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1 **Preparation of HKUST-1/PEI mixed-matrix membranes: adsorption-diffusion**
2 **coupling control of small gas molecules**

3

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19

20 **Abstract**

21 HKUST-1 nanocrystals (50-80 nm) were homogeneously dispersed in a
22 polyetherimide (PEI) polymer matrix. The use of a capping agent (sodium formate)

1 prevented the agglomeration of HKUST-1 nanocrystals in the casting solution. The
2 highly dispersed HKUST-1 nanocrystals were found to strengthen the interactions
3 with the PEI and minimize the interfacial holes by providing more accessible Cu
4 unsaturated metal sites for the C=O bonds on the five-membered rings of the PEI
5 matrix. The PEI membrane loaded with 30 wt. % HKUST-1 nanocrystals
6 (30-N-HKUST-1/PEI) showed a high H₂ permeability (193.3 Barrer at 25 °C under
7 1.5 bar) and good ideal H₂/CH₄ and H₂/CO₂ selectivity factor of 101.7 and 20.6 in a
8 single gas test, respectively. In the gas mixture test, it also showed a good separation
9 performance, i.e., a H₂/CH₄ and H₂/CO₂ selectivity factor of 82.4 and 16.5 was
10 measured, respectively. The 30-N-HKUST/PEI membrane was tested in a gas mixture
11 at different temperatures (25 - 100 °C), different pressures (0 - 3 bar) and various time
12 (5 - 72 h) to study the performance in more realistic conditions thus to be further
13 considered in the separation of syngas.

14

15 **Keywords:** HKUST-1 nanocrystals; capping agent; mixed-matrix membrane;
16 interfacial defects; gas separation

17

1 **Introduction**

2 Metal organic frameworks (MOFs)/polymer mixed-matrix membranes (MMMs)
3 have recently attracted much attention [1, 2] thanks to their growing interest for
4 challenging gas separation/purification processes. These MMMs combine the
5 advantages of MOFs' excellent physicochemical features with the high selectivity,
6 desirable mechanical properties and economical processability of the polymer matrix
7 [3, 4]. MOFs are made from an assembly of metal ions and organic linkers, which
8 allow them to interact favorably with the bulk polymeric chain, thus achieving higher
9 compatibility and avoiding the formation of micro-gaps [5, 6]. It is critical to control
10 the noncovalent interactions and covalent bonds between the filler and polymer
11 during the synthesis step in order to obtain a homogeneous dispersion within the
12 polymeric matrix [7-9]. Adequate solvent dispersion and slight mechanical force is
13 usually sufficient to avoid large agglomeration of MOF crystals in the suspension.
14 Another method, which has been proven to effectively enhance the overall dispersion,
15 consists of using MOF composites or MOFs modified by long-chain organic
16 compounds as fillers. Finally, fine tuning of the particle morphology is also of
17 importance for MOF-based membranes. MOF nanosheets [10], nanorods and
18 nanoparticles [11] are often preferred because they provide larger interfacial areas at
19 the MOF-polymer boundary interface, ultimately allowing a better integration.

20 It is important to improve the compatibility of the filler and the polymer matrix.
21 One should not forget that the core of a MOFs-MMMs membrane process is the
22 membrane material itself. Selecting the ideal MOF/polymer pair for a given
23 separation process (e.g., hydrogen separation and purification) is not straightforward
24 and include several parameters to be considered such as the durability, the mechanical
25 integrity at operating conditions as well as the productivity and separation efficiency

1 to name only a few. Ultimately, the separation performance is always limited by the
2 “trade-off” phenomenon between gas selectivity and permeability [12]. As
3 summarized in Table. 1, numerous strategies have already been developed to improve
4 MOFs-MMMs performance. These pioneering studies include the incorporation of
5 MOFs with small pore size and high gas selectivity to fabricate MOFs-MMMs
6 including PIM-1, 6FDA, Matrimid, PSf and PEI. Compared with the commercially
7 available Matrimid and polyetherimide (PEI) membranes, the PIM-1 and 6FDA
8 exhibit high permeability, but they do require expensive polymers that may hindered
9 their industrial potential [13-17]. Therefore, cheap commercial polymers such as PEI,
10 Matrimid and PSf appear as more attractive options for membrane separation
11 processes, especially considering their exceptional chemical and physical properties.
12 However, these polymers suffer from a low permeability. Here also, even if the
13 combination of commercial polymers and MOFs can greatly improve this latter point,
14 it remains that the choice of optimal filler and polymer materials is not really
15 predictable and still highly relies on tedious trial and errors strategies [18-25].
16 Furthermore, several critical aspects regarding the design of MOFs hybrid membranes
17 for an optimal gas separation mechanism, including solution-diffusion where
18 performance is dominated by the polymer, size screening where fillers with small pore
19 size regulate the performance, and Knudsen diffusion in which the large pore of the
20 polymer and the filler control the separation process have been put forward and
21 studied [3]. However, due to an insufficient characterization of the real pore structure
22 and pore size distribution of experimental MOFs-MMMs, the relationship between
23 structure and performance is not yet well understood and more research is urgently
24 needed.

25 Herein, we propose a novel homogeneous MOFs-MMMs membranes based on

1 the combination of HKUST-1 nanocrystals and PEI. PEI, commercially known as
2 ULTEM, is a high-performance thermoplastic polymer with imide, isopropylidene
3 and ether groups [26, 27]. It is cheap, has a good chemical and heat resistance as well
4 as a good processability. These features make it very suitable as a polymer matrix.
5 However, as said above, membranes made from PEI polymers have a low
6 permeability, far below the acceptable permeation performance for versatile operating
7 conditions. To overcome this issue, inspired by previous studies on the high
8 permeability of HKUST-1 in liquid separation [28, 29], we propose the addition of
9 HKUST-1 fillers. It is a highly permeable MOF with a unit structure made of four
10 carboxylic acid bridge forming a paddle-wheel structure. The main pore size is about
11 9 Å and its open three-dimensional architecture is expected to improve substantially
12 the permeability of PEI membranes in gas separation. Meanwhile, the high adsorption
13 CO₂ and CH₄ in of HKUST-1 is beneficial for selectivity improvement. Of particular
14 importance, the Cu unsaturated metal sites of the MOF should favor the C=O bonds
15 on the five-membered ring of the PEI polymer matrix, resulting in improved
16 compatibility and homogeneity. HKUST-1 nanocrystals were prepared with the
17 addition of a capping agent (sodium formate) which act as a chemical linker and
18 prevent the agglomeration in suspension [30]. After sonication and stirring, the
19 resulting highly dispersed HKUST-1 nanocrystals are thus uniformly dispersed in the
20 Polyetherimide (PEI) polymer matrix. Finally, the MMM was scrapped with an
21 automatic coating machine. The MMMs show high H₂ permeability and promising
22 H₂/CO₂ and H₂/CH₄ selectivity. This behavior is attributed to (i) the controlled and
23 homogeneous dispersion of HKUST-1 nanocrystals in PEI, and (ii) the favorable
24 electrostatic interactions between HKUST-1 and PEI, which reduce the interface
25 defects.

1

2

3 **Table 1.** State-of-the-art studies combining MOFs with polymer matrices.

