

*Electronic Supplementary Information for*

**Regulating the proton conductivity of metal organic framework  
materials through solvent control**

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**Synthesis of 4-[2-(4-pyridinyl) vinyl] -benzoic acid(PyebH):** 4-formylbenzoic acid(4.61 g), 4-methylpyridine(2.60 mL) and acetic anhydride(30 mL) were placed to a 250 mL three-necked flask under the condition of nitrogen. The reaction solution was heated to reflux for 12 hours, and then water(60 mL) was added to stop the reaction when the temperature of the reaction solution dropped to room temperature. Then the solution is suction filtered and washed with a mixed solution of methanol and ethanol. Finally, the product was dried in a vacuum oven at 50°C for 24 hours to obtain a light yellow solid. Yield: 70%. <sup>1</sup>H NMR (400M Hz, CDCl<sub>3</sub>) δ 13.00(s, H), δ 8.57(d, 2H), δ 7.96(d, 2H), δ 7.76(d, 2H), δ 7.60(d, 2H), δ 7.43(s, H), δ 7.38(s, H). Elemental analysis calcd. (%) for C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>: C, 74.65; H, 4.92; N, 6.21. Found: C, 73.83; H, 4.84; N, 6.13. IR (KBr, cm<sup>-1</sup>, Fig. S1 ): 3030(m), 2791(w), 1924(w), 1629(vs), 1603(vs), 1286(vs).

**Synthesis of {[Zn(pyeb)<sub>2</sub>](DMF)(H<sub>2</sub>O)}<sub>n</sub> (1):** Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O(0.5 mmol, 0.1487 g) and PyebH(0.5 mmol, 0.1126 g) were dissolved in a mixed solution of DMF(12 mL) and anhydrous ethanol(12 mL) . The solution was ultrasonized for 1 hour and transferred to a Teflon-lined steel autoclave, and heated up to 90°C for 72 h. After cooling to room temperature, colorless and transparent needle-like crystals are obtained, which are dried under vacuum to obtain **1**. Yield:43%. Elemental analysis calcd. (%) for C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>O<sub>6</sub>Zn: C, 61.54; H, 4.83; N, 6.94. Found: C, 60.82; H, 4.53; N, 6.02. IR (KBr, cm<sup>-1</sup>, Fig. 3 ): 3039(w), 1612(s), 1537(m), 1367(m).

**Synthesis of {[Zn(pyeb)<sub>2</sub>](MeCN)}<sub>n</sub> (2):** The dry **1** were soaked in acetonitrile at room temperature for 12 hours. The solvent molecules in the pores were replaced by acetonitrile. Then drying product to get **2**. Yield: 87%. Elemental analysis calcd. (%) for C<sub>30</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>Zn: C, 64.88; H, 4.15; N, 7.57. Found: C, 63.59; H, 4.02; N, 7.43. IR (KBr, cm<sup>-1</sup>, Fig. 3 ): 2235(s), 1612(s), 1367(m).

**Synthesis of {[Zn(pyeb)<sub>2</sub>](Me<sub>2</sub>CO)}<sub>n</sub> (3):** The dry **1** were soaked in acetone at room temperature for 12 hours. The solvent molecules in the pores were replaced by acetone. Then drying product to get **3**. Yield: 88%. Elemental analysis calcd. (%) for C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>Zn: C, 65.04; H, 4.55; N, 4.90. Found: C, 64.82; H, 4.33; N, 4.78. IR (KBr, cm<sup>-1</sup>, Fig.3 ): 1716(m), 1612(s), 1367(m).

**Synthesis of {[Zn(pyeb)<sub>2</sub>](DMF)}<sub>n</sub> (4):** The dry **2** were soaked in DMF at room temperature for 12 hours. Then drying product to get **4**. Yield: 89%. Elemental analysis calcd. (%) for C<sub>31</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub>Zn: C, 63.38; H, 4.60; N, 7.16. Found: C, 63.21; H, 4.55; N, 7.10. IR (KBr, cm<sup>-1</sup>, Fig. 3 ): 1668(m), 1612(s), 1367(m).

