Electronic Supporting Information

Method for increasing permeability for O_2/N_2 separation with mixed-matrix membranes of water-stable MIL-101 and polysulfone

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1 Experimental

1.1 Materials

Chromium nitrate nonahydrate ($Cr(NO_3)_2{\cdot}9H_2O$, 99%) and hydrofluoric acid (analysis grade) were obtained from Acros Organics. Benzene-1,4-dicarboxylic acid (H_2BDC, 99%) was acquired from Aldrich. Dichloromethane (DCM, >99.9%), N,N-dimethylformamide (DMF, 99.9%) and Ethanol (99.9%) were purchased from Prolabo. Polysulfone (PSF) Ultason S 6010 Natural was provided by BASF AG, Ludwigshafen, Germany. O_2 and N_2 gas were supplied by Air Liquide (Germany) and used as received (purity 99.99%).

1.2 Synthesis of MIL-101

3D-$\{[Cr_3(O)(BDC)_3(X)(H_2O)_2]\ {\cdot}{\sim}25H_2O\}$, BDC = benzene-1,4-dicarboxylate (terephthtalate), X = F or OH depending on synthesis conditions, MIL-101 was synthesized according to the previously reported reported procedure.[1] A typical synthesis involves a solution containing chromium(III) nitrate $Cr(NO_3)_3{\cdot}9H_2O$ (400 mg, $1{\cdot}10^{-3}$ mol), $1{\cdot}10^{-3}$ mol of hydrofluoric acid, 1,4-benzene dicarboxylic acid H_2BDC (164 mg, $1{\cdot}10^{-3}$ mol) in 5 ml H_2O; the mixture is transferred to the Teflon line in a hydrothermal autoclave which is heated for 6 h at 210°C and cooled afterwards slowly to room temperature over a time period of 8 h. The mixture was then isolated from the autoclave and the solid separated from the solution through centrifugation (4200 U/min for 50 min). A significant amount of recrystallized terephthalic acid is present. To eliminate most of the carboxylic acid, the product was redispersed and centrifuged two times in DMF (20 ml), one time in ethanol (10ml) and one time in water (10 ml). The final product was then dried at room temperature.

1.3 Preparation of mixed matrix membranes

The polymer (PSF) was dissolved in dichloromethane (CH_2Cl_2) and the solution was filtered through a syringe filter (PTFE membrane, 0.45 µm pore size). 1.25, 1.88 and 2.5 wt% of polymer in CH_2Cl_2 were used. The MOF material (MIL-101) was added to the previously prepared polymer solution, and the obtained dispersion was stirred for one week. 8, 16, and 24 wt% MIL-101 was added to the polymer. To achieve a homogeneous dispersion of the inorganic particles the casting solution was treated for 30 min in ultrasonic bath (ELMA Transsonic 310, 35 Hz), afterwards it was stirred for 30 min again. This cycle was repeated three times. Before casting, the dispersion was kept under stirring for 30 more minutes. The dispersion was cast into metal rings, 7 cm in diameter, which were placed on a flat glass surface. All the casting equipment was placed on top of an adjustable table to assure horizontal alignment during the membrane formation. To prevent membrane contamination by dust particles during the evaporation of the solvent, funnels were used to cover the metal. A paper tissue covered the funnels to avoid contamination. This system also exerts some control on the evaporation rate. As soon as all solvent was evaporated, the membrane was removed from the metal ring and the glass surface by flushing the ring with distilled water. The membrane was finally dried in a vacuum oven at 120 °C and 80 mbar overnight. In addition, the pure polymer membranes were dried in the same way.

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[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, and I. Margiolaki, *Science*, 2005, **309**, 2040.

