed on Bruker AVANCE III 300 spectrometer at the Basic Sciences Research Institute of Ewha Womans University. Elemental analyses were performed at the Organic Chemistry Research Centre of Sogang University. Thermogravimetric analyses (TGA) was performed under N₂ at a scan rate of 5 °C min⁻¹, using a TGA Q50 from TA instruments. X-ray powder diffraction (XRPD) data were recorded on a Bruker D2 phaser diffractometer at 30 kV and 10 mA for Cu K α (λ = 1.54050Å), with a step size of 0.02 ° in 2. N₂ sorption and water vapor isotherms of the samples were obtained using a BELSORP-max (Microtrac BEL Corp.,Japan) at 77 K and 298 K until *P*/*P*₀ = 0.95 respectively. Prior to the adsorption measurements, the samples were evacuated (*p* < 10⁻⁵ mbar) at 120 °C for overnight. Infrared spectra were performed with a ThermoFisher Scientific iS10 FT-IR spectrometer.

Single-crystal X-ray crystallography

All of the single crystals of Zn₈FDC, Zn₇FDC and Zn₅FDCs were coated with Parabar 10312 (Hampton Research Inc.). Single-crystal X-ray diffraction patterns were collected using a synchrotron-based X-ray source produced from a PLS II 2D bending magnet ($\lambda = 0.70000$ Å) with a silicon(111) double crystal monochromator and Rayonix MS225HS CCD area detector at 173, 100, and 220 K respectively. The PAL BL2D-SMDC program^{S2} was used for one set of data collection as follow conditions: detector distance of 66 mm, 1-axis omega scan: $\Delta \omega$ of 1°, exposure time of 1 s/frame. HKL3000sm (Ver. 717.6)^{S3} was used for cell

refinement, reduction, and absorption correction. The structures were solved by the intrinsic phasing method using SHELXT-2018/2^{S4} and refined by full-matrix least-squares on F^2 using SHELXL-2019/3.^{S5} All non-hydrogen atoms were refined anisotropically, and H atoms (except the H atom of coordinated hydroxy) were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.95 – 0.99 Å and with U_{iso} (H) values of 1.2 and 1.5 U_{eq} of the parent atoms. O-bound H-atoms of coordinated hydroxy were assigned based on a difference Fourier map and were refined with distance restraints of 0.92 Å using DFIX command, and U_{iso} (H) values of 1.5 U_{eq} of oxygen atom. Thus, the final refinement was performed with the structural factors modified based on the disordered structural solvent electron densities obtained from the SQUEEZE routine of PLATON.^{S6} Some SHELXL restrains (DFIX, DANG, SIMU, DELU, and RIGU) and the thermal parameters of the corresponding atoms.

Further details may be obtained from the Cambridge Crystallographic Data Centre (CCDC) using www.ccdc.cam.ac.uk/deposit. CCDC entries 2300231, 2300232, 2300233 and 2300234 contain the supplementary crystallographic data for this article.

Moisture Exposure Experiments

The moisture exposure experiment was conducted using a saturated KNO₃ aqueous solution to maintain the relative humidity at a fixed temperature (94.6% at 25 °C).^{S7} 5 mL of the saturation solution was placed in a 20 mL vial, and a separate 5 mL vial containing 10 mg of MOFs was immersed in the solution. After tightly sealing the 20 mL vial cap, it was left to stand for 48 h in a 25 °C water bath to maintain the temperature.

Geometry optimization

Geometry optimization was performed for Zn_5FDC -OMS and Zn_5FDC -DEF to compare with experimental structures. This optimization was conducted utilizing the universal force field (UFF)^{S8} with QEq^{S9} charge assignment through the Forcite module in Materials Studio. The cell parameters of these structures were also optimized. The optimized structures, denoted Zn_5FDC -DEF_{opt} and as Zn_5FDC -OMS_{opt}, were visualized in Fig. S19, with the detailed cell parameters provided in Table S10.

NVT simulation

The proton conductivity of Zn_5FDC -DEF exhibits a rapid increase at relatively low humidity levels compared to Zn_5FDC -OMS. This can be attributed to the interaction between the MOF and water. Monte Carlo (MC) simulations were executed using RASPA software to calculate the interaction between the MOF and water. NVT simulations were conducted at 25 degrees, employing the previously optimized structures and water uptake experimental values at relative humidity levels of 30, 70, and 95. The atoms of MOFs were described by Lennard-Jones (LJ) potential with the parameters of the universal force field (UFF). The partial charge of the atoms within MOFs was computed via the Qeq method. The water molecules were illustrated by Tip4P model.^{S10} The Lorentz-Berthelot mixing rule was applied for the pairwise atomic interaction. Additionally, the structures were assumed to be fixed during the RASPA simulation. The average interaction energy between the MOF and water is detailed in Table S8.

At 30% humidity, the average energy between water and MOF was lower in the presence of DEF, indicating that $Zn_5FDC-H_2O_{DEF}$ was more stable than $Zn_5FDC-H_2O_{OMS}$. The configuration at 30% humidity can be found in Fig. S20. Consequently, water can adhere to it rapidly at lower humidity. At higher humidity levels, $Zn_5FDC-DEF$ and $Zn_5FDC-OMS$ exhibit similar average energies between water and MOF.

Alternating current (A.C.) impedance measurement.

