



**HAL**  
open science

## Is amino-modification of HKUST-1 in PEI mixed-matrix membranes always favorable to CO<sub>2</sub> separation?

Ge Yang, Yanjiao Wang, Mengling Sun, Panpan Xu, Chunzheng Wang, Ke Huang, Heqing Jiang, Svetlana Mintova, Hailing Guo

### ► To cite this version:

Ge Yang, Yanjiao Wang, Mengling Sun, Panpan Xu, Chunzheng Wang, et al.. Is amino-modification of HKUST-1 in PEI mixed-matrix membranes always favorable to CO<sub>2</sub> separation?. *Microporous and Mesoporous Materials*, 2023, 359, pp.112649. 10.1016/j.micromeso.2023.112649 . hal-04283467

**HAL Id: hal-04283467**

**<https://hal.science/hal-04283467>**

Submitted on 13 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# 1 Is amino-modification of HKUST-1 in PEI mixed-matrix membranes 2 always favorable to CO<sub>2</sub> separation?

3  
4 Ge Yang<sup>a,b</sup>, Yanjiao Wang<sup>a</sup>, Mengling Sun<sup>a</sup>, Panpan Xu<sup>a</sup>, Chunzheng Wang<sup>a</sup>, Ke  
5 Huang<sup>a</sup>, Heqing Jiang<sup>c</sup>, Svetlana Mintova<sup>a,d</sup>, Hailing Guo<sup>a,\*</sup>  
6  
7

8 a State Key Laboratory of Heavy Oil Processing, College of Chemistry and Chemical Engineering,  
9 China University of Petroleum (East China) Qingdao, 266555 (P.R. China).

10 b College of Science, China University of Petroleum (East China), Qingdao, 266555 (P.R. China).

11 c Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences,  
12 Laoshan District, Qingdao CN-266101, China

13 d Laboratoire Catalyse et Spectrochimie (LCS), ENSICAEN, UNICAEN, CNRS, Normandie  
14 Université, 6 boulevard du Marechal Juin, 14050 Caen (France).

15  
16 \* Corresponding Author Email: [guohl@upc.edu.cn](mailto:guohl@upc.edu.cn)  
17

## 18 1 Introduction

19 Gas separation processes play important roles in industry production and daily life.  
20 Compared with chemical separation processes with high energy consumption,  
21 membrane based separation technology shows the advantages of high energy  
22 efficiency and easy operation<sup>[1,2]</sup>. Polymeric membranes are attractive for membrane  
23 separation since they are economical and easily fabricated. While, due to the trade-off  
24 effect between permeability and selectivity in polymeric membranes, mixed matrix  
25 membranes (MMMs) loaded with various fillers including porous materials have  
26 received considerable attention since they combine the properties of the filler and the  
27 matrix, showing the potential to break performance limits<sup>[3,5]</sup>. Among the various  
28 fillers used, the MOFs are widely considered because the organic linkers enable  
29 potentially stronger interaction with the polymers.

30  
31 However, the separation performance of most MMMs is under the performance upper  
32 boundary due to the effects of multiple factors such as loading, dispersion in casting  
33 solvent, and interface compatibility<sup>[6]</sup>. These factors determine the efficiency of the  
34 filler phase and the state of non-selective interfacial voids in MMMs. Although MOFs  
35 materials have shown stronger and better regulated “polymer-filler” interactions,  
36 compared with other porous materials, the structural optimization of MOFs-based  
37 MMMs is still the critical factor to develop high-performance MMMs<sup>[7,9]</sup>. The main  
38 effective structural optimization strategies include reduction of filler’s particle size,  
39 synthesis of nanosheets, modification of filler’s surface or polymer chains by  
40 functional groups, *in-situ* membrane preparation<sup>[6,9,11]</sup>. In general, grafting functional  
41 groups onto MOFs has been considered as one of the best techniques since is easily  
42 achieved by substituting the MOFs’ functional ligand. Vankelecom’s research on  
43 UiO-66-based MMMs found that NH<sub>2</sub>-UiO-66 could not only enhanced the  
44 interactions between the filler and the matrix, but also improve the adsorption of CO<sub>2</sub>  
45 in NH<sub>2</sub>-UiO-66, which was conducive to the separation of CO<sub>2</sub>/CH<sub>4</sub><sup>[12]</sup>. Similar  
46 performance optimizations have been reported for NH<sub>2</sub>-UiO-66/PMMA MMMs<sup>[13]</sup>,

1 NH<sub>2</sub>-MIL-53/Pebax MMMs<sup>[14]</sup>, NH<sub>2</sub>-MIL-53/PI MMMs<sup>[15]</sup>, NUS-8/PIM-1<sup>[16]</sup>. The  
2 main focus is on the design of high-performing MOF-based MMMs with molecule  
3 sieving features and reinforced interface.

4  
5 According to previous reports, the MMMs are not effective in H<sub>2</sub>/CO<sub>2</sub> separation<sup>[6,</sup>  
6 <sup>17]</sup>. Due to the close molecular kinetic diameters of H<sub>2</sub> and CO<sub>2</sub> molecules and the  
7 stronger polarity of CO<sub>2</sub>, neither sieving effect nor adsorption enhancement effect can  
8 significantly improve the performance of MMMs, especially the H<sub>2</sub>/CO<sub>2</sub> selectivity. In  
9 our recent work, we combined HKUST-1 nanoparticles with Polyetherimide(PEI) and  
10 the resulted MMMs were used for H<sub>2</sub>/CO<sub>2</sub> separation<sup>[18]</sup>. The PEI is a  
11 high-performance polymer with superior processability, which could be molded into  
12 different forms<sup>[19]</sup>. HKUST-1 (Cu<sub>3</sub>(BTC)<sub>2</sub>) is a porous materials with channels size of  
13 9 Å, allowing the rapid permeation of gas molecules, but with low molecule sieving  
14 property<sup>[17]</sup>. The HKUST-1 has not been widely used for preparation of MMMs like  
15 the UiO series, MIL series and ZIFs crystals<sup>[6]</sup>. Our work took advantage of the large  
16 pore of HKUST-1 nanocrystals to accelerate H<sub>2</sub> diffusion with low diffusion  
17 resistance. Whereas, the permeability of CO<sub>2</sub> molecules was affected by  
18 adsorption-desorption process in the HKUST-1, resulting in a higher diffusion  
19 resistance. The phenomenon of increased H<sub>2</sub> permeability accompanied by decreased  
20 CO<sub>2</sub> permeability was also observed by Liu<sup>[20]</sup>. The separation mechanism of  
21 HKUST-1/PEI MMMs controlled by “adsorption-diffusion” of H<sub>2</sub>/CO<sub>2</sub> was proposed.  
22 Based on this mechanism, we postulated that by increasing the adsorption-desorption  
23 resistance of HKUST-1 to CO<sub>2</sub>, permeance could improve the MMMs’ performance  
24 by amino-functionalization of the HKUST-1. The *in-situ* functionalization of  
25 HKUST-1 is difficult, as its ligands (Trimesic acid, BTC) cannot be completely  
26 replaced by functional ligands. NH<sub>2</sub>-functionalized HKUST-1 has been prepared by  
27 partial replacement of the BTC with NH<sub>2</sub>-BDC<sup>[21,23]</sup>. Sun reported on the synthesis of  
28 sub-NH<sub>2</sub>-Cu-BTC with 2 μm crystal size resulting in stronger affinity between  
29 NH<sub>2</sub>-Cu-BTC and CO<sub>2</sub> molecules<sup>[21]</sup>. Concerning the NH<sub>2</sub>-HKUST-1 crystals, the  
30 final substitution ratio and position of amino-functionalized ligands have not been  
31 studied before, thereby the actual effect from the incomplete amino-functionalization  
32 is not clear.

33  
34 Herein, we report the amino- functionalization of HKUST-1 crystals for enhancement  
35 of the diffusion resistance of CO<sub>2</sub> in MMMs. The modification procedure and the  
36 position of the amino groups on HKUST-1 crystals were studied in details.

## 37 38 **2 Experimental section**

### 39 **2.1 Materials**

40 Copper (II) nitrate trihydrate (Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 99.0%–102%) and sodium formate  
41 (HCOONa, ≥99%) were bought from Sinopharm Chemical Reagent Co., Ltd. (China).  
42 1,3,5-benzenetricarboxylic acid, 2-aminoterephthalic acid, ethanol (C<sub>2</sub>H<sub>5</sub>OH) and  
43 dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were obtained from Shanghai Aladdin Biochemical  
44 Technology Co., Ltd. (China). Polyetherimide (PEI) particles was supplied by

1 SABIC. The deionized water was homemade.

## 2 3 **2.2 Synthesis of HKUST-1 and NH<sub>2</sub>-HKUST-1 materials**

4 The HKUST-1 nanocrystals were synthesized following the methodology reported  
5 earlier<sup>[18]</sup>. Solution A was obtained by dissolving Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.09 g) in  
6 deionized water (36.0 ml), and solution B was prepared by mixing  
7 1,3,5-benzenetricarboxylic acid (0.63 g) with sodium formate (0.94g) in ethanol (36.0  
8 mL). Then, solution B was slowly added in drops to solution A with magnetic stirring  
9 (600 rpm), and then the mixture was transferred to a teflon autoclave for  
10 crystallization at 120 °C for 3 h. The as-synthesized product was purified using a  
11 centrifuge (5000 rpm, 15 min) and re-dispersed in deionized water; the procedure was  
12 repeated three times and finally stabilized in ethanol. The product was freeze-dried  
13 and the sample was denoted as HKUST-1. The *in-situ* ammonia functionalized sample  
14 named NH<sub>2</sub>-HKUST-1 was prepared only changing the solution B including  
15 dissolution of 0.47g 1,3,5-Benzenetricarboxylic acid, 0.14g 2-Aminoterephthalic acid  
16 and 0.94g sodium formate in 36.0 ml ethanol; the other steps remained the same.