Polymer	MOF				Permeability (Barrer)	Selectivity	ref	
	Name	Pore size (nm)	Particle size	Loading (wt %)				
PIM-1	MOF-74	1.1	10-15 μm	20	11469.0 (H ₂)	$\frac{21269 (\text{CO}_2)}{1114.0 (\text{CH}_4)}$	$\frac{0.54}{10.3}$	13
	ZIF-8	0.34	20-60 nm	28	10650.0 (H ₂)	$\frac{17050 (\text{CO}_2)}{1440 (\text{CH}_4)}$	$\frac{0.62}{7.4}$	14
6FDA-DAM	ZIF-8	0.4-0.42	50-80 nm	23.8	899 (H ₂)	41.2 (CH ₄)	21.8	15
6FDA-Durene	ZIF-71	0.42	< 100 nm	30	4533.0 (H ₂)	$\frac{7750.0 (\text{CO}_2)}{813.0 (\text{CH}_4)}$	$\frac{0.59}{5.6}$	16
6FDA-TP	ZIF-90	0.35	60-105 nm	50	179 (H ₂)	$\frac{63.0 (\text{CO}_2)}{1.8 (\text{CH}_4)}$	$\frac{2.8}{99.4}$	17
Matrimid 5218	ZIF-8	0.34	50-150 nm	60	35.8 (H ₂)	0.1 (CH ₄)	358.2	18
	ZIF-8	0.34	\approx 60 nm	20	56.5 (H ₂)	0.4 (CH ₄)	157	19
	MIL-53	0.85	nanoscale	37	103.0 (H ₂)	1.1 (CH ₄)	93.6	20
	MOF-5	0.87	100 nm	30	53.8 (H ₂)	$\frac{20.2 (\text{CO}_2)}{0.5 (\text{CH}_4)}$	$\frac{2.7}{119.6}$	21
Psf	MCM-41	0.85	2-4 μm	12/4	26.8 (H ₂)	0.4 (CH ₄)	67.0	23
	MIL-53		0.5-1 μm					
PEI	MOF-5	0.867	30-80 nm	5	14.09 (H ₂)	2.3 (CO ₂)	6.13	24
	ZIF-11	0.3	280 nm	20	27.1 (H ₂)	$\frac{6.95 (\text{CO}_2)}{0.32 (\text{CH}_4)}$	$\frac{3.89}{84.68}$	25

4

1 **2. Experiments**

2 *2.1. Materials*

3 Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.0 %-102 %) and sodium formate
4 (HCOONa , $\geq 99\%$) were received from Sinopharm Chemical Reagent Co., Ltd.
5 (China). Trimesic acid ($\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$) and dichloromethane (CH_2Cl_2 , analytical
6 reagent) were provided by Shanghai Aladdin Biochemical Technology Co., Ltd.
7 (China). Polyetherimide (PEI) was supplied by SABIC. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$,
8 analytical reagent) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. (China).
9 All chemicals were used as received without further treatment.

10 *2.2. Synthesis of HKUST-1 nanocrystals and microcrystals*

11 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.09 g) was dissolved in 36.0 mL of deionized water to form
12 solution A. 1,3,5-Benzenetricarboxylic acid (0.63 g) and Sodium formate (0.94 g)
13 were dissolved in another 36.0 mL of ethanol to form solution B. Then, solution B
14 was poured into solution A under magnetic stirring (600 rpm) for 15 min and
15 subjected to crystallization at 120 °C for 3 h. The product (denoted N-HKUST-1) was
16 collected by centrifugation (5000 rpm, 15 min) and re-dispersed in deionized water
17 (three times) and once in ethanol [31]. Finally, the N-HKUST-1 were freeze dried for
18 24 h. They were further dispersed in 5.0 mL of CH_2Cl_2 (MMMs solvent), and then
19 treated prior membrane preparation (10 minutes mechanical stirring and 10 minutes
20 sonication repeated three times). The crystals (denoted CH_2Cl_2 -N-HKUST-1) were
21 collected by centrifugation and freeze dried for 24 h. The synthesis process of
22 HKUST-1 microcrystals is the same as that of nanocrystals, except that the dosage of
23 sodium formate is reduced to 0.31g. Other conditions remain unchanged. The crystals
24 (denoted M-HKUST-1) were collected by centrifugation and freeze dried for 24 h.

1 *2.3. Preparation of HKUST-1-MMMs*

2 The 5.0 wt % polymer solution was prepared by dissolving 0.25 g PEI in CH₂Cl₂ (5.0
3 mL) at room temperature until a clear yellowish uniform viscous solution was
4 obtained. Different loadings of HKUST-1 were then dispersed in the above solution,
5 following three rounds of 10-minute mechanical stirring and 10-minute sonication to
6 ensure uniformity. The casting solutions were further scraped on a clean glass plate
7 with an automatic coating machine to control the membrane thickness. After adequate
8 evaporation of CH₂Cl₂ (at room temperature for 24 h, at 60 °C for 24 h, and at 120 °C
9 for 24 h), the prepared HKUST-1/PEI MMMs were carefully peeled off from the glass
10 plate. The loading amounts of N-HKUST-1 in the MMMs were 10.0 wt. %, 30 wt. %
11 and 50.0 wt. %, which are denoted as 10-N-HKUST-1/PEI, 30-N-HKUST-1/PEI and
12 50-N-HKUST-1/PEI, respectively. The loading amounts of M-HKUST-1 in the
13 MMMs were 30.0 wt. %, which are denoted as 30-M-HKUST-1/PEI. All the
14 membranes were re-activated in vacuum oven at 120 °C for 24 h before gas
15 permeability tests.

16 *2.4. Characterization*

17 HKUST-1 crystals and all the prepared MMMs were characterized by X-ray
18 diffraction (XRD, Bruker, D8 Advance) at a scanning rate of 8° min⁻¹ and 3-75°
19 2Theta range. The morphology and size of HKUST-1 crystals and the MMMs surface
20 features were observed with a scanning electron microscope (SEM, JEOL-7900F).
21 Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Bruker
22 Vertex 70V spectrometer with an average of 32 scans in the range 400-4000 cm⁻¹. The
23 surface morphology of MMMs was characterized with atomic force microscopy
24 (SHIMADZU, SMP-9700). X-Ray photoelectron spectroscopy (XPS) measurements
25 were carried out on a PH 5000 Versaprobe spectrometer with a source gun of Al K α .

1 N₂ sorption measurements were measured at 77 K using a Quantachrome, Autosorb
2 IQ instrument. Prior to the measurements, the samples were degassed at 100 °C for 7
3 h under vacuum. The apparent surface area was calculated using the
4 Brunauer-Emmet-Teller (BET) equation and following the procedure recommended
5 by Rouquerol et al. for microporous sorbents [32]. Relevant pore size distributions
6 were calculated from the adsorption branch of the isotherms by applying the kernel of
7 (metastable) non-local density functional theory (NLDFT) adsorption isotherms
8 considering an amorphous SiO₂ surface and a cylindrical pore model. Micro- and total
9 pore volumes were also determined using the same kernel. The calculations were
10 carried out using the ASiQwin 5.2 software provided by Quantachrome.
11 Thermogravimetric analyses, TGA and DSC, were measured using a NETZSCH (STA
12 449 F5) analyzer under N₂ atmosphere from room temperature to 800 °C with a
13 heating rate of 5 °C min⁻¹.

14 *2.5. Gas-separation experiments*

15 For the gas-separation measurement, the MMMs were placed in a stainless-steel cell
16 and permeated to a steady state. The Wicke-Kallenbach technique was used to
17 characterize the performance of one-component gas permeability and two-component
18 mixed gas separation (1.5 bar upstream (feed gas) and 1 bar downstream (sweeping
19 gas of argon (Ar)) with 0.5 bar transmembrane pressure drop). The membrane area
20 tested was 0.785 cm². Gas feed was provided at 100 cm³ min⁻¹ (for mixture of gases,
21 100 cm³ min⁻¹ is the total flow of the two gases, i.e. 50 cm³ min⁻¹ for each gas), while
22 the permeate side was swept by argon gas with a flow rate of 40 cm³ min⁻¹. The
23 permeated gas composition was determined using a gas chromatography (456-GC,
24 Scion) equipped with a thermal conductivity detector (TCD). All the permeation

1 results were averaged from at least three different MMMs. The permeability, termed
2 permeance P_i in Barrer (1 Barrer = $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \text{ s}^{-1} \cdot \text{cmHg}^{-1}$), of the
3 MMMs was calculated with the following Equation (1):

$$P_i = \frac{10^{-10} l N_i}{A \Delta p_i} \quad (1)$$

4 where N_i ($\text{cm}^3(\text{STP}) \cdot \text{s}^{-1}$) is the permeate flow rate of component i , l (cm) is the
5 thickness of membrane ΔP_i (cmHg) is the transmembrane pressure drop of component
6 i , and A (m^2) is the membrane area.