The proton conductivity was measured by conventional two-probe alternating current (A.C.) impedance spectroscopy using Solartron SI 1260 impedance/gain-phase analyzer and 1296 dielectric interface. The applied the frequency range was from 1 Hz to 1 MHz at the applied voltage of 100 mV. The powder sample was pelletized and both sides of pellet (dia. 4 mm) was painted by gold paste. The pellet was placed in a homemade sample holder and put in a commercial temperature and humidity control chamber. The impedance was recorded at various temperatures and humidities. The proton conductivity (σ) was calculated using Equation 1.

$$\sigma = \frac{L}{RS} \tag{1}$$

where *L* is the thickness of the sample pellet, S denotes the cross-sectional area, and *R* represents the measured impedance. Furthermore, the activation energies (E_a) were evaluated from the Arrhenius plot by temperature dependents conductivity measurement using equation 2,

$$\sigma T = A e^{-Ea}/_{kT}$$
(2)

where A and k are pre-exponential factors and the Boltzmann constant, respectively.

Supplementary Figures

Compound	Zn ₅ FDC-DEF	Zn ₅ FDC-DCM
formula	$C_{70}H_{56}O_{20}Zn_5$	$C_{60.80}H_{35.60}Cl_{1.60}O_{18}Zn_5$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pccn	Pccn
Fw	1572.01	1437.66
<i>a</i> , Å	23.260(5)	21.495(4)
<i>b</i> , Å	26.3366(5)	26.719(5)
<i>c</i> , Å	31.857(6)	31.702(6)
α, deg	90°	90°
β, deg	90°	90°
γ, deg	90°	90°
$V, Å^3$	19515(7)	18207(6)
Z	4	4
$ ho_{\rm calcd}, { m g~cm^{-3}}$	0.535	0.524
Temp , K	220(2)	100(2)
λ, Å	0.700	0.700
μ, mm ⁻¹	0.606	0.667
goodness-of-fit (F ²)	1.052	0.839
<i>F</i> (000)	3200	2886
reflections collected	43139	32367
independent reflections	22282 [$R(int) = 0.0119$]	16775 [$R(int) = 0.0517$]
completeness to θ_{\max} , %	99.8%	99.9%
data/restraints/parameters	22282 / 97 / 441	16775 / 26 / 405
θ range for data	1.471 to 27.000	1.197 to 25.000
diffraction limits (<i>h</i> , <i>k</i> , <i>l</i>)	-30≤ <i>h</i> ≤30, -34≤ <i>k</i> ≤34, -41≤ <i>l</i> ≤41	-25≤h≤25, -32≤k≤32, -38≤l≤38
refinement method	Full-matrix le	ast-squares on F^2
$R_1, wR_2[I > 2\sigma(I)]$	$R_1 = 0.0453$ ^[a] , $wR_2 = 0.1499$ ^[b]	$R_1 = 0.0828$ [a], $wR_2 = 0.2320$ [b]
R_1, wR_2 (all data)	$R_1 = 0.0510$ [a], $wR_2 = 0.1530$ [b]	$R_1 = 0.1518$ [a], $wR_2 = 0.2707$ [b]
largest peak, hole, eÅ ⁻³	0.425, -0.859	0.570, -0.635

Table S1. X-ray Crystallographic data of Zn₅FDC-DEF and Zn₅FDC-DCM

^[a] $R = \Sigma ||F_o| - |Fc|| / \Sigma |F_o|$. ^[b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1119P)^2 + (0.0000)P]$ for Zn₅FDC-DEF, and $w = 1/[\sigma^2(Fo^2) + (0.1622P)^2 + (0.0000)P]$ for Zn₅FDC-DCM, $P = (F_o^2 + 2F_c^2)/3$.