1.4 Gas permeation experiments

The prepared membranes were used for gas permeation experiments. Single-gas permeabilities were evaluated for O_2 and N_2 using the permeation cell described elsewhere.[2] Before affixing the membrane to the permeation cell, the thickness of the membrane was measured on 10 different points using a micrometer. The gas permeation measurements were performed at steady state conditions using the pressure rise method at 30 °C. The membrane is placed into the cell while the permeate side is evacuated, then the feed side is evacuated too. After that the valve on the feed side is closed and put under defined pressure (e.g. 3 bars) with a single gas (beginning with the slower permeating gas, i.e. nitrogen if oxygen/nitrogen separation is investigated). After pressurizing the feed side for 2 h the permeation measurements can be started. The line between the permeate side and the vacuum pump is closed and the feed pressure adjusted. Since the gas permeates from the feed side through the membrane to the permeate side the pressure there increases. The linear pressure rise is recorded with an x-y printer and used to calculate the permeability P in barrer units (1 barrer = 1×10^{-10} cm^3 (STP) cm/cm^2 s cmHg). Such single-gas measurements are also termed isochoric permeation experiment where the membrane separates a high pressure feed volume from a low pressure permeate volume (R. Adams, C. Carson, J. Ward, R. Tannenbaum, W. Koros, *Microporous Mesoporous Mater.* 2010, **131**, 13–20).

From the single-gas permeabilities the ideal gas selectivity was calculated according to the following equation (1)

$$\alpha_{\mathrm{ideal}\left(\frac{O_2}{N_2}\right)} = \frac{P_{O_2}}{P_{N_2}} \qquad (1)$$

For the pure polymer, four individual membranes with an area of 11.3 cm^2 and thicknesses of about 30 µm were analyzed in gas permeation experiments. In the case of the MMMs, samples with an area of around 11.3 cm^2 and thicknesses between 19 and 60 µm were analyzed.

The unit Barrer is a non-SI-unit in the cgs-system for the gas permeability of thin materials (in honor of the New Zealand chemist Richard M. Barrer (1910-1996), who was a leader in research on the diffusion of gases).

Permeability is defined to be the gas flow rate multiplied by the thickness of the material, divided by the area and by the pressure difference across the material (equation 2). To measure this quantity, the barrer is the permeability represented by a flow rate of 10^{-10} cubic centimeters per second (volume at standard temperature and pressure, 0 °C and 1 atmosphere), times 1 centimeter of thickness, per square centimeter of area and centimeter of mercury difference in pressure.

That is, 1 barrer = 10^{-10} $cm^2 \cdot s^{-1} \cdot cmHg^{-1}$ (equation 3), or, in SI units, 7.5005 x 10^{-18} $m^2 \cdot s^{-1} \cdot Pa^{-1}$.

$$\text{Permeability } (P) = \frac{\text{flow rate x thickness}}{\text{area x pressure difference}} \qquad (2)$$

$$P(\text{barrer}) = 10^{-10}\,\frac{\mathrm{cm^3(STP)\cdot cm}}{\mathrm{cm^2\cdot s\cdot cmHg}} \qquad (3)$$

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[2] J. U. Wieneke and C. Staudt, *Polymer Degradation and Stability*, 2010, **95**, 684.

Table S1 Gas permeation results on PSF membranes containing selected MOFs.[a]

Membrane		**P (O_2) [barrer]**	**P (N_2) [barrer]**	**S (O_2/N_2)**
MOF	**Membrane Thickness (d) [µm]**			
Pure polymer	29.2	1.47	0.25	5.89
MIL-101(Cr)	54.7	2.53	0.47	5.42
MOF-508a(Zn)	52.7	1.65	0.45	3.70
MIL-53(Al)	49.4	1.48	0.35	4.27
MIL-100(Fe)	54.0	2.03	0.35	5.80
MANS-1(Ni)	54.5	1.72	1.1	1.55

[a] experiments performed at 30 °C and 3 bar total feed pressure. PSF + 8wt% MOF P = Permeability, S = Selectivity