7 The MMMs permselectivity was evaluated by the separation factor ($\alpha_{i/j}$), which was
8 obtained according to Equation (2):

$$\alpha_{i/j} = \frac{X_i/X_j}{Y_i/Y_j} \quad (2)$$

9 where i, j are the two components in the mixture and X, Y are the mole fractions in the
10 permeate and feed solution, respectively.

11 Assuming that the gas transport processes through the 30-N-HKUST-1/PEI membrane
12 are thermally activated, the E_{act} values can be calculated using the Arrhenius empirical
13 equation (3):

$$\ln P = \frac{E_{act}}{RT} + C \quad (3)$$

14 where P (Barrer) is the permeation coefficient, E_{act} (kJ/mol) corresponds to the
15 activation energy of permeation.

16 The isotherms of 30-N-HKUST-1/PEI membrane at 273K and 298K were measured
17 and the E_{ast} values can be calculated using the integral equation of Van't Hoff
18 isovolumic equation (4):

$$\ln P = -\frac{E_{ast}}{R} \frac{1}{T} + C \quad (4)$$

1 where P (Torr) is the adsorption equilibrium pressure, R is the gas constant, T (K) is
2 the analysis temperature, E_{ast} (kJ/mol) corresponds to the heat of adsorption.

3 The E_{act} is related to the diffusion activation energy (ED) and heat of adsorption (E_{ast})
4 (5):

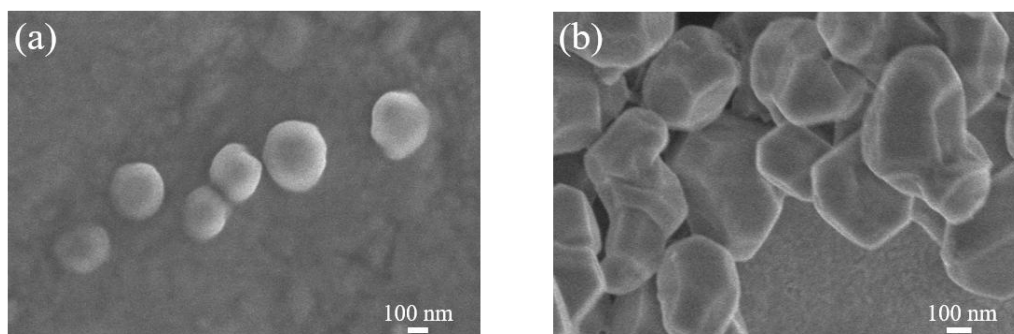
$$E_{act} = ED + E_{ast} \quad (5)$$

5 **3. Results and discussion**

6 *3.1 Characterization of HKUST-1 crystals*

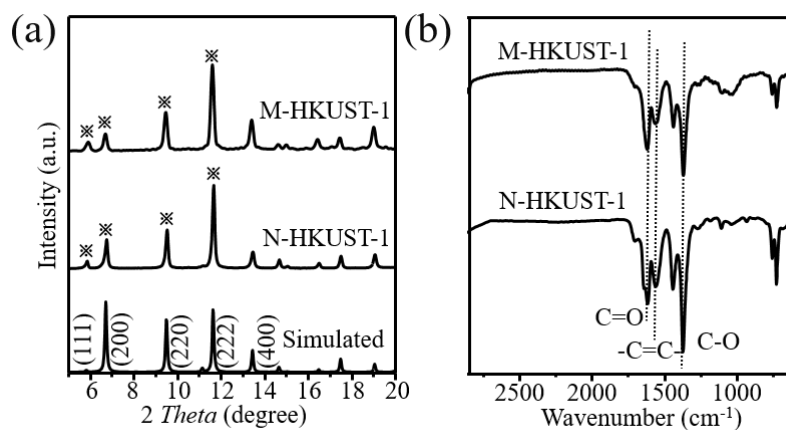
7 Sodium formate was used as an end-capping reagent to optimize both the shape and
8 size of HKUST-1 crystals. Its addition results in fairly uniform bean-shaped
9 nanocrystals with a crystal size of around 50-80 nm (Fig 1a) and sub microcrystals
10 with crystal size of 300-500 nm (Fig 1b). The XRD diffraction pattern (Fig 2a) of the
11 synthesized HKUST-1 crystals is in good agreement with the literature suggesting a
12 proper phase purity [33] and a pristine MOF structure. The crystallite size of the
13 N-HKUST-1 was calculated to be approximately 63 nm using the Scherer's equation
14 (using all peaks), which is consistent with the SEM results. From the synthesis point
15 of view, sodium formate allows to optimize the crystal morphology mainly from two
16 aspects: (i) it reduces the average crystal size thanks to its modulating effect on the
17 coordinating interactions between the metal ions and the organic linkers. Indeed, in
18 the initial stage of the crystallization, sodium formate acts as a competitor of the
19 organic linker BTC and coordinate to Cu cations. It results in an inhibited crystal
20 growth and it allows more nuclei to be formed. (ii) This competitive coordination of
21 the capping reagent appears to prevent the agglomeration of nanocrystals by

1 regulating the overall rate of crystal growth, ultimately leading to smaller and highly
2 dispersed nanoparticles. The FTIR spectrum of as-synthesized HKUST-1 crystals is
3 presented in Fig 2b. The typical bands found at 1375 cm^{-1} , 1564 cm^{-1} and 1644 cm^{-1}
4 are attributed to the symmetrical vibrations of C-O, skeleton vibrations of the benzene
5 and the stretching vibrations of the C=O, respectively.



6
7 **Fig 1.** SEM pictures of (a) N-HKUST-1 and (b) M-HKUST-1

8



9

10 **Fig 2.** (a) XRD patterns and (b) FT-IR spectra of N-HKUST-1 and M-HKUST-1

11

12 Fig 3 exhibits the N₂ at 77 K adsorption-desorption isotherm of the MOF crystals. The
13 HKUST-1 sample exhibits a hybrid type I/type IV isotherm that is nowadays
14 commonly seen with modern micro/mesoporous (nano) materials. However, the main

1 component of the isotherm can be attributed to type I(a), being characteristic of
2 microporous materials with pores below 1 nm. The isotherm also revealed a small H4
3 hysteresis loop indicative of the presence of intercrystalline mesoporosity (e.g.
4 porosity present in-between nanocrystals) and a steep uptake at higher relative
5 pressures (i.e., above $P/P_0 = 0.98$), typically associated with the presence of
6 nanoparticles. A sharp and narrow pore size distribution with a mode pore size
7 centered at around 0.8 nm (calculated using state-of-the-art NLDFT kernels), and a
8 micropore volume of $0.45 \text{ cm}^3 \text{ g}^{-1}$ were obtained (Table S1 and Fig 3). An apparent
9 surface area, calculated using the BET model and verifying the Rouquerol's criteria
10 for predominantly microporous samples, of $793 \text{ m}^2/\text{g}$ and $667 \text{ m}^2/\text{g}$ were determined
11 for N-HKUST-1 and M-HKUST-1 respectively (Table S1), which is consistent with
12 previously reported data [34]. All the physico-chemical data extracted from
13 physisorption measurements confirmed the high-quality of the synthesized MOF
14 sample. TGA curve of N-HKUST-1 and M-HKUST-1 are shown in Fig S1. The
15 weight loss below $305 \text{ }^\circ\text{C}$ is attributed to the desorption of weakly physisorbed and
16 confined water molecules, while the weight loss in the temperature range $305\text{--}365 \text{ }^\circ\text{C}$
17 arises from the release of coordinated water molecules. The MOF starts to degrade at
18 $365 \text{ }^\circ\text{C}$. In this region, the continuous weight loss originates from the decomposition
19 of the organic linkers within the framework associated with a release of CO_2 up to
20 $\sim 750 \text{ }^\circ\text{C}$.