Zn(1)-O(7)	1.9456(13)	Zn(2)-O(8) ^{#4}	2.0844(11)
Zn(1)-O(2)	1.9614(13)	Zn(2)-O(1)#3	2.1208(11)
Zn(1)-O(1)	1.9633(11)	Zn(2)-O(1)#4	2.1208(11)
Zn(1)-O(10) ^{#1}	1.9770(13)	Zn(3)-O(5)	1.9482(13)
Zn(2)-O(4)	2.0698(12)	Zn(3)-O(6)	1.9482(16)
Zn(2)-O(4) ^{#2}	2.0698(12)	Zn(3)-O(1)#3	1.9609(12)
Zn(2)-O(8) ^{#3}	2.0844(11)	Zn(3)-O(9)#5	1.9633(13)
O(7)-Zn(1)-O(2)	118.38(6)	O(1) ^{#3} -Zn(2)-O(1) ^{#4}	92.81(6)
O(7)-Zn(1)-O(1)	112.80(5)	O(5)-Zn(3)-O(6)	106.72(7)
O(2)-Zn(1)-O(1)	111.87(5)	O(5)-Zn(3)-O(1)#3	122.20(5)
O(7)-Zn(1)-O(10)#1	101.48(6)	O(6)-Zn(3)-O(1)#3	113.53(6)
O(2)-Zn(1)-O(10) ^{#1}	103.69(6)	O(5)-Zn(3)-O(9)#5	102.44(6)
O(1)-Zn(1)-O(10) ^{#1}	106.92(5)	O(6)-Zn(3)-O(9)#5	104.73(8)
O(4)-Zn(2)-O(4) ^{#2}	90.98(8)	O(1) ^{#3} -Zn(3)-O(9) ^{#5}	105.29(5)
O(4)-Zn(2)-O(8)#3	87.12(5)	C(16)-O(6)-Zn(3)	127.2(2)
O(4) ^{#2} -Zn(2)-O(8) ^{#3}	92.65(5)	Zn(3)#6-O(1)-Zn(1)	115.13(5)
O(4)-Zn(2)-O(8)#4	92.65(5)	Zn(3)#6-O(1)-Zn(2)#7	103.74(5)
O(4) ^{#2} -Zn(2)-O(8) ^{#4}	87.12(5)	Zn(1)-O(1)-Zn(2)#7	112.24(5)
O(8) ^{#3} -Zn(2)-O(8) ^{#4}	179.67(6)	Zn(3)#6-O(1)-H(1O1)	97.0(13)
$O(4)$ -Zn(2)- $O(1)^{#3}$	89.14(5)	Zn(1)-O(1)-H(1O1)	116.8(13)
O(4) ^{#2} -Zn(2)-O(1) ^{#3}	169.08(4)	Zn(2) ^{#7} -O(1)-H(1O1)	110.3(13)
O(8) ^{#3} -Zn(2)-O(1) ^{#3}	98.26(5)	C(1)-O(2)-Zn(1)	107.09(11)
O(8) ^{#4} -Zn(2)-O(1) ^{#3}	81.97(5)	C(15)-O(4)-Zn(2)	130.78(11)
O(4)-Zn(2)-O(1)#4	169.08(4)	C(15)-O(5)-Zn(3)	113.26(11)
O(4) ^{#2} -Zn(2)-O(1) ^{#4}	89.14(5)	C(21)-O(7)-Zn(1)	124.99(11)
O(8) ^{#3} -Zn(2)-O(1) ^{#4}	81.97(5)	C(21)-O(8)-Zn(2)#7	139.08(12)
O(8) ^{#4} -Zn(2)-O(1) ^{#4}	98.26(5)	C(35)-O(9)-Zn(3)#5	134.33(13)
		C(35)-O(10)-Zn(1)#8	130.65(12)

Table S2. Selected bond length (Å) and angles (deg.) of Zn_5FDC -DEF

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1,-z+1/2	#2 -x+1/2,-y+3/2,z	#3 -x+1/2,y,z+1/2	2 #4 x,-y+3/2,z+1/2		
#5 -x+1,-y+1,-z+1	#6 -x+1/2,y,z-1	/2 #7	x,-y+3/2,z-1/2	#8	x+1/2,-y+1,-z+1/2

Zn(1)-O(2)	1.928(5)	$Zn(2)-O(7)^{#3}$	2.082(5)
Zn(1)-O(6)	1.959(4)	Zn(2)-O(1)#3	2.107(4)
Zn(1)-O(1)	1.959(4)	Zn(2)-O(1)#2	2.107(4)
Zn(1)-Cl(1D)	2.060(7)	Zn(3)-O(4)	1.932(5)
Zn(2)-O(5)	2.069(4)	Zn(3)-O(8)#4	1.963(4)
Zn(2)-O(5) ^{#1}	2.069(4)	Zn(3)-O(1) ^{#3}	1.968(4)
Zn(2)-O(7) ^{#2}	2.082(5)	Zn(3)-O(3)#3	1.975(5)
O(2)-Zn(1)-O(6)	102.9(2)	O(7) ^{#3} -Zn(2)-O(1) ^{#2}	169.51(17)
O(2)-Zn(1)-O(1)	106.05(18)	O(1) ^{#3} -Zn(2)-O(1) ^{#2}	92.2(2)
O(6)-Zn(1)-O(1)	123.3(2)	O(4)-Zn(3)-O(8)#4	119.7(2)
O(2)-Zn(1)-Cl(1D)	107.4(3)	O(4)-Zn(3)-O(1)#3	112.77(17)
O(6)-Zn(1)-Cl(1D)	105.5(2)	O(8)#4-Zn(3)-O(1)#3	111.19(17)
O(1)-Zn(1)-Cl(1D)	110.5(2)	O(4)-Zn(3)-O(3)#3	100.2(2)
C(1D)-Cl(1D)-Zn(1)	162.1(11)	O(8)#4-Zn(3)-O(3)#3	105.1(2)
O(5)-Zn(2)-O(5) ^{#1}	177.0(2)	O(1)#3-Zn(3)-O(3)#3	105.99(19)
O(5)-Zn(2)-O(7) ^{#2}	91.76(18)	Zn(1)-O(1)-Zn(3)#5	115.00(17)
O(5) ^{#1} -Zn(2)-O(7) ^{#2}	86.17(18)	Zn(1)-O(1)-Zn(2)#6	102.94(15)
O(5)-Zn(2)-O(7) ^{#3}	86.18(18)	Zn(3)#5-O(1)-Zn(2)#6	112.07(19)
O(5) ^{#1} -Zn(2)-O(7) ^{#3}	91.77(18)	Zn(1)-O(1)-H(1O1)	109(4)
O(7) ^{#2} -Zn(2)-O(7) ^{#3}	93.8(3)	Zn(3)#5-O(1)-H(1O1)	118(4)
O(5)-Zn(2)-O(1) ^{#3}	98.67(16)	Zn(2)#6-O(1)-H(1O1)	98(4)
O(5) ^{#1} -Zn(2)-O(1) ^{#3}	83.44(16)	C(1)-O(2)-Zn(1)	133.7(5)
O(7) ^{#2} -Zn(2)-O(1) ^{#3}	169.51(16)	C(1)-O(3)-Zn(3)#5	127.9(5)
O(7) ^{#3} -Zn(2)-O(1) ^{#3}	87.97(17)	C(15)-O(4)-Zn(3)	124.7(4)
O(5)-Zn(2)-O(1) ^{#2}	83.44(16)	C(15)-O(5)-Zn(2)	136.3(5)
O(5) ^{#1} -Zn(2)-O(1) ^{#2}	98.67(16)	C(16)-O(6)-Zn(1)	110.5(5)
O(7) ^{#2} -Zn(2)-O(1) ^{#2}	87.97(17)	C(16)-O(7)-Zn(2)#6	129.5(4)
		C(30)-O(8)-Zn(3)#4	107.1(4)