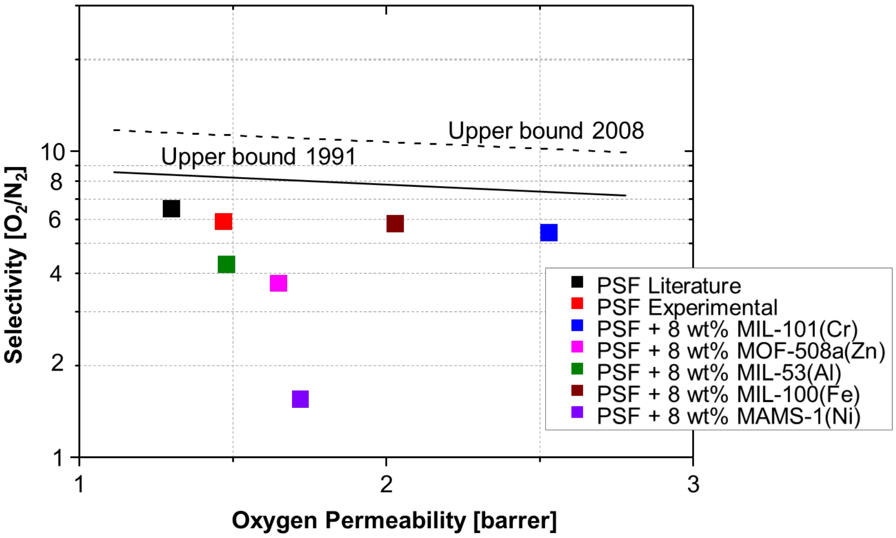

Fig. S1 O_2/N_2 Separation performance of selected MOFs-PSF mixed-matrix membranes. The Robeson upper bounds for polymer performance as defined in 1991[3] and 2008[4] are shown.

Table S2 Gas permeation results on MIL-101-PSF membranes, experiments performed at 30 °C and 3 bar total feed pressure.

Membrane			**P (O_2) [barrer]**	**P (N_2) [barrer]**	**S (O_2/N_2)**
Polymer amount	**MIL-101(Cr) load**	**Membrane thickness (d) [µm]**			
300 mg	***Pure polymer***	29.2	1.47	0.25	5.89
400 mg	*8 wt%*	54.7	2.53	0.47	5.42
	16 wt%	59.2	4.11	0.68	6.02
	24 wt%	60.0	5.25	0.97	5.42
300 mg	*8 wt%*	31.4	2.51	0.47	5.33
	16 wt%	35.1	4.60	0.91	5.03
	24 wt%	47.3	5.83	0.89	6.52
200mg	*8 wt%*	19.2	2.91	0.60	4.83
	16 wt%	23.3	4.75	0.96	4.97
	24 wt%	26.2	6.03	1.10	5.49

