Electronic Supplementary Material (ESI) for Chemical Science

From Metal-Organic Framework (MOF) to MOF/Polymer Composite Membrane: Enhancement of Low-Humidity Proton Conductivity

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Table S1 Selected bond lengths (Å) and angles (°) for **1**

	Complex **1**		
Ca(1)−O(1)	2.319(3)	Ca(1)−O(1W)	2.383(3)
Ca(1)−O(2a)	2.389(4)	Ca(1)−O(2b)	2.411(3)
Ca(1)−O(2W)	2.487(3)	Ca(1)−O(4c)	2.502(3)
Ca(1)−O(5c)	2.664(3)	Ca(1)−O(1b)	2.769(3)
O(1)−Ca(1)−O(1W)	84.18(11)	O(1)−Ca(1)−O(2a)	136.43(11)
O(1W)−Ca(1)−O(2a)	76.88(11)	O(1)−Ca(1)−O(2b)	79.31(12)
O(1W)−Ca(1)−O(2b)	157.61(11)	O(2a)−Ca(1)−O(2b)	125.47(9)
O(1)−Ca(1)−O(2W)	78.82(12)	O(1W)−Ca(1)−O(2W)	107.13(11)
O(2a)−Ca(1)−O(2W)	70.15(12)	O(2b)−Ca(1)−O(2W)	84.47(10)
O(1)−Ca(1)−O(4c)	132.50(11)	O(1W)−Ca(1)−O(4c)	85.48(12)
O(2a)−Ca(1)−O(4c)	85.03(11)	O(2b)−Ca(1)−O(4c)	94.58(11)
O(2W)−Ca(1)−O(4c)	148.06(12)	O(1)−Ca(1)−O(5c)	82.25(11)
O(1W)−Ca(1)−O(5c)	81.31(11)	O(2a)−Ca(1)−O(5c)	131.60(11)
O(2b)−Ca(1)−O(5c)	81.57(10)	O(2W)−Ca(1)−O(5c)	158.25(12)
O(4c)−Ca(1)−O(5c)	50.35(10)	O(1)−Ca(1)−O(1b)	132.24(9)
O(1W)−Ca(1)−O(1b)	143.03(11)	O(2a)−Ca(1)−O(1b)	71.22(9)
O(2b)−Ca(1)−O(1b)	56.75(10)	O(2W)−Ca(1)−O(1b)	79.23(10)
O(4c)−Ca(1)−O(1b)	73.79(10)	O(5c)−Ca(1)−O(1b)	106.38(10)

Symmetry codes : a) *x*−1, *y*, *z*; b) *x*−1/2, −*y*+1/2, −*z*+1; c) *x*−1, *y*−1, *z* for **1**.

Table S2 Hydrogen-bonding geometry parameters (Å, °) for compound **1**

D−H···A	d(D−H)	d(H···A)	d(D···A)	∠(DHA)
	Complex **1**			
N(1)−H(1)···O(2Wd)	0.91	2.24	3.080(5)	153.9
N(6)−H(1)···O(2)	0.91	2.36	2.911(5)	119.0
O(1W)−H(1Y)···O(3a)	0.96	1.84	2.782(4)	167.4
O(2W)−H(2X)···O(5e)	0.96	1.89	2.837(5)	167.2
O(2W) −H(2Y) ···O(4f)	0.96	1.81	2.722(5)	157.8

Symmetry codes: a) *x*−1, *y*, *z*; d) *x*+1, *y*, *z*; e) *x*−3/2, −*y*+3/2, −*z*+1; f) *x*−1/2, −*y*+3/2, −*z*+1 for **1**.

Table S3 Proton Conductivity of the MOFs under Ambient Conditions

compound	σ (S cm^{-1})	RH (%)	T (K)	reference
$Mn(dhbq)(H_2O)_2$[a]	3.5×10^{-9}	60	298	Ref21
$(HOC_2H_4)_2dtoaCu$[b]	5.9×10^{-8}	70	300	Ref22
$Zn_3(L)(H_2O)_2\cdot2H_2O$[c]	1.4×10^{-6}	75	298	Ref23
$(NH_4)_2(adp)[Zn_2(ox)_3]\cdot2H_2O$[d]	6.0×10^{-6}	70	298	Ref24
$\{NH(prol)_3\}[MnCr(ox)_3]\cdot2H_2O$[e]	2.0×10^{-6}	65	298	Ref25
$Co[Cr(CN)_6]_{2/3}\cdot zH_2O$	2.9×10^{-5}	69	293	Ref26
$(NH_4)_4[MnCr_2(ox)_6]\cdot4H_2O$	3.0×10^{-5}	69	295	Ref27
$\{NMe_3(CH_2COOH)\}[FeCr(ox)_3]\cdot n H_2O$	8×10^{-5}	65	298	Ref28
$\{[Ca(D\text{-}Hpmpc)(H_2O)_2]\cdot2HO_{0.5}\}_n$ composite membrane	2.8×10^{-5}	53	298	this work

[a] H_2dhbq = 2,5-dihydroxy-1,4-benzoquinone.

[b] prol = $-C_3H_7OH$.

[c] adp = adipic acid.

[d] L = 1,3,5-benzenetriphosphonate.

[e] dtoa = dithiooxamide.

