Electronic Supplementary Information

A Novel Route for Preparing Highly Proton Conductive Membrane materials with Metal-Organic Frameworks (MOFs)

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1 Experimental

1.1 Materials

Sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO) (Sulfonation degree: 28.6%) in Na⁺ form is kindly supplied by Tianwei Membrane Co. Ltd., Shandong of China. Dimethyl aminoterephthalate (99%) is acquired from Alfa Aesar. The other reagents, including ferric chloride hexahydrate (FeCl₃·6H₂O, 99%), N-methyl-2-pyrrolidone (NMP, \geq 98.0%), N, N-dimethyl formamide (DMF, \geq 99.5%), dichloromethane (DCM, \geq 99.5%), trichloromethane (TCM, \geq 99.0%), thionyl chloride (\geq 99.0%), ninhydrin(\geq 95%), ethanol (99.9%) and HCl are all of analytical grade and commercially obtained from domestic chemical reagents companies. Deionized water was used throughout.

1. 2 Synthesis, Purification and activation of Fe-MIL-101-NH₂

The MOFs, 3D-{[Fe₃ (O) (BDC-NH₂)₃(OH) (H₂O) ₂] \cdot pH₂O}, BDC=benzene -1, 4 -dicarboxylate (terephthtalate), designated as Fe-MIL-101-NH₂, MIL (Materials of Institut Lavoisier). Fe-MIL-101-NH₂ is synthesized from a mixture of dimethyl aminoterephthalate (323.8mg, 1.5mmol) in 15ml of DMF with a solution of FeCl₃·6H₂O (540.6mg, 2.0mmol) in 15ml of aqueous solution of DMF; the mixture is transferred to the Teflon line in a hydrothermal autoclave which is heated for 24 h at 150° C and cooled afterwards slowly to room temperature over a time period. The mixture is then isolated from the autoclave and the solid separated from the solution through filtration, washed with three times DMF and then three times dichloromethane. After drying under vacuum at room temperature overnight, a powder consisting of crystals of Fe- MIL-101-NH₂ was obtained.

However, it is hard to obtain crystalline Fe- MIL-101-NH₂, because of the presence of organic or inorganic impurities in the pores as well as outside pores. To eliminate most of the carboxylic acid, the product is washed in hot DMF(100°C, 8h, 2time) and in hot EtOH(80° C, 8h, 2times), filtered off, and dried overnight in an oven at 75 °C.

In order to better for the next step, the Fe- MIL-101-NH₂ is activated by guest exchange and removal with CHCl₃. The crystal is then soaked in 10 mL of CHCl₃ for three days with fresh CHCl₃ added every 24 h. After 3 days of soaking the crystals are stored in the last CHCl₃ solution until needed.

1. 3 Preparation of mixed matrix membranes

The Sulfonated Poly (2, 6-dimethyl-1, 4-phenylene oxide) (SPPO) is dissolved in DMF and the chlorosulfonylation reaction of SPPO is carried out under reflux of a DMF solution containing of thionyl chloride. The chlorosulfonylation of SPPO (PPO-SO₂Cl) is obtained by filtration, washed with water. The Hinsberg reaction is realized into PPO-SO₂Cl of NMP solution blending with 2, 4, 6, 8 and 10 wt% of Fe-MIL-101-NH₂ and NaOH solution (0.1mol/L). To achieve a homogeneous dispersion of the MOFs particles the solution is treated for 40 min in ultrasonic bath (KUDOS Ultrasonic 310, 53Hz), afterwards it stirred 3d to prepare a uniform membrane solution.

The membranes are formed by casting the membrane solution onto a flat glass surface. All the casting equipment was placed on top of table an adjustable drying apparatus to assure horizontal alignment during the membrane formation and then evaporating the solvent at 60°C for 24 h. To prevent membrane contamination by dust particles during the evaporation of the solvent, evaporation pan were used to cover the glass. As soon as all solvent was evaporated, the membrane was removed from the glass surface by flushing with distillated water. The membrane was finally dried in a vacuum oven at 60°C. In addition, the pure polymer membranes were dried in the same way.

All the resulting membranes are treated with 1M HCl aqueous solution for 24 h at room temperature. Finally, the membranes are washed with deionized water and stored in deionized water before use.

2 characterization methods

2.1 Morphology analyses



Fig.S1 SEM images of Fe-MIL-101-NH₂ microcrystals(a) and of surface hybrid membrane (b). Scanning electron microscope (SEM, FEI-Sirion200) was applied to investigate the morphology. It is shown that the Fe-MIL-101-NH₂ crystals are of the octagonal structure in Fig.S1.