Table S3. Selected bond length (Å) and angles (deg.) of Zn_5FDC -DCM

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+3/2,z #2 -x+1,y+1/2,-z+3/2 #3 x-1/2,-y+1,-z+3/2

#4 -x+1,-y+1,-z+1 #5 x+1/2,-y+1,-z+3/2 #6 -x+1,y-1/2,-z+3/2

Compound	Zn ₈ FDC	Zn ₇ FDC
formula	$C_{90}H_{54}O_{29}Zn_8$	$C_{90}H_{54}O_{28}Zn_7$
Crystal system	Trigonal	Trigonal
Space group	<i>R-3c</i>	<i>R-3c</i>
Fw	2122.29	2040.92
<i>a</i> , Å	22.815(3)	23.8166(8)
<i>b</i> , Å	22.815(3)	23.8166(8)
<i>c</i> , Å	71.082(14)	67.9071(18)
α, deg	90°	90°
β, deg	90°	90°
γ, deg	120°	120°
$V, Å^3$	32043(11)	33358(2)
Z	6	12
$ ho_{\text{calcd}}, \text{g cm}^{-3}$	0.660	1.219
Temp , K	173(2)	100(2)
λ, Å	0.700	0.71073
μ, mm ⁻¹	0.878	1.547
goodness-of-fit (F ²)	1.394	1.063
<i>F</i> (000)	6396	12336
reflections collected	25164	104167
independent reflections	6565 [$R(int) = 0.0279$]	8509 [R(int) = 0.1476]
completeness to θ_{max} , %	99.8%	99.8%
data/restraints/parameters	6565 / 306 / 198	8509 / 7 / 382
heta range for data	1.471 to 27.000	2.311 to 27.484
diffraction limits (<i>h, k, l</i>)	-30≤ <i>h</i> ≤30, -34≤ <i>k</i> ≤34, -41≤ <i>l</i> ≤41	-29≤ <i>h</i> ≤30, -30≤ <i>k</i> ≤30, -88≤ <i>l</i> ≤78
refinement method	Full-matrix lea	ast-squares on F^2
$R_1, wR_2[I > 2\sigma(I)]$	$R_1 = 0.0453$ ^[a] , $wR_2 = 0.1499$ ^[b]	$R_1 = 0.0624$ ^[a] , $wR_2 = 0.1705$ ^[b]
R_1, wR_2 (all data)	$R_1 = 0.0510$ ^[a] , $wR_2 = 0.1530$ ^[b]	$R_1 = 0.1127$ ^[a] , $wR_2 = 0.1932$ ^[b]
largest peak, hole, eÅ ⁻³	0.425, -0.859	0.595, -1.541

Table S4. X-ray Crystallographic data of Zn_8FDC and Zn_7FDC

^[a] $R = \Sigma ||F_o| - |Fc|| / \Sigma |F_o|$. ^[b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo2) + (0.2000P)^2 + (0.0000)P]$ for Zn₈FDC, and $w = 1/[\sigma^2(F_o^2) + (0.09690P)^2 + (78.8977)P]$ for Zn₇FDC, $P = (F_o^2 + 2F_c^2)/3$.