Table S4 Relative atomic ratio (%) of main elements in pure PVP and composite membranes, and MOF **1** samples

Sample	Element		Peak position (eV)	Relative atomic ratio (%)
PVP	Ca 2p	Ca $2p_{1/2}$	-	0
		Ca $2p_{3/2}$	-	
	P 2p		-	0
	N 1s	NR_3 [a]	399.40	100
		HNR_3^+ [b]	-	
MOF **1**/PVP-3	Ca 2p	Ca $2p_{1/2}$	350.80	1.23
		Ca $2p_{3/2}$	346.95	
	P 2p		132.72	1.46
	N 1s	NR_3 [a]	399.35	97.31
		HNR_3^+ [b]	401.61	
MOF **1**/PVP-5	Ca 2p	Ca $2p_{1/2}$	350.80	1.82
		Ca $2p_{3/2}$	346.95	
	P 2p		132.73	1.76
	N 1s	NR_3 [a]	399.25	96.42
		HNR_3^+ [b]	401.66	
MOF **1**/PVP-10	Ca 2p	Ca $2p_{1/2}$	350.80	3.81
		Ca $2p_{3/2}$	346.9	
	P 2p		132.80	3.69
	N 1s	NR_3 [a]	399.34	92.50
		HNR_3^+ [b]	401.64	
MOF **1**/PVP-20	Ca 2p	Ca $2p_{1/2}$	350.60	7.41
		Ca $2p_{3/2}$	346.78	
	P 2p		132.78	6.93
	N 1s	NR_3 [a]	399.28	85.66
		HNR_3^+ [b]	401.68	
MOF **1**/PVP-30	Ca 2p	Ca $2p_{1/2}$	350.40	11.12
		Ca $2p_{3/2}$	346.75	
	P 2p		132.76	10.47
	N 1s	NR_3 [a]	399.38	78.41
		HNR_3^+ [b]	401.69	
MOF **1**/PVP-50	Ca 2p	Ca $2p_{1/2}$	350.30	18.43
		Ca $2p_{3/2}$	346.81	
	P 2p		132.78	17.12
	N 1s	NR_3 [a]	399.34	64.45
		HNR_3^+ [b]	401.61	
MOF **1**	Ca 2p	Ca $2p_{1/2}$	350.52	31.89
		Ca $2p_{3/2}$	347.01	
	P 2p		132.78	33.94
	N 1s	NR_3 [a]	-	34.17
		HNR_3^+ [b]	401.68	

a: the tertiary nitrogen;

b: the protonated tertiary nitrogen.

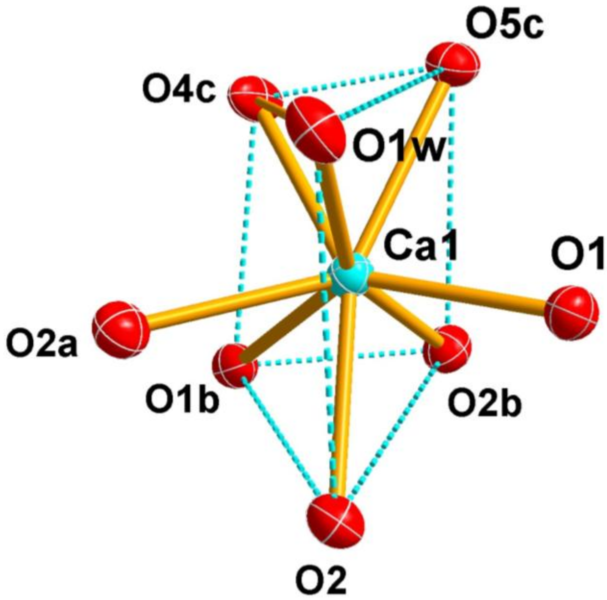

Fig. S1 Local coordination geometry of Ca (II) ion in MOF **1** (Cyan: Ca^{2+}, Red: O). (Symmetry codes: a) x−1, y, z; b) x−1/2, −y+1/2, −z+1; c) x−1, y−1, z).

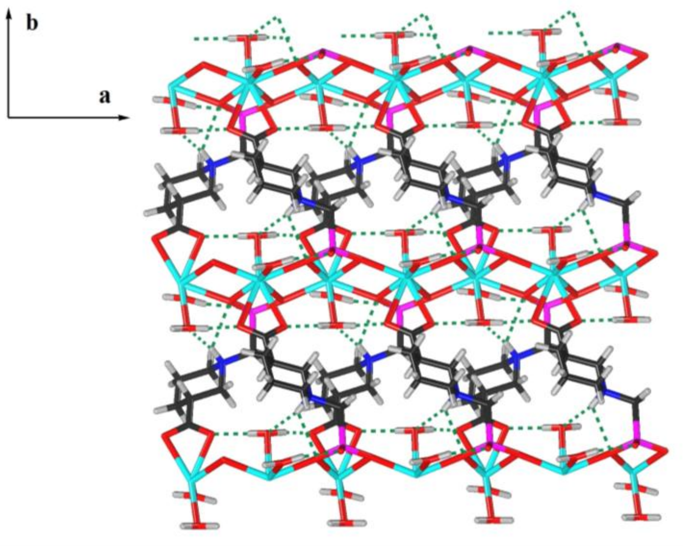

Fig. S2 Versatile hydrogen-bonding interactions observed in MOF **1** (Black, C; blue, N; Red, O; Cyan, Ca; Magenta, P; Light Gray, H).