2. 2 X-ray diffraction analyses



Fig.S2 Power XRD for Fe-MIL-101-NH₂ (black) compared to that of the simulated framework for MIL-101(Cr) (gray).¹



Fig.S3 Powder X-ray diffraction patterns of the pure Fe-MIL-101-NH₂(black), Fe-MIL-101-NH₂ soaked in water for one day(red), Fe-MIL-101-NH₂ soaked in CHCl₃ for three days(blue) and hybrid membranes with the loading of 10%(green).

The samples were characterized by X-ray powder diffraction (XRD) with a Japan Rigaku Dmax X-ray diffractometer equipped with graphite monochromatized high-intensity Cu-K α radiation (λ =1.54178 Å).

A typical XRD pattern of the Fe-MIL-101-NH₂ is shown in Fig.S2 together with the simulated XRD pattern for MIL-101(Cr).¹ The comparison between the experimental and the simulated XRD patterns demonstrates the formation of a pure phase Fe-MIL-101-NH₂ under the applied synthesis conditions.

The powder XRD of Fe-MIL-101-NH₂ soaked in water and CHCl₃ wee shown in Fig.S3. The peaks shape and position of the XRD is found similar to pure phase Fe-MIL-101-NH₂, it make sure that the crystalline Fe-MIL-101-NH₂ structure is still there after immersing in water and CHCl₃.

The powder XRD of the hybrid membrane with loading of 10% Fe-MIL-101-NH₂ is depicted in Fig.S3. Although the crystal of Fe-MIL-101-NH₂ is wrapped by PPO-SO₂Cl, the structure of MOFs is similar to as-synthesized material.



2.3 The Fourier transforms infrared analyses

Fig.S4 IR spectrum of Fe-MIL-101-NH₂

The FT-IR spectra were measured on a Bruker Vector-22 FT-IR spectrometer at room temperature. The IR-spectrum of the Fe-MIL-101-NH₂ is showed in Fig. S4.

In the IR-spectrum of Fe-MIL-101-NH₂ synthesized from DMF, a band at 1659 cm^{-1} shows the presence of DMF molecules. Bands at 1576 and 1432 cm^{-1} correspond

to the symmetric and antisymmetric C-O stretching vibrations of carboxylates and indicate the presence of 2- aminoterephthalate anions in the structure.²

The doublet at 3441 and 3379 cm⁻¹ corresponds to the asymmetrical and symmetrical stretchings of the amine moieties.^{3, 4} These absorptions seem to be formed by the contribution of two different bands, pointing at two amine species in the framework.

When focusing on the lower frequency region, in spite of the abundance of vibrations in this area, two other characteristic bands of the amino group can be perceived: the N-H bending (scissoring) vibration observed as a shoulder at 1623 cm⁻¹ and the C-N stretching absorption distinctive of aromatic amines at 1339 cm⁻¹.⁴



Fig.S5 IR spectrum of (a) SPPO, (b) PPO-SO₂Cl and (c) mixed matrix membranes

The spectrum for SPPO (a) is characterized by a band at 1192 cm⁻¹ corresponding to the -S=O bond, and those corresponding to $-SO_3^-$ groups were observed at 1026 and 1066 cm⁻¹. After chlorosulfonation of the SPPO with thionyl chloride, a new band corresponding to $-SO_2Cl$ group appeared at 1374cm⁻¹ on the spectrum for PPO-SO₂Cl (b). This observation is in agreement with previous FTIR studies on chlorosulfonated membranes.⁵ After reaction with Fe-MIL-101-NH₂, the $-SO_2Cl$ band totally disappeared and a new band at 1170cm⁻¹, corresponding to

 $-SO_2NH-$ group, confirmed the acid-amine bonding about the spectrum for mixed matrix membranes.⁵ For the aminated, the $-SO_3^-$ bands at 1025 and 1062cm⁻¹ are observed again together with a shift of the -S=O band from 1192 to 1202 cm⁻¹.



2.4 Thermogravimetric analyses

Fig.S6 TGA of Fe-MIL-101-NH₂ and hybrid membrane under nitrogen atmosphere.

The thermal behaviors of Fe-MIL-101-NH₂ determined were by thermo-gravimetric analyzer (TGA-50H, Shimadzu) in 20 ml/min nitrogen atmosphere with a heating rate of 10°C/min (Fig. S6). A crystalline sample of Fe-MIL-101-NH₂ was heated from 50 to 600°C. Three weight-loss steps were observed about MOFs: the first, corresponding to about 10%, occurs in the range 50-100°C relates to the departure of water on the surface of the sample; the second (10 %) is due to the sample releases of water followed by desorption of some DMF between 150 and 280°C; the last one (55%) is due to the departure of OH groups and the decomposition of the framework from 290 to 400°C (calculated: %). The framework decomposes at temperatures above 280°C, in line with the highly stable Fe unfunctionalized counterpart, that decomposes at $\approx 290^{\circ}$ C.