Zn(1)-O(5) ^{#1}	1.962(4)	Zn(2)-O(1)#4	1.994(5)
Zn(1)-O(3)	1.970(5)	Zn(2)-O(1) ^{#5}	1.994(5)
Zn(1)-O(4) ^{#2}	2.002(4)	Zn(2)-O(2)	2.073(6)
Zn(1)-O(1)	2.011(4)	Zn(2)-O(2)#4	2.073(6)
Zn(1)- $Zn(1)$ ^{#3}	2.9693(14)	Zn(2)-O(2)#5	2.073(6)
Zn(2)-O(1)	1.994(5)	$Zn(2)$ - $Zn(2)^{#3}$	2.231(3)
O(5) ^{#1} -Zn(1)-O(3)	110.8(2)	O(1)-Zn(2)-O(2) ^{#5}	169.6(2)
O(5) ^{#1} -Zn(1)-O(4) ^{#2}	105.21(18)	O(1)#4-Zn(2)-O(2)#5	83.79(17)
$O(3)$ -Zn(1)- $O(4)^{#2}$	106.4(2)	O(1)#5-Zn(2)-O(2)#5	97.7(2)
O(5) ^{#1} -Zn(1)-O(1)	105.15(16)	O(2)-Zn(2)-O(2) ^{#5}	87.5(2)
O(3)-Zn(1)- $O(1)$	124.5(2)	O(2)#4-Zn(2)-O(2)#5	87.5(2)
$O(4)^{#2}$ -Zn(1)-O(1)	103.05(17)	O(1)-Zn(2)-Zn(2) ^{#3}	55.98(11)
$O(5)^{#1}$ -Zn(1)-Zn(1) ^{#3}	82.81(14)	$O(1)^{#4}$ -Zn(2)-Zn(2) ^{#3}	55.97(11)
O(3)-Zn(1)-Zn(1) ^{#3}	164.9(2)	O(1)#5-Zn(2)-Zn(2)#3	55.98(11)
O(4) ^{#2} -Zn(1)-Zn(1) ^{#3}	74.77(13)	O(2)-Zn(2)-Zn(2) ^{#3}	126.98(15)
O(1)-Zn(1)-Zn(1) ^{#3}	42.43(13)	$O(2)^{#4}$ -Zn(2)-Zn(2) ^{#3}	126.98(15)
O(1)-Zn(2)-O(1)#4	91.74(15)	$O(2)^{\#5}$ -Zn(2)-Zn(2) ^{#3}	126.98(15)
O(1)-Zn(2)-O(1) ^{#5}	91.74(15)	Zn(2)-O(1)-Zn(2)#3	68.0(2)
O(1) ^{#4} -Zn(2)-O(1) ^{#5}	91.73(15)	Zn(2)-O(1)-Zn(1)#3	143.12(8)
O(1)-Zn(2)-O(2)	97.7(2)	$Zn(2)^{\#3}-O(1)-Zn(1)^{\#3}$	108.57(5)
O(1) ^{#4} -Zn(2)-O(2)	169.6(2)	Zn(2)-O(1)-Zn(1)	108.57(5)
$O(1)^{#5}$ -Zn(2)-O(2)	83.78(17)	$Zn(2)^{\#3}-O(1)-Zn(1)$	143.12(8)
O(1)-Zn(2)-O(2) ^{#4}	83.78(17)	$Zn(1)^{#3}-O(1)-Zn(1)$	95.1(3)
O(1) ^{#4} -Zn(2)-O(2) ^{#4}	97.7(2)	C(1)-O(2)-Zn(2)	146.6(6)
O(1) ^{#5} -Zn(2)-O(2) ^{#4}	169.6(2)	C(1)-O(3)-Zn(1)	111.2(5)
O(2)-Zn(2)-O(2) ^{#4}	87.5(2)	C(15)-O(4)-Zn(1)#7	132.5(4)
		C(15)-O(5)-Zn(1)#8	123.9(5)

Table S5. Selected bond leng	gth (Å) and	angles (deg.)	of Zn ₈ FDC
------------------------------	-------------	---------------	------------------------

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1/3,y-1/3,z+1/6 #3 y+1/3,x-1/3,-z+7/6 #4 -y+1,x-y,z #2 y,-x+y,-z+1