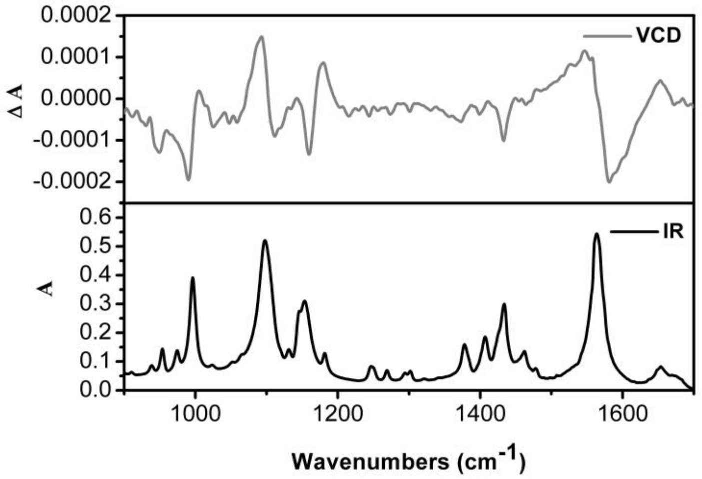

Fig. S3 The VCD (top) and IR absorption spectrum (bottom) of MOF **1** in the solid state at room temperature.

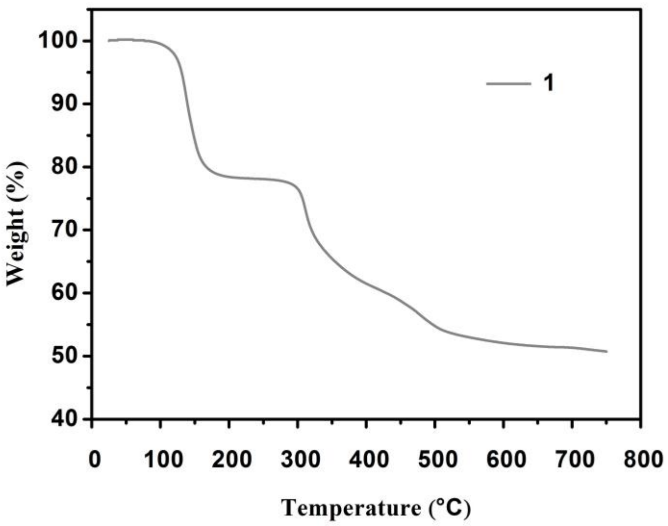

Fig. S4 Thermogravimetric curve for MOF **1**.

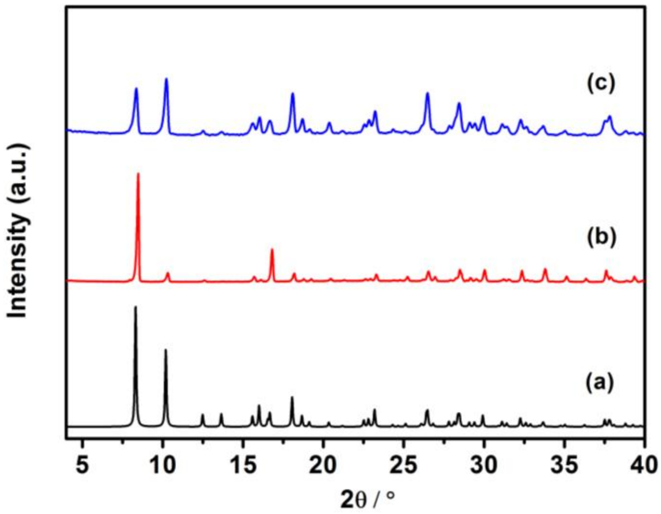

Fig. S5 PXRD patterns of (a) a simulation based on single-crystal analysis of MOF **1**, (b) as-synthesized bulk crystals of MOF **1**, and (c) as-synthesized submicrorods of MOF **1**.

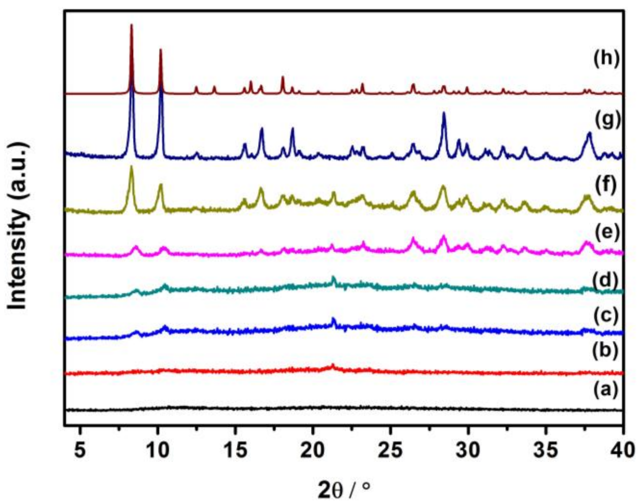

Fig. S6 PXRD patterns of pure PVP, MOF/polymer composite membranes and MOF **1** single crystal simulation ((a) pure PVP, (b) MOF **1**/PVP-3, (c) MOF **1**/PVP-5, (d) MOF **1**/PVP-10, (e) MOF **1**/PVP-20, (f) MOF **1**/PVP-30, (g) MOF **1**/PVP-50, and (h) the simulated one from single crystal).