## 17 18 **2.3 Preparation of HKUST-1(NH<sub>2</sub>-HKUST-1)/PEI mixed matrix membranes**

19 Polyetherimide matrix solution (5.0 w.t. %) was obtained by dissolving pre-dried  
20 treated PEI particles (0.25 g) in dichloromethane (5.0 g) until the mixture became a  
21 clear uniform viscous solution. This concentration of the matrix solution was  
22 beneficial for the dispersion of the MOF crystals uniformly in the casting solution.  
23 Casting solution was prepared by dispersing different amounts of fillers (HKUST-1  
24 and NH<sub>2</sub>-HKUST-1 crystals after being vacuum-dried overnight) in the PEI matrix  
25 solution, via three rounds of magnetic stirring (10 min) and sonication (10 min) to  
26 ensure the uniformity of crystal particles. After thorough de-bubbling, the casting  
27 solutions were carefully poured onto a horizontally placed glass plate, and scraped by  
28 an automatic coating machine. The prepared mixed matrix membranes loading  
29 HKUST-1 and NH<sub>2</sub>-HKUST-1 crystals could be taken from the glass plate after the  
30 solvent (CH<sub>2</sub>Cl<sub>2</sub>) was completely removed by drying at 25 °C, 60 °C, and 120 °C for  
31 24h. The loading amount of HKUST-1 and NH<sub>2</sub>-HKUST-1 crystals in the membranes  
32 was 10.0 w.t. % and 30 w.t. %, and these membranes were denoted as  
33 HKUST-1-10%/PEI, HKUST-1-30%/PEI, NH<sub>2</sub>-HKUST-1-10%/PEI, and  
34 NH<sub>2</sub>-HKUST-1-30%/PEI, respectively. The pristine PEI membrane was prepared  
35 without the addition of any HKUST-1 and NH<sub>2</sub>-HKUST-1 crystals.

## 36 37 **2.4 Characterization**

38 X-ray diffraction (XRD, Bruker D8 Advance) was used to characterize the crystalline  
39 phase and structure of HKUST-1 and NH<sub>2</sub>-HKUST-1 nanocrystals with a scanning  
40 rate of 2° min<sup>-1</sup> in the 3-90° 2 *Theta* range, and the mixed matrix membranes with a  
41 scanning rate of 8° min<sup>-1</sup> in the 3-75° 2 *Theta* range. Scanning electron microscope  
42 (SEM, JEOL-7900F) was applied to observe the crystal morphology and particle size  
43 of HKUST-1 and NH<sub>2</sub>-HKUST-1 crystals and the top-view and cross-sectional surface  
44 features of mixed matrix membranes. Elementar (ELEMENTAR, UNICUBE) did the

1 element analysis (EA) under CHNS mode. Infrared spectrometer (Bruker Vertex 70V)  
 2 recorded the fourier transform infrared (FT-IR) spectra of both MOFs crystals and  
 3 MMMs with an average 64 scans in the 400-4000  $\text{cm}^{-1}$  range. X-Ray photoelectron  
 4 spectroscopy (XPS) was obtained by an ESCALAB 250Xi ThermoFischer  
 5 spectrometer with an Al  $K\alpha$  source gun.  $\text{N}_2$  sorption measurements were carried out  
 6 on a Quantachrome, Autosorb IQ instrument to study the porous structure of  
 7 HKUST-1 and  $\text{NH}_2$ -HKUST-1 crystals at  $-196\text{ }^\circ\text{C}$ .  $\text{H}_2$  and  $\text{CO}_2$  adsorption capacities  
 8 were also measured by a Quantachrome, Autosorb IQ instrument at  $0\text{ }^\circ\text{C}$  and  $25\text{ }^\circ\text{C}$ ,  
 9 and the measurement was taken at  $0\text{ }^\circ\text{C}$  for crystal sample. The degassing condition of  
 10 the samples was  $120\text{ }^\circ\text{C}$  for 10 h. Thermogravimetric analyses (TG and DSC) were  
 11 performed from  $35\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$  under nitrogen atmosphere with a  $5\text{ }^\circ\text{C min}^{-1}$  heating  
 12 rate by using a NETZSCH (STA 449 F5) analyzer

13

## 14 **2.5 Gas separation performance test of MMMs**

15 The gas separation performance test was based on the Wicke-Kallenbach technique.  
 16 Before testing, membranes were activated at  $120\text{ }^\circ\text{C}$  for 24h under vacuum. Then, all  
 17 the mixed matrix membrane were place a stainless-steel module with an effective  
 18 membrane area of  $1.77\text{ cm}^2$ . Both the one-component gas ( $\text{H}_2$ ,  $\text{CO}_2$ ) permeability and  
 19 mixed two-component gas permeability and separation ( $\text{H}_2/\text{CO}_2$ ) would be  
 20 characterized. The flow rate of feed gas was  $100\text{ ml min}^{-1}$ , and the flow rate of  
 21 sweeping gas (Ar) at the permeate side was  $40\text{ ml min}^{-1}$  in order to avoid  
 22 concentration polarization. For two-component mixed gas, the gas flow ratio was 1:1.  
 23 A transmembrane pressure drop of 0.5 bar was maintained for all tests. The  
 24 composition of the permeated gases was detected by a gas chromatography (Scion,  
 25 456-GC). Each membrane sample would be tested at least 3 times to get the average  
 26 permeation data. The gas permeability of component  $i$  ( $P_i$ ) in *Barrer* ( $1\text{ Barrer} = 1 \times$   
 27  $10^{-10}\text{ cm}^3\text{ (STP)}\cdot\text{cm}\cdot\text{cm}^{-2}\text{s}^{-1}\cdot\text{cmHg}^{-1}$ ) of mixed matrix membranes was evaluated  
 28 based on Equation (1):

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

29 where  $N_i$  is the volume flow rate ( $\text{cm}^3\text{(STP)}\cdot\text{s}^{-1}$ ),  $l$  is the membrane's thickness (m),  
 30  $\Delta P_i$  is the transmembrane pressure drop (cmHg), and  $A$  is the effective membrane's  
 31 area ( $\text{m}^2$ ).

32 The MMMs' selectivity ( $\alpha_{i/j}$ ) was calculated according to Equation (2):

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

33 where  $X_i/X_j$  and  $Y_i/Y_j$  are the volumetric fractions of the permeate and feed gas,  
 34 respectively.

35

## 36 **2.6 Thermodynamic calculation of gas permeation behavior of MMMs**

37 In this work,  $E_p$ ,  $E_D$  and  $\Delta H_S$  were used to describe the permeation behavior of gases  
 38 in MMM, which are the activation energies of permeation and diffusion and enthalpy

1 of sorption<sup>[24, 25]</sup>. The relation between  $E_P$ ,  $E_D$  and  $\Delta H_S$  is presented by Equation (3):

$$E_P = E_D + \Delta H_S \quad (3)$$

2  $E_P$  was calculated according to the Arrhenius empirical Equation (4):

$$\ln P = a - \frac{E_P}{RT} \quad (4)$$

3 Where  $P$  is the gas permeability,  $T$  is the measurement temperature (K), and  $R$  is the  
4 ideal gas constant.

5  $\Delta H_S$  can be calculated using the Clausius-Clapperron Equation (5):

$$\ln p = \frac{\Delta H_S}{R} \frac{1}{T} + C \quad (5)$$

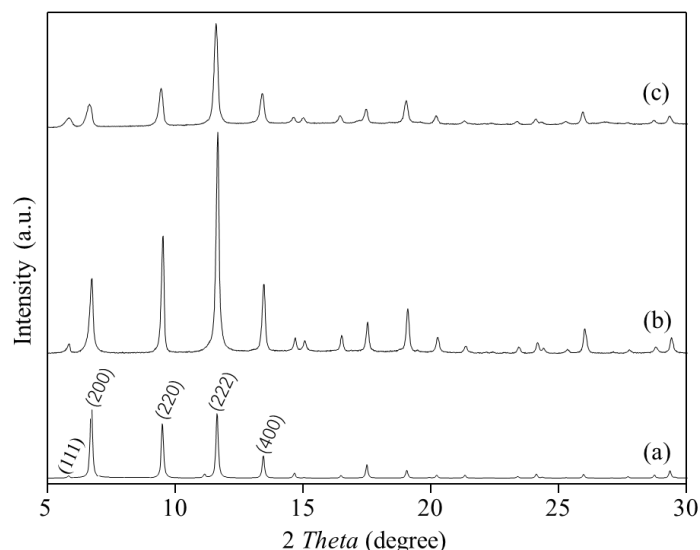
6 Where  $p$  (MPa) is the testing pressure,  $T$  (K) is the measurement temperature, and  $R$  is  
7 the ideal gas constant.

8

### 9 **3 Results and discussion**

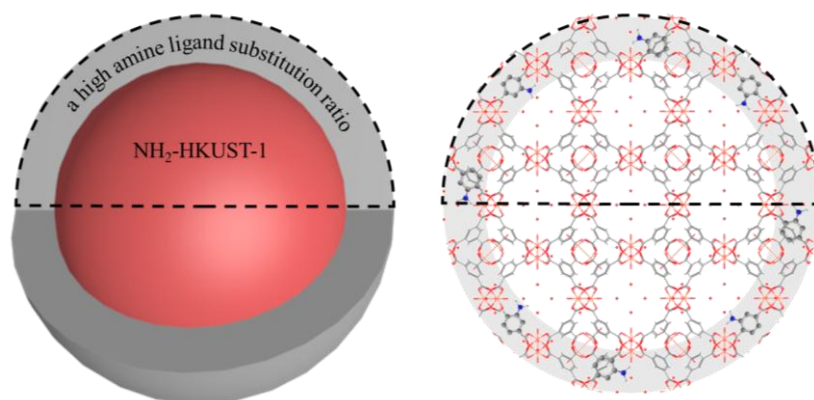
#### 10 **3.1 Structure analysis of NH<sub>2</sub>-HKUST-1 and HKUST-1 samples**

