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1 Is amino-modification of HKUST-1 in PEI mixed-matrix membranes 2 always favorable to CO₂ separation?

3
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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^[1,2]. 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^[3,5]. 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^[6]. 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^[7,9]. 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^[6,9,11]. 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 NH₂-UiO-66 could not only enhanced the
44 interactions between the filler and the matrix, but also improve the adsorption of CO₂
45 in NH₂-UiO-66, which was conducive to the separation of CO₂/CH₄^[12]. Similar
46 performance optimizations have been reported for NH₂-UiO-66/PMMA MMMs^[13],

1 NH₂-MIL-53/Pebax MMMs^[14], NH₂-MIL-53/PI MMMs^[15], NUS-8/PIM-1^[16]. 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 H₂/CO₂ separation^{[6,}
6 ^{17]}. Due to the close molecular kinetic diameters of H₂ and CO₂ molecules and the
7 stronger polarity of CO₂, neither sieving effect nor adsorption enhancement effect can
8 significantly improve the performance of MMMs, especially the H₂/CO₂ selectivity. In
9 our recent work, we combined HKUST-1 nanoparticles with Polyetherimide(PEI) and
10 the resulted MMMs were used for H₂/CO₂ separation^[18]. The PEI is a
11 high-performance polymer with superior processability, which could be molded into
12 different forms^[19]. HKUST-1 (Cu₃(BTC)₂) 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^[17]. The HKUST-1 has not been widely used for preparation of MMMs like
15 the UiO series, MIL series and ZIFs crystals^[6]. Our work took advantage of the large
16 pore of HKUST-1 nanocrystals to accelerate H₂ diffusion with low diffusion
17 resistance. Whereas, the permeability of CO₂ molecules was affected by
18 adsorption-desorption process in the HKUST-1, resulting in a higher diffusion
19 resistance. The phenomenon of increased H₂ permeability accompanied by decreased
20 CO₂ permeability was also observed by Liu^[20]. The separation mechanism of
21 HKUST-1/PEI MMMs controlled by “adsorption-diffusion” of H₂/CO₂ was proposed.
22 Based on this mechanism, we postulated that by increasing the adsorption-desorption
23 resistance of HKUST-1 to CO₂, 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. NH₂-functionalized HKUST-1 has been prepared by
27 partial replacement of the BTC with NH₂-BDC^[21,23]. Sun reported on the synthesis of
28 sub-NH₂-Cu-BTC with 2 μm crystal size resulting in stronger affinity between
29 NH₂-Cu-BTC and CO₂ molecules^[21]. Concerning the NH₂-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 CO₂ 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 (NO₃)₂·3H₂O, 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 (C₂H₅OH) and
43 dichloromethane (CH₂Cl₂) 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 NH₂-HKUST-1 materials**

4 The HKUST-1 nanocrystals were synthesized following the methodology reported
5 earlier^[18]. Solution A was obtained by dissolving Cu (NO₃)₂·3H₂O (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 NH₂-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(NH₂-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 NH₂-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 NH₂-HKUST-1 crystals could be taken from the glass plate after the
30 solvent (CH₂Cl₂) was completely removed by drying at 25 °C, 60 °C, and 120 °C for
31 24h. The loading amount of HKUST-1 and NH₂-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, NH₂-HKUST-1-10%/PEI, and
34 NH₂-HKUST-1-30%/PEI, respectively. The pristine PEI membrane was prepared
35 without the addition of any HKUST-1 and NH₂-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 NH₂-HKUST-1 nanocrystals with a scanning
40 rate of 2° min⁻¹ in the 3-90° 2 *Theta* range, and the mixed matrix membranes with a
41 scanning rate of 8° min⁻¹ 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 NH₂-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 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. N_2 sorption measurements were carried out
 6 on a Quantachrome, Autosorb IQ instrument to study the porous structure of
 7 HKUST-1 and NH_2 -HKUST-1 crystals at $-196\text{ }^\circ\text{C}$. H_2 and 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 cm^2 . Both the one-component gas (H_2 , CO_2) permeability and
 19 mixed two-component gas permeability and separation (H_2/CO_2) would be
 20 characterized. The flow rate of feed gas was 100 ml min^{-1} , and the flow rate of
 21 sweeping gas (Ar) at the permeate side was 40 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 $10^{-10}\text{ cm}^3\text{ (STP)}\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$) 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 ΔP_i is the transmembrane pressure drop (cmHg), and A is the effective membrane's
 31 area (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 ΔH_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^[24, 25]. The relation between E_P , E_D and ΔH_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 ΔH_S can be calculated using the Clausius-Clapperron Equation (5):