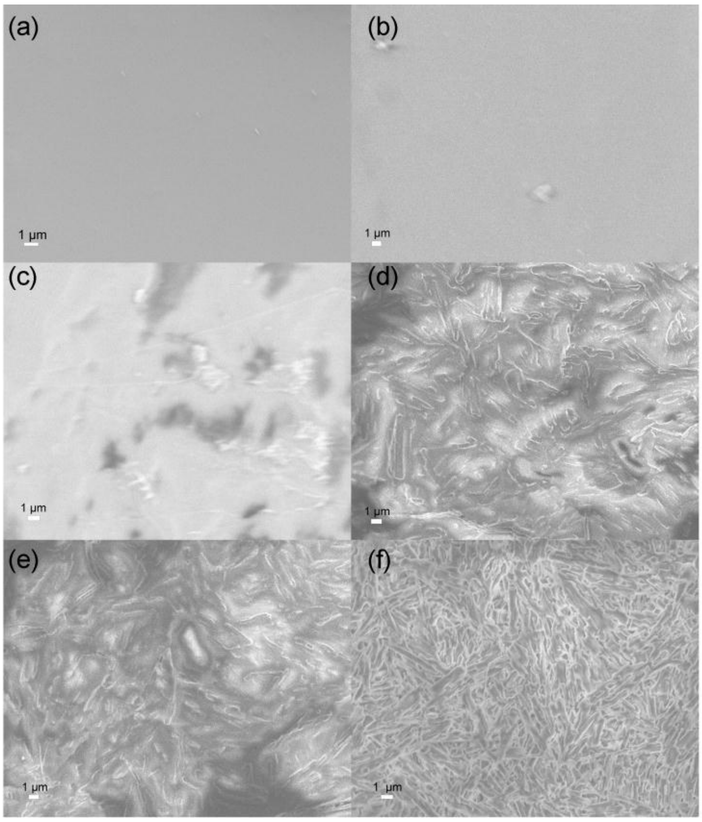

Fig. S7 Top views of SEM images of (a) pure PVP, (b) MOF **1**/PVP-3, (c) MOF **1**/PVP-5, (d) MOF **1**/PVP-10, (e) MOF **1**/PVP-20, and (f) MOF **1**/PVP-30 composite membranes.

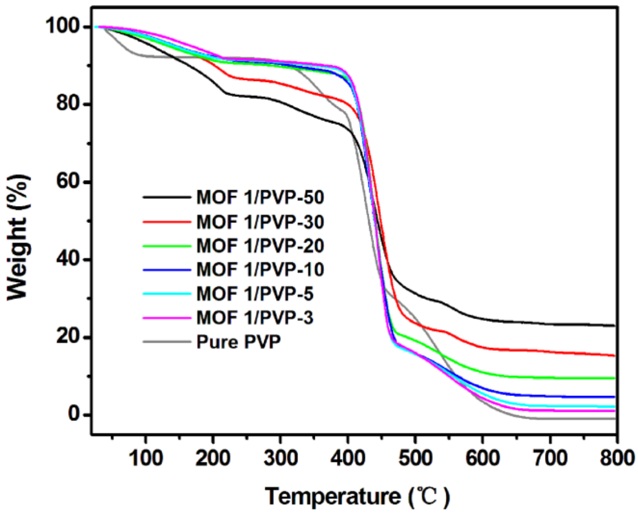

Fig. S8 Thermogravimetric curves for pure PVP and MOF/PVP composite membranes with different contents of MOF **1**.

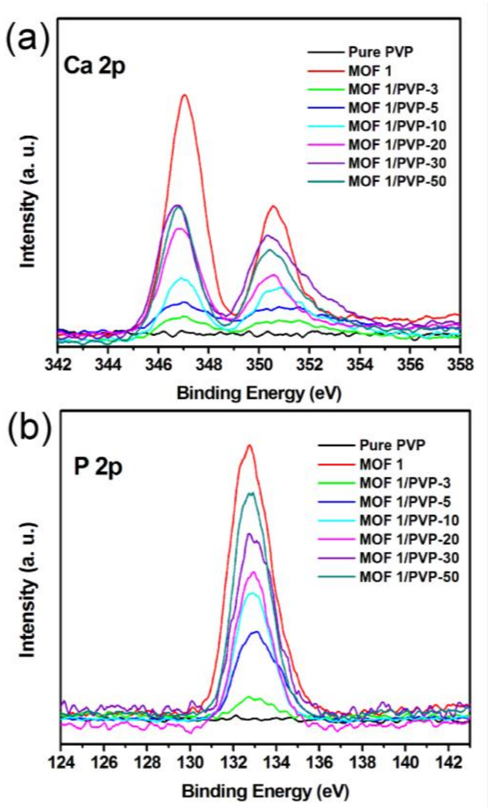

Fig. S9 XPS spectra of MOF/PVP composite membranes with different contents of MOF **1**; XPS signals of the core-level (a) Ca 2p, (b) P 2p for pure PVP, MOF **1** and the composite membranes.

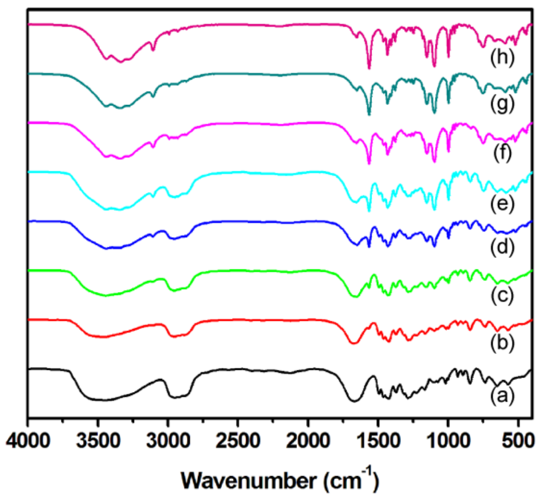

Fig. S10 FTIR spectra of pure PVP, MOF **1** and the composite membranes ((a) pure PVP, (b) MOF **1**/PVP-3, (c) MOF **1**/PVP-5, (d) MOF **1**/PVP-10, (e) MOF **1**/PVP-20, (f) MOF **1**/PVP-30, (g) MOF **1**/PVP-50, and (h) MOF **1**).

