

Humidity-mediated Anisotropic Proton Conductivity through the 1D Channels of Co-MOF-74

Supplementary Material

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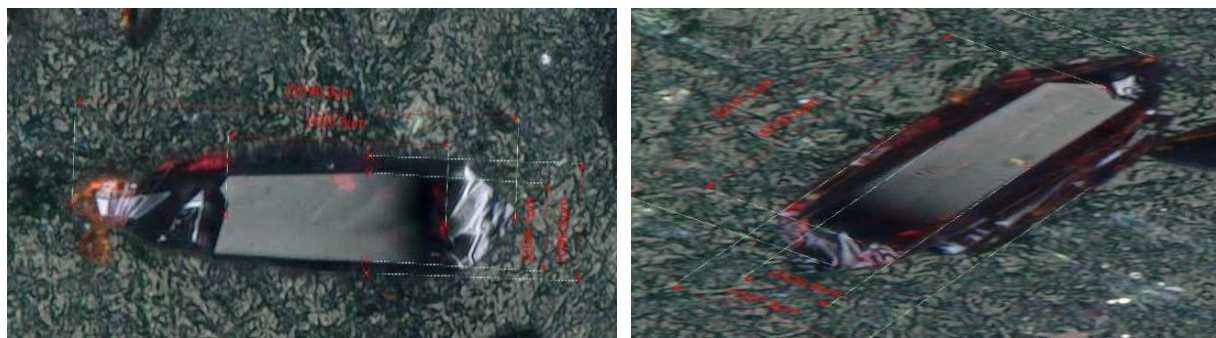


Figure S1. Microscopic images of two Co-MOF-74 crystals for the evaluation of the contact area in equation S1.

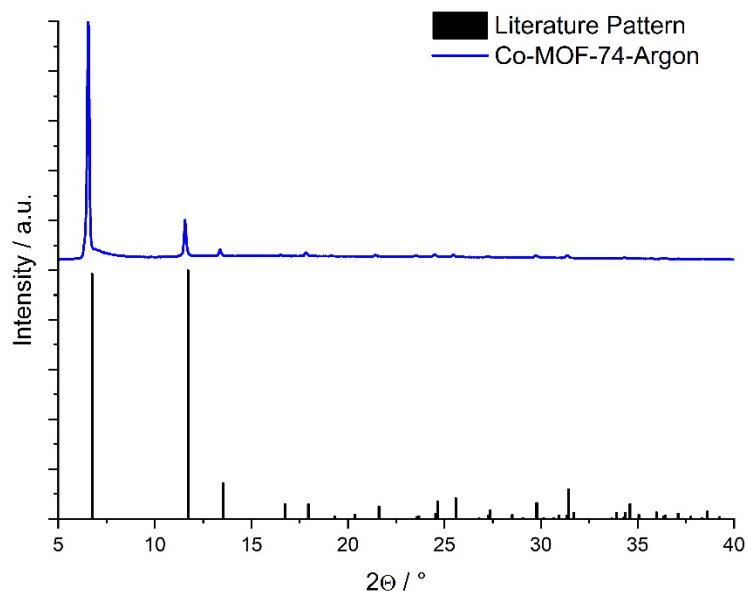


Figure S2. Experimental and simulated powder XRD pattern of Co-MOF-74 [1].

[1] Strauss, I.; Mundstock, A.; Hinrichs, D.; Himstedt, R.; Knebel, A.; Reinhardt, C.; Dorfs, D.; Caro, J. *Angew. Chemie Int. Ed.* **2018**, *57*, 7434–7439.

Table S1. Dimensions of Co-MOF-74 single crystals and contact lengths/widths with underlaying flat substrate, determined from Figure S1. The values are used as correcting factors for the assessment of the contact area in equation S1.

crystal #	length	contact length	width	contact width
1	45.6 μm	34.1 μm (74.8%)	190.9 μm	95 μm (49.8%)
2	141.2 μm	105.0 μm (74.8%)	57 μm	26 μm (45.6%)

Equation S1. Calculation of the proton conductivity σ from the measured proton resistance R and the contact area with the Pt electrodes (A : contact area between sample and the Pt electrode array; n : number of spacings between electrodes, D : inter-electrode distance (20 μm), d : electrode width (20 μm), a : width of crystal) [2].

$$\sigma = n \cdot (D / (R \cdot A)) = n \cdot (D / (R \cdot a \cdot d)) \quad (\text{S1})$$

Table S2. Fit results for the spectra in Figure 4.

	along micropore axis	orthogonal to axis
χ^2	0.015	0.014
$CPE-T$	1.8753×10^{-11}	1.4715×10^{-11}
$CPE-P$	0.88579	0.89969
R / Ω	1.278×10^7	2.072×10^7

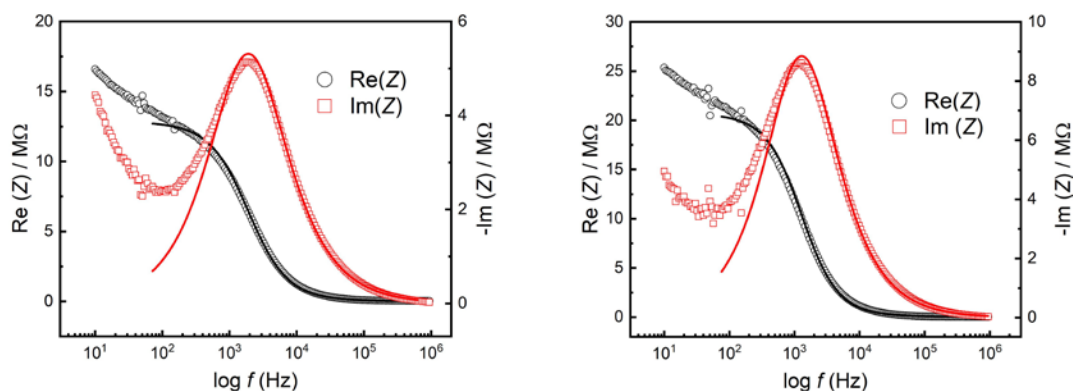


Figure S3. Real and imaginary parts of the impedance *vs.* frequency of a single Co-MOF-74 crystal in two different orientations relative to the contacting electrodes (25 °C, 92% r.h.): along (left) and orthogonal (right) to the micropore axis.

Table S3. All measured proton conductivity values of Co-MOF-74 crystals under variable conditions.

sample name	proton current direction	$T / ^\circ\text{C}$	r.h. / %	proton conductivity $\sigma / \mu\text{S cm}^{-1}$
Co-74_1	=	25	92	123
	≠	25	92	11.7
Co-74_2	=	21	75	0.732
	=	21	80	2.29
	=	21	85	7.38
	=	21	90	20.4
	=	22	90	34.4
Co-74_3	=	26	90	45.5
	=	30	90	49.6
	≠	21	90	0.862
Co-74_4	≠	24	90	1.46
	≠	27	90	1.85
	≠	30	90	2.40
	=	30	70	0.27
Co-74_5	=	30	75	1.18
	=	30	80	4.48
	=	30	85	15.7
	=	30	90	49.8
	(=)	(30)	(95)	(2590) ²
	=	40	90	52.3
	=	50	90	77.7
	=	60	90	137
	=	60	90	137

¹ "=": along *c* axis; "≠": orthogonal ² (presumed bulk water condensation)