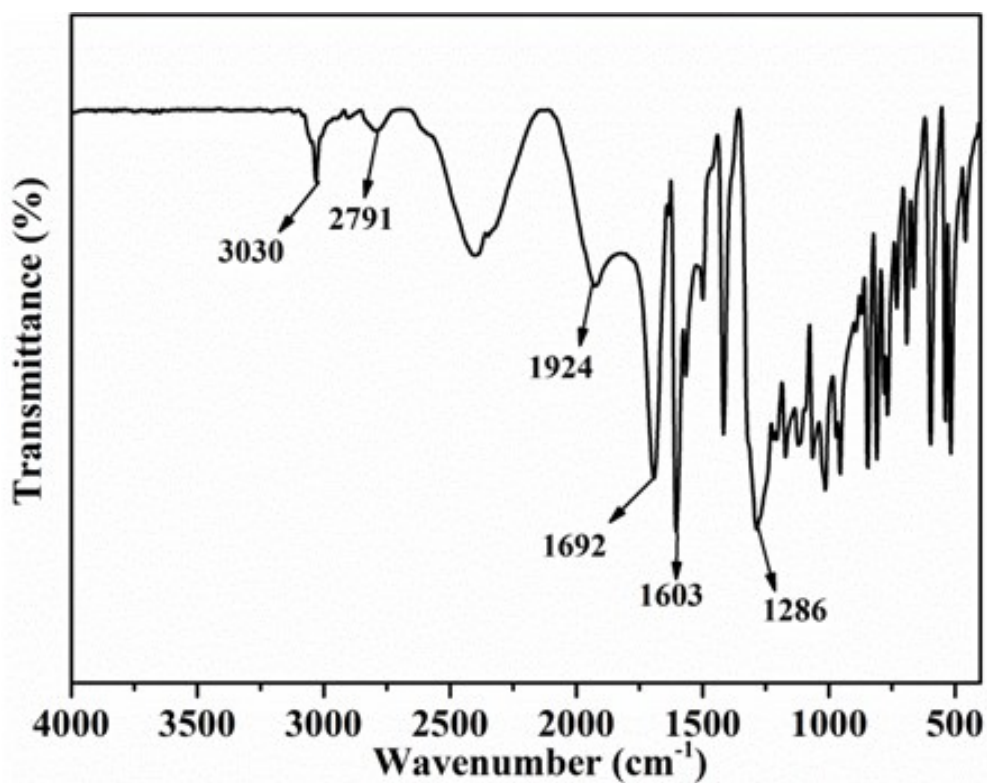


Fig. S1 FT-IR spectra of 4-[2-(4-pyridyl)vinyl]-benzoic acid ligand

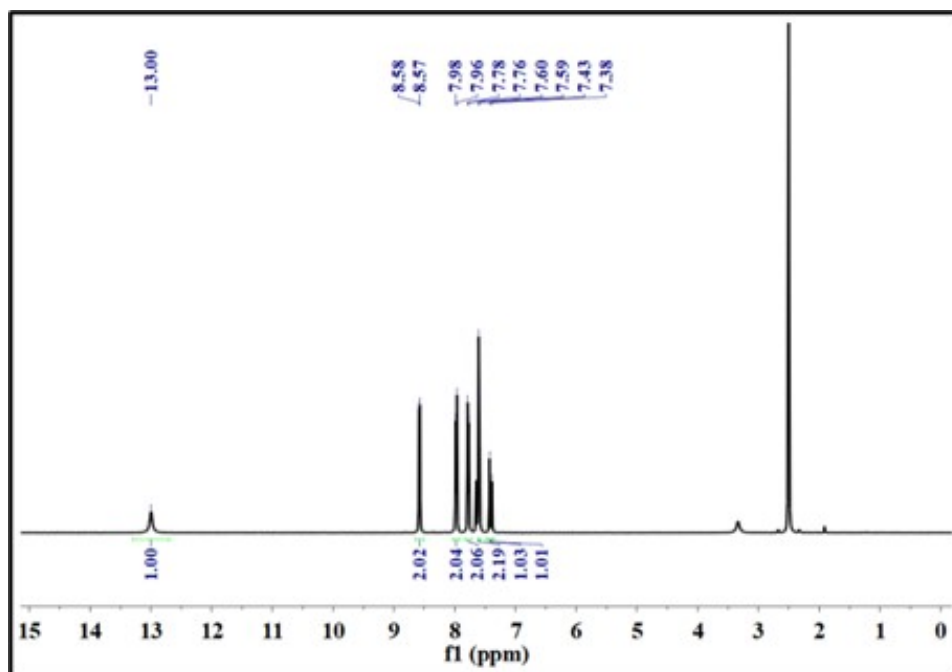


Fig. S2 Nuclear magnetic resonance hydrogen spectrum diagram of 4-[2-(4-pyridyl)vinyl]-benzoic acid ligand