21

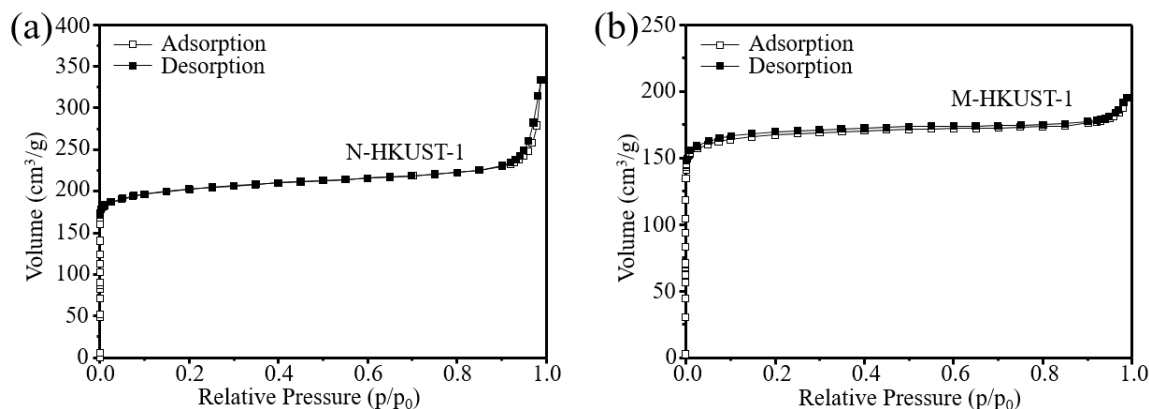
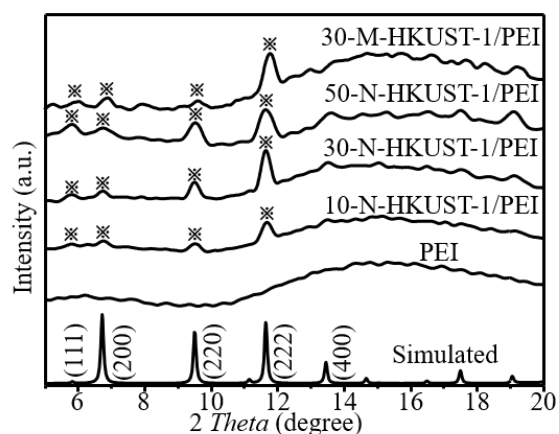


Fig 3. N₂ at 77 K physisorption isotherms of (a) N-HKUST-1 and (b) M-HKUST-1

Finally, in order to assess the stability and the suitability of the as-synthesized HKUST-1 crystals as a filler in the fabrication of MMM, CH₂Cl₂-N-HKUST-1 and CH₂Cl₂-M-HKUST-1 (MOF crystals treated three times with a 10-minute mechanical stirring and 10-minute sonication protocol) were also analyzed by XRD. The resulting pattern (Fig S2) shows that the crystal structure of HKUST-1 is perfectly maintained after this treatment, confirming the pertinence to use HKUST-1 crystals suspended in CH₂Cl₂ for fabricating MMMs.

3.2 Characterization of HKUST-1/PEI MMMs

A series of HKUST-1/PEI MMMs were prepared and the corresponding XRD patterns are shown in Fig 4. The pattern of the pure PEI membrane, exhibiting a broad peak centered at $\sim 15^\circ$ 2θ is consistent with data reported in the literature [35, 36]. The XRD patterns of the different HKUST-1/PEI MMMs all exhibit the Bragg peaks representative of the HKUST-1. As expected, a gradual increase in the intensity of the peaks located at 5.8° , 6.7° , 9.5° , 11.7° and 13.5° is observed with an increase in the HKUST-1 crystals loading (Fig 4).



1

2 **Fig 4.** XRD patterns of pure PEI membrane and HKUST-1/PEI MMMs with different HKUST-1

3 loadings

4 The membrane forming process was further evaluated via optical imaging. As shown

5 in Fig 5, all MMMs are of high-quality with an apparent homogeneous crystals

6 dispersion and one can directly correlate the deepening of the blue color with the

7 increasing of loading of HKUST-1 crystals. Of particular interest, SEM images,

8 shown in Fig 6, revealed the textural differences in the MMMs. Indeed, while the

9 surface of the pure PEI membrane is smooth (Fig 6a), the HKUST-1/PEI MMMs have

10 a significant surface roughness which is increasing as a function of the particle's

11 loading. The SEM pictures depicted in Fig 6b-d also confirmed the homogenous

12 dispersion of the HKUST-1 nanocrystals. No obvious or major defects were found on

13 the surface of the MMMs. The EDS results of Cu mapping also prove the

14 homogeneous dispersion of HKUST-1 nanocrystals (Fig 6b-d) except for the

15 30-M-HKUST-1/PEI sample (see below). Such homogeneity is attributed to the use of

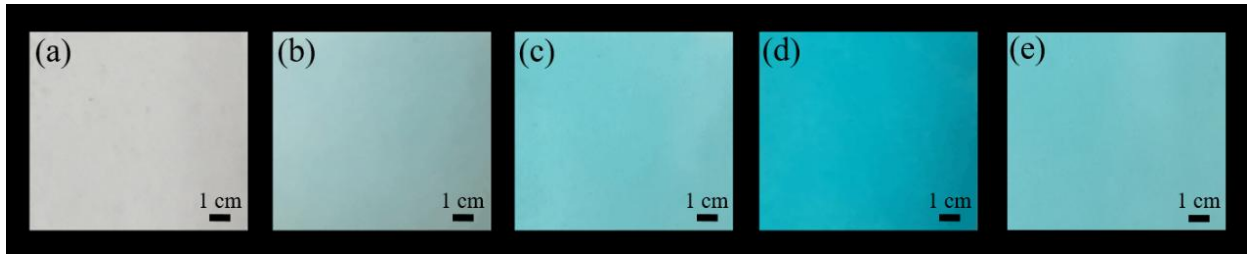
16 the capping agent (sodium formate) during the synthesis which, as already said above,

17 is believe to prevent the agglomeration of the MOF nanocrystals in suspension. From

18 the cross-sectional views (Fig 7), the thickness of the PEI and HKUST-1/PEI MMMs

1 were determined to be 12.5–13.5 μm . These images revealed the polymer veins due to
2 plastic deformation, which has also been found in other MOF-based MMMs. This
3 effect is usually attributed to a strong interaction between the polymer and the filler
4 [37] and will therefore result in a better integration and dispersion of the MOF filler
5 within the host matrix. However, there are visible voids at the interfaces between the
6 N-HKUST-1 and the polymer in the 50-N-HKUST-1/PEI membrane (Fig 7d). This
7 result indicates an excessive loading of N-HKUST-1 resulting in irreversible damages
8 in the PEI chain composing the polymer. According to the EDS results of the
9 cross-section of the membrane, the Cu distribution in the N-HKUST-1/PEI MMMs is
10 relatively homogeneous (Fig 7b-d). In the 30-M-HKUST-1/PEI membrane (Fig 7e),
11 the agglomeration leads to inhomogeneous distribution of M-HKUST-1 as shown by
12 EDS mapping. In addition, the larger size crystal also results in irreversible damages
13 in the PEI chain composing the polymer. The surface morphology (Fig 8) and
14 roughness (Table S2) of the HKUST-1/PEI MMMs were finally investigated by AFM.
15 The average roughness of the HKUST-1/PEI MMMs increased substantially as
16 compared with the one of the pristine PEI membrane, and became rougher with
17 increasing loading of HKUST-1 crystals (Table S2). As illustrated in the TG curves
18 (Fig 9), all HKUST-1/PEI MMMs are thermally stable up to 300 $^{\circ}\text{C}$ (initial weight
19 loss being attributed to solvent), which make them suitable for gas separation
20 applications.

