Supplementary Materials: Thickness and Humidity on Proton Conductivity in MOF-508 Thin Film by Twin-Zinc-Source Method

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Figure S1 shows that the XRD peaks do not correspond to the characteristic peaks of MOF-508a prepared by the solvent thermal method, which showed that the preparation of a zinc foil using this method was not successful.

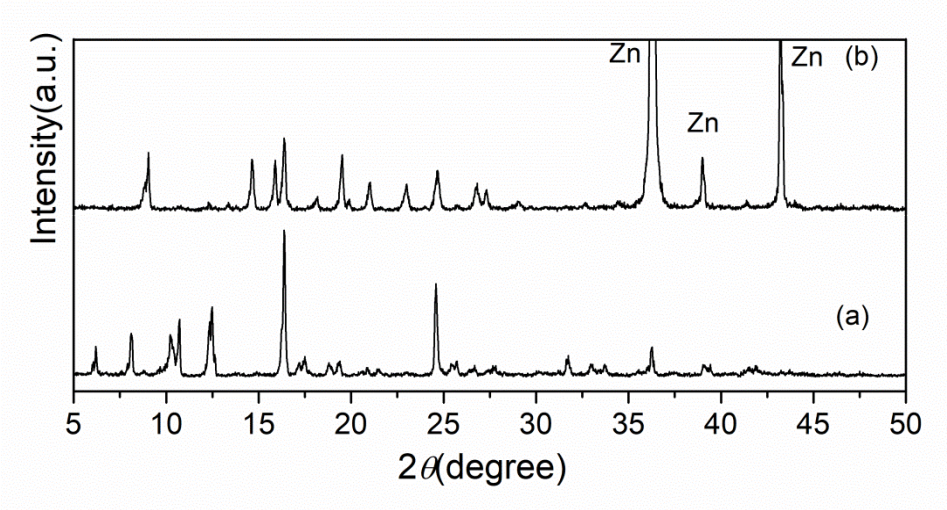


Figure S1. PXRD pattern of (a) the standard powder, (b) the thin film incorporated on the Zn foil via the solvent thermal method.

Figure S2 depicts the thin films composed of MOF-508a/Zn and MOF-508b/Zn when the additional molecules were removed.

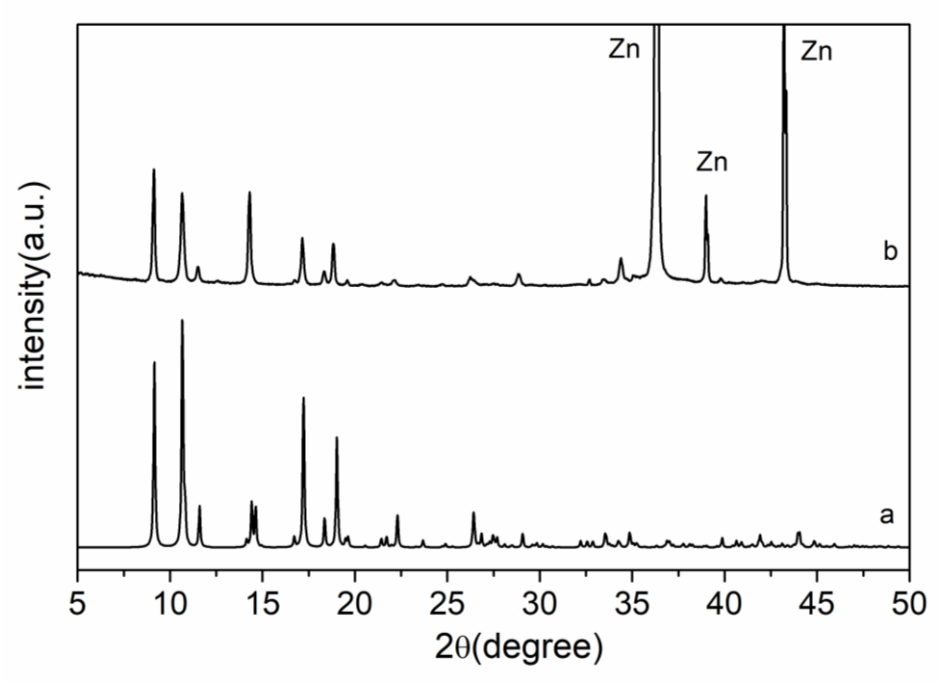
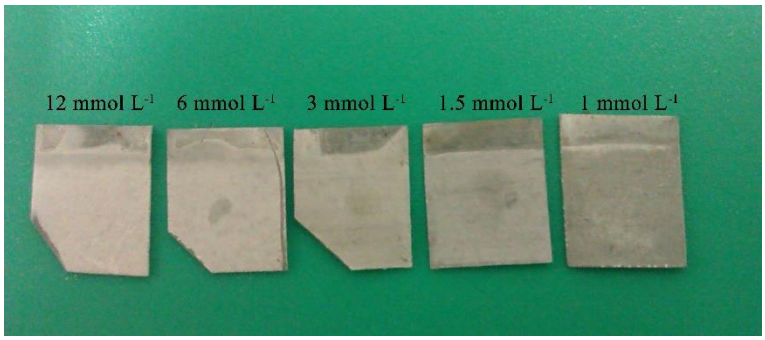