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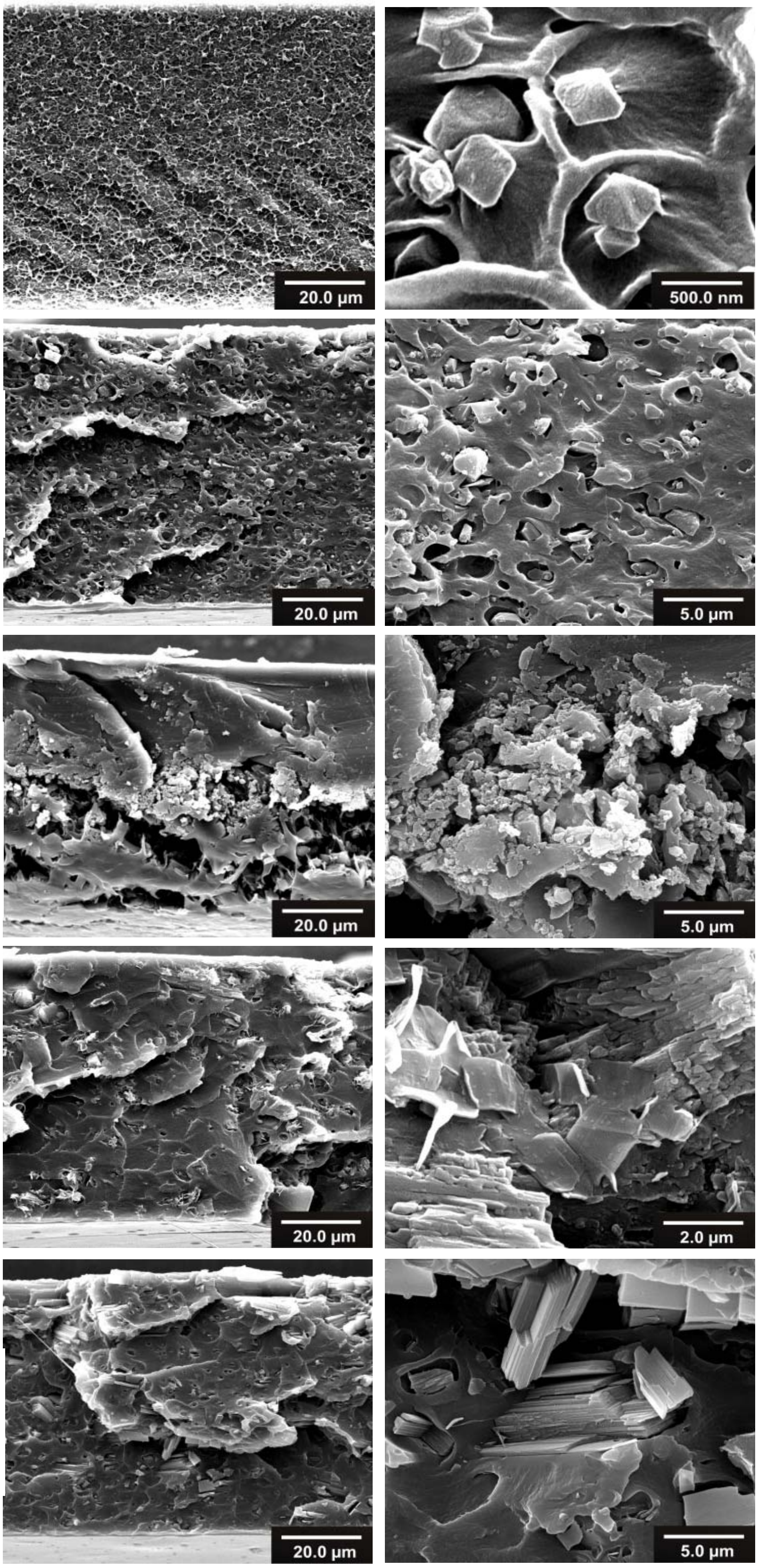
[3] L. M. Robeson, *J. Membrane Sci.*, 1991, **62**, 165.

[4] L. M. Robeson, *J. Membrane Sci.* 2008, **320**, 390.



PSF-MIL-101
MIL-101 particle size
100 – 370 nm

PSF-MIL-100(Fe)
MIL-100(Fe) particle size
450 – 950 nm

PSF-MIL-53(Al)
MIL-53(Al) particle size
conglomerate, no
individual particles
discernable

PSF-MOF508a (Zn)
MOF508a particle size
540 nm – 2.3 µm with
agglomerate

PSF-MAMS-1(Ni)
MAMS-1 particle size
640 nm – 5.1 µm with
agglomerate

Fig. S2 SEM cross-sections of MOF-PSF membranes based on 400 mg of PSF with 8 wt% loadings of selected MOFs (as indicated).

2 Comment on gas permeation in MMMs

If impermeable inorganic additives are used for the preparation of MMMs in most cases the path length of the major component is reduced more than the one of the minor component leading to an improvement of selectivity compared to the pure polymer material.