21

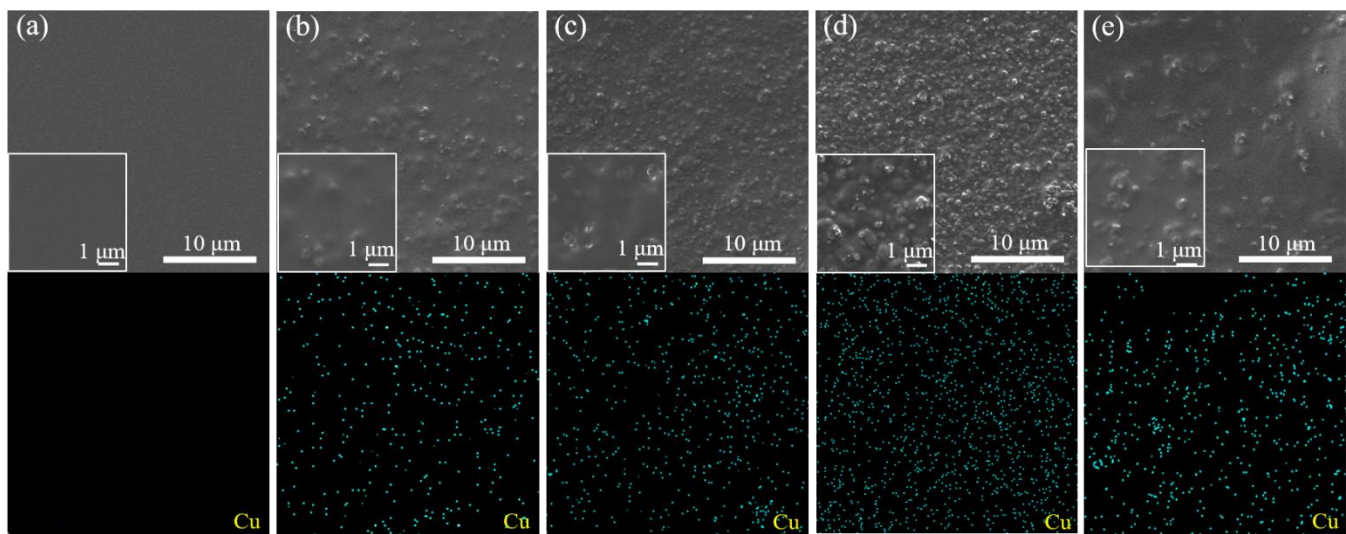


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2 **Fig 5.** Optical images of (a) pure PEI membrane, (b) 10-N-HKUST-1/PEI, (c)

3 30-N-HKUST-1/PEI, (d) 50-N-HKUST-1/PEI and (e) 30-M-HKUST-1/PEI

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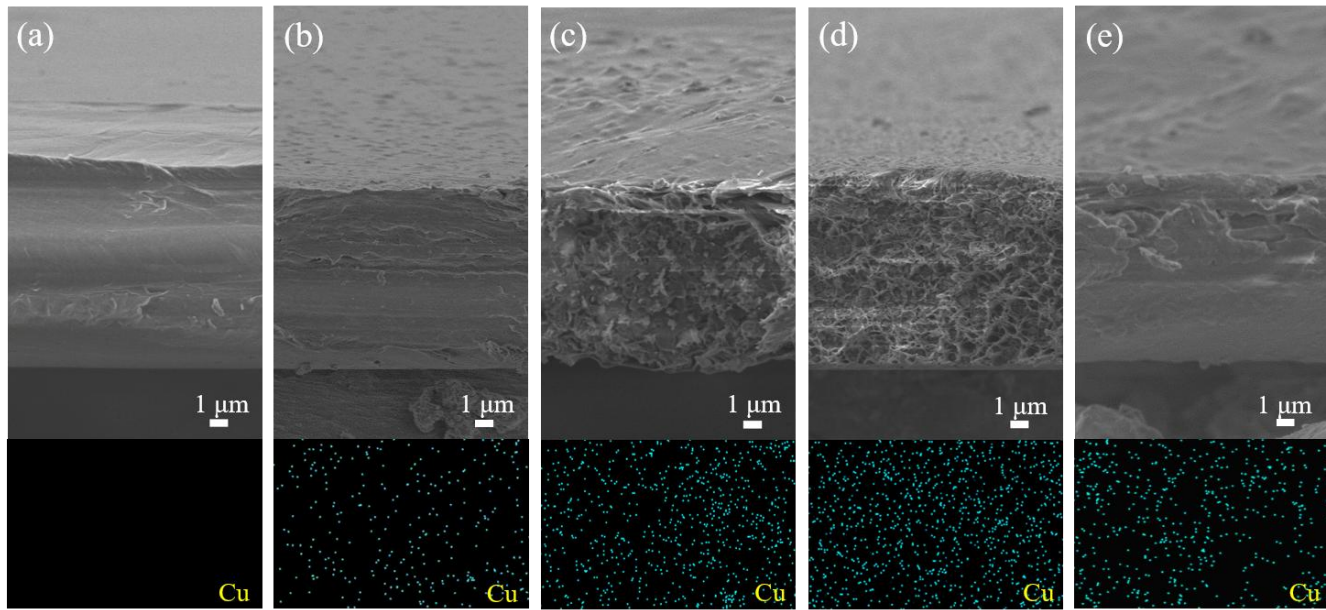


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6 **Fig 6.** SEM images and EDS mapping of (a) pure PEI, (b) 10-N-HKUST-1/PEI, (c)

7 30-N-HKUST-1/PEI, (d) 50-N-HKUST-1/PEI and (e) 30-M-HKUST-1/PEI membranes

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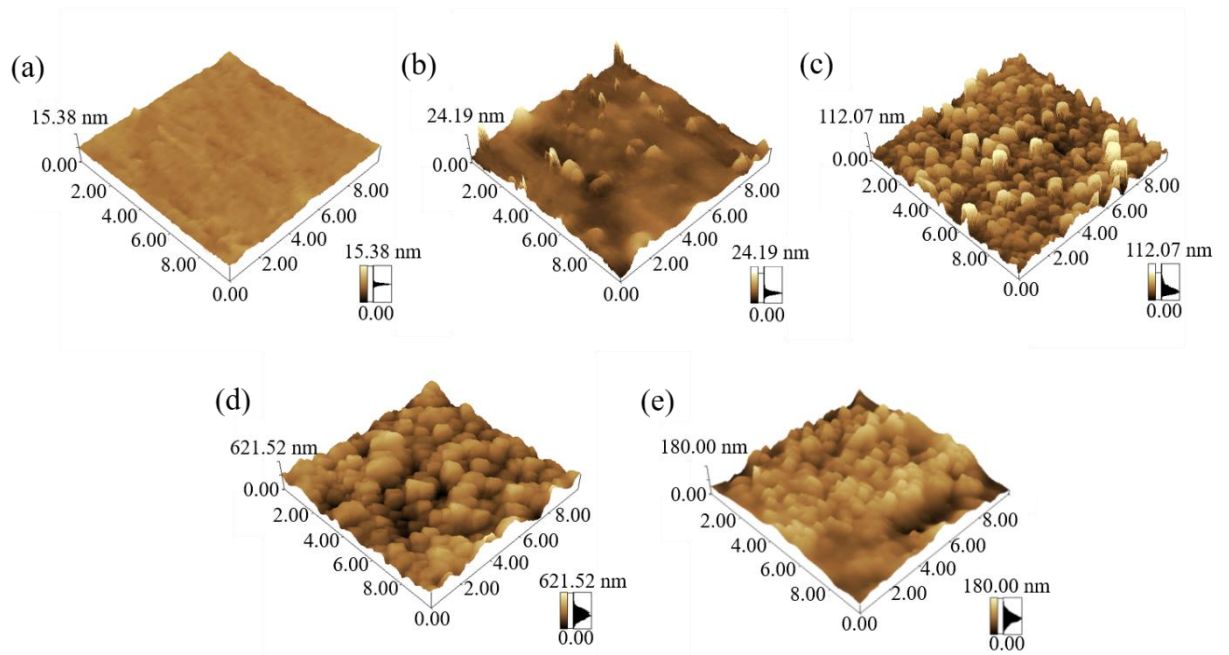


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2 **Fig 7.** Cross-section SEM images and EDS mapping of (a) pure PEI, (b) 10-N-HKUST-1/PEI, (c)