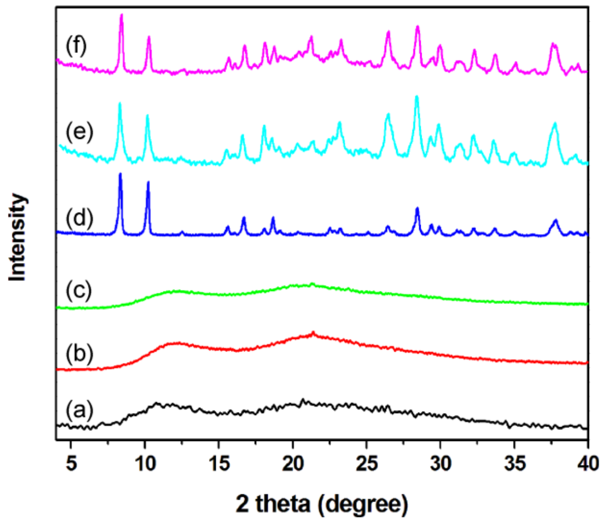

Fig. S11 PXRD patterns of (a) pure PVP, (b) PVP exposed to air, (c) PVP exposed to oxygen, (d) MOF **1**/PVP-50, (e) MOF **1**/PVP-50 exposed to air, and (f) MOF **1**/PVP-50 exposed to oxygen at 333 K for 24 h for the test of oxidative stability.

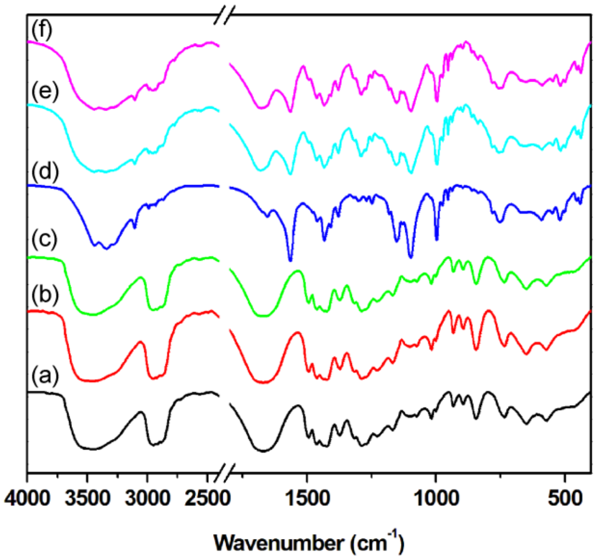

Fig. S12 FTIR spectra of (a) pure PVP, (b) PVP exposed to air, (c) PVP exposed to oxygen, (d) MOF **1**/PVP-50, (e) MOF **1**/PVP-50 exposed to air, and (f) MOF **1**/PVP-50 exposed to oxygen at 333 K for 24 h for the test of oxidative stability.

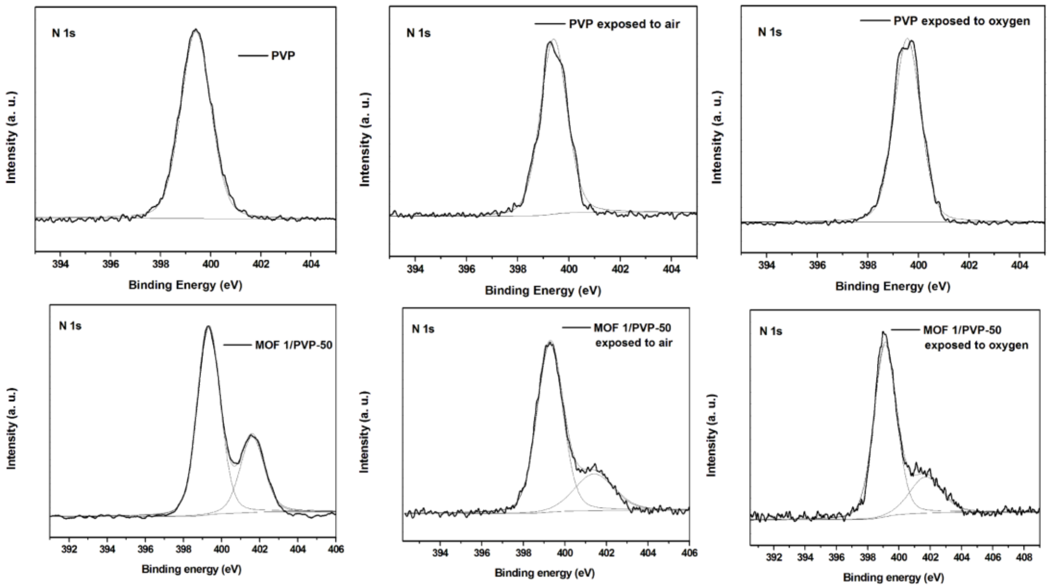

Fig. S13 XPS spectra of N 1s signal of pure PVP, and MOF **1**/PVP-50 without and with exposure to air and oxygen flows at 333 K for 24 h for the test of oxidative stability.