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

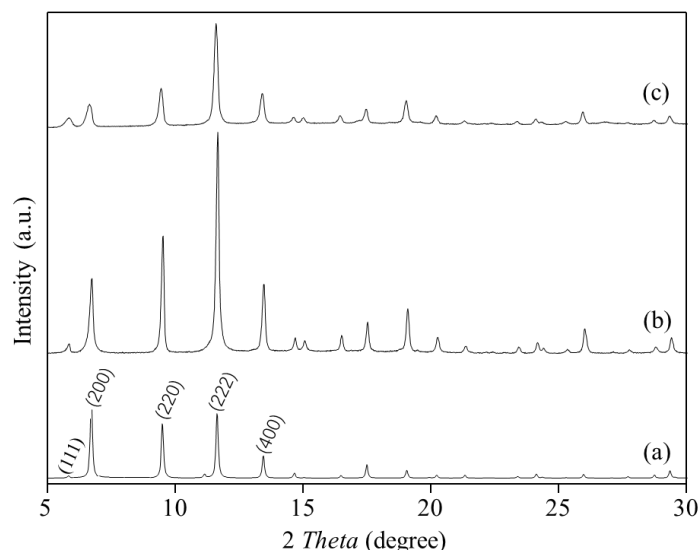
6 Where p (MPa) is the testing pressure, T (K) is the measurement temperature, and R is
7 the ideal gas constant.

8

9 **3 Results and discussion**

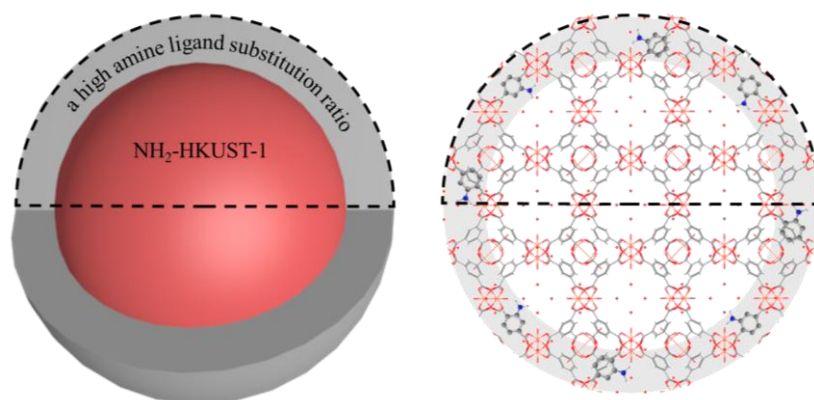
10 **3.1 Structure analysis of NH₂-HKUST-1 and HKUST-1 samples**

11 The X-Ray diffraction patterns of NH₂-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 NH₂-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 NH₂-HKUST-1 is 88.52%. The average crystal size of HKUST-1
18 determined using Scheller's formula is 110 nm and of NH₂-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 NH₂-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 NH₂-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 NH₂-HKUST-1 sample.