#5 -x+y+1,-x+1,z #6 x-y+2/3,-y+4/3,-z+5/6 #7 x-y,x,-z+1 #8 -x+y+2/3,y+1/3,z-1/6

Zn(1)-O(1A)	1.947(5)	Zn(2)-O(1)	1.974(3)
Zn(1)-O(3A) ^{#1}	1.967(4)	Zn(3)-O(3B) ^{#3}	2.067(4)
Zn(1)-O(1)	1.985(3)	Zn(3)-O(3B) ^{#2}	2.067(4)
Zn(1)-O(1B)	1.987(4)	Zn(3)-O(3B)#4	2.067(4)
Zn(1)-Zn(2)	2.9588(8)	Zn(3)-O(1)#5	2.111(3)
Zn(2)-O(4B) ^{#2}	1.908(4)	Zn(3)-O(1)	2.111(3)
Zn(2)-O(2B)	1.939(4)	Zn(3)-O(1)#6	2.111(3)
O(1A)-Zn(1)-O(3A) ^{#1}	105.2(2)	O(3B)#4-Zn(3)-O(1)	87.23(14)
O(1A)-Zn(1)-O(1)	133.0(2)	O(1)#5-Zn(3)-O(1)	89.09(13)
O(3A) ^{#1} -Zn(1)-O(1)	105.35(15)	O(3B) ^{#3} -Zn(3)-O(1) ^{#6}	87.24(14)
O(1A)-Zn(1)-O(1B)	105.2(2)	O(3B) ^{#2} -Zn(3)-O(1) ^{#6}	173.11(14)
O(3A) ^{#1} -Zn(1)-O(1B)	103.28(17)	O(3B)#4-Zn(3)-O(1)#6	96.68(15)
O(1)-Zn(1)-O(1B)	101.42(15)	$O(1)^{#5}$ -Zn(3)-O(1) ^{#6}	89.08(13)
O(1A)-Zn(1)-Zn(2)	174.3(2)	O(1)-Zn(3)-O(1) ^{#6}	89.08(13)
$O(3A)^{#1}-Zn(1)-Zn(2)$	79.47(12)	O(3B) ^{#3} -Zn(3)-O(2)	127.08(11)
O(1)-Zn(1)-Zn(2)	41.50(10)	O(3B) ^{#2} -Zn(3)-O(2)	127.08(11)
O(1B)-Zn(1)-Zn(2)	76.47(11)	O(3B)#4-Zn(3)-O(2)	127.08(11)
$O(4B)^{#2}$ -Zn(2)-O(2B)	112.81(18)	O(1)#5-Zn(3)-O(2)	54.09(9)
O(4B) ^{#2} -Zn(2)-O(4A) ^{#1}	108.20(17)	O(1)-Zn(3)-O(2)	54.09(9)
O(2B)-Zn(2)-O(4A) ^{#1}	104.25(18)	O(1)#6-Zn(3)-O(2)	54.09(9)
$O(4B)^{#2}$ -Zn(2)-O(1)	119.36(16)	Zn(2)-O(1)-Zn(1)	96.71(15)
O(2B)-Zn(2)-O(1)	104.27(16)	Zn(2)-O(1)-Zn(3)	107.14(14)
O(4A) ^{#1} -Zn(2)-O(1)	106.82(16)	Zn(1)-O(1)-Zn(3)	136.40(18)
$O(4B)^{#2}$ -Zn(2)-Zn(1)	160.33(13)	Zn(2)-O(1)-H(1O1)	90(3)
O(2B)-Zn(2)-Zn(1)	82.15(12)	Zn(1)-O(1)-H(1O1)	122(3)
$O(4A)^{#1}$ -Zn(2)-Zn(1)	78.68(12)	Zn(3)-O(1)-H(1O1)	95(3)
O(1)-Zn(2)-Zn(1)	41.79(10)	Zn(3)-O(2)-H(1O2)	103.6(16)
O(3B) ^{#3} -Zn(3)-O(3B) ^{#2}	87.41(16)	Zn(3)-O(2)-H(1O2) ^{#6}	103.6(16)
O(3B) ^{#3} -Zn(3)-O(3B) ^{#4}	87.41(16)	Zn(3)-O(2)-H(1O2) ^{#5}	103.6(16)
O(3B) ^{#2} -Zn(3)-O(3B) ^{#4}	87.40(16)	C(1A)-O(1A)-Zn(1)	107.4(6)
O(3B) ^{#3} -Zn(3)-O(1) ^{#5}	96.68(14)	C(15A)-O(3A)-Zn(1)#7	127.2(4)
O(3B) ^{#2} -Zn(3)-O(1) ^{#5}	87.24(14)	C(15A)-O(4A)-Zn(2)#7	129.6(3)
O(3B)#4-Zn(3)-O(1)#5	173.11(15)	C(1B)-O(1B)-Zn(1)	130.0(4)
O(3B) ^{#3} -Zn(3)-O(1)	173.10(15)	C(1B)-O(2B)-Zn(2)	124.7(4)
O(3B) ^{#2} -Zn(3)-O(1)	96.68(15)	C(15B)-O(3B)-Zn(3)#8	145.0(4)
		$C(15B)-O(4B)-Zn(2)^{\#8}$	118.4(4)

Table S6. Selected bond length (Å) and angles (deg.) of Zn₇FDC

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+1/3,y-1/3,z+1/6 #2 -y+1/3,-x+2/3,z+1/6 #3 -x+y+1/3,y+2/3,z+1/6

#4 x+1/3,x-y+2/3,z+1/6 #5 -x+y,-x+1,z #6 -y+1,x-y+1,z

#7 -x+y+2/3,y+1/3,z-1/6 #8 -y+2/3,-x+1/3,z-1/6

Table S7. The cell parameters of Zn_5FDC -OMS_{opt} and Zn_5FDC -DEF_{opt}

	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α(°)	$\beta(°)$	γ(°)
Zn ₅ FDC-OMS _{opt}	25.3749	22.5614	30.6565	90	90	90
Zn ₅ FDC-DEF _{opt}	21.8227	25.6415	31.8416	90	90	90

Table S8. Tables of interaction energies of water-water and water-MOF calculated to RASPA of NVT simulation

Water-Water interaction energy (units: kJ/mol)

	Zn ₅ FDC-OMS _{opt}	Zn ₅ FDC-DEF _{opt}	
RH 30%	-17.05	-7.319	
RH 70%	-22.12	-21.83	
RH 95%	-25.63	-27.13	

Water-MOF interaction energy (units: kJ/mol)

	Zn ₅ FDC-OMS _{opt}	Zn ₅ FDC-DEF _{opt}
RH 30%	-15.36	-22.49
RH 70%	-12.29	-12.32
RH 95%	-9.18	-9.03

Condi	tions	Conductivity (S cm ⁻¹)	
Temp (K)	RH (%)	Zn ₅ FDC-DEF	Zn ₅ FDC-OMS
	30	$1.10 imes 10^{-12}$	2.75×10^{-13}
	40	1.65×10^{-12}	$2.60 imes 10^{-13}$
	50	2.60×10^{-12}	3.46×10^{-13}
208	60	4.84×10^{-12}	4.81×10^{-13}
298	70	7.28×10^{-11}	$6.95 imes 10^{-13}$
	80	4.67×10^{-7}	1.18×10^{-12}
	90	$8.97 imes 10^{-6}$	3.33×10^{-12}
	95	$2.94 imes 10^{-4}$	$9.46 imes 10^{-8}$
303		2.61 × 10 ⁻⁴	3.08 × 10 ⁻⁶
313		3.07×10^{-4}	1.51×10^{-5}
323		3.43×10^{-4}	2.85×10^{-5}
333	95	4.27×10^{-4}	4.30×10^{-5}
343		3.23×10^{-4}	5.05×10^{-5}
353		7.53×10^{-5}	8.41×10^{-5}
363		1.93×10^{-5}	5.96 × 10 ⁻⁵