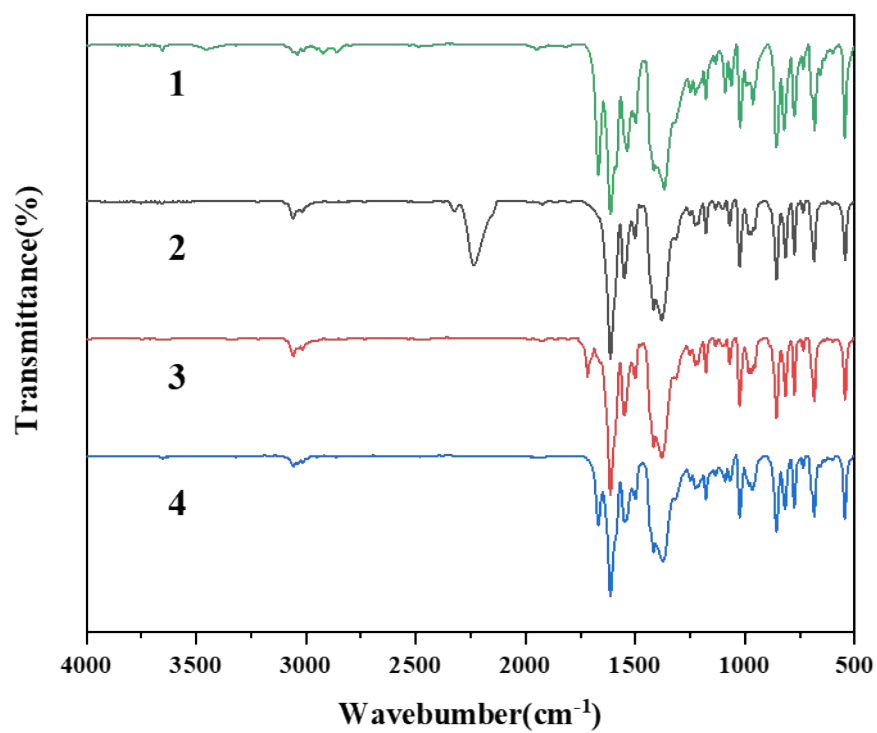


Fig. S3 IR spectra of 1, 2, 3, and 4 tested after proton conduction

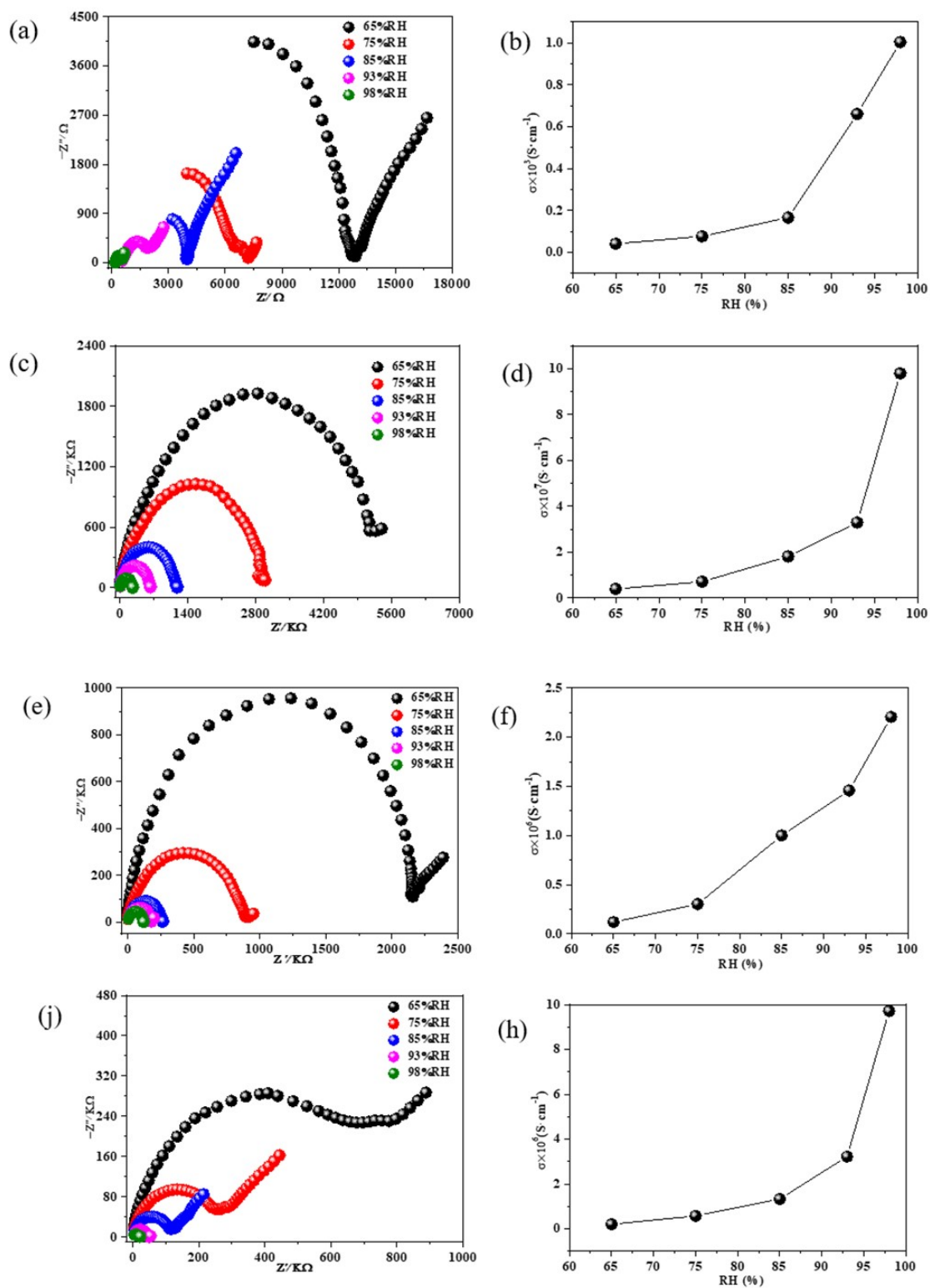