1
2 **Figure 1 XRD patterns of (a) HKUST-1 (simulated), (b) HKUST-1 and (c)**
3 **NH₂-HKUST-1 samples**

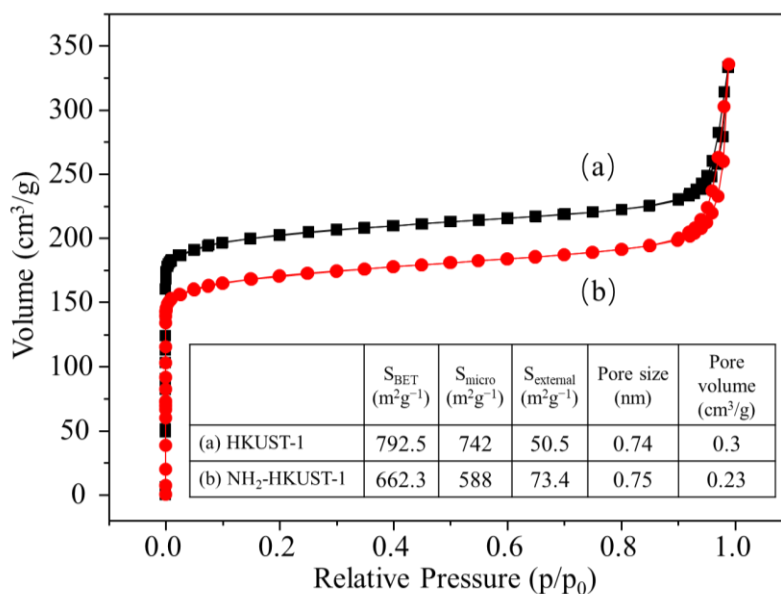
4 The substitution ratio of the 2-aminoterephthalic acid in the NH₂-HKUST-1 was
5 calculated based on the elemental analysis (Table S1). The ratio of m
6 (2-aminoterephthalic acid): m (1,3,5-trihydroxybenzene) is calculated to be 1 : 5,
7 which is lower than the feeding ratio 1 : 2 in the initial precursor 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 NH₂-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 NH₂-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 NH₂-HKUST-1 “core-shell” structure: the gray band**
17 **is the outer surface of NH₂-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 NH₂-HKUST-1 samples
21 show a reduction of the BET surface area from 792.5 m²g⁻¹ to 662.3 m²g⁻¹,
22 respectively. While, the external surface area increased, due to the smaller particle

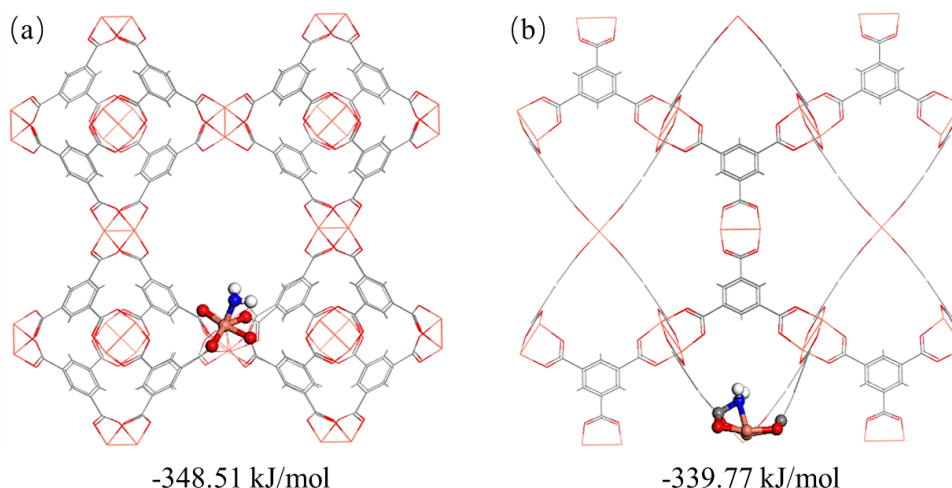
1 size of NH₂-HKUST-1, the micropore volume decreased. The pore size remained the
 2 same in both samples, which is consistent with XRD results. However, the decrease of
 3 pore volume from 0.30 cm³/g to 0.23 cm³/g indicates the occupation of the pores by
 4 -NH₂ groups.