Figure S2. PXRD pattern of (a) the standard powder of MOF-508b, (b) the MOF-508b/Zn thin film with the additional molecules removed at 120 °C.

Figure S3 shows the real materials of the MOF-508a/Zn thin film with different concentrations of Zn^{2+} or different reaction times. The width of the film was 1 cm and the length of the film was 1.2 cm. It is also visible from the picture that the thickness of the MOF-508a thin film decreased with the reduction in the concentration of Zn^{2+} or different reaction times.



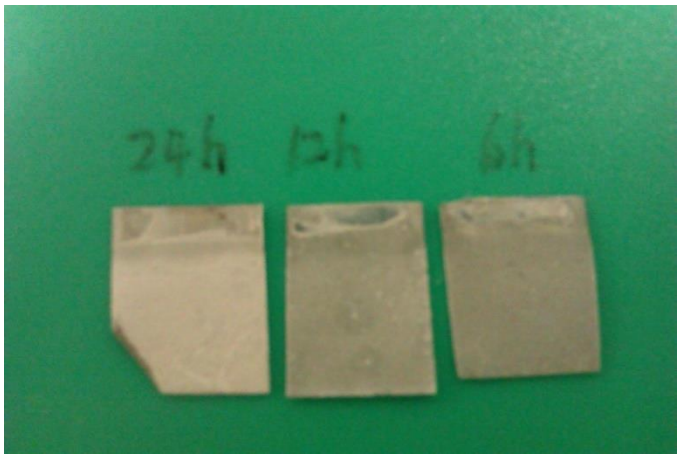


Figure S3. The photo of the MOF-508a/Zn thin film with different concentrations of Zn^{2+} and different reaction times.

In order to verify the results presented in this study, the concentration of Zn^{2+} was selected as 2 mmol L^{-1}. The SEM image displays that the thickness of the thin film was about 20 μm (Fig s4), which verified the integrity of the mathematical modeling.

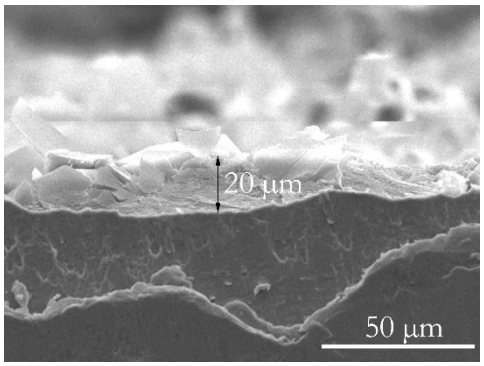


Figure S4. The thickness of the thin film when the concentration of Zn^{2+} was 2 mmol L^{-1}.

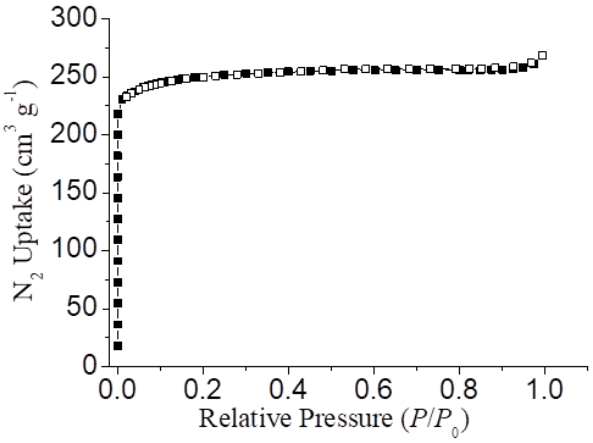


Figure S5. N_2 sorption isotherms of the MOF-508b at 77 K.