Table S9. Proton conductivities of Zn_5FDC -DEF and Zn_5FDC -OMS

Sample	Proton Conductivity (S cm ⁻¹)	Experimental Conditions	ON/OFF ratio	Activation Energy (eV)	Responsive Conditions	Ref
Zn ₅ FDC-DEF	4.27 x 10 ⁻⁴	60 °C 95% RH	2.85 x 10 ⁸	0.11	humid environment	This work
Zn ₅ FDC-OMS	8.41 x 10 ⁻⁵	80 °C 95% RH	3.23 x 10 ⁸	0.39	humid environment	This work
$(NH_4)_2(adp)[Zn_2(ox)_3]$ · nH_2O	8×10^{-3}	25 °C 95% RH	114 ^[a]	0.63	water vapor	S11
((CH ₃) ₂ NH ₂) ₂ [Li ₂ Zr(C ₂ O ₄) ₄]	3.9×10^{-5}	17 °C 67% RH	$7.8\times10^{3[a]}$	0.64	humid environment	S12
BUT-8(Cr)A	7.61 × 10 ⁻²	25 °C 100% RH	$1.82\times 10^{4\text{[a]}}$	0.11	humid environment	S13
ZZU-1	8.9 × 10 ⁻⁴	100 °C 98% RH	~35 ^[b]	1.37	formic acid vapor	S14
ZZU-2	4.63 × 10 ⁻⁴	100 °C 98% RH	~9 [b]	1.65	formic acid vapor	S14
$[Cu(HL)(DMSO) \cdot (Me OH)]_n$	7.4 × 10 ⁻⁴	25 °C 95% RH	1.2×10 ⁴ [a]	0.52	H ₂ O vapor or DMSO/MeOH vapor	S15
[Pt ₂ (MPC) ₄ Cl ₂ Co(DM A)(HDMA)·guest	7.1 × 10 ⁻³	60 °C 95% RH	105	0.4	dimethylammo nium cation (HDMA ⁺) and H_2O	S16
Zr-TCPBP	5.8 × 10 ⁻⁴	25 °C 98% RH	240	0.17	HCl, different pH	S17

 Table S10. List of switchable proton conductive MOFs

^[a] calculated.

^[b] Taken from the figures of the original papers.



Fig. S1 Crystal structure of Zn_5FDC -DEF. (a) The coordination environment in the asymmetric unit of Zn_5FDC -DEF. (b) The secondary building units (SBUs) of Zn_5FDC , $[Zn_5(OH)_2(O_2C)_8(DEF)_2]$. (c) Single network of Zn_5FDC -DEF. Colour scheme: Zn, bluish silver; O, red; C, grey; H, white; N, blue.



Fig. S2. TGA trace of Zn₅FDC-DEFs obtained under a nitrogen atmosphere with 5 °C/min ramping rate.



Fig. S3 NMR spectra of Zn_5FDC -DEF after DCM solvent exchange. This spectrum showed the remaining DEF solvent in Zn_5FDC after DCM solvent exchange.



Fig. S4 Crystal structure of Zn₇FDC. (a) The coordination environment in the asymmetric unit of Zn₇FDC.
(b) The secondary building units (SBUs) of Zn₇FDC, [Zn₇(OH)₃(O₂C)₁₂](H₃O). (c) Single network of Zn₇FDC. Colour scheme: Zn, steel blue; O, red; C, grey; H, white. (d) Structural motifs of Zn₇FDC with two-fold interpenetrated networks. (e) Hydrogen bond interaction of carboxylate oxygen at with hydronium cations or hydroxy group in SBUs.



Fig. S5 Crystal structure of Zn_8FDC . (a) The coordination environment in the asymmetric unit of Zn_8FDC . (b) The secondary building units (SBUs) of Zn_8FDC , $[Zn_8O_3(O_2C)_{12}]^2$. (c) Single network of Zn_8FDC . Colour scheme: Zn, bluish silver; O, red; C, grey; H, white.



Fig. S6 XRPD patterns of as-synthesized mixture MOFs (Zn_7FDC and Zn_8FDC) and Zn_8FDC obtained after immersion in three days. These were compared with the simulated patterns of Zn_8FDC and Zn_7FDC .



Fig. S7 (a) Illustration of structural transformation of Zn_8FDC and Zn_7FDC with simplified structures. (b) A proposed mechanism from ref. S18. It is clearly shown reversible interpenetration in a metal-organic framework induced by reassembly of ligands and SBUs.



Fig. S8 Crystal structure of Zn_5FDC -DCM. (a) The coordination environment in the asymmetric unit of Zn_5FDC -DCM. (b) The secondary building units (SBUs) of Zn_5FDC , $[Zn_5(OH)_2(O_2C)_8(DCM)_2]$. (c) Single network of Zn_5FDC -DCM. Colour scheme: Zn, bluish silver; O, red; C, grey; H, white; Cl, green.