3 30-N-HKUST-1/PEI, (d) 50-N-HKUST-1/PEI and (e) 30-M-HKUST-1/PEI membranes

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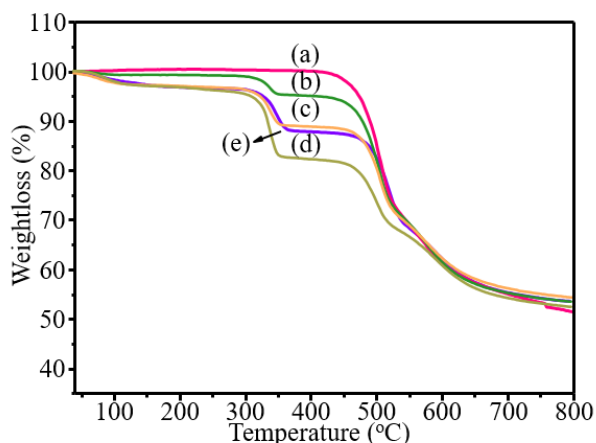


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6 **Fig 8.** AFM images of (a) pure PEI, (b) 10-N-HKUST-1/PEI, (c) 30-N-HKUST-1/PEI, (d)

7 50-N-HKUST-1/PEI and (e) 30-M-HKUST-1/PEI membranes

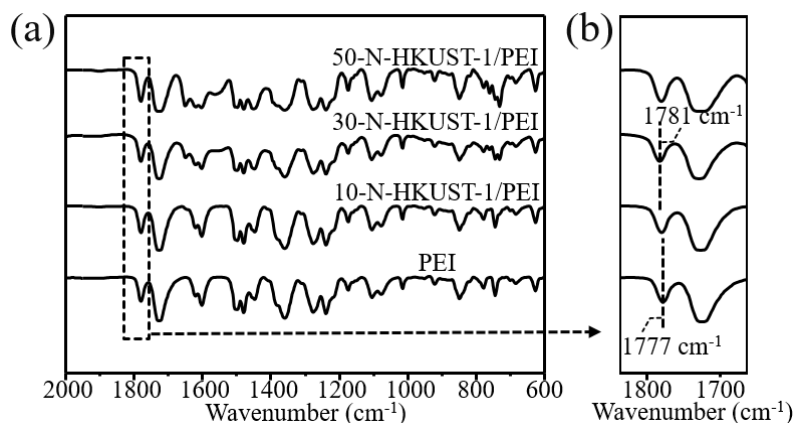
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1
 2 **Fig 9.** TG curves of (a) pure PEI, (b) 10-N-HKUST-1/PEI, (c) 30-N-HKUST-1/PEI, (d)
 3 50-N-HKUST-1/PEI and (e) 30-M-HKUST-1/PEI membranes

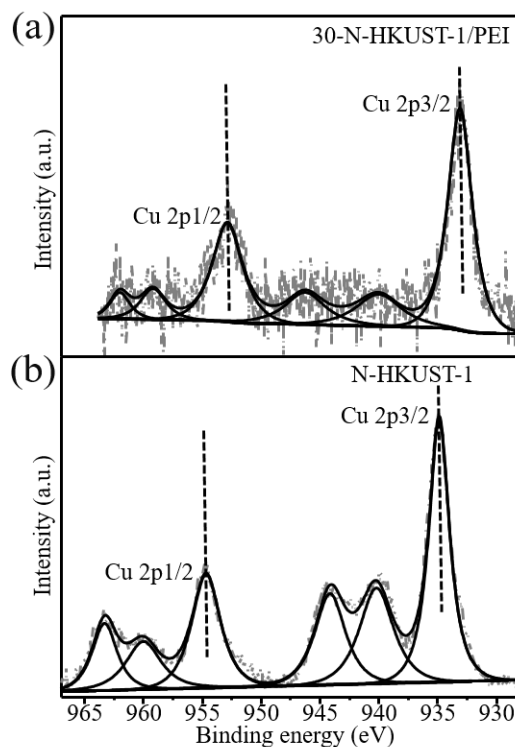
4
 5 The FTIR spectra of pure PEI membrane and HKUST-1/PEI MMMs are shown in Fig
 6 10. The characteristic peaks coming from the PEI polymer can be clearly identified in
 7 all the different MOF/PEI MMMs. Namely, the peak at 1724 cm^{-1} and 1777 cm^{-1} can
 8 be attributed to the symmetric and asymmetric C=O stretching vibrations at the
 9 five-membered rings in PEI. The peaks at 1375 cm^{-1} , 1564 cm^{-1} and 1644 cm^{-1} belong
 10 to the symmetrical vibrations of C-O, skeleton vibrations of the benzene and the
 11 stretching vibrations of the C=O in HKUST-1, respectively, thus confirming the stable
 12 existence of N-HKUST-1 in the MMMs. It can also be noted that the intensity of the
 13 characteristic peak of N-HKUST-1 increases in accordance with the crystals loading.
 14 More important, an evident blue shift of the C=O peak in the FTIR spectra of the
 15 HKUST-1/PEI MMMs was observed (Fig 10b, from 1777 cm^{-1} to 1781 cm^{-1}). This
 16 result indicates an alteration in the electron distribution of the C=O group. It is
 17 suggested to originate from the action of the copper unsaturated metal sites in
 18 HKUST-1 onto oxygen atoms, making them more electronegative and resulting in a

1 tendency to withdraw the electron clouds of the chemical bonds. The existence of this
2 electrostatic interaction was confirmed via XPS analysis (copper, Cu 2p) of
3 N-HKUST-1 and 30-N-HKUST-1/PEI membrane (Fig 11). Compared to the
4 N-HKUST-1, the binding energy for Cu 2p^{1/2} and Cu 2p^{3/2} shifted to the lower values
5 for the 30-N-HKUST-1/PEI sample (from 954.8 eV to 953.2 eV and from 934.8 eV to
6 932.8 eV for Cu 2p^{1/2} and Cu 2p^{3/2}, respectively), thus confirming that the density of
7 the electron cloud near the copper unsaturated metal site increases. This is consistent
8 with the results obtained by FTIR (Fig 10). To sum up, the copper unsaturated metal
9 site interacts with the C=O of PEI polymer, reducing the binding energy of Cu 2p^{1/2}
10 and Cu 2p^{3/2}. This electrostatic interaction will therefore enhance the bonding strength
11 of the PEI and the N-HKUST-1. As shown in Fig 12, these enhanced electrostatic
12 interactions reduce the fluidity of PEI chains, ultimately leading to a higher glass
13 transition temperature for the 30-N-HKUST-1/PEI membrane (213.8 °C) as compared
14 to the pure PEI (208.5 °C) as shown in Fig 12, being consistent with all the previously
15 discussed results.
16



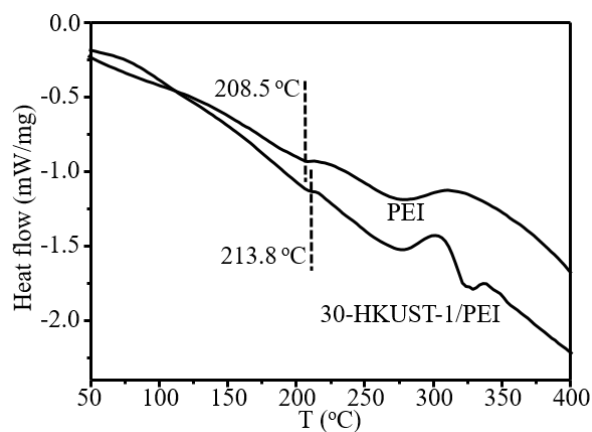
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18 **Fig 10.** FTIR spectra of the pure PEI membrane and HKUST-1/PEI MMMs with different loading

1 amounts of N-HKUST-1 in the range (a) 600-2000 cm^{-1} and (b) 1600-1900 cm^{-1}



2

3 **Fig 11.** XPS spectra (Cu 2p) of (a) N-HKUST-1 and (b) 30-N-HKUST-1/PEI membranes



4

5 **Fig 12.** Differential scanning calorimetry (DSC) curves of pure PEI membrane and