5
 6 **Figure 3** N₂ adsorption isotherms of (a) HKUST-1 and (b) NH₂-HKUST-1 recorded at
 7 -196 °C; *Inset*: results deduced from the N₂ adsorption measurements.

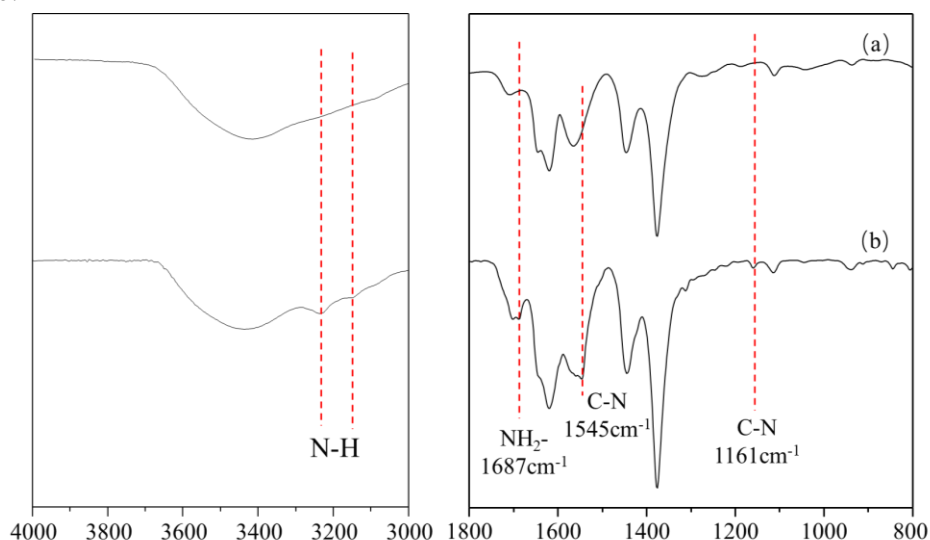
8 The adsorption results of HKUST-1 and NH₂-HKUST-1 samples further confirmed
 9 the occupation of the pore space by the -NH₂ groups. Additionally, the NH₂-HKUST-1
 10 exhibits lower CO₂ adsorption capacity as shown in Figure S3 in contrast to previous
 11 reports on surface functionalized MOFs materials^[26, 27]. This result can be explained
 12 with the reduced free pore volume of NH₂-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 NH₂-HKUST-1's surface.

15
 16 The form of the 2-aminoterephthalic acid ligand in the NH₂-HKUST-1 structure under
 17 the action of the central metal Cu²⁺ was calculated using the pm6^[28] method of
 18 Gaussian^[29]. The binding energy of -NH₂ groups in the pores of the NH₂-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 NH₂-HKUST-1 which is consistent with the N₂ adsorption results
 22 presented above.



1
2 **Figure 4 Binding energy of amino group in the NH₂-HKUST-1 sample: (a) inside the**
3 **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 NH₂-HKUST-1 were subjected to FT-IR characterization
6 (Figure 5). The bands corresponding to the vibrations of C-O (1375 cm⁻¹), benzene
7 ring (1564 cm⁻¹) and C=O (1644 cm⁻¹) are observed in both samples. Two new bands
8 in the spectrum of NH₂-HKUST-1's at 3237 cm⁻¹ and 3151 cm⁻¹ appeared and they are
9 attributed to the vibration of N-H^[21, 30] (Figure 5b). Also the peak at 1687 cm⁻¹ is
10 related to -NH₂^[15]. The bands at 1161 cm⁻¹ and 1545 cm⁻¹ are corresponding to the
11 C-N bond^[21]. The new bands proved the presence of amino groups in NH₂-HKUST-1
12 sample.