11 The X-Ray diffraction patterns of NH<sub>2</sub>-HKUST-1 and HKUST-1 samples, together  
12 with a simulated XRD pattern of HKUST-are shown in Figure 1 a-c. The  
13 characteristic peaks for NH<sub>2</sub>-HKUST-1 and HKUST-1 assigned to (111), (200), (220),  
14 (222), and (400) planes are present in the patterns and they are in good agreement  
15 with the simulated XRD, thus indicating the purity of the *in-situ* amino-modified  
16 sample. Assuming that the crystallinity of the HKUST-1 is 100%, the relative  
17 crystallinity of the NH<sub>2</sub>-HKUST-1 is 88.52%. The average crystal size of HKUST-1  
18 determined using Scheller's formula is 110 nm and of NH<sub>2</sub>-HKUST-1 is 70 nm. The  
19 difference in crystal size was also confirmed by SEM (Figure S1). The changes in  
20 crystallinity and crystal size of NH<sub>2</sub>-HKUST-1 are probably due to the introduction of  
21 hetero-structured amine based organic ligands (2-Aminoterephthalic acid). The  
22 deprotonation ability of 2-Aminoterephthalic acid ( $pK_a \approx 3.95$ ) is stronger than that of  
23 trimesic acid ( $pK_1=2.12$ ,  $pK_2=4.10$ ,  $pK_3=5.18$ ), causing 2-Aminoterephthalic acid to  
24 act as an capping agent thus inhibiting further growth of the crystals and leading to  
25 the reduction of the crystal size. The structures of HKUST-1 and NH<sub>2</sub>-HKUST-1  
26 samples have been refined and a slight increase of crystal cell parameter  $a$  from 26.32  
27 to 26.33 Å after amination, due to the partial substitution of organic ligands in the  
28 crystal structure is observed for NH<sub>2</sub>-HKUST-1 sample.



1  
2 **Figure 1 XRD patterns of (a) HKUST-1 (simulated), (b) HKUST-1 and (c)**  
3 **NH<sub>2</sub>-HKUST-1 samples**

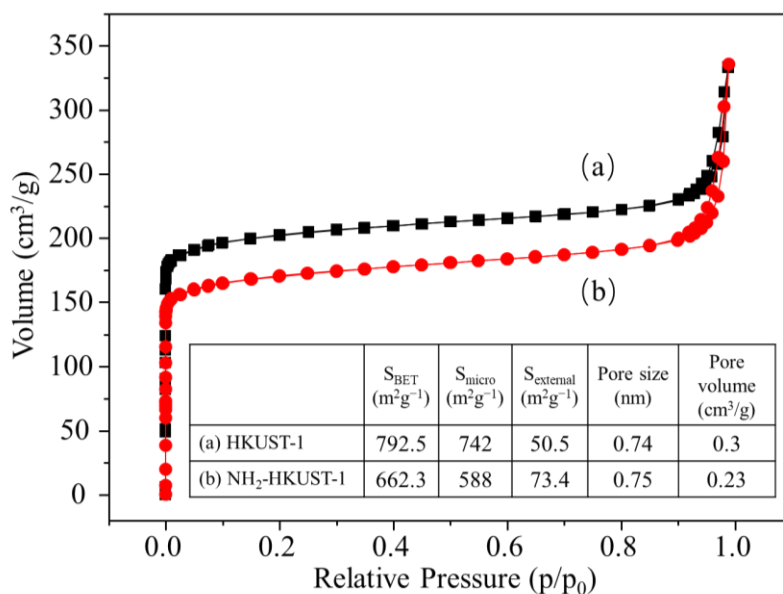
4 The substitution ratio of the 2-aminoterephthalic acid in the NH<sub>2</sub>-HKUST-1 was  
5 calculated based on the elemental analysis (Table S1). The ratio of m  
6 (2-aminoterephthalic acid): m (1,3,5-trihydroxybenzene) is calculated to be 1 : 5,  
7 which is lower than the feeding ratio 1 : 2 in the initial precursor mixture. Based on  
8 the XPS result (Figure S2), the ratio of m (2-aminoterephthalic acid): m  
9 (1,3,5-trihydroxybenzene) (1 : 1.3) of the outer surface of NH<sub>2</sub>-HKUST-1 was found  
10 to be higher than that of the bulk crystals suggesting the role of amine ligand as an  
11 inhibitor. Thus we hypothesized that the amino-modified NH<sub>2</sub>-HKUST-1 sample  
12 exhibits a “core-shell” structure as schematically presented in Figure 2. Due to the  
13 capping effect of the 2-aminoterephthalic acid entering the skeleton, the crystals stop  
14 growing, forming an outer surface with a higher amino ligand concentration.



15  
16 **Figure 2 Schematic presentation of NH<sub>2</sub>-HKUST-1 “core-shell” structure: the gray band**  
17 **is the outer surface of NH<sub>2</sub>-HKUST-1 crystals with a higher amine ligand**  
18 **(2-aminoterephthalic acid) amount**

19 The effect of amination on the crystals porous structure was studied by nitrogen  
20 adsorption (Figure 3). After amination, the HKUST-1 and NH<sub>2</sub>-HKUST-1 samples  
21 show a reduction of the BET surface area from 792.5 m<sup>2</sup>g<sup>-1</sup> to 662.3 m<sup>2</sup>g<sup>-1</sup>,  
22 respectively. While, the external surface area increased, due to the smaller particle

1 size of NH<sub>2</sub>-HKUST-1, the micropore volume decreased. The pore size remained the  
 2 same in both samples, which is consistent with XRD results. However, the decrease of  
 3 pore volume from 0.30 cm<sup>3</sup>/g to 0.23 cm<sup>3</sup>/g indicates the occupation of the pores by  
 4 -NH<sub>2</sub> groups.

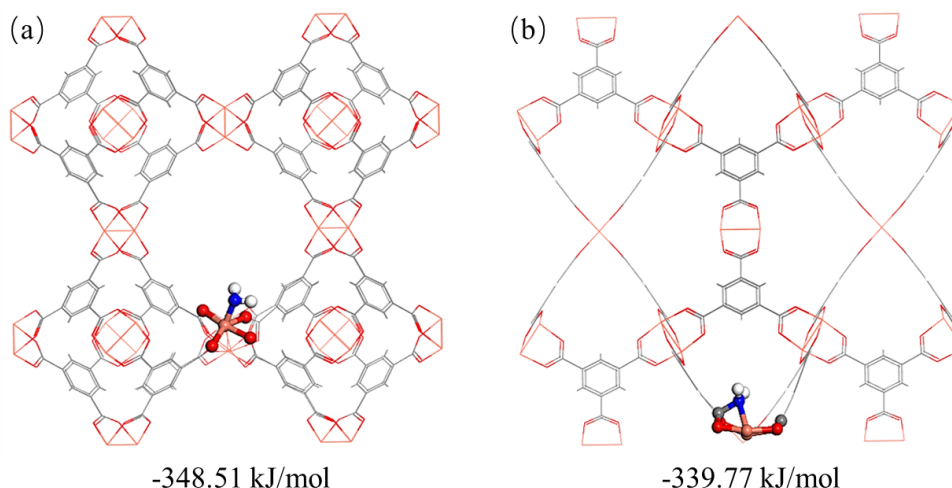


5  
 6 **Figure 3** N<sub>2</sub> adsorption isotherms of (a) HKUST-1 and (b) NH<sub>2</sub>-HKUST-1 recorded at  
 7 -196 °C; *Inset*: results deduced from the N<sub>2</sub> adsorption measurements.

8 The adsorption results of HKUST-1 and NH<sub>2</sub>-HKUST-1 samples further confirmed  
 9 the occupation of the pore space by the -NH<sub>2</sub> groups. Additionally, the NH<sub>2</sub>-HKUST-1  
 10 exhibits lower CO<sub>2</sub> adsorption capacity as shown in Figure S3 in contrast to previous  
 11 reports on surface functionalized MOFs materials<sup>[26, 27]</sup>. This result can be explained  
 12 with the reduced free pore volume of NH<sub>2</sub>-HKUST-1 occupied by the amino groups.  
 13 The decreased adsorption rate indicates that the amino groups do not act as active  
 14 sites on NH<sub>2</sub>-HKUST-1's surface.

15  
 16 The form of the 2-aminoterephthalic acid ligand in the NH<sub>2</sub>-HKUST-1 structure under  
 17 the action of the central metal Cu<sup>2+</sup> was calculated using the pm6<sup>[28]</sup> method of  
 18 Gaussian<sup>[29]</sup>. The binding energy of -NH<sub>2</sub> groups in the pores of the NH<sub>2</sub>-HKUST-1 is  
 19 -348.51 kJ/mol, while outside, at the surface of the crystals is -339.77 kJ/mol (Figure  
 20 4). This result indicates that amino groups are more likely to be confined in the  
 21 channels of the NH<sub>2</sub>-HKUST-1 which is consistent with the N<sub>2</sub> adsorption results  
 22 presented above.