6 30-N-HKUST-1/PEI membrane

7 3.3. Gas permeation measurements of HKUST-1/PEI MMMs

8 The single gas permeability of the pure PEI membrane and the HKUST-1/PEI MMMs

9 were measured by the Wicke-Kallenbach technique at 25 °C and 1.5 bar. The

1 permeability and ideal selectivity values are summarized in Table S7, SI and Table 2.
2 The HKUST-1/PEI MMMs exhibit a higher H₂ permeability as compared to the pure
3 PEI membrane. Adding a 30 wt.% N-HKUST-1 to the PEI membrane resulted in a
4 2.55-fold increase in the H₂ permeability (75.8 barrer for pristine PEI membrane vs
5 193.3 barrer for 30-N-HKUST-1/PEI). This result can be rationalized by the
6 intersecting three-dimensional pore network of the HKUST-1 embedded in PEI which
7 provides faster and resistance-less through-pore channels for small and non-polar H₂
8 molecules (0.29 nm). On the contrary, the permeability of bigger gas molecules, such
9 as CO₂ and CH₄ decreases due to their strong adsorption in the MOF nanocrystals.
10 Indeed, the presence of Cu metal sites ensures a strong adsorption effect and a slow
11 desorption of CO₂ and CH₄ in MOFs' channels, ultimately controlling their transport
12 properties. Regarding the H₂/CO₂ and H₂/CH₄ ideal selectivity, among all the
13 HKUST-1/PEI MMMs, the best ones were obtained for the 30-N-HKUST-1/PEI
14 sample, being of 20.6 and 101.7, respectively. Quite remarkably, it represents a
15 5.7-fold increase as compared to the H₂/CO₂ ideal selectivity of the pure PEI
16 membrane and 6.2-fold increase for the H₂/CH₄ one. In addition, the improved
17 electrostatic interactions between the C=O bonds on the five-membered ring of PEI
18 and the Cu²⁺ of HKUST-1 ensure a certain membrane's density with no loss of
19 selectivity. However, it is to be noted that for the 50-N-HKUST-1/PEI membrane,
20 with high loading of N-HKUST-1, the permeability of H₂, CO₂ and CH₄ increased and
21 the H₂/CO₂ as well as the H₂/CH₄ ideal selectivity decreased. Here, the excessive
22 amount of N-HKUST-1 in the PEI polymer matrix damaged the PEI chains, resulting

1 in the apparition of non-selective voids at the interface between the two materials, as
2 shown in the SEM image (Fig 7d). Nevertheless, it remains that even with these voids,
3 the CO₂ and CH₄ permeability of 50-N-HKUST-1/PEI was still lower than the pure
4 PEI membrane, demonstrating the strong incorporation of HKUST-1 filler in MMMs.
5 In addition, adding a 30 wt.% M-HKUST-1 to the PEI membrane resulted in a
6 8.62-fold increase in the H₂ permeability (75.8 barrer for pristine PEI membrane vs
7 529.2 barrer for 30-M-HKUST-1/PEI). The damages of the PEI chains induced by the
8 larger crystal size of M-HKUST-1 and their inhomogeneous distribution lead to
9 non-selective voids, ultimately resulting in a loss of selectivity (11.6 for H₂/CO₂ and
10 33.1 for H₂/CH₄) (Fig 7e).

11 Activation energy of permeation (E_{act}) values of 5.3 kJ/mol for H₂, 11.0 kJ/mol for
12 CO₂ and 8.6 kJ/mol for CH₄ in single gas permeability were calculated for the best
13 performing membrane, the 30-N-HKUST-1/PEI (Fig 13a and Table S3). The E_{act} of
14 H₂ is extremely small due to the low diffusion resistance faced within the membrane,
15 leading to fast diffusion of smaller H₂ molecules (0.29 nm) as compared to larger CO₂
16 (0.33 nm) and CH₄ (0.38 nm) ones. The calculated E_{ast} values are -0.6 kJ/mol for H₂,
17 -25.4 kJ/mol for CO₂ and -11.2 kJ/mol for CH₄ through 273K and 298K isothermal
18 adsorption test of 30-N-HKUST-1/PEI membrane (Fig 13b and Table. S4). Following
19 Eq. 5, the calculated ED values are 5.9 kJ/mol for H₂, 36.4 kJ/mol for CO₂ and 19.8
20 kJ/mol for CH₄. The E_{ast} of CO₂ and CH₄ is much higher than the E_{ast} of H₂ due to the
21 strong adsorption of these molecules by the HKUST-1 crystals. This effect can be
22 attributed to the presence of Cu unsaturated metal sites in the MOF. Through carefully

1 comparing E_{ast} and ED of H_2 , CO_2 and CH_4 , the permeation of CO_2 and CH_4 is
 2 dominated by adsorption phenomena, while the permeation of H_2 is dominated by
 3 diffusion ones. The adsorption capacity of CO_2 in HKUST-1 is stronger than that of
 4 CH_4 , which is also the reason why the permeation of CO_2 is higher than that of CH_4 .
 5 Finally, the single gas separation performance of the 30-N-HKUST-1/PEI was found
 6 to outperform the well-known Robeson's upper bound (Fig S3) confirming the
 7 potential of N-HKUST-1 for the preparation of effective and economically relevant
 8 PEI-based MMMs.

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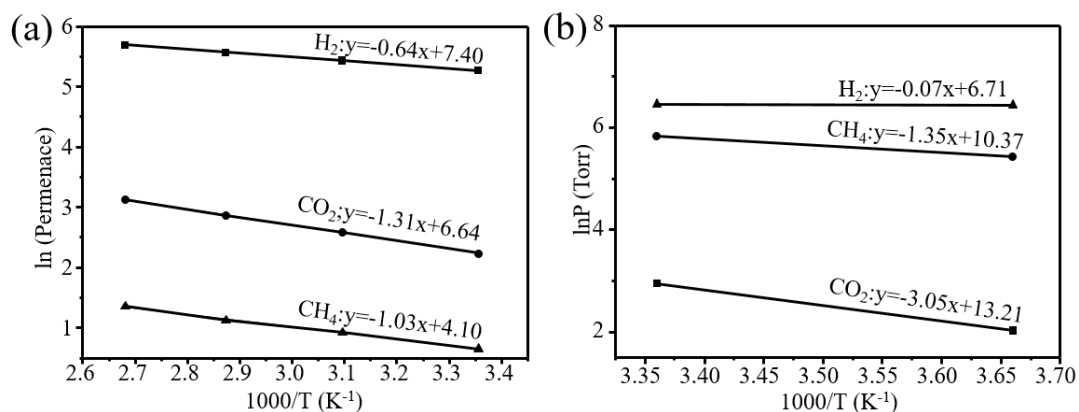
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12 **Table 2.** Gas permeability and ideal selectivity of pure PEI and HKUST-1/PEI MMMs at 25 °C
 13 and 1.5 bar

Membrane	Gas Permeability (Barrer)			Ideal selectivity (α)	
	H_2	CO_2	CH_4	H_2/CO_2	H_2/CH_4
Pure PEI	75.8	21.2	4.6	3.6	16.5
10-N-HKUST-1/PEI	120.8	11.2	2.7	10.8	44.7
30-N-HKUST-1/PEI	193.3	9.4	1.9	20.6	101.7
50-N-HKUST-1/PEI	241.8	19.3	4.1	12.5	59.0
30-M-HKUST-1/PEI	529.2	45.8	17.0	11.6	31.1

14



1
 2 **Fig 13.** (a) Arrhenius temperature dependence of H₂, CO₂ and CH₄ permeances for the
 3 30-N-HKUST-1/PEI membrane; (b) Van't Hoff plots of H₂, CO₂, and CH₄ recorded at 273 K and
 4 298 K

5
 6 Finally, the H₂/CO₂ and H₂/CH₄ mixed gas permeation of HKUST-1/PEI MMMs were
 7 evaluated. As summarized in Table 3, a similar trend as the one found for single gas
 8 permeation was obtained. Focusing on 30-N-HKUST-1/PEI, while a slight decrease of
 9 the H₂ permeability (from 193.3 barrer to 136.8 barrer and 189.6 barrer in H₂/CO₂ and
 10 H₂/CH₄, respectively) was found due to the competitive permeation mechanism [38],
 11 the CO₂ and CH₄ permeability did not change significantly (from 9.4 barrer to 8.3
 12 barrer and from 1.9 barrer to 2.3 barrer, respectively). A slight decrease in the H₂/CO₂
 13 and H₂/CH₄ selectivity (16.5 and 82.4) was also noted.