13
14 **Figure 5 FT-IR spectra of (a) HKUST-1 and (b) NH₂-HKUST-1 crystals**

15 The TG study of both HKUST-1 and NH₂-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^[31, 32]. 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 NH₂-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 NH₂-HKUST-1 started
7 at a lower temperature, due to the -NH₂ groups which decomposed at lower
8 temperature^[33].

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^[18]. 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 NH₂-HKUST-1 filled membranes, which is
19 consistent with crystals' XRD patterns (Figure 1).

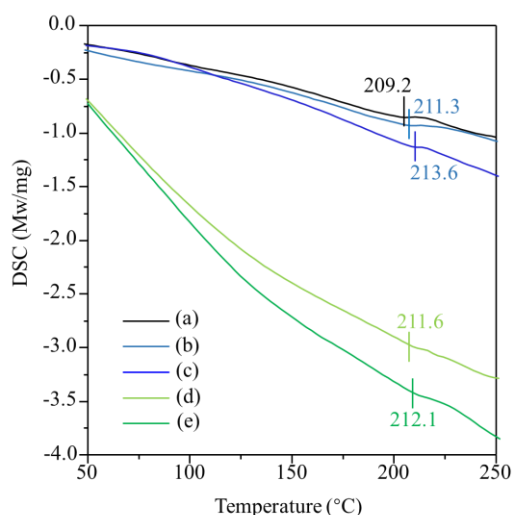
20
21 As can be seen in SEM images (Figure S6), all the mixed matrix membranes are
22 continuous and the HKUST-1 particles are evenly distributed. It is worth noting that
23 when the filling amount reaches 30%, the cross-section morphology of
24 HKUST-1-30%/PEI MMM exhibited more obvious polymer veins than that of
25 NH₂-HKUST-1-30%/PEI, which was caused by plastic deformation^[34]. This was
26 related to the different interaction strength between the NH₂-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 NH₂-HKUST-1-10%/PEI and NH₂-HKUST-1-30%/PEI
31 show an additional peak at 3237 cm⁻¹ representative of N-H bond^[21] (Figure S7).
32 Previous works reported on amino-functional fillers forming hydrogen bonds with
33 organic matrix, and the vibration of -NH₂ showed a significant blue shift^[26, 35, 36].
34 While, no significant shift of this peak in the NH₂-HKUST-1-10%/PEI and
35 NH₂-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 Cu²⁺
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⁻¹ to
41 1779.8 cm⁻¹. However, in the NH₂-HKUST-1-30%/PEI (Figure S7 e), the band
42 shifting is less only from 1777.3 cm⁻¹ to 1778.3 cm⁻¹. The electron donor -NH₂ group
43 led to an increase in the electron cloud density of the NH₂-HKUST-1 crystal,
44 which might weakened the interaction between the PEI polymer and NH₂-HKUST-1

1 crystals in the membranes. In summary, the amination of HKUST-1 does not improve
2 the interactions between the NH₂-HKUST-1 and the PEI as expected.

3
4 The XPS results also showed that the interaction between NH₂-HKUST-1 and PEI
5 was not further enhanced. The XPS spectra for Cu 2p_{3/2} of the pure crystals and
6 membranes are shown in Figure S8. The XPS spectra of HKUST-1 (Figure S8a) and
7 NH₂-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^[37, 38], respectively. The
9 NH₂-HKUST-1(Cu) is similar to HKUST-1(Cu), suggesting that the -NH₂ groups do
10 not coordinate with Cu²⁺ but may be protruding into the pores^[39]. By comparing the
11 spectra recorded on the membranes and pure HKUST-1, NH₂-HKUST-1 crystals, the
12 signal intensity of Cu 2p_{3/2} decreased. In the HKUST-1-30%/PEI membrane, the peak
13 shift is due to the effect of C=O on Cu²⁺ resulting in an increase of the electron cloud
14 density of Cu²⁺. While, the shift decreases for the NH₂-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, NH₂-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_g*) 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_g* rises after filling appropriate amount
23 of HKUST-1 and NH₂-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_g* of 213.6 °C, thus further explaining the higher effect of HKUST-1 than
26 NH₂-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) NH₂-HKUST-1-10%/PEI and (e)**
30 **NH₂-HKUST-1-30%/PEI with the glass transition temperature (*T_g*)**