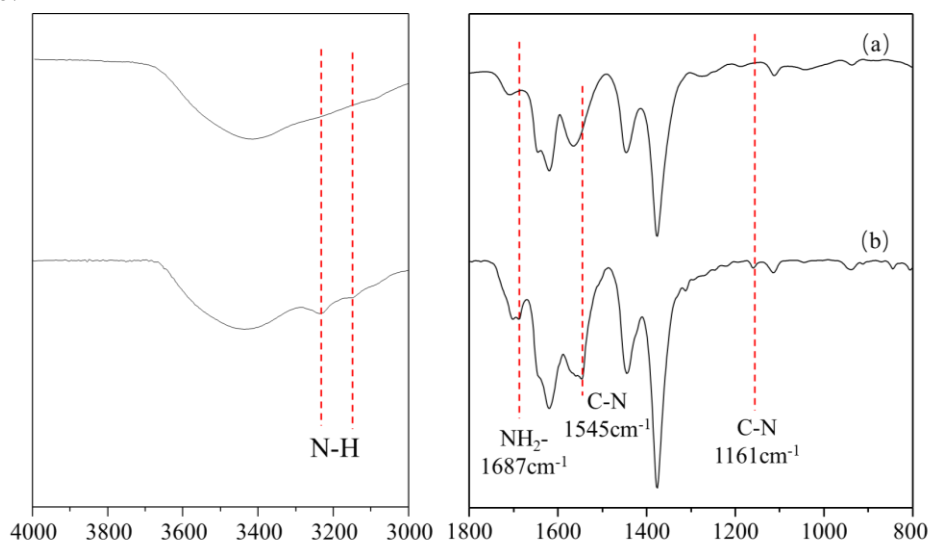




1  
2  
3

**Figure 4 Binding energy of amino group in the NH<sub>2</sub>-HKUST-1 sample: (a) inside the channels and (b) outside the crystals**

4 In order to further prove that the amino ligand enters in the pores of the crystals, both  
5 samples HKUST-1 and NH<sub>2</sub>-HKUST-1 were subjected to FT-IR characterization  
6 (Figure 5). The bands corresponding to the vibrations of C-O (1375 cm<sup>-1</sup>), benzene  
7 ring (1564 cm<sup>-1</sup>) and C=O (1644 cm<sup>-1</sup>) are observed in both samples. Two new bands  
8 in the spectrum of NH<sub>2</sub>-HKUST-1's at 3237 cm<sup>-1</sup> and 3151 cm<sup>-1</sup> appeared and they are  
9 attributed to the vibration of N-H<sup>[21, 30]</sup> (Figure 5b). Also the peak at 1687 cm<sup>-1</sup> is  
10 related to -NH<sub>2</sub><sup>[15]</sup>. The bands at 1161 cm<sup>-1</sup> and 1545 cm<sup>-1</sup> are corresponding to the  
11 C-N bond<sup>[21]</sup>. The new bands proved the presence of amino groups in NH<sub>2</sub>-HKUST-1  
12 sample.



13  
14

**Figure 5 FT-IR spectra of (a) HKUST-1 and (b) NH<sub>2</sub>-HKUST-1 crystals**

15 The TG study of both HKUST-1 and NH<sub>2</sub>-HKUST-1 reveals the structural change at  
16 270 °C and a residual mass of around 40% suggesting that the amine ligand has little  
17 effect on the structure (Figure S4). Before the decomposition and combustion of the  
18 organic ligand (270 °C), the weight loss of MOF crystal is mainly due to dehydration  
19 process, including the first step related to the removal of physically absorbed water

1 and the second step related to the release of chemisorbed water<sup>[31, 32]</sup>. Two  
2 endothermic peaks between 100 °C and 270 °C could be observed from the DTG  
3 curves (Figure S4 inserted figure), which correspond to the two dehydration processes.  
4 In NH<sub>2</sub>-HKUST-1, the first physical dehydration step ended at 187 °C, higher than  
5 that in HKUST-1 (164 °C), due to the stronger interaction formed by amino groups  
6 and water molecules. Additionally, the thermal degradation of NH<sub>2</sub>-HKUST-1 started  
7 at a lower temperature, due to the -NH<sub>2</sub> groups which decomposed at lower  
8 temperature<sup>[33]</sup>.

### 9 10 **3.2 Structural analysis of membranes**

11 In our previous work we demonstrated that loading of crystals in the membranes with  
12 less than 30% can avoid their agglomeration<sup>[18]</sup>. Therefore, in this work, we will focus  
13 on the MMMs with 10% and 30% filling amount. Seen from Figure S5, mixed matrix  
14 membranes with different amounts of fillers have XRD patterns belonging to PEI and  
15 MOF crystals, proving that HKUST-1 maintained its structure during the membrane  
16 preparation. The intensity of crystal peaks of MMMs with the same filler enhanced  
17 with the increase of loading amount. The signal intensity of HKUST-1 filled  
18 membranes are more obvious than that of NH<sub>2</sub>-HKUST-1 filled membranes, which is  
19 consistent with crystals' XRD patterns (Figure 1).

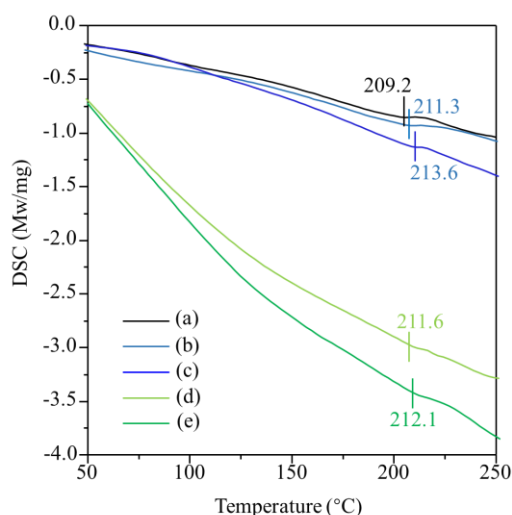
20  
21 As can be seen in SEM images (Figure S6), all the mixed matrix membranes are  
22 continuous and the HKUST-1 particles are evenly distributed. It is worth noting that  
23 when the filling amount reaches 30%, the cross-section morphology of  
24 HKUST-1-30%/PEI MMM exhibited more obvious polymer veins than that of  
25 NH<sub>2</sub>-HKUST-1-30%/PEI, which was caused by plastic deformation<sup>[34]</sup>. This was  
26 related to the different interaction strength between the NH<sub>2</sub>-HKUST-1 crystals and  
27 the PEI, which will be discussed below.

28  
29 Compared with membranes with HKUST-1 (HKUST-1-10%/PEI and  
30 HKUST-1-30%/PEI), the NH<sub>2</sub>-HKUST-1-10%/PEI and NH<sub>2</sub>-HKUST-1-30%/PEI  
31 show an additional peak at 3237 cm<sup>-1</sup> representative of N-H bond<sup>[21]</sup> (Figure S7).  
32 Previous works reported on amino-functional fillers forming hydrogen bonds with  
33 organic matrix, and the vibration of -NH<sub>2</sub> showed a significant blue shift<sup>[26, 35, 36]</sup>.  
34 While, no significant shift of this peak in the NH<sub>2</sub>-HKUST-1-10%/PEI and  
35 NH<sub>2</sub>-HKUST-1-30%/PEI membranes is observed, indicating that the chemical  
36 environment of N-H bond has not changed after loading in PEI matrix. It is suggested  
37 that the amino groups are mainly present in the pores rather than on the outer surface.  
38 The C=O band belonging to the PEI's 5-membered ring due to react with the Cu<sup>2+</sup>  
39 unsaturated metal sites exhibits an obvious blue shift in all samples. In the  
40 HKUST-1-30%/PEI MMM (Figure S7 c), the C=O band shifts from 1777.3 cm<sup>-1</sup> to  
41 1779.8 cm<sup>-1</sup>. However, in the NH<sub>2</sub>-HKUST-1-30%/PEI (Figure S7 e), the band  
42 shifting is less only from 1777.3 cm<sup>-1</sup> to 1778.3 cm<sup>-1</sup>. The electron donor -NH<sub>2</sub> group  
43 led to an increase in the electron cloud density of the NH<sub>2</sub>-HKUST-1 crystal,  
44 which might weakened the interaction between the PEI polymer and NH<sub>2</sub>-HKUST-1

1 crystals in the membranes. In summary, the amination of HKUST-1 does not improve  
2 the interactions between the NH<sub>2</sub>-HKUST-1 and the PEI as expected.

3  
4 The XPS results also showed that the interaction between NH<sub>2</sub>-HKUST-1 and PEI  
5 was not further enhanced. The XPS spectra for Cu 2p<sub>3/2</sub> of the pure crystals and  
6 membranes are shown in Figure S8. The XPS spectra of HKUST-1 (Figure S8a) and  
7 NH<sub>2</sub>-HKUST-1 (Figure S8b) contain a distinct peak at 934.97 eV and 934.95 eV, and  
8 a satellite peaks ranged from 948 eV to 937 eV<sup>[37, 38]</sup>, respectively. The  
9 NH<sub>2</sub>-HKUST-1(Cu) is similar to HKUST-1(Cu), suggesting that the -NH<sub>2</sub> groups do  
10 not coordinate with Cu<sup>2+</sup> but may be protruding into the pores<sup>[39]</sup>. By comparing the  
11 spectra recorded on the membranes and pure HKUST-1, NH<sub>2</sub>-HKUST-1 crystals, the  
12 signal intensity of Cu 2p<sub>3/2</sub> decreased. In the HKUST-1-30%/PEI membrane, the peak  
13 shift is due to the effect of C=O on Cu<sup>2+</sup> resulting in an increase of the electron cloud  
14 density of Cu<sup>2+</sup>. While, the shift decreases for the NH<sub>2</sub>-HKUST-1-30%/PEI membrane,  
15 confirming the weakened interactions.

16  
17 The TG of the membranes shows a significant inflection point around 300 °C, which  
18 is consistent with the TG results of pure HKUST-1, NH<sub>2</sub>-HKUST-1 materials,  
19 resulting from the collapse of their structure (Figure S9). DSC analysis before 300 °C  
20 reveals the glass transition temperature (*T<sub>g</sub>*) of the PEI polymer. Glass transition  
21 temperature reflects the lowest temperature at which molecular segments in a polymer  
22 can move. As can be seen from Figure 6, the *T<sub>g</sub>* rises after filling appropriate amount  
23 of HKUST-1 and NH<sub>2</sub>-HKUST-1 particles. The HKUST-1-30%/PEI membrane with  
24 the strongest interactions between PEI matrix and HKUST-1 crystals, has the highest  
25 *T<sub>g</sub>* of 213.6 °C, thus further explaining the higher effect of HKUST-1 than  
26 NH<sub>2</sub>-HKUST-1 on the PEI.