The weight loss below 100°C is attributed to the loss of moisture. In this stage,

MOFs loses more weight than MMMs due to its high hydrophilicity.⁶ The next stage of weight loss is from 200°C to 350°C and is ascribed to the decomposition of sulfamide groups of MMMs. The weigh loss of MMMs starts at 200°C and its main decomposition peak is around 300°C. Considering the poor thermal stability of SPPO-Na, the MOFs—PPO-SO₂Cl chemical interaction imparts better thermal stability to the other sulfonic acid groups; moreover, its decomposition temperature is even higher than the MOFs.

2.5 Determination of free NH₂ group in hybrid membrane

To the best of our knowledge, the determinations of free NH_2 after the formation of membranes have the following ways:

(a) Ninhydrin reation.

The ninhydrin and free NH₂ group in Fe-MIL-101-NH₂ happens the color reaction in heating conditions. This reaction is very sensitive. According to the color depth of reaction product (color solution absorption rate and the content of free amino is proportional in a certain concentration range), the contents of free amino in the hybrid membrane can examine with colorimetry and spectrophotometer. We can get molar number of free amino in membrane with different amount of MOFs by this method, if the solution is color change.

In our experiments, the hybrid membrane with the loading of 10% the Fe-MIL-101-NH₂ was soaked in ninhydrin solution at 60° C for 3 day. We considered that the free NH₂ did not exist in the Fe-MIL-101-NH₂ after the formation of membranes, because there is no obvious color change in the solution.

(b) FT-IR spectrometry.

Within the region of 3250cm⁻¹~3500cm⁻¹ in FTIR spectra, there are two peaks of stretching vibration assigned to the primary amine, only one peak assigned to the secondary amine and no peak assigned to the tertiary amine because of the existence of the nitrogen hydrogen bond.

In our experiments, there are two peaks in the region of 3250cm⁻¹~3500cm⁻¹ from FT-IR of the pure Fe-MIL-101-NH₂, but there is one peak in FT-IR of the hybrid

membrane with the loading of 10% the Fe-MIL-101-NH₂, so it is not the free NH₂ in Fe-MIL-101-NH₂ after the formation of membranes(Fig.S7). As a result of this experiment, we can infer the other hybrid membrane with the low loading of MOFs do not possess free amino group.



Fig.S7 the FT-IR of the pure Fe-MIL-101-NH₂(black) and the hybrid membrane with the loading of 10% Fe-MIL-101-NH₂(red).

2.6 Ion exchange capacity (IEC)

Initially, the membrane sample in the H^+ form was soaked in 0.5 mol/l NaCl solutions for 24 h. Then, the sample was taken out and washed with deionized water. The water used for washing was collected and mixed with the remaining solution. This mixture solution was titrated with a 0.01mol/l NaOH standard solution. The IEC value was calculated according to the following equation:

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{W_{drv}}$$

where w_{dry} is the dry weight of the sample in the H⁺ form, V_{NaOH} is the titrated volume of the NaOH solution, and C_{NaOH} is the concentration of the NaOH solution (0.01mol/L).

2.7 Water uptake

The membrane sample in the H^+ form was soaked in deionized water at room temperature for 24 h. After becoming completely swollen, the sample was taken out, wiped with a tissue paper to remove the excess water, and weighed immediately. The wet sample was dried at 50°C under vacuum until the constant weight was reached. The water uptake W was calculated according to the following equation:

$$W = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where w_{wet} and w_{dry} are the wet and dry weights of the membrane, respectively.

A series of blend membranes were prepared: the membranes prepared by blending SPPO with Fe-MIL-101-NH₂. As a reference, a membrane was also prepared with SPPO by following the same procedure. The main properties of the membranes, such as IEC and water uptake are listed in Table S1.

As a result, some sulfonic acid groups were reacted during the subsequent chlorosulfonation reaction. This may be the reason why the hybrid membranes have lower IEC values than SPPO blank (SM-0). Meanwhile, as the content of MOFs increases, IEC value decreases. This is because MOFs does not possess ion exchange capability. When its content reaches some extent, IEC value decreases due to a decrease in the relative weight ratio of SPPO. The water uptake has the opposite changing trend as IEC, which is related to the MOFs of hydrophilicity.⁶

Membrane	Number	MOFs (wt %)	IEC (meq/g)	Water uptake (%)			
	SM-0	0	2.01	44.7			
	SM-2	2	1.97	46.6			
	SM-4	4	1.93	48.4			
SPPO-MOFs	SM-6	6	1.87	50.7			
	SM-8	8	1.85	52.5			
	SM-10	10	1.82	55.1			

Table S1 Composition and properties of the membranes.

