# Proton transport in crystalline, porous covalent organic frameworks

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## Experimental

#### 1. Sample synthesis and preparation

**Synthesis of TPB-DMTP-COF**. TPB-DMTP-COF was synthesized as previously reported in the literature.<sup>1</sup> Typically, 0.08 mmol of 1,3,5-tri(4-aminophenyl) benzene (TPAB, purchased from Tokyo Chemical Industry) and 0.12 mmol of 2,5-dimethoxyterephthalaldehyde (DMTA) was mixed with 0.5 ml of o-dichlorobenzene (o-DCB, purchased from Sigma) and 0.5 ml of BuOH. Acetic acid (6M, 0.1 ml) was used as the catalyst. The mixture was degassed thoroughly, sealed and then heated at 120 °C for three days. The precipitated product was centrifuged, washed with THF, and then Soxhlet extracted with THF for one day to remove any trapped guest molecules. The resultant (yellow) powder was collected and dried at 120 °C under vacuum for 24h. The final product yield was approximately 70%.

**Synthesis of 2,5-dimethoxyterephthalaldehyde (DMTA)**. The DMTA used above was synthesized via a lithium halogen exchange reaction between o-dichlorobenzene with 3 equivalents of n-BuLi at -78 °C in THF and then treated with DMF and 3 M HCL as described in literature.<sup>2</sup>

**Preparation of carbonized COF material (C-COF)**. C-COF was prepared by pyrolysis of the TPB-DMTP-COF under a  $N_2$  atmosphere using a tube-furnace. The nitrogen flow was set to 80 mL/min. The sample was heated up to 800 °C at a heating rate of 5 °C/min. Then the furnace was held at 800 °C for an additional 2 h and then was cooled naturally. The resulting carbonized material (black) was ground and stored in glovebox for future use.

Synthesis of  $H_2O$ -in-COF. Both the TPB-DMTP-COF and carbonized COF materials were degassed by heating to 120 °C under vacuum for 12h to remove guest molecules. The  $H_2O$  was added into the container, and heated to 100 °C, the valve between two sample containers was then opened slowly (as shown in Figure 1(c) in the main text), and the solvents were pressurized/vaporized into the COFs. The

$$V \% = \frac{(m_1 - m_0)/\rho_{sol}}{m_1 + m_0}$$

solvent loading (*V*%) is calculated by  $m_0 \cdot v$ , where  $m_0$  and  $m_1$  are the mass of COFs before and after loading,  $\rho_{sol}$  is the density of solvents, and v is the porosity of COFs. The TGA curve of the TPB-DMTP-COF<sup>1</sup> shows a decomposition process with an onset temperature of ~ 420 °C and an approximately 20% weight loss, and is followed by a relatively gradually weight loss process up to 700 °C.

### 2. Characterization

#### 2.1 Solid state NMR

All the solid-state NMR experiments were performed on a Bruker Avance III 500 MHz wide-bore NMR spectrometer, operating at <sup>1</sup>H Lamor Frequency of 500.03 MHz. A 4 mm double resonance MAS probe was used for the static <sup>1</sup>H experiments. The sample temperatures were calibrated with the isotropic chemical shifts of lead nitrate at different temperatures using the method described in literature.<sup>3</sup>

### 2.2 Pulsed Field Gradient (PFG) - NMR

<sup>1</sup>H and <sup>19</sup>F diffusion coefficients were measured on a Bruker Avance III 300M Hz wide-bore spectrometer equipped with a Diff50 probe. The maximum gradient strength is 29.4 T/m. The samples were first sealed in a 4 mm solid-state NMR rotor in an argon-filled glovebox. The rotors were then inserted into a standard 5 mm NMR glass tube for measurements. Pulse-field gradient stimulated echo (PGSTE) sequence was used to measure the diffusion coefficients, which were calculated from the Stejskal-Tanner equation:<sup>4</sup>

$$\ln(\frac{I}{I_0}) = -D^{NMR}\gamma^2(\Delta - \frac{\delta}{3})\delta^2 g^2 \tag{1}$$

Where I and I<sub>0</sub> are the signals in the presence and absence of the pulse field gradient, respectively,  $\gamma$  is the gyromagnetic ratio of the proton,  $\Delta$  is the interval between the gradient pulses,  $\delta$  is the length of the gradient pulse, and *g* is the magnitude of the gradient pulse. In the present study,  $\Delta$  was varied from 10 ms to 100 ms,  $\delta$  was set to 5 ms and *g* was optimized to a suitable gradient strength range from 0.05 to 20 T/m according to the diffusion coefficient. Recycle delay was 2 s for all the measurements. Sample temperature in the diffusion probe was calibrated by using the relative chemical shift separation between OH and methyl group resonances of dry methanol.<sup>5</sup>



**Figure S1.** Wide Angel X-ray Diffraction (WAXD) spectrum of the *COF* sample. This result is essentially the same as the WAXD pattern of the same materials published by Xu and coworkers (See Figure S1 in Supporting Information of Ref <sup>6</sup>). The average grain size of *COF* crystallites is about 15.8

nm, estimated from the Scherrer equation:  $d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta}$ , where *K* is a shape factor with a typical value of 0.9.  $\lambda = 0.154056$  nm is the x-ray wave length.  $\beta = 0.00873$  [rad] is the line broadening at half the maximum.



Figure S2. <sup>13</sup>C NMR of the *COF* and *C-COF* samples measured at 8 kHz magic angle spinning. The *C-COF* spectrum was measured using a single pulse excitation sequence with recycle delay of 5s, 10 k scans. No NMR signal was observed for the *C-COF* sample by <sup>1</sup>H $\rightarrow$ <sup>13</sup>C CP-MAS sequence after 2048 scans. *COF* spectrum was measured by a CP-MAS sequence with recycle delay of 2s and 4096 scans.



**Figure S3.** Time dependency of <sup>1</sup>H diffusion coefficients of *COF* measured at 80, 90 and 100 °C. The diffusion coefficient of bulk water molecules at 80 °C is marked as a dotted dash line in the figure for comparison. The sample was sealed in a closed 4 mm NMR rotor, therefore the boiling temperature of the water should be well-above 100 °C. The dots in the figure are experimental data, and the solid line are the best fit to the experimental values using fast-diffusion limit approach:<sup>7</sup>

$$\frac{D_{eff}(t)}{D_0} = 1 - \frac{4S}{9\sqrt{\pi}V} (D_0 t)^{\frac{1}{2}}$$
. The surface-to-volume ratios obtained from the fitting is about 1.5 × 10<sup>4</sup> m<sup>-1</sup> for all three temperatures. Assuming a 1D channel structure, this S/V value corresponds to a

characteristic length scale of  $\sim 130~\mu m.$ 



**Figure S4.** <sup>1</sup>H inversion recovery profiles of  $H_2O$  in *COF* and *C-COF* samples, measured at 20 °C. The experimental data (black squares) can be fitted with a single component exponential decay.

Spin-lattice (T<sub>1</sub>) relaxation of water in the *COF* and *C-COF* systems was first estimated with a saturation recovery sequence with delays varying from 1  $\mu$ s to 100s in a log scale, then precisely measured using inversion-recovery ( $\pi - \tau 1 - \pi/2$ ) pulse sequence using delays 10 times of the estimated T<sub>1</sub>.

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