27  
28 **Figure 6 Differential scanning calorimetry (DSC) curves of (a) pure PEI membrane, (b)**  
29 **HKUST-1-10%/PEI, (c) HKUST-1-30%/PEI, (d) NH<sub>2</sub>-HKUST-1-10%/PEI and (e)**  
30 **NH<sub>2</sub>-HKUST-1-30%/PEI with the glass transition temperature (*T<sub>g</sub>*)**

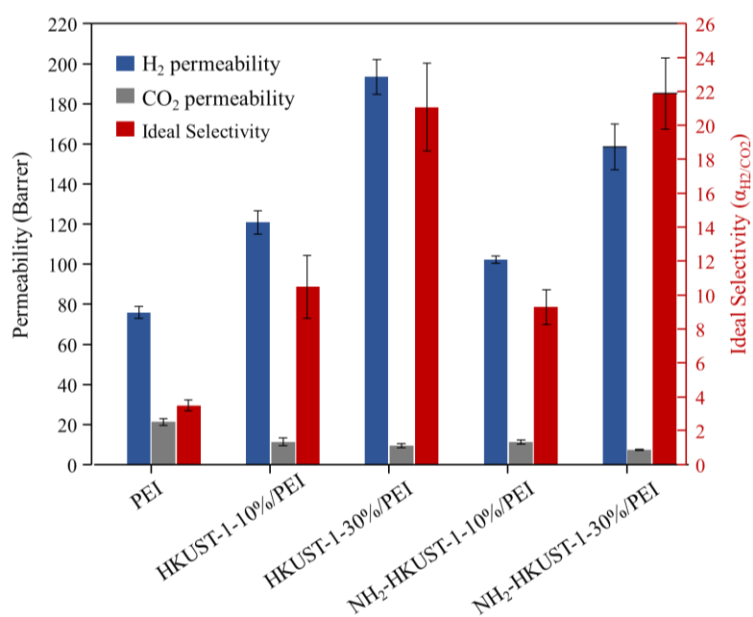
### 31 3.3 Gas separation performance of membranes

32 The H<sub>2</sub> and CO<sub>2</sub> single gas permeability of the pure PEI membrane and the mixed

1 matrix membranes were measured at 25 °C. The permeability and ideal selectivity  
 2 obtained for all membranes are depicted in Figure 7 and summarized in Table S2.  
 3 Overall, the H<sub>2</sub> permeability and selectivity of the MMMs improved with the addition  
 4 of both HKUST-1 and NH<sub>2</sub>-HKUST-1 compared with the parent PEI membrane. With  
 5 the increase of the loading amount of the same filler (HKUST-1 or NH<sub>2</sub>-HKUST-1),  
 6 the H<sub>2</sub> permeability increased. However, all MMMs exhibited reduced CO<sub>2</sub>  
 7 permeability, suggesting that both HKUST-1 and NH<sub>2</sub>-HKUST-1 fillers did not affect  
 8 the CO<sub>2</sub> permeance. The different trends in permeability of H<sub>2</sub> and CO<sub>2</sub> stated that the  
 9 effect of non-selective interface defects was low in MMMs. This is consistent with the  
 10 results presented in Figure S7, where the interactions between the filler (HKUST-1  
 11 and NH<sub>2</sub>-HKUST-1) and the PEI matrix were proved.

12

13 In order to further understand the effect of amino-modification of HKUST-1 on  
 14 MMMs, the performance of NH<sub>2</sub>-HKUST-1-30%/PEI and HKUST-1-30%/PEI was  
 15 compared. NH<sub>2</sub>-HKUST-1 sample has smaller crystal size than the HKUST-1 (Figure  
 16 S1). Generally, the reduction in crystal size leads to enhanced interfacial forces  
 17 between the filler and the matrix. While, according to the IR and TG analysis of  
 18 MMMs, we found that the interfacial interactions were not enhanced in the  
 19 NH<sub>2</sub>-HKUST-1-30%/PEI membrane. Therefore, we assume that the effect of  
 20 interfacial voids caused by size reduction has little effect on membrane's permeability.  
 21 The lower permeability of NH<sub>2</sub>-HKUST-1-30%/PEI membrane for both H<sub>2</sub> and CO<sub>2</sub>  
 22 was mainly due to the pore blockage by -NH<sub>2</sub> groups. While, there was a little  
 23 increase in ideal selectivity from 21.0 (HKUST-1-30%/PEI) to 21.9  
 24 (NH<sub>2</sub>-HKUST-1-30%/PEI), since the diffusion of large CO<sub>2</sub> molecule was more easily  
 25 limited by the narrowed diffusion channels. Thus, the amino groups located in the  
 26 pores caused a loss of membranes' permeability; there membranes  
 27 (NH<sub>2</sub>-HKUST-1-10%/PEI and NH<sub>2</sub>-HKUST-1-30%/PEI) were not subjected to  
 28 optimization.

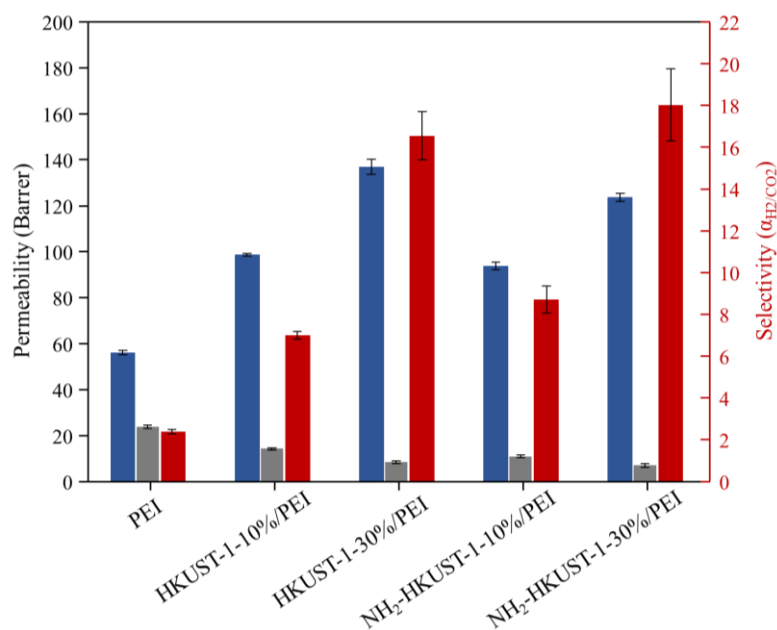


29  
30

**Figure 7 Single gas separation performance of pristine PEI membrane and mixed**

1 **matrix membranes HKUST-1/PEI and NH<sub>2</sub>-HKUST-1 measured at 25 °C**

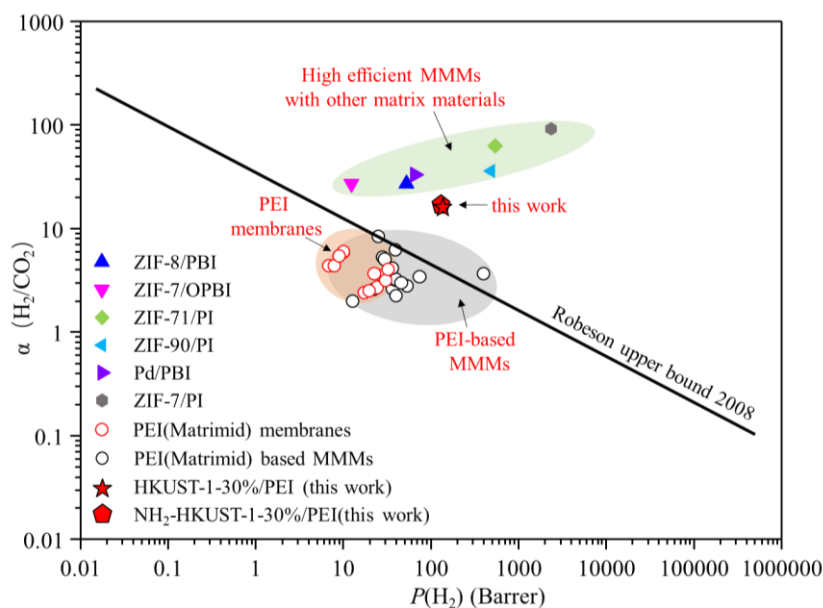
2 The mixed gas separation performance of the MMMs has the similar trend as the  
3 single component gas separation testing (Figure 8 and Table S3). The  
4 NH<sub>2</sub>-HKUST-1-30%/PEI membrane showed a decrease gas permeability for both H<sub>2</sub>  
5 and CO<sub>2</sub> with a slight improved selectivity. However, due to the competitive  
6 adsorption of H<sub>2</sub> and CO<sub>2</sub>, the mixed gas separation performance (both permeability  
7 and selectivity) of this membrane was lower than that of the single component gas  
8 separation performance.



9  
10 **Figure 8 Mixed gas separation performance of pristine PEI membrane and mixed**  
11 **matrix membranes HKUST-1/PEI and NH<sub>2</sub>-HKUST-1 measured at 25 °C**

12 The Robeson upper boundary (2008) was used to evaluate the H<sub>2</sub>/CO<sub>2</sub> separation  
13 performance of HKUST-1-30%/PEI and NH<sub>2</sub>-HKUST-1-30%/PEI MMMs (Figure 9  
14 and Table S5)<sup>[40]</sup>. First, we found that the H<sub>2</sub>/CO<sub>2</sub> separation performances of  
15 PEI-based MMMs, filling small pore MOFs (such as ZIF-8, ZIF-90, ZIF-12), were  
16 close to the upper boundary. Compared with pure PEI membranes, the main  
17 contribution of filler materials was the improvement of H<sub>2</sub> permeability. After adding  
18 HKUST-1 or NH<sub>2</sub>-HKUST-1, the H<sub>2</sub> permeability of HKUST-1-30%/PEI and  
19 NH<sub>2</sub>-HKUST-1-30%/PEI MMMs was improved more significantly, and the selectivity  
20 also increased. As HKUST-1 does not have molecular sieving property for H<sub>2</sub>/CO<sub>2</sub>  
21 separation, its highly permeable channels mainly contributed to the performance's  
22 optimization under the “adsorption-diffusion coupling control” mechanism.  
23 Nevertheless, the amino-functionalization exhibited a negative effect on the high  
24 permeability of MMMs due to the pore blockage. Second, there is a performance  
25 gap between our work and other high efficient MMMs, which is mainly related to the  
26 intrinsic separation performance of the matrix materials. Efficient matrices, such as  
27 polybenzimidazole (PBI), polyimides (PIs), and polymers of intrinsic microporosity  
28 (PIMs), generally exhibit high intrinsic gas permeability and selectivity. However, the  
29 price, synthesis process, processibility and mechanical strength of matrices should

1 also be considered. The PBI matrix is an expensive and difficult to process, the PIMs  
 2 matrix shows poor mechanical properties. Compared with them, the PEIs showed  
 3 high mechanical stability and economically viable for applications.