The N_2 sorption-desorption isotherms of the MOF-508b at 77 K are similar to the compound reported in the literature, 24. It could not affect their proton conductivity. The BET surface area of the samples calculated using the Langmuir equation from the N_2 sorption isotherm is 992.0178 m^2/g.

The MOF-508b/Zn thin film was kept at different relative humidities (63%, 85%, 75%, and 98%) for 1-3 days; the respective PXRD patterns are shown in Figures 6. When the relative humidity was 63% or 75%, there was no change in the phase of the MOF-508b/Zn thin film, but when it was increased to 85% and kept at this value for 1 day, the phase of the film changed. This shows that increasing the relative humidity also causes an increase in additional water molecules that are absorbed into the channel; as a result of which, the structure of MOF-508b/Zn also changes which may lead to the collapse of the structure. This indicates that the MOF-508b/Zn adsorbed a large number of water molecules when kept at a high humidity, and the structure of MOF-508b was not able to stably accept water molecules.

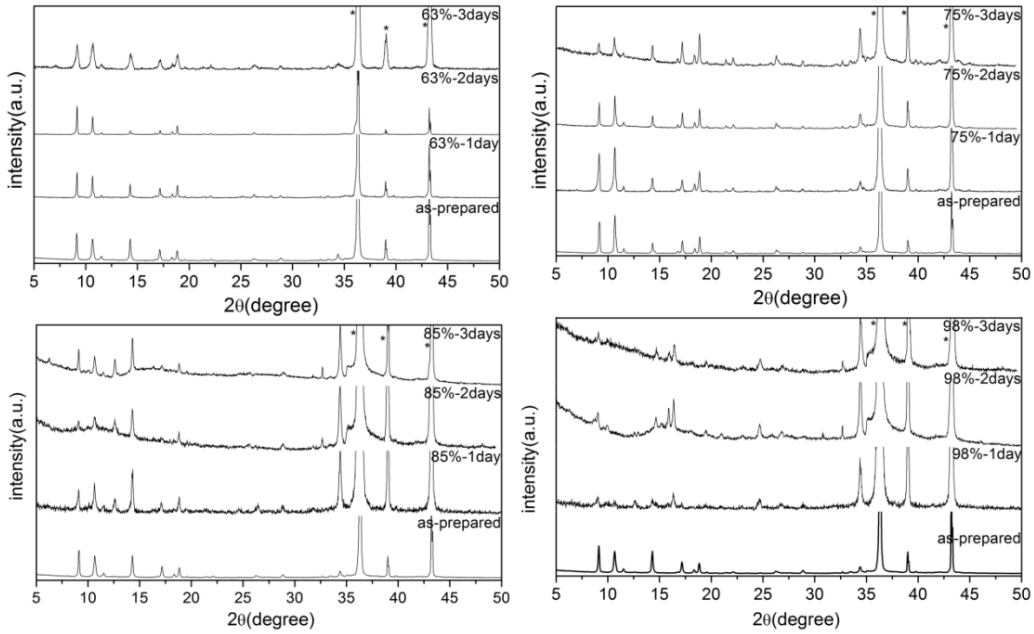


Figure S6. The PXRD pattern of MOF-508b/Zn thin film kept at different relative humidity values (63%, 85%, 75%, and 98%) for 1-3 days (* is Zn).

Figure s7 shows the thermogravimetric curve of the as-made MOF-508b kept at varying relative humidity values, i.e., 63%, 75%, 85%, and 98% RH, and at room temperature for 1 to 3 days. The increase rate was 10 °C min^{-1}. The TGA values of the MOF-508b confirm that the quantity of additional water molecules adsorbed increased significantly with humidity and time.

