

Synthesis of Hydrophobic Metal-Organic Frameworks for Proton Conduction

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One of the key factors for high proton conduction lies in hydrophilic environments. However, a recent paper demonstrated that, although water clusters cannot be formed in hydrophobic channels, hydrophobic channel can exhibit a fast diffusion of water by a virtue of unique arrangements under hydrophobic interactions.¹ In this study, a series of isorecticular metal-organic frameworks (MOFs), $\text{Zn}_2(\text{BDC-F}_x)_2(\text{DABCO})$ (BDC^{2-} : terephthalate; $x = 0, 1, 2$, and 4) with 1D square channels having different hydrophilicity/hydrophobicity, were synthesized to clarify the correlation between proton conduction behavior and hydrophobicity.

Four above-mentioned frameworks were prepared by a solvothermal method. As shown in Figure 1a, all the present MOFs exhibited similar powder XRD patterns. Taking $\text{Zn}_2(\text{BDC-F})_2(\text{DABCO})$ (**1**), which was newly synthesized, as an example, the mono-F substituted terephthalate, BDC-F, coordinates to Zn ions to form two-dimensional layers in the *ab* plane (Figure 1b). At the same time, the diamine ligand, DABCO, connects both sides of Zn_2 paddlewheel units to bridge the layers along the *c*-axis (Figure 1c). Different hydrophobic channels while keeping the channel structure unchanged can be acquired by varying the number of F atoms on the ligands. This may lead to a different water network manner from those in reported frameworks. The relationship between proton conduction behavior and hydrophobicity is discussed.

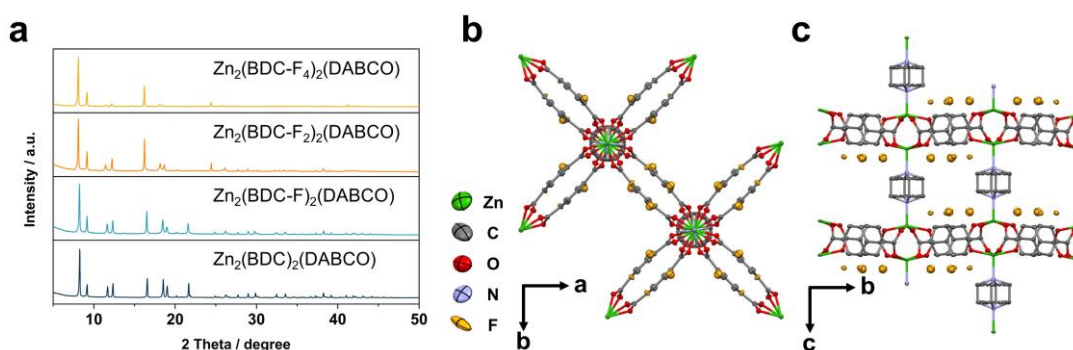


Figure 1. (a) Powder XRD patterns of $\text{Zn}_2(\text{BDC-F}_x)_2(\text{DABCO})$. Crystal structure of **1** at 100 K (*P4/ncc* form) view along (b) *c*-axis and (c) *a*-axis, where hydrogen atoms and DMF molecules are omitted for clarity.

1) Y. Itoh *et al.*, *Science* **2022**, 376, 738.