4

5 **Figure 9 H<sub>2</sub>/CO<sub>2</sub> separation performance of MMMs via Robeson upper bound (2008)<sup>[40]</sup>;**  
 6 **details are shown in Table S5<sup>[41, 60]</sup>**

7 As discussed in the introduction section, the main challenge for MMMs for H<sub>2</sub>/CO<sub>2</sub>  
 8 separation is the high adsorption and solubility of CO<sub>2</sub> in MMMs, which results in  
 9 lower H<sub>2</sub>/CO<sub>2</sub> selectivity compared to other gas pairs that requires high CO<sub>2</sub>  
 10 permeability, such as CO<sub>2</sub>/CH<sub>4</sub>. This work provides new strategy to achieve H<sub>2</sub>/CO<sub>2</sub>  
 11 separation by utilizing HKUST-1 crystals with big pores. While, the amino-functionalization  
 12 of the HKUST-1 crystals leading to pore blockage has a negative effect on the separation.  
 13

14

### 15 3.4 Gas separation mechanism

16 In our previous work, we reported the “adsorption-diffusion coupling control”  
 17 separation mechanism under addition of large-pore HKUST-1 in the MMM for  
 18 separation of small H<sub>2</sub> molecules from CO<sub>2</sub> molecules, thus suggesting the diffusion  
 19 control H<sub>2</sub> permeation and adsorption prevention of CO<sub>2</sub> permeation<sup>[18]</sup>. Here, we  
 20 studied the role of amino groups in the HKUST-1 crystals. According to the gas  
 21 separation results, we found that the diffusion of gas molecules was blocked by the  
 22 amino-functional groups of the NH<sub>2</sub>-HKUST-1-30%/PEI mainly occupying the  
 23 permeable channels, resulting in decreased permeability for both H<sub>2</sub> and CO<sub>2</sub>. In  
 24 addition, the small NH<sub>2</sub>-HKUST-1 crystals used in this work did not show obvious  
 25 enhancement of the interfacial voids. Thermodynamic study was used to elucidate the  
 26 pore blockage and adsorption effect of -NH<sub>2</sub> groups (Table 1 and Figure S4). Firstly,  
 27 the activation energy of permeation (E<sub>p</sub>) of the small H<sub>2</sub> molecules is lower than that  
 28 of the big CO<sub>2</sub> molecules, resulting in high H<sub>2</sub>/CO<sub>2</sub> selectivity of the membranes.  
 29 Secondly, the decreased ΔH<sub>S</sub> (H<sub>2</sub> and CO<sub>2</sub>) of NH<sub>2</sub>-HKUST-1-30%/PEI membrane

1 showed that the amino groups has little effect on the adsorption property of the  
 2 MMMs, which may be due to the unexposed adsorption sites. The higher  $E_{D(H_2 \text{ and } CO_2)}$   
 3 for  $NH_2$ -HKUST-1-30%/PEI than for HKUST-1-30%/PEI probably is resulted from  
 4 the pore blockage. The  $\Delta E_{D(CO_2)}$  is bigger than the  $\Delta E_{D(H_2)}$ , indicating that the pore  
 5 blockage with  $-NH_2$  groups had a greater effect on the  $CO_2$  molecules. Thereby, the  
 6 presence of amino groups in the HKUST-1's pores results in pore blockage, and  
 7 eventually led to the deterioration of the membranes permeability.

8 **Table 1 Thermodynamic calculations of mixed matrix membranes**

Gas	Membrane	$E_p$ (kJ/mol)	$\Delta H_S$ (kJ/mol)	$E_D$ (kJ/mol)
$H_2$	HKUST-1-30%/PEI	5.3	-12.4	17.7
	$NH_2$ -HKUST-1-30%/PEI	6.0	-11.9	17.9
$CO_2$	HKUST-1-30%/PEI	10.9	-24.8	35.7
	$NH_2$ -HKUST-1-30%/PEI	15.8	-21.8	37.6

9

#### 10 **4 Conclusions**

11  $NH_2$ -HKUST-1 was synthesized successfully and thoroughly characterized in  
 12 comparison to the parent HKUST-1 sample. FT-IR results confirmed the introduction  
 13 of  $-NH_2$  in the HKUST-1's sample. The crystallinity and spatial distribution of amino  
 14 groups showed that the amino ligand (2-Aminoterephthalic acid) mainly is present on  
 15 the outer surface of  $NH_2$ -HKUST-1 due to the end-capping effect, forming a  
 16 "core-shell" crystal structure. While, the  $N_2$  adsorption results and theoretical  
 17 calculation suggested that the  $-NH_2$  groups of the ligand tend to be constrained in the  
 18 pores of  $NH_2$ -HKUST-1 crystals under the action of  $Cu^{2+}$  resulting in pore blockage.  
 19 As a result, the mixed matrix membranes prepared ( $NH_2$ -HKUST-1/PEI) did not  
 20 exhibit enhanced interfacial interactions. Furthermore, the pore blockage seriously  
 21 affected the diffusion of the gas molecules, leading to decrease of the gas permeability  
 22 of the  $NH_2$ -HKUST-1-30%/PEI membrane. Despite the little improvement in  
 23 selectivity, the sacrifice of permeability makes the amino-modification not an  
 24 appropriate optimization strategy for preparation of MMMs. This work demonstrated  
 25 the negative effect of amino-modification/functionalization to the HKUST-1 materials  
 26 on MMMs performance. Further the spatial distribution of amino groups in the  
 27 HKUST-1 should be considered and optimize prior using for MMMs fabrication.

28

#### 29 **Declaration of Competing Interest**

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

32

#### 33 **Acknowledgements**

34 This work was supported by National Key Research and Development Program of  
 35 China of Ministry of Science and Technology (2022YFE0116000), National Natural

1 Science Foundation of China (No. 22175200, No. 21975285), the Fundamental  
2 Research Funds for the Central Universities (No. 21CX06024A), and Qingdao  
3 Postdoctoral Research Project (No. qddy20210005), Fujian Province Science and  
4 Technology Program, Innovation Fund (2022C0021).

## 6 References

- 7 [1]L. Shao, B. T. Low, T. Chung, A. R. Greenberg, Polymeric Membranes for the Hydrogen  
8 Economy: Contemporary Approaches and Prospects for the Future, *J. Membrane Sci.*,  
9 327 (2009) 18-31. <https://doi.org/10.1016/j.memsci.2008.11.019>.
- 10 [2]D. Sholl, R. Lively, Seven Chemical Separations to Change the World, *Nature*, 532 (2016)  
11 435-437. <https://doi.org/10.1038/532435a>.
- 12 [3]M. Galizia, W. S. Chi, Z. P. Smith, T. C. Merkel, R. W. Baker, B. D. Freeman, 50Th  
13 Anniversary Perspective : Polymers and Mixed Matrix Membranes for Gas and Vapor  
14 Separation: A Review and Prospective Opportunities, *Macromolecules*, 50 (2017)  
15 7809-7843. <https://doi.org/10.1021/acs.macromol.7b01718>.
- 16 [4]M. Ahmadi, S. Janakiram, Z. Dai, L. Ansaloni, L. Deng, Performance of Mixed Matrix  
17 Membranes Containing Porous Two-Dimensional (2D) and Three-Dimensional (3D)  
18 Fillers for CO<sub>2</sub> Separation: A Review, *Membranes*, 8 (2018) 1-50.  
19 <https://doi.org/10.3390/membranes8030050>.
- 20 [5]A. R. Kamble, C. M. Patel, Z. V. P. Murthy, A Review On the Recent Advances in Mixed  
21 Matrix Membranes for Gas Separation Processes, *Renew. Sust. Energ. Rev.*, 145 (2021)  
22 111062. <https://doi.org/10.1016/j.rser.2021.111062>.
- 23 [6]Q. Qian, P. A. Asinger, M. J. Lee, G. Han, K. Mizrahi Rodriguez, S. Lin, F. M. Benedetti,  
24 A. X. Wu, W. S. Chi, Z. P. Smith, MOF-Based Membranes for Gas Separations, *Chem.*  
25 *Rev.*, 120 (2020) 8161-8266. <https://doi.org/10.1021/acs.chemrev.0c00119>.
- 26 [7]W. K. Setiawan, K. Chiang, Silica Applied as Mixed Matrix Membrane Inorganic Filler  
27 for Gas Separation: A Review, *Sustain. Environ. Res.*, 29 (2019) 29-32.  
28 <https://doi.org/10.1186/s42834-019-0028-1>.
- 29 [8]D. Bastani, N. Esmaeili, M. Asadollahi, Polymeric Mixed Matrix Membranes Containing  
30 Zeolites as a Filler for Gas Separation Applications: A Review, *J. Ind. Eng. Chem.*, 19  
31 (2013) 375-393. <https://doi.org/10.1016/j.jiec.2012.09.019>.
- 32 [9]S. H. Goh, H. S. Lau, W. F. Yong, Metal–Organic Frameworks (MOFs)- Based Mixed  
33 Matrix Membranes (MMMs) for Gas Separation: A Review On Advanced Materials in  
34 Harsh Environmental Applications, *Small*, 18 (2022) 2107536.  
35 <https://doi.org/10.1002/sml.202107536>.
- 36 [10]Y. Cheng, S. J. Datta, S. Zhou, J. Jia, O. Shekhah, M. Eddaoudi, Advances in  
37 Metal-Organic Framework-Based Membranes, *Chem. Soc. Rev.*, 51 (2022) 8300-8350.  
38 <https://doi.org/10.1039/d2cs00031h>.
- 39 [11]M. Kalaj, K. C. Bentz, S. Ayala, J. M. Palomba, K. S. Barcus, Y. Katayama, S. M. Cohen,  
40 MOF-Polymer Hybrid Materials: From Simple Composites to Tailored Architectures,  
41 *Chem. Rev.*, 120 (2020) 8267-8302. <https://doi.org/10.1021/acs.chemrev.9b00575>.
- 42 [12]M. W. Anjum, F. Vermoortele, A. L. Khan, B. Bueken, D. E. De Vos, I. F. J.  
43 Vankelecom, Modulated UiO-66-Based Mixed-Matrix Membranes for CO<sub>2</sub> Separation,