Fig. S4 Proton conductivity of 1, 2, 3 and 4 at different humidity

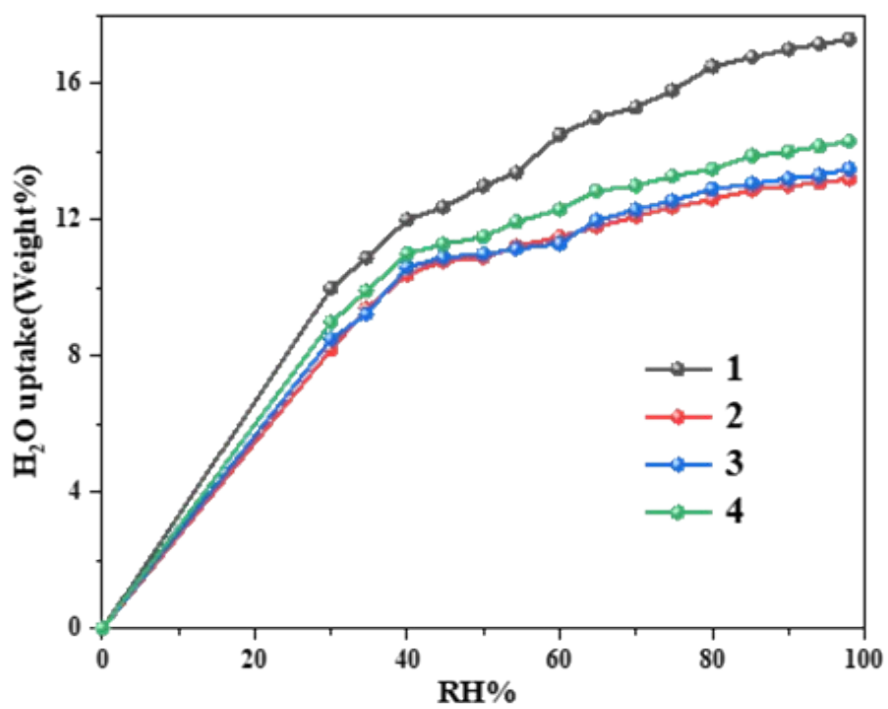


Fig. S5 Water adsorption of 1, 2, 3 and 4.