Table S5 Chemical environment of nitrogen for the tertiary nitrogen in pure PVP and MOF **1**/PVP-50

Sample	Element	Peak position (eV)	Band area	Nitrogen relative atomic ratio (%)
PVP	N 1s (NR_3)[a]	399.40	25197.96	100
PVP exposed to air flows	N 1s (NR_3)[a]	399.41	20140.39	100
PVP exposed to oxygen flows	N 1s (NR_3)[a]	399.41	23582.33	100
MOF **1**/PVP-50	N 1s (HNR_3^+)[b]	401.61	9110.03	26.05
	N 1s (NR_3)[a]	399.34	25855.04	73.95
MOF **1**/PVP-50 exposed to air flows	N 1s (HNR_3^+)[b]	401.40	5332.07	25
	N 1s (NR_3)[a]	399.28	15999.99	75
MOF **1**/PVP-50 exposed to oxygen flows	N 1s (HNR_3^+)[b]	401.43	4304.17	22.88
	N 1s (NR_3)[a]	399.32	14505.07	77.12

a: the tertiary nitrogen;

b: the protonated tertiary nitrogen.

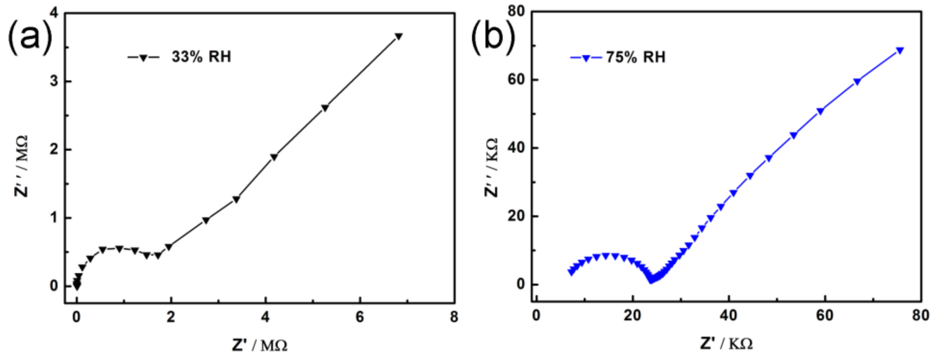

Fig. S14 Nyquist plots of MOF **1** submicrorods (a) ~33% RH and (b) ~75% RH at 298 K.

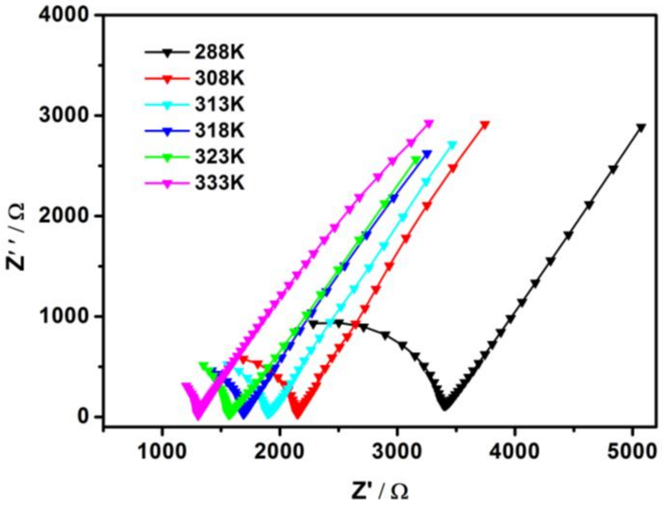

Fig. S15 Nyquist plots of MOF **1** submicrorods at different temperatures and ~97% RH (relative humidity).