14 Industrial syngas usually contains H₂, CO₂, CH₄, and their separation play a critical
 15 role in many synthesis and valorization processes. To further explore the “realistic”
 16 performance of 30-N-HKUST-1/PEI membrane in this separation, it was tested at
 17 different temperatures (25-100 °C) (Table. S5) and pressures (0-3 bar) (Table. S6)
 18 under mixed gas permeation. As shown in Fig 14 and Fig 15, an increase in the

1 temperature and pressure resulted in a gradual increase of the permeability of H₂, CO₂
 2 and CH₄. Under such conditions an induced desorption of CO₂ and CH₄ is observed
 3 [39]. The same effect explains the loss of selectivity even for 30-N-HKUST-1/PEI
 4 membrane, it remains much higher than the one of pure PEI. In addition, the stability
 5 test (72 h) revealed that the permeability and selectivity of the 30-N-HKUST-1/PEI
 6 membrane remains unchanged (Fig 16). Our results clearly demonstrate the potential
 7 of the MOF/PEI MMMs for practical applications in harsh conditions as well as
 8 continuous and extended on-stream time.

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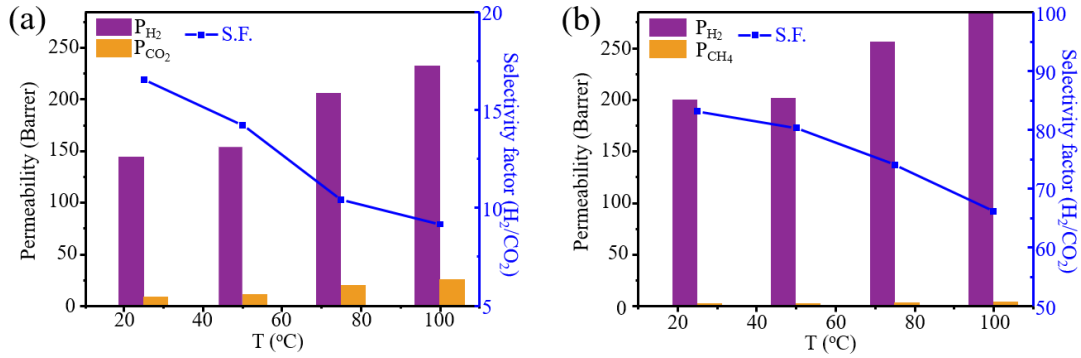
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14 **Table 3.** Mixed gas permeation (H₂/CO₂ and H₂/CH₄) results of the PEI and HKUST-1/PEI
 15 MMMs at 25 °C and 1.5 bar

Membrane	Gas Permeability		Selectivity	Gas Permeability		Selectivity
	(Barrer)		(α)	(Barrer)		(α)
	H ₂	CO ₂	H ₂ /CO ₂	H ₂	CH ₄	H ₂ /CH ₄
Pure PEI	56.0	23.7	2.4	58.3	4.3	13.6
10-N-HKUST-1/PEI	98.6	14.1	7.0	109.0	3.6	30.3
30-N-HKUST-1/PEI	136.8	8.3	16.5	189.6	2.3	82.4
50-N-HKUST-1/PEI	176.2	27.7	6.4	202.0	5.0	40.4

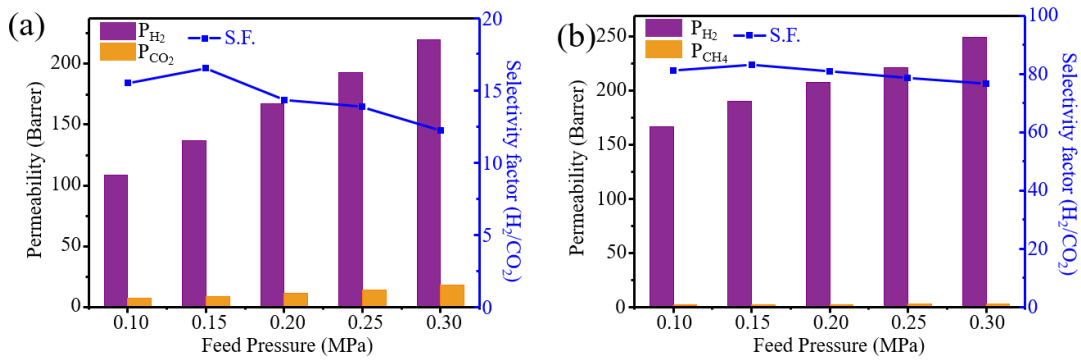
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2

3 **Fig 14.** (a) Permeability and separation (H₂/CO₂) of 30.0-HKUST-1/PEI membrane at different
 4 temperatures (25 – 100 °C); (b) Permeability and separation (H₂/CH₄) of 30.0-HKUST-1/PEI
 5 membrane at different temperatures (25 – 100 °C)

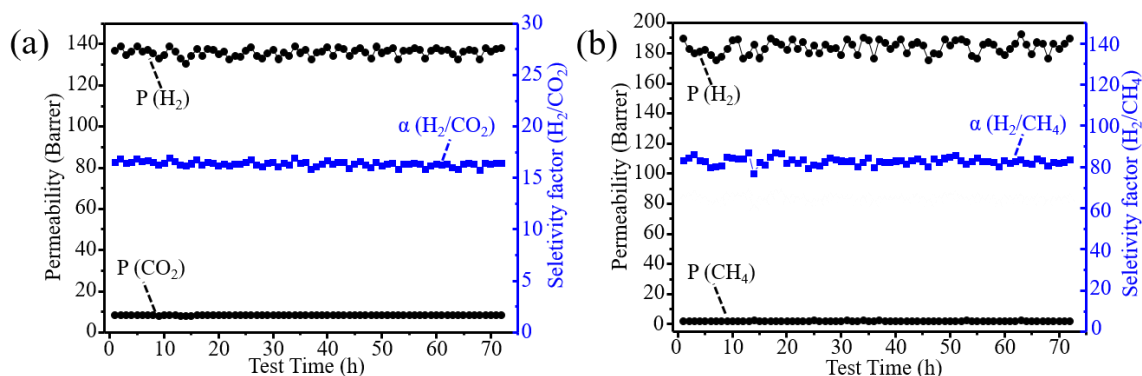
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8 **Fig 15.** (a) Permeability and separation (H₂/CO₂) of 30.0-HKUST-1/PEI membrane at different
 9 feed pressure (0.10 – 0.30 MPa); (b) Permeability and separation (H₂/CH₄) of 30.0-HKUST-1/PEI
 10 membrane at different temperatures (0.10 – 0.30 MPa)

11



1

2 **Fig 16.** Stability of 30-N-HKUST-1/PEI membrane in (a) H₂/CO₂ and (b) H₂/CH₄ mixed gas
 3 separation tests performed continuously for 72 hours

4

5 **4. Conclusions**

6 Mixed matrix membranes were prepared by deposition of various amount of
 7 HKUST-1 nanocrystals (50-80 nm) in the polyetherimide matrix. The agglomeration
 8 of the HKUST-1 nanocrystals in the coating suspension was eliminated by using a
 9 capping agent (sodium formate). The MMMs show high H₂ permeability and H₂/CO₂
 10 and H₂/CH₄ selectivity. This is attributed to the homogeneous dispersion of HKUST-1
 11 nanocrystals in the PEI and the electrostatic interaction between the HKUST-1
 12 nanocrystals and PEI, which reduced the interface defects. The optimum H₂
 13 permeability (193.3 barrer) and ideal selectivity (20.6 in H₂/CO₂ and 101.7 in H₂/CH₄)
 14 are obtained for the 30-N-HKUST-1/PEI membrane. According to the energy
 15 calculation, an adsorption-diffusion coupling separation mechanism is proposed. The
 16 exceptional gas separation performance along with the high stability of the MMMs
 17 render them attractive for hydrogen separation application.

18

19

1 **Declaration of Competing Interest**

2 The authors declare that they have no known competing financial interests or personal
3 relationships that could have appeared to influence the work reported in this paper.

4 5 **Acknowledgements**

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9 International Associated Laboratory LIA “Zeolite”.

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