- 1 ACS Appl. Mater. Inter., 7 (2015) 25193-25201. <https://doi.org/10.1021/acsami.5b08964>.
- 2 [13]H. Molavi, A. Shojaei, S. A. Mousavi, Improving Mixed-Matrix Membrane  
3 Performance via Pmma Grafting From Functionalized NH<sub>2</sub>-UiO-66, *J. Mater. Chem. A*, 6  
4 (2018) 2775-2791. <https://doi.org/10.1039/C7TA10480D>.
- 5 [14]S. Meshkat, S. Kaliaguine, D. Rodrigue, Mixed Matrix Membranes Based On Amine and  
6 Non-Amine MiL-53(Al) in Pebax® MH-1657 for CO<sub>2</sub> Separation, *Sep. Purif. Technol.*,  
7 200 (2018) 177-190. <https://doi.org/10.1016/j.seppur.2018.02.038>.
- 8 [15]N. Tien-Binh, H. Vinh-Thang, X. Y. Chen, D. Rodrigue, S. Kaliaguine, Polymer  
9 Functionalization to Enhance Interface Quality of Mixed Matrix Membranes for High  
10 CO<sub>2</sub>/CH<sub>4</sub> Gas Separation, *J. Mater. Chem. A*, 3 (2015) 1522-15213.  
11 <https://doi.org/10.1039/c5ta01597a>.
- 12 [16]Y. Pu, Z. Yang, V. Wee, Z. Wu, Z. Jiang, D. Zhao, Amino-Functionalized NUS-8  
13 Nanosheets as Fillers in PIM-1 Mixed Matrix Membranes for CO<sub>2</sub> Separations, *J.*  
14 *Membrane Sci.*, 641 (2022) 119912. <https://doi.org/10.1016/j.memsci.2021.119912>.
- 15 [17]F. N. Al-Rowaili, M. Khaled, A. Jamal, U. Zahid, Mixed Matrix Membranes for H<sub>2</sub>/CO<sub>2</sub>  
16 Gas Separation-A Critical Review, *Fuel*, 333 (2023) 126285.  
17 <https://doi.org/10.1016/j.fuel.2022.126285>.
- 18 [18]Y. Wang, G. Yang, H. Guo, X. Meng, G. Kong, Z. Kang, R. Guillet-Nicolas, S. Mintova,  
19 Preparation of HKUST-1/PEI Mixed-Matrix Membranes: Adsorption-Diffusion Coupling  
20 Control of Small Gas Molecules, *J. Membrane Sci.*, 643 (2022) 120070.  
21 <https://doi.org/10.1016/j.memsci.2021.120070>.
- 22 [19]F. Hamidavi, A. Kargari, A. Eliassi, Sorption and Permeation Study of  
23 Polyetherimide/Hydrophobic Silica Nanocomposite Membrane for Effective Syngas  
24 (H<sub>2</sub>/CO/CO<sub>2</sub>) Separation, *Sep. Purif. Technol.*, 279 (2021) 119774.  
25 <https://doi.org/10.1016/j.seppur.2021.119774>.
- 26 [20]J. Hu, H. Cai, H. Ren, Y. Wei, Z. Xu, H. Liu, Y. Hu, Mixed-Matrix Membrane Hollow  
27 Fibers of Cu<sub>3</sub>(BTC)<sub>2</sub> MOF and Polyimide for Gas Separation and Adsorption, *Ind. Eng.*  
28 *Chem. Res.*, 49 (2010) 12605-12612. <https://doi.org/10.1021/ie1014958>.
- 29 [21]B. Ge, Y. Xu, H. Zhao, H. Sun, Y. Guo, W. Wang, High Performance Gas Separation  
30 Mixed Matrix Membrane Fabricated by Incorporation of Functionalized  
31 Submicrometer-Sized Metal-Organic Framework, *Materials*, 11 (2018) 1421.  
32 <https://doi.org/10.3390/ma11081421>.
- 33 [22]K. Pirzadeh, K. Esfandiari, A. A. Ghoreyshi, M. Rahimnejad, CO<sub>2</sub> and N<sub>2</sub> Adsorption and  
34 Separation Using Aminated UiO-66 and Cu<sub>3</sub>(BTC)<sub>2</sub>: A Comparative Study, *Korean J.*  
35 *Chem. Eng.*, 37 (2020) 513-524. <https://doi.org/10.1007/s11814-019-0433-5>.
- 36 [23]Y. Wang, H. Ge, Y. Wu, G. Ye, H. Chen, X. Hu, Construction of an Electrochemical  
37 Sensor Based On Amino-Functionalized Metal-Organic Frameworks for Differential  
38 Pulse Anodic Stripping Voltammetric Determination of Lead, *Talanta*, 129 (2014)  
39 100-105. <https://doi.org/10.1016/j.talanta.2014.05.014>.
- 40 [24]K. A. Stevens, J. D. Moon, H. Borjigin, R. Liu, R. M. Joseph, J. S. Riffle, B. D. Freeman,  
41 Influence of Temperature On Gas Transport Properties of Tetraaminodiphenylsulfone  
42 (TADPS) Based Polybenzimidazoles, *J. Membrane Sci.*, 593 (2020) 117427.  
43 <https://doi.org/10.1016/j.memsci.2019.117427>.
- 44 [25]A. Fuoco, B. Satilmis, T. Uyar, M. Monteleone, E. Esposito, C. Muzzi, E. Tocci, M.

- 1 Longo, M. P. De Santo, M. Lanč, K. Friess, O. Vopička, P. Izák, J. C. Jansen,  
2 Comparison of Pure and Mixed Gas Permeation of the Highly Fluorinated Polymer of  
3 Intrinsic Microporosity PIM-2 Under Dry and Humid Conditions: Experiment and  
4 Modelling, *J. Membrane Sci.*, 594 (2020) 117460.  
5 <https://doi.org/10.1016/j.memsci.2019.117460>.
- 6 [26]O. G. Nik, X. Y. Chen, S. Kaliaguine, Functionalized Metal Organic  
7 Framework-Polyimide Mixed Matrix Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation, *J. Membrane*  
8 *Sci.*, 413-414 (2012) 48-61. <https://doi.org/10.1016/j.memsci.2012.04.003>.
- 9 [27]H. Molavi, A. Shojaei, Mixed-Matrix Composite Membranes Based On UiO-66-Derived  
10 MOFs for CO<sub>2</sub> Separation, *ACS Appl. Mater. Inter.*, 11 (2019) 9448-9461.  
11 <https://doi.org/10.1021/acsami.8b20869>.
- 12 [28]J. J. P. Stewart, Optimization of Parameters for Semiempirical Methods V: Modification  
13 of NDDO Approximations and Application to 70 Elements, *J. Mol. Model.*, 13 (2007)  
14 1173-1213. <https://doi.org/10.1007/s00894-007-0233-4>.
- 15 [29]M. Jfg, W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G.  
16 Scalmani, V. Barone, B. Mennucci, G. A. Petersson, *Gaussian 09, Revision a. 1;*  
17 *Gaussian* (2009).
- 18 [30]B. C. E. Silva, K. Irikura, R. C. G. Frem, M. V. B. Zanoni, Effect of Cu(BDC-NH<sub>2</sub>) Mof  
19 Deposited On Cu/Cu<sub>2</sub>O Electrode and its Better Performance in Photoelectrocatalytic  
20 Reduction of CO<sub>2</sub>, *J. Electroanal. Chem.*, 880 (2021) 114856.  
21 <https://doi.org/10.1016/j.jelechem.2020.114856>.
- 22 [31]F. Israr, D. K. Kim, Y. Kim, S. J. Oh, K. C. Ng, W. Chun, Synthesis of Porous Cu- BTC  
23 with Ultrasonic Treatment: Effects of Ultrasonic Power and Solvent Condition, *Ultrason.*  
24 *Sonochem.*, 29 (2016) 186-193. <https://doi.org/10.1016/j.ultsonch.2015.08.023>.
- 25 [32]A. Domán, J. Madarász, K. László, In Situ Evolved Gas Analysis Assisted  
26 Thermogravimetric (Tg-FTIR and Tg/DTA-MS) Studies On Non-Activated Copper  
27 Benzene-1,3,5-Tricarboxylate, *Thermochim. Acta*, 647 (2017) 62-69.  
28 <https://doi.org/10.1016/j.tca.2016.11.013>.
- 29 [33]R. Abedini, M. Omidkhah, F. Dorosti, Highly Permeable  
30 Poly(4-Methyl-1-Pentyne)/NH<sub>2</sub>-MiL53(Al) Mixed Matrix Membrane for CO<sub>2</sub>/CH<sub>4</sub>  
31 Separation, *RSC Adv.* (2014) 36522-36537. <https://doi.org/10.1039/C4RA07030E>.
- 32 [34]E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, Metal-Organic Polyhedra 18  
33 Mixed-Matrix Membranes for Gas Separation, *J. Membrane Sci.*, 463 (2014) 82-93.  
34 <https://doi.org/10.1016/j.memsci.2014.03.045>.
- 35 [35]Q. Xin, J. Ouyang, T. Liu, Z. Li, Z. Li, Y. Liu, S. Wang, H. Wu, Z. Jiang, X. Cao,  
36 Enhanced Interfacial Interaction and CO<sub>2</sub> Separation Performance of Mixed Matrix  
37 Membrane by Incorporating Polyethylenimine-Decorated Metal-Organic Frameworks,  
38 *ACS Appl. Mater. Inter.*, 7 (2015) 1065-1077. <https://doi.org/10.1021/am504742q>.
- 39 [36]B. Zornoza, A. Martinez-Joaristi, P. Serra-Crespo, C. Tellez, J. Coronas, J. Gascon, F.  
40 Kapteijn, Functionalized Flexible MOFs as Fillers in Mixed Matrix Membranes for  
41 Highly Selective Separation of CO<sub>2</sub> From CH<sub>4</sub> at Elevated Pressures, *Chem. Commun.*,  
42 47 (2011) 9522-9524. <https://doi.org/10.1039/c1cc13431k>.
- 43 [37]A. S. Duke, E. A. Dolgoplova, R. P. Galhenage, S. C. Ammal, A. Heyden, M. D. Smith,  
44 D. A. Chen, N. B. Shustova, Active Sites in Copper-Based Metal-Organic Frameworks:

- 1 Understanding Substrate Dynamics, Redox Processes, and Valence-Band Structure, *J.*  
2 *Phys Chem. C*, 119 (2015) 27457-27466. <https://doi.org/10.1021/acs.jpcc.5b08053>.
- 3 [38]Y. Wu, H. Zhang, Y. Yan, J. Peng, High Efficient HKUST-1 Membrane Over Paper-Like  
4 Steel Fibers for Direct Catalytic Wet Peroxide Oxidation of Phenol, *Mater. Chem. Phys.*,  
5 252 (2020) 123119. <https://doi.org/10.1016/j.matchemphys.2020.123119>.
- 6 [39]H. Wang, X. Yuan, Y. Wu, G. Zeng, X. Chen, L. Leng, Z. Wu, L. Jiang, H. Li, Facile  
7 Synthesis of Amino-Functionalized Titanium Metal-Organic Frameworks and their  
8 Superior Visible-Light Photocatalytic Activity for Cr(VI) Reduction, *J. Hazard. Mater.*,  
9 286 (2015) 187-194. <https://doi.org/10.1016/j.jhazmat.2014.11.039>.
- 10 [40]L. M. Robeson, The Upper Bound Revisited, *J. Membrane Sci.*, 320 (2008) 390-400.  
11 <https://doi.org/10.1016/j.memsci.2008.04.030>.
- 12 [41]G. Li, Z. Si, S. Yang, Y. Zhuang, S. Pang, Y. Cui, J. Baeyens, P. Qin, A Defects-Free  
13 ZIF-90/6FDA-Durene Membrane Based On the Hydrogen Bonding/Covalent Bonding  
14 Interaction for Gas Separation, *J. Membrane Sci.*, 661 (2022) 120910.  
15 <https://doi.org/10.1016/j.memsci.2022.120910>.
- 16 [42]X. Jiang, S. He, G. Han, J. Long, S. Li, C. H. Lau, S. Zhang, L. Shao, Aqueous One-Step  
17 Modulation for Synthesizing Monodispersed ZIF-8 Nanocrystals for Mixed-Matrix  
18 Membrane, *ACS Appl. Mater. Inter.*, 13 (2021) 11296-11305.  
19 <https://doi.org/10.1021/acsami.0c22910>.
- 20 [43]M. Usman, M. Y. Khan, T. Anjum, A. L. Khan, B. Hoque, A. Helal, A. S. Hakeem, B. A.  
21 Al-Maythaly, Controlled Covalent Functionalization of ZIF-90 for Selective CO<sub>2</sub>  
22 Capture & Separation, *Membranes*, 12 (2022) 1055.  
23 <https://doi.org/10.3390/membranes12111055>.
- 24 [44]M. Boroglu, I. Boz, B. Kaya, Effect of New Metal-Organic Framework (Zeolitic  
25 Imidazolate Framework [ZIF-12]) in Mixed Matrix Membranes On Structure,  
26 Morphology, and Gas Separation Properties, *J. Polym. Eng.*, 41 (2021) 259-270.  
27 <https://doi.org/10.1515/polyeng-2020-0288>.
- 28 [45]M. Safak Boroglu, M. Ugur, I. Boz, Enhanced Gas Transport Properties of Mixed Matrix  
29 Membranes Consisting of Matrimid and RHO Type ZIF-12 Particles, *Chem. Eng. Res.*  
30 *Des.*, 123 (2017) 201-213. <https://doi.org/10.1016/j.cherd.2017.05.010>.
- 31 [46]S. Japip, K. Liao, Y. Xiao, T. Chung, Enhancement of Molecular-Sieving Properties by  
32 Constructing Surface Nano-Metric Layer Via Vapor Cross-Linking, *J. Membrane Sci.*,  
33 497 (2016) 248-258. <https://doi.org/10.1016/j.memsci.2015.09.045>.
- 34 [47]L. Hu, V. T. Bui, S. Pal, W. Guo, A. Subramanian, K. Kisslinger, S. Fan, C. Y. Nam, Y.  
35 Ding, H. Lin, In Situ Growth of Crystalline and Polymer- Incorporated Amorphous ZIFs  
36 in Polybenzimidazole Achieving Hierarchical Nanostructures for Carbon Capture, *Small*,  
37 18 (2022) 2201982. <https://doi.org/10.1002/sml.202201982>.
- 38 [48]D. Carter, F. H. Tezel, B. Kruczek, H. Kalipcilar, Investigation and Comparison of Mixed  
39 Matrix Membranes Composed of Polyimide Matrimid with ZIF-8, Silicalite, and SAPO-  
40 34, *J. Membrane Sci.*, 544 (2017) 35-46. <https://doi.org/10.1016/j.memsci.2017.08.068>.
- 41 [49]L. Diestel, N. Wang, A. Schulz, F. Steinbach, J. Caro, Matrimid-Based Mixed Matrix  
42 Membranes: Interpretation and Correlation of Experimental Findings for Zeolitic  
43 Imidazolate Frameworks as Fillers in H<sub>2</sub>/CO<sub>2</sub> Separation, *Ind. Eng. Chem. Res.*, 54 (2015)  
44 1103-1112. <https://doi.org/10.1021/ie504096j>.

- 1 [50]S. Yang, Y. Wang, P. Lu, H. Jin, F. Pan, Z. Shi, X. Jiang, C. Chen, Z. Jiang, Y. Li,  
2 Metal–Organic Frameworks Corset with a Thermosetting Polymer for Improved  
3 Molecular-Sieving Property of Mixed-Matrix Membranes, *ACS Appl. Mater. Inter.*, 12  
4 (2020) 55308-55315. <https://doi.org/10.1021/acsami.0c17426>.
- 5 [51]R. Martinez-Tirado, N. Yuriychuk, M. Iglesias, M. López-González, E. M. Maya, Mixed  
6 Matrix Membranes Containing a Biphenyl-Based Knitting Aryl Polymer and Gas  
7 Separation Performance, *Membranes*, 11 (2021) 914.  
8 <https://doi.org/10.3390/membranes11120914>.
- 9 [52]M. Arjmandi, M. Pakizeh, Mixed Matrix Membranes Incorporated with Cubic-MOF-5 for  
10 Improved Polyetherimide Gas Separation Membranes: Theory and Experiment, *J. Ind.*  
11 *Eng. Chem.*, 20 (2014) 3857-3868. <https://doi.org/10.1016/j.jiec.2013.12.091>.
- 12 [53]S. Zid, P. Alcouffe, M. Zinet, E. Espuche, Mixed-Matrix Membranes Based On  
13 Polyetherimide, Metal–Organic Framework and Ionic Liquid: Influence of the  
14 Composition and Morphology On Gas Transport Properties, *Polymers*, 14 (2022) 3489.  
15 <https://doi.org/10.3390/polym14173489>.
- 16 [54]Y. Zhang, K. J. Balkus, I. H. Musselman, J. P. Ferraris, Mixed-Matrix Membranes  
17 Composed of Matrimid® and Mesoporous ZSM-5 Nanoparticles, *J. Membrane Sci.*, 325  
18 (2008) 28-39. <https://doi.org/10.1016/j.memsci.2008.04.063>.
- 19 [55]E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, Mixed-Matrix Membranes  
20 Containing MOF-5 for Gas Separations, *J. Membrane Sci.*, 328 (2009) 165-173.  
21 <https://doi.org/10.1016/j.memsci.2008.12.006>.
- 22 [56]X. Ma, X. Wu, J. Caro, A. Huang, Polymer Composite Membrane with Penetrating  
23 ZIF-7 Sheets Displays High Hydrogen Permselectivity, *Angew. Chem. Int. Edit.*, 131  
24 (2019) 16302-16306. <https://doi.org/10.1002/ange.201911226>.
- 25 [57]L. Zhu, D. Yin, Y. Qin, S. Konda, S. Zhang, A. Zhu, S. Liu, T. Xu, M. T. Swihart, H. Lin,  
26 Sorption- Enhanced Mixed Matrix Membranes with Facilitated Hydrogen Transport for  
27 Hydrogen Purification and CO<sub>2</sub> Capture, *Adv. Funct. Mater.*, 29 (2019) 1904357.  
28 <https://doi.org/10.1002/adfm.201904357>.
- 29 [58]A. I. Romero, M. L. Parentis, A. C. Habert, E. E. Gonzo, Synthesis of  
30 Polyetherimide/Silica Hybrid Membranes by the Sol–Gel Process: Influence of the  
31 Reaction Conditions On the Membrane Properties, *J. Mater. Sci.*, 46 (2011) 4701-4709.  
32 <https://doi.org/10.1007/s10853-011-5380-4>.
- 33 [59]M. Arjmandi, M. Pakizeh, O. Pirouzram, The Role of Tetragonal-Metal-Organic  
34 Framework-5 Loadings with Extra ZnO Molecule On the Gas Separation Performance of  
35 Mixed Matrix Membrane, *Korean J. Chem. Eng.*, 32 (2015) 1178-1187.  
36 <https://doi.org/10.1007/s11814-014-0315-9>.
- 37 [60]Q. Song, S. K. Nataraj, M. V. Roussanova, J. C. Tan, D. J. Hughes, W. Li, P. Bourgoïn,  
38 M. A. Alam, A. K. Cheetham, S. A. Al-Muhtaseb, E. Sivaniah, Zeolitic Imidazolate  
39 Framework (ZIF-8) Based Polymer Nanocomposite Membranes for Gas Separation,  
40 *Eng. Environ. Sci.*, 5 (2012) 8359-8369. <https://doi.org/10.1039/c2ee21996d>.