Fig. S9 Structural transformation of Zn_8FDC to Zn_5FDC -DCM. In a red box, there are structure of Zn_8FDC with a single framework, simplified structure with ligands represented as a linear and the oxo or hydroxy groups of the SBUs represented as dots and the ligand as lines. In a blue box, there are structure of Zn_5FDC -DCM with a single framework, simplified structure with ligands and DCM represented as a linear and the hydroxy group of SBUs represented as a red point, ligand as a linear and DCM as a blue point. The structure transformation from Zn_8FDC to Zn_5FDC -DCM induced by DCM results from loss of metals, oxygen of SBUs and ligands.



Fig. S10 XRPD patterns of Zn_5FDC -DEF and Zn_5FDC -DCM measured after activation. Those are compared with simulated patterns of geometry optimized structures, Zn_5FDC -DEF_{opt} and Zn_5FDC -DCM_{opt}.



Fig. S11 Simulated XRPD patterns of Zn₅FDC-DEF, Zn₅FDC-DEF_{opt}, Zn₅FDC-DCM, and Zn₅FDC-OMS_{opt}.



Fig. S12 Bond lengths and angles of Zn_5FDC -DCM and Zn_5FDC -OMS_{opt}.



Fig. S13 Bond lengths and angles of Zn₅FDC-DEF and Zn₅FDC-DEF_{opt}.



Fig. S14 N_2 isotherm of Zn_5FDC -OMS and Zn_5FDC -DEF at 77K.



Fig. S15. Nyquist plots for (a) Zn_5FDC -OMS (b) Zn_5FDC -DEF under various relative humidity at 298 K. Nyquist plot for (c) Zn_5FDC -OMS (d) Zn_5FDC -DEF at the variable temperature and 95% RH.



Fig. S16. Comparison of XRPD patterns of Zn_5FDC -DEF exposed to RH 70% for 2 d and Zn_5FDC -H₂O_{DEF} with simulated patterns from single crystal structures.



Fig. S17 XRPD of Zn₅FDCs before and after proton conductivity experiments.



Fig. S18. Cycling test Zn₅FDC-DEF between 30% and 95% RH at 298 K



Fig. S19 The visualization of the optimized structures (a) Zn_5FDC -OMS_{opt} (b) Zn_5FDC -DEF_{opt}



Fig. S20 The adsorption configuration of NVT simulation (a) Zn₅FDC-OMS_{opt} (b) Zn₅FDC-DEF_{opt}

References

- S1. C. M. G. Henríquez, L. H. Tagle, C. A. Terraza, A. B. González, A. L. Cabrera and U. G. Volkmann, *J. Appl. Polym. Sci.*, 2012, **125**, 477-487.
- S2. J. W. Shin, K. Eom and D. Moon, J. Synchrotron Radiat., 2016, 23, 369-373.
- S3. Z. Otwinowski and W. Minor, in *Methods Enzymol.*, Academic Press, 1997, vol. 276, pp. 307-326.
- S4. G. Sheldrick, *Acta Cryst.* 2015, A71, 3-8.
- S5. G. Sheldrick, Acta Crystallogr. Sect. C: Cryst. Struct. Commun., 2015, 71, 3-8.
- S6. A. Spek, Acta Cryst. 2015, C71, 9-18.
- S7. L. Greenspan, J. Res. NBS. A. Phys. Ch., 1977, 81, 89-96.
- S8. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, III and W. M. Skiff, J. Am. Chem. Soc., 1992, 114, 10024-10035.
- S9. A. K. Rappé and W. A. Goddard, J. Phys. Chem., 1991, 95, 3358-3363.
- S10. J. L. F. Abascal and C. Vega, J. Chem. Phys., 2005, 123, 234505-234516.
- S11. M. Sadakiyo, T. Yamada and H. Kitagawa, J. Am. Chem. Soc., 2009, 131, 9906-9907.
- S12. S. Tominaka, F.-X. Coudert, T. D. Dao, T. Nagao and A. K. Cheetham, J. Am. Chem. Soc., 2015, 137, 6428-6431.
- S13. F. Yang, G. Xu, Y. Dou, B. Wang, H. Zhang, H. Wu, W. Zhou, J.-R. Li and B. Chen, *Nature Energy*, 2017, 2, 877-883.
- S14. R.-L. Liu, W.-T. Qu, B.-H. Dou, Z.-F. Li and G. Li, Chem. Asian J., 2020, 15, 182-190.
- S15. S. Nakatsuka, Y. Watanabe, Y. Kamakura, S. Horike, D. Tanaka and T. Hatakeyama, *Angew. Chem. Int. Ed.*, 2020, **59**, 1435-1439.
- S16. K. Otsubo, S. Nagayama, S. Kawaguchi, K. Sugimoto and H. Kitagawa, JACS Au, 2022, 2, 109-115.
- S17. S.-L. Yang, G. Li, M.-Y. Guo, W.-S. Liu, R. Bu and E.-Q. Gao, J. Am. Chem. Soc., 2021, 143, 8838-8848.

S18. S. B. Choi, H. Furukawa, H. J. Nam, D.-Y. Jung, Y. H. Jhon, A. Walton, D. Book, M. O'Keeffe, O. M. Yaghi and J. Kim, Angew. Chem. Int. Ed., 2012, 51, 8791-8795.