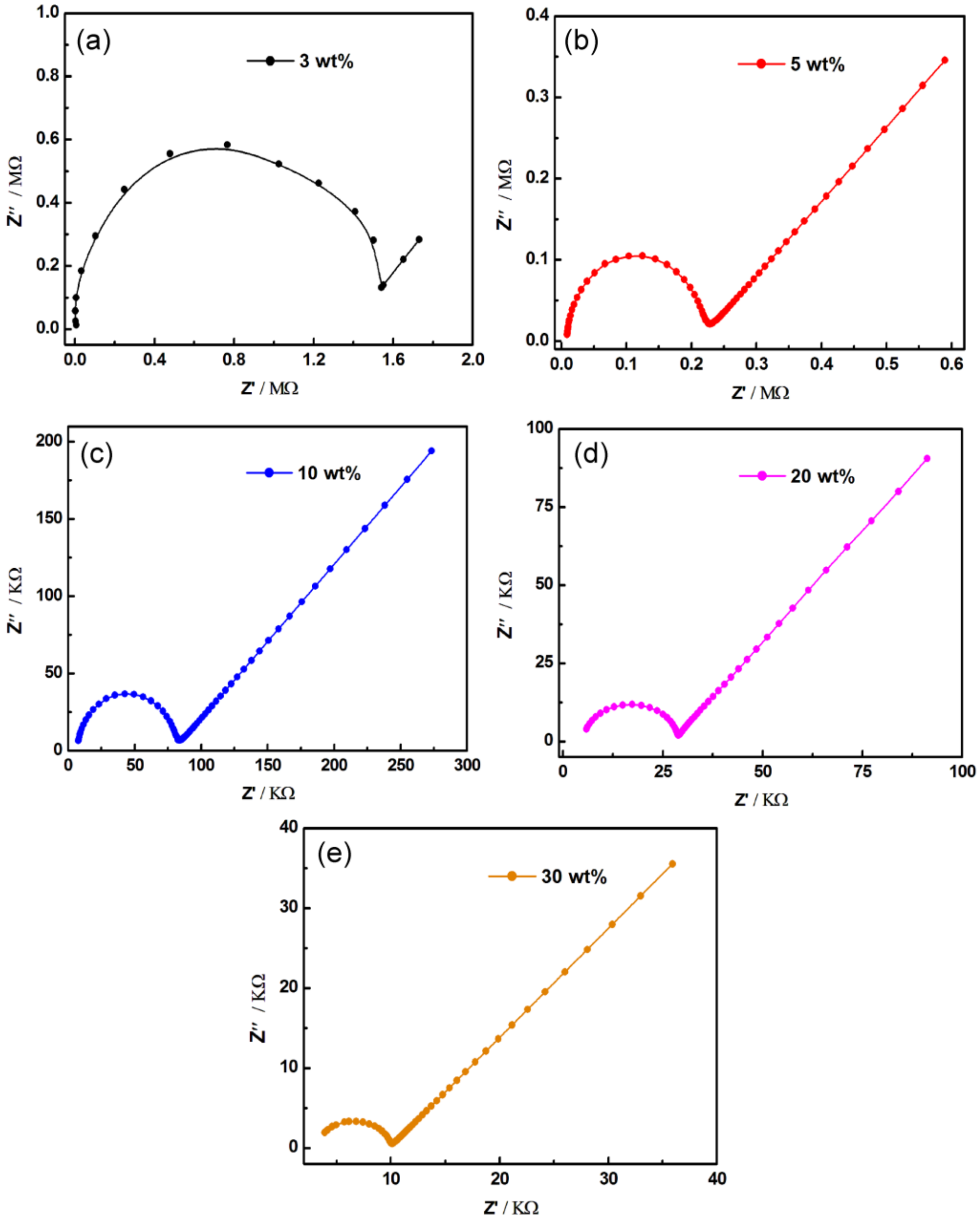

Fig. S16 Nyquist plots of MOF/PVP composite membranes with different contents of MOF **1** at ~53% RH and 333 K; (a) MOF **1**/PVP-3, (b) MOF **1**/PVP-5, (c) MOF **1**/PVP-10, (d) MOF **1**/PVP-20 and (e) MOF **1**/PVP-30.

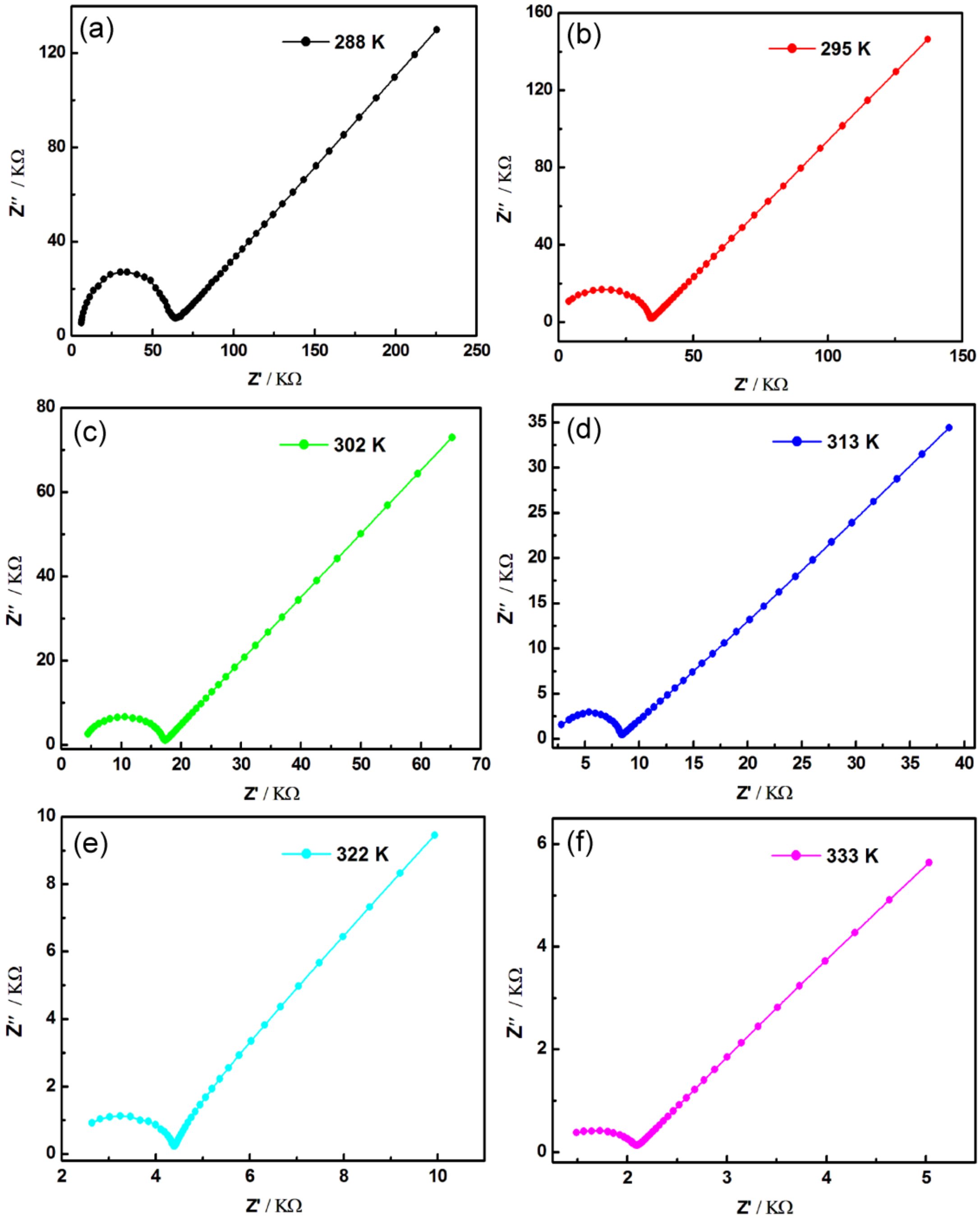

Fig. S17 Nyquist plots of MOF/PVP composite membranes containing 50% MOF **1** at different temperatures ((a) 288 K, (b) 295 K, (c) 302 K, (d) 313 K, (e) 322 K, and (f) 333 K) and ~53% RH.