Successful preparation of flat sheet MMM with MOFs has been shown for a commercially available polyimide (matrimid) and Cu-BPY-HFS (BPY = 4,4'-bipyridine, HFS = hexafluorosilicate).[5] For the O_2/N_2 separation the oxygen permeability could only slightly be increased from 1.46 barrer (pure polymer) to 3.06 barrer (MMM with 40 wt% of Cu-BPY-HFS), whereas the selectivity of 6.64 did not change much (Table 1, Fig. S3). A somewhat stronger increase of permeability has been found for MMMs prepared with MOF-5 and matrimid. If 30wt% of MOF-5 is used for the preparation of a MMM, the oxygen permeability increased from 1.9 to 4.12 barrer (Table S3, Fig. S3). Again the oxygen/nitrogen selectivity of 7.60 changed by less than 5%.[6] Still for economically feasible MMMs a permeability of 6 would be needed. Similar effects were also observed for different polymers used as matrix. An increase in oxygen permeability, approximately 20%, with a very small increase in selectivity (from 6.56 to 6.84) was found for a MMM membrane consisting of polyvinyl acetate (PVAc) and copper terephthalate (CuTPA).[7] Furthermore it has been demonstrated recently that MMMs can be produced as hollow fibers using a polyimide (PMDA-ODA) and $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate).[8] The production process of hollow fibers is very versatile with regard to additives and highly important for large scale applications. The reason for this is that hollow fiber modules obtain ratios of membrane area to module volume of up to 6000 m^2/m^3.

Table S3 Compiled gas permeation data of mixed-matrix membranes with MOFs from literature.

Polymer	**MOF**	**MOF (wt-%)**	**P (O_2) [barrer]**	**P (N_2) [barrer]**	**S (O_2/N_2)**	**Ref.**
Matrimid 5218	Cu-bpy-hfs	*0 wt%*	1.46	0.22	6.64	5
		10 wt%	1.44	0.24	6.04	
		20 wt%	1.77	0.31	5.76	
		30 wt%	1.98	0.31	6.33	
		40 wt%	3.06	0.49	6.27	
Matrimid 5218	MOF-5	*0 wt%*	1.90	0.25	7.6	6
		10 wt%	2.30	0.28	8.4	
		20 wt%	2.90	0.40	7.2	
		30 wt%	4.12	0.52	7.9	
PSF	Cu-btc	*0 wt%*	1.7	0.4	4.3	9
		5 wt%	1.1	0.3	3.7	
		10 wt%	2.5	1	2.5	
PSF	$Mn(HCOO)_2$	*0 wt%*	1.5	0.3	5	9
		5 wt%	1	0.3	3.3	
		10 wt%	1.1	0.2	5.5	

PSF: Polysulfone

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[5] Y. Zhang, I. H. Musselman, J. P. Ferraris and K. J. Balkus Jr., *J. Membrane Sci.*, 2008, **313**, 170.

[6] E. V. Perez, K. J. Balkus Jr., J. P. Ferraris and I. H. Musselman, *J. Membrane Sci.*, 2009, **328**, 165

[7] R. Adams, C. Carson, J. Ward, R. Tannenbaum and W. Koros, *Microporous and Mesoporous Mater.*, 2010, **131**, 13.

[8] J. Hu, H. Cai, H. Ren, Y. Wei, Z. Xu, H. Liu and Y. Hu, *Ind. Eng. Chem. Res.*, 2010, **49**,12605.

[9] A. Car, C. Stropnik and K-V. Peinemann, *Desalination*, 2006, **200**, 42.