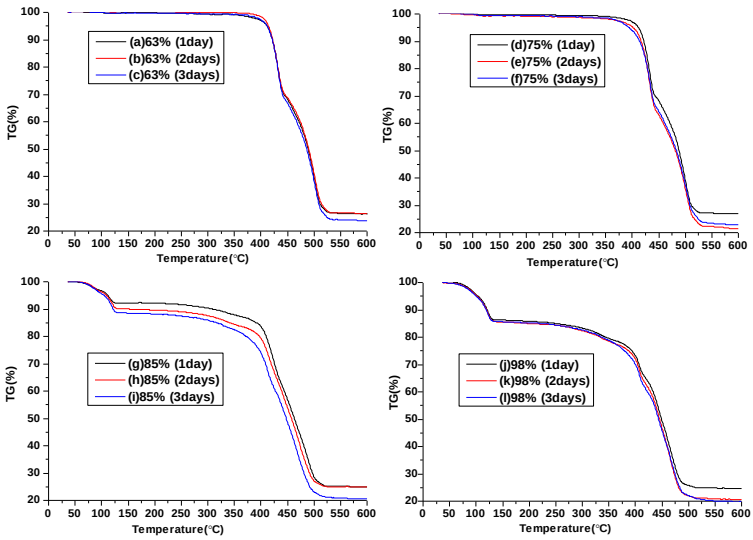


Figure S7. Thermogravimetric analysis curve of the as-made MOF-508b/Zn thin film kept at different relative humidity values, i.e., 63%, 75%, 85%, and 98% RH, and at room temperature for 1 to 3 days. The ramp rate was 10 °C min^{-1}.

When the relative humidity values were 63% and 75%, the sample remained stable up to around 350 °C, which agrees with findings in the literature[S1]. The drop in the TG curve occurred after 350 °C, that is, when the sample was at a relative humidity of less than 75%, no water molecules were absorbed. The samples at relative humidity values of 85% and 98% began to decline, indicating that following the adsorption of water molecules and an increase in temperature, the water molecules in the channel began to exit. At 100 °C, the TG curve continued its decline, indicating that the structure of the MOF-508b

began to change with increasing temperature; this result also coincides with the PXRD data in Figure s6. Although the quantity of adsorbed water molecules in the channel increased with the increase in relative humidity, the structure of the MOF-508b also changed accordingly. As shown in Figure s6, when the relative humidity was 85% the molecular structure began to collapse, indicating that MOF-508b was extremely unstable when exposed to water.

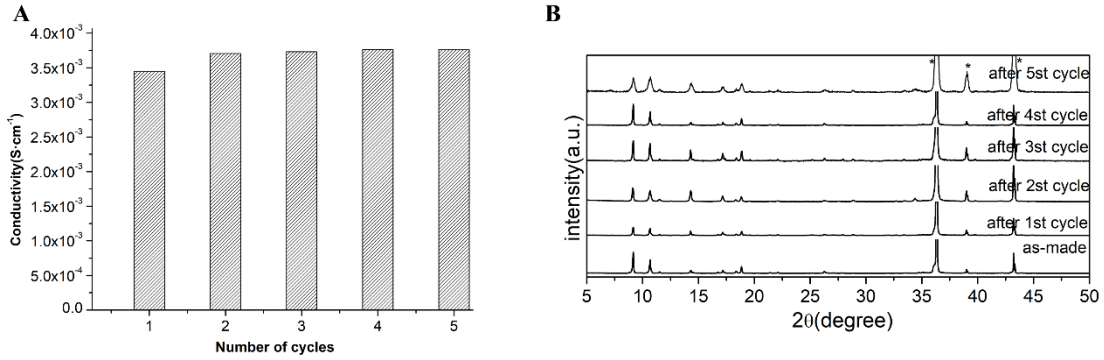


Figure S8. A) Representative diagrams for the conductivity recovery studies, with the conductivity of MOF-508b/Zn thin film after five runs of recycling experiments. (B) PXRD of the MOF-508b/Zn thin film after each step of relative humidity atmosphere of 63%.

This relative humidity atmosphere was repeated; its conductivity was unchanged up to five cycles, demonstrating its good recyclability and stability for the detection applications (Figure 4A). After every AC impedance experiment, the PXRDs of the MOF-508b/Zn thin film and the relative humidity sealed product (postspeciation sample) were recorded. By comparison of the PXRDs, it was evident that the MOF retains its crystallinity even after this recycling process (Figure 4B).