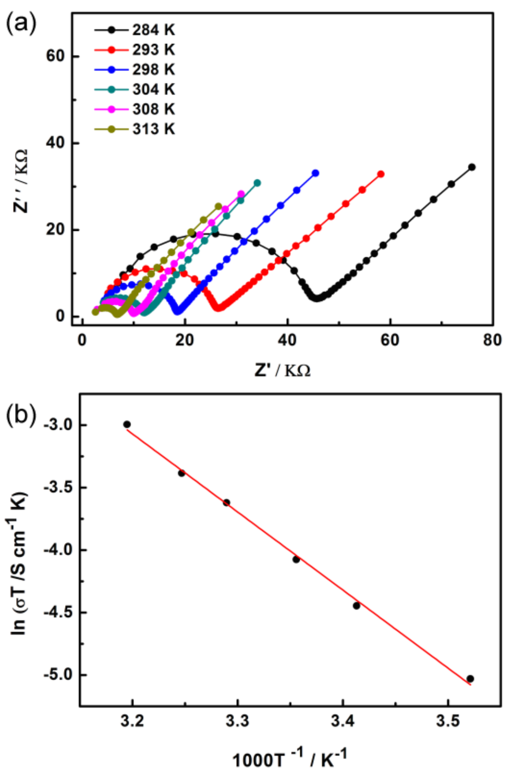

Fig. S18 (a) Nyquist plots of MOF **1**/PVP-50 composite membrane at different temperatures and ~65% RH (relative humidity); (b) Arrhenius-type plot of conductivity for the MOF **1**/PVP-50 composite membrane in function of temperature and under ~65% RH condition.

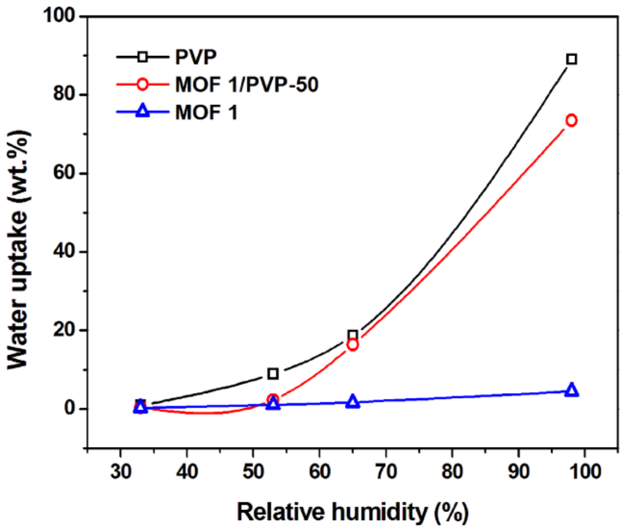

Fig. S19 Water uptakes of pure PVP, MOF **1**/PVP-50 composite membrane and MOF **1** at 298 K in function of relative humidity.

Cost estimation for composite membranes

In order to estimate the gross cost of as-prepared MOF/PVP composite membranes, the price of each starting chemical is listed below:

DL-piperidine-3-carboxylic acid hydrochloride: 0.48-0.80 USD/g
H_3PO_3: 0.024 USD/g
HCHO: 0.0067 USD/mL (36%)
Solvent: 0.0192 USD/mL
Energy: 0.0601 USD/g
Productivity: 60.0% (based on DL-piperidine-3-carboxylic acid hydrochloride)
H_3pmpc ligand: 1.24-1.60 USD/g (H_3pmpc=D, L-1-(phosphonomethyl)piperidine-3-carboxylic acid)

H_3pmpc ligand: 1.24-1.60 USD/g,
CaO: 0.039 USD/g,
Solvent: 0.41 USD/100 mL,
Energy cost: 0.29 USD/g,
Productivity of MOF **1**: 61.5% (based on H_3pmpc compound),
MOF **1**: 1.86-2.27 USD/g (MW = 315.27),

PVP: 0.283 USD/g,

The weight and the area of the MOF **1**/PVP-50 membrane are estimated to be 0.03-0.032 g and 1.92 cm^2.

The gross cost of MOF **1**/PVP-50 composite membrane per square meter can be calculated as follows:

$$\text{Cost (USD /m}^2) = \frac{\text{Membrane mass (g)} \times [\text{MOF price (RMB/g)} + \text{PVP price (RMB/g)}]}{2 \times \text{Membrane surface (m}^2)}$$
$$= \frac{0.03 \times (1.86 + 0.283)}{2 \times 1.92 \times 10^{-4}}$$
$$= 167.42 \text{ USD /m}^2$$

The cost of commercial Nafion membrane is about 600-1200 USD/m^2[1,2] and the price of Nafion® 117 membrane (CAS No.: 31175-20-9) is 377.5 USD for 8 inch × 10 inch (7314 USD/m^2) from Sigma-Aldrich. By comparison, it is found that the MOF **1**/PVP-50 composite membrane is more economic than Nafion® 117 membrane.

[1] S. K. Kamarudina, F. Achmada, W. R. W. Dauda, Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices, *International Journal of Hydrogen Energy*, **2009**, 34, 6902-6916.

[2] E. E. Unverena, T. Erdogana, S. S. Çelebib, T. Y. Inan, *International Journal of Hydrogen Energy*, **2010**, 35, 3736–3744.