2.8 Proton conductivity of membranes

The proton conductivity of the membrane was measured using the normal four-point probe technique.^{7, 8} The membrane samples were in the hydrogen form and fully hydrated. The impedance was determined using an Autolab PGSTAT 30 (Eco Chemie, Netherlands) set at galvanostatic mode with an ac current amplitude of 0.1mA over the frequency range from 1MHz to 50 Hz. Using a Bode plot, the frequency region over which the impedance had a constant value was recognized, and the resistance was then obtained from a Nyquist plot. The proton conductivity is calculated according to the following equation:

$$\kappa = \frac{L}{RWd}$$

where R is the obtained membrane resistance, L is the distance between potential-sensing electrodes, and W and d are the width and thickness of the membrane, respectively.

2.9 Proton conductivity of pure Fe-MIL-101-NH₂

For the electrical conductivity measurements , the pellets of Fe-MIL-101-NH₂ with a diameter of 5 mm and thickness of 1 mm were obtained by uniaxially cold pressing (600MPa) for 2min. AC measurements were performed with impedance at frequencies ranging between 100000Hz and 1Hz (AC voltage of 0.2V, nickel electrodes) . Fig.S8 shows the Nyquist plot of the impedance spectrum acquired from the pure Fe-MIL-101-NH₂. The impedance spectra were analyzed using the commercial software ZSimpwin. The proton conductivity is calculated according to the following equation:

$$\kappa' = \frac{L'}{R'S'}$$

where R' is the obtained pure Fe-MIL-101-NH₂ resistance, L' is the thickness of pellets of Fe-MIL-101-NH₂, and S' is the area of the pellet of Fe-MIL-101-NH₂, respectively.

The conductivity associated with the high frequency semicircle is on the order of 2.83×10^{-7} S/cm at 298K in air. The conductivity of the Fe-MIL-101-NH₂ is far less

the hybrid membrane shown in Table S2.



Fig.S8 Impedance Nyquist plot of a spectrum collected from the pure Fe-MIL-101-NH₂

No.	MOFs	Conditions	conductivity	Reference
			(S/cm)	
1	PCMOF-3	298K,	3.5×10 ⁻⁵	J. Am. Chem. Soc.,
		98% RH		2010, 132 , 14055.
2	MIL-53(Fe)-(COOH) ₂	298K,	2.0×10 ⁻⁶	
		95% RH		J. Am. Chem. Soc.,
		353K,	0.7×10 ⁻⁵	2011, 133 , 2034.
		95% RH		
3	$(NH_4)_4[MnCr_2(ox)_6]\cdot 4H_2O$	298K,	1.1×10 ⁻³	J. Am. Chem. Soc.,
		98% RH		2011, 133 , 15328.
4	$[Zn(d-L_{Cl})(Cl)](H_2O)_2$	304K,	4.45×10 ⁻⁵	J. Am. Chem. Soc.,
		98% RH		2011, 133 , 17950.
5	$\begin{array}{l} Mg_2(dobdc) \cdot 0.35 LiO^i Pr \cdot 0.25 LiB \\ F_4 \cdot EC \cdot DEC \end{array}$	300K	3.1×10 ⁻⁴	J. Am. Chem. Soc.,
				2011, 133 , 14522.
6	Cucurbit[6]uril	298K,	1.1×10 ⁻³	Angew. Chem. Int. Ed.,
		98% RH		2011, 50 , 7870.
7	(b-PCMOF2(Tz) _{0.45})	423K	5.0×10^{-4}	Nat. Chem., 2009, 1, 705.
8	$[Al(\mu_2-OH)(1,4-ndc)]_n$ >imidazole	393K	1.0×10^{-5}	Nat. Mater., 2009, 8, 831.
9	[Al([D6]ndc)(OH)] _n >Histamine	423K	1.0×10 ⁻³	Angew. Chem. Int. Ed.,
				2011, 50 , 11706.
10	HKUST-1	298K,	K, anol 1.5×10 ⁻⁴ or	I Am Chem Soc
		methanol		2012 134 51
		vapor		2012, 137, 31.

Table S2: Comparison of proton conductivity with other MOFs

11	$[Zn(H_2PO_4)_2(TzH)_2]_n.$	423K	1.2×10^{-4}	J. Am. Chem. Soc., 2012, 134 , 12780	
12	Fe- MIL-101-NH ₂ -SPPO	363K, 98% RH	2.5×10 ⁻¹	this work	
13	Pure Fe- MIL-101-NH ₂	298K	1.0×10^{-1} 2.8×10^{-7}		

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