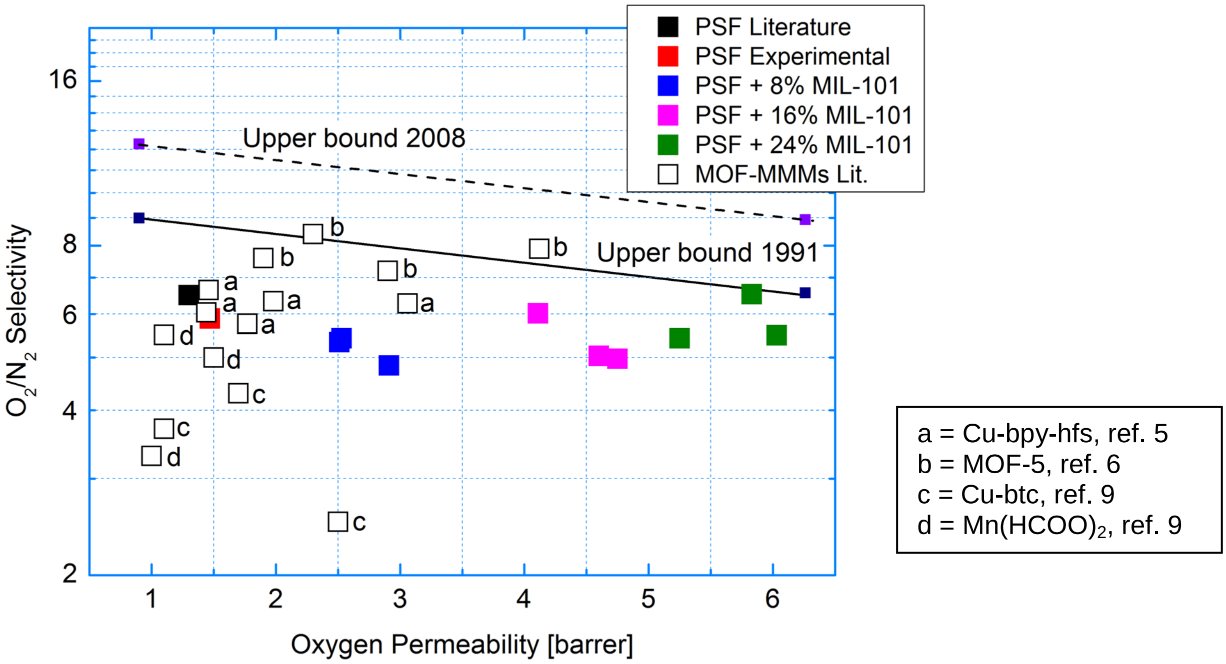

Fig. S3 O_2/N_2 Separation performance of MIL-101-PSF mixed-matrix membranes, compared with the compiled data on MOF containing mixed-matrix membranes. Three blue, pink and green points each present the results for different membrane thicknesses for the respective PSF-MIL-101 membranes with different weight loads (cf. Table S2). The thickness of MMMs with MOFs in literature was not given (cf. Table S3). Letter a-d refer to the literature numbers for other MOF-MMMs (see legend). The upper bounds for polymer performances as defined by Robeson in 1991[3] and 2008[4] are shown.

3 Further membrane characterization methods

X-ray diffraction analyses were carried out on a PANalytical X'Pert PRO diffractometer using Cu $K\alpha_1/\alpha_2$ radiation with $\lambda = 1.5418$ Å and a Ni-foil as K_β-filter.

Nitrogen and oxygen sorption were measured at 77K using a Quantachrome Autosorb iQ gas sorption analyzer. Ultra high purity (UHP, grade 5.0, 99.999%) nitrogen, oxygen and helium gases were used; the latter was used for performing cold and warm free space correction measurements. MIL-101 BET surface area (3239 m^2/g) and pore size were calculated using sample weights after degassing for 2 h at 120°C using the built-in oil-free vacuum system of the instrument (ultimate vacuum $<10^{-8}$ mbar).

To acquire **scanning electron microscopy (SEM) images**, the MIL-101 nanocrystals and the membranes cross-sections were coated with gold. The coated samples were then imaged using an ESEM Quanta 400 FEG SEM equipped with a secondary electron (SE) detector and operated at 20 keV.

The high crystallinity and framework type of the synthesized particles were verified by powder X-ray diffraction (XRPD) analysis (Fig. S4). Also, the polymeric matrix does not alter the crystalline pattern of MIL-101 (Fig. S4). Oxygen and nitrogen sorption isotherms of MIL-101 particles, as well as pore volumes and BET surface areas calculated from the isotherms, are shown in Fig. S5. As-synthesized MIL-101 samples have high pore volumes and surface areas close to samples in literature reports.[1]