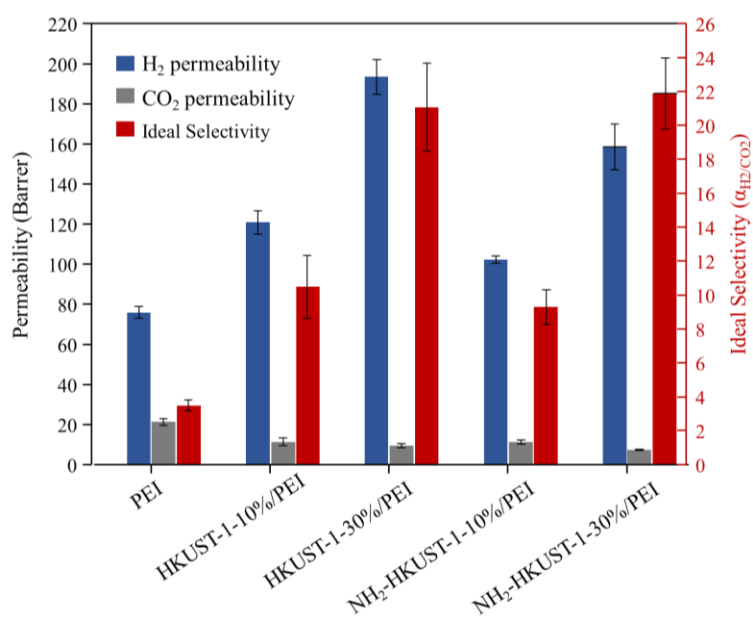
31 3.3 Gas separation performance of membranes

32 The H₂ and CO₂ 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 H₂ permeability and selectivity of the MMMs improved with the addition
 4 of both HKUST-1 and NH₂-HKUST-1 compared with the parent PEI membrane. With
 5 the increase of the loading amount of the same filler (HKUST-1 or NH₂-HKUST-1),
 6 the H₂ permeability increased. However, all MMMs exhibited reduced CO₂
 7 permeability, suggesting that both HKUST-1 and NH₂-HKUST-1 fillers did not affect
 8 the CO₂ permeance. The different trends in permeability of H₂ and CO₂ 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 NH₂-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 NH₂-HKUST-1-30%/PEI and HKUST-1-30%/PEI was
 15 compared. NH₂-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 NH₂-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 NH₂-HKUST-1-30%/PEI membrane for both H₂ and CO₂
 22 was mainly due to the pore blockage by -NH₂ groups. While, there was a little
 23 increase in ideal selectivity from 21.0 (HKUST-1-30%/PEI) to 21.9
 24 (NH₂-HKUST-1-30%/PEI), since the diffusion of large CO₂ 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 (NH₂-HKUST-1-10%/PEI and NH₂-HKUST-1-30%/PEI) were not subjected to
 28 optimization.

