Supporting Information

for

The role of sulfonate groups and hydrogen bonding in the proton conductivity of two coordination networks

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Supplementary data
**Figure S1:** Linker molecule \( \text{(H}_2\text{O}_3\text{PCH}_2)_2\text{-NCH}_2\text{-C}_6\text{H}_4\text{-SO}_3\text{H} \) \( (\text{H}_5\text{L}) \)

**Figure S2:** Exemplary Nyquist plots at various applied potentials for (a) \([\text{Mg(H}_2\text{O)}_2(\text{H}_3\text{L})]\cdot\text{H}_2\text{O} \) (22 °C, 70% r.h.) and (b) \([\text{Pb}_2(\text{HL})]\cdot\text{H}_2\text{O} \) (22 °C, 90% r.h.).

**Figure S3:** Powder XRD patterns of (a) \([\text{Mg(H}_2\text{O)}_2(\text{H}_3\text{L})]\cdot\text{H}_2\text{O} \) and (b) \([\text{Pb}_2(\text{HL})]\cdot\text{H}_2\text{O} \). All measurements were performed at 25 °C and 90% relative humidity (r.h.). No significant change is observed after activation of the samples (i.e., exposure to 80 °C for 24 h).
Figure S: Powder XRD patterns of (a) [Mg(H₂O)₂(H₃L)]·H₂O and (b) [Pb₂(HL)]·H₂O at variable temperature and humidity.

Figure S5: Equivalent circuit models used: (a) Activated [Mg(H₂O)₂(H₃L)]·H₂O and for activated/non-activated [Pb₂(HL)]·H₂O, (b) non-activated [Mg(H₂O)₂(H₃L)]·H₂O.

Table S1: Some proton-conducting coordination networks containing sulfonate groups [1,2]

| sample name                              | conditions     | $\sigma$ (S/cm) | $E_a$ (eV) |
|------------------------------------------|----------------|-----------------|------------|
| {[Zn(bpeH)(5-sip)(H₂O)]·(H₂O)}ₙ         | 65 °C, 95% r.h.| $2.5 \times 10^{-6}$ | 0.54       |
| {[Cu(py)(5-Hsip)(H₂O)]ₙ·(H₂O)}₂ₙ        | 65 °C, 95% r.h.| $3.5 \times 10^{-5}$ | 0.35       |
| {[Cu(bpee)₀.₅(5-sip)(H₂O)]ₙ·(H₂O)₄(bpeeH₂)₀.₅}ₙ | 65 °C, 95% r.h.| $9.9 \times 10^{-8}$ | 0.40       |
| {[Cu(bpy)(5-Hsip)(H₂O)]·(H₂O)}₂ₙ        | 65 °C, 95% r.h.| $5.8 \times 10^{-6}$ | 0.43       |
| {[Cu(bpy)(5-H2sip)(H₂O)]ₙ·(H₂O)}ₙ       | 65 °C, 95% r.h.| $1.4 \times 10^{-6}$ | 0.45       |
| {[Cu₂(bpy)(5-sip)(H₂O)]·(H₂O)}₂ₙ        | 80 °C, 95% r.h.| $9.4 \times 10^{-3}$ | 0.64       |
| Cu₄(5-sip)₃(OH)₂(DMF)₂                  | 95 °C, 95% r.h.| $7.4 \times 10^{-4}$ | 1.32       |
| UiO-66(SO₃H)₂                            | 80 °C, 90% r.h.| $8.4 \times 10^{-2}$ | 0.32       |
| MIL-101-SO₃H                             | 70 °C, 90% r.h.| $4.3 \times 10^{-5}$ | 0.27       |
References

1. Liu, R.; Wang, D.-Y.; Shi, J.-R.; Li, G. *Coord. Chem. Rev.* **2021**, *431*, 213747. doi:10.1016/j.ccr.2020.213747

2. Lim, D.-W.; Kitagawa, H. *Chem. Rev.* **2020**, *120*, 8416. doi:10.1021/acs.chemrev.9b00842