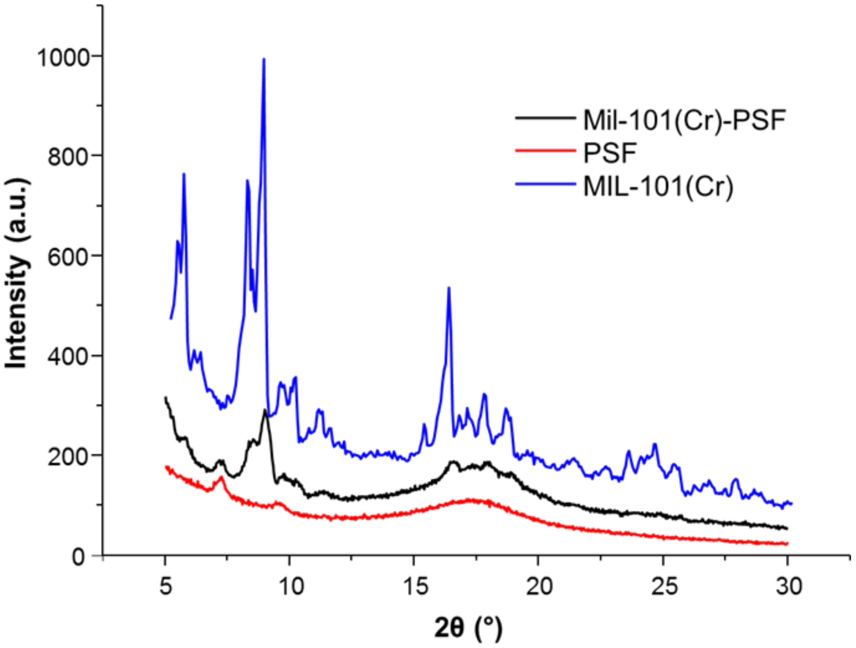

Fig. S4 X-ray powder diffraction pattern; (black: 16% MIL-101-PSF membrane of 59 μm thickness).

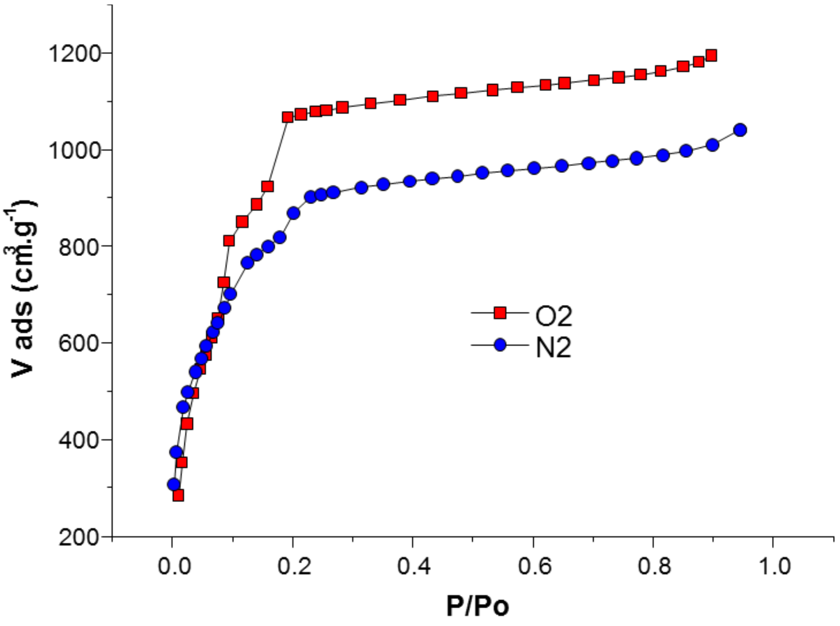

Fig. S5 O_2 and N_2 adsorption isotherms of a synthesized and activated MIL-101 sample; These sorption isotherms were fitted by the Brunauer–Emmett–Teller (BET) and Langmuir (L) equations (at $p/p_0 = 0.06 – 0.16$) to give S_{BET} (3239 m^2/g) and S_L (4617 m^2/g) surface areas and a total pore volume of 1.61 cm^3/g.