Table S1. The specific saturated salt solutions and corresponding relative humidity (RH)% values[S2,S3].

t/℃	Relative Humidity (RH)%								
	LiBr	LiCl	MgCl	K_2CO_3	NaBr	KI	NaCl	KCl	K_2SO_4
5	7.4±0.8	13(3)	33.6±0.3	43.1±0.5	63.5±0.8	73.3±0.4	75.7±0.3	87.7±0.5	98.5±1.0
10	7.1±0.7	13(4)	33.5±0.3	43.1±0.4	62.2±0.6	72.1±0.4	75.7±0.3	86.8±0.4	98.2±0.8
15	6.9±0.7	12	33.3±0.3	43.2±0.4	60.7±0.6	71.0±0.3	75.6±0.2	85.9±0.4	97.9±0.7
20	6.6±0.6	12	33.1±0.2	43.2±0.4	59.1±0.5	69.9±0.3	75.5±0.2	85.1±0.3	97.6±0.6
25	6.4±0.6	11.3±0.3	32.8±0.2	43.2±0.4	57.6±0.4	68.9±0.3	75.3±0.2	84.2±0.3	97.3±0.5
30	6.2±0.5	11.3±0.3	32.4±0.2	43.2±0.5	56.0±0.4	67.9±0.3	75.1±0.2	83.6±0.3	97.0±0.4
35	6.0±0.5	11.3±0.3	32.1±0.2	—	54.6±0.4	67.0±0.3	74.9±0.2	83.0±0.3	97.7±0.4
40	5.8±0.4	11.2±0.3	31.6±0.2	—	53.2±0.5	66.1±0.3	74.7±0.2	82.3±0.3	96.4±0.4
45	5.7±0.4	11.2±0.3	31.1±0.2	—	52.0±0.5	65.3±0.3	74.5±0.2	81.7±0.3	96.1±0.4
50	5.5±0.4	11.1±0.3	30.5±0.2	—	50.9±0.6	64.5±0.3	74.5±0.9	81.2±0.4	95.8±0.5
55	5.4±0.3	11.0±0.3	29.9±0.2	—	50.2±0.7	63.8±0.4	74.5±0.9	80.7±0.4	—
60	5.3±0.3	11.0±0.3	29.3±0.2	—	49.7±0.8	63.1±0.4	74.4±0.9	80.3±0.5	—
65	5.3±0.3	10.9±0.3	28.5±0.3	—	49.5±1.0	62.5±0.4	74.2±0.9	79.9±0.5	—
70	5.2±0.3	10.8±0.4	27.8±0.3	—	49.7±1.1	61.9±0.4	74.1±0.9	79.5±0.6	—
75	5.2±0.2	10.6±0.4	26.9±0.3	—	50.3±1.3	61.4±0.5	74.0±0.9	79.2±0.7	—
80	5.2±0.2	10.5±0.5	26.1±0.4	—	51.4±1.5	61.0±0.5	73.9±0.9	78.9±0.8	—

A comparison of the conductivity of MOFs is reported in the literature; the conductivity of our synthesized MOF (4× 10^{-4} S/cm) is in good agreement with some of the literature reporting on MOFs, as shown in Table S2, a comparison of the conductivity of MOFs reported in the literature.

Table S2. The proton conductivities of carboxylate-based MOF.

Materials Name	σ(S cm^{-1})	References
$[Fe(ox)(H_2O)_2]$	1.5×10^{-3} (25℃, 100% RH)	RSC Adv. 4 (2014) 54382–54387
$K_2(H_2adp)[Zn_2(ox)_3]_3H_2O$	1.2×10^{-4} (25℃, 98% RH)	J. Am. Chem. Soc. 136 (2014) 13166–13169
$(NH_4)_4[MnCr_2(ox)_6]_4H_2O$	1.7×10^{-3} (40℃, 96% RH)	J. Am. Chem. Soc. 133 (2011) 15328–15331
$\{[Gd(ma)(ox)(H_2O)]n_3H_2O\}$	4.7×10^{-4} (80℃ 95% RH)	Inorg.Chem. 56 (2017) 4956–4965
$(N_2H_5)[CeEu(ox)_4(N_2H_5)]_4H_2O$	3.42×10^{-3} (25℃, 100% RH)	Adv. Mater. 29 (2017) 1701804
$[Zn_2(HCOO)(trz)_3]_n$	7.95×10^{-7} (50℃, 98% RH)	Eur. J. Inorg. Chem. 6(2019) 794–799.
$[[Zn(2\text{-}MeBIM)(Pht)(H_2O)]\cdot2H_2O]_n$	1.0×10^{-5}S cm^{-1} (25℃, 100% RH)	Inorganica Chimica Acta, 2015, 437: 167.
MOF-508a/Zn thin film	4× 10^{-4}(16 μm, 25℃, air RH)	This work

References

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