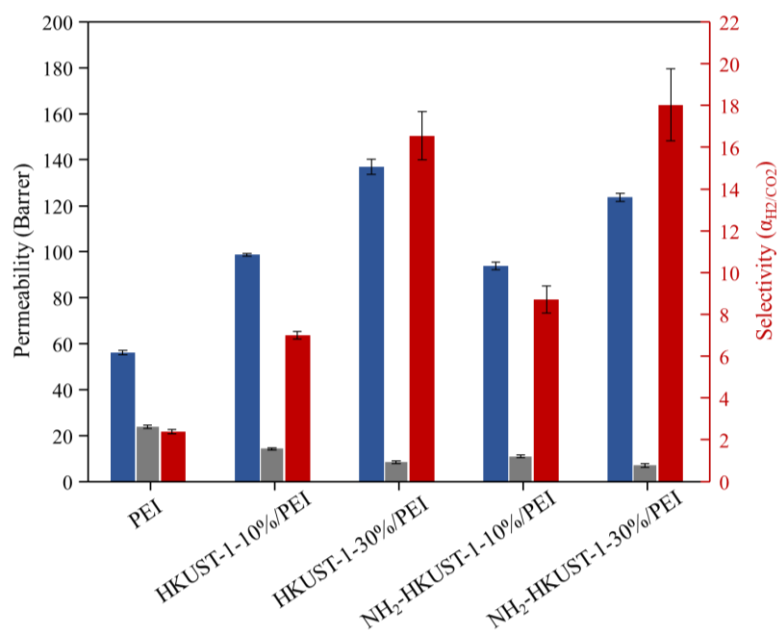


29
30

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

1 **matrix membranes HKUST-1/PEI and NH₂-HKUST-1 measured at 25 °C**

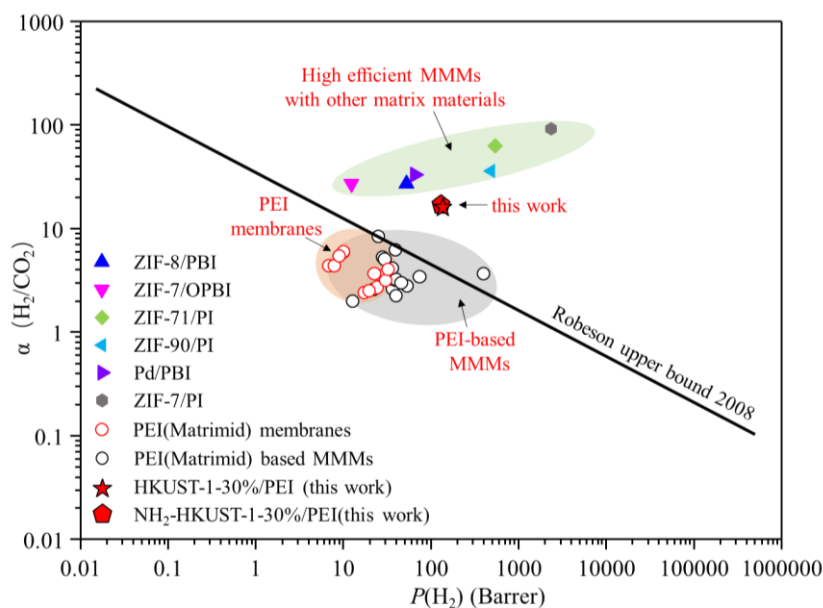
2 The mixed gas separation performance of the MMMs has the similar trend as the
3 single component gas separation testing (Figure 8 and Table S3). The
4 NH₂-HKUST-1-30%/PEI membrane showed a decrease gas permeability for both H₂
5 and CO₂ with a slight improved selectivity. However, due to the competitive
6 adsorption of H₂ and CO₂, 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 NH₂-HKUST-1 measured at 25 °C**

12 The Robeson upper boundary (2008) was used to evaluate the H₂/CO₂ separation
13 performance of HKUST-1-30%/PEI and NH₂-HKUST-1-30%/PEI MMMs (Figure 9
14 and Table S5)^[40]. First, we found that the H₂/CO₂ 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 H₂ permeability. After adding
18 HKUST-1 or NH₂-HKUST-1, the H₂ permeability of HKUST-1-30%/PEI and
19 NH₂-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 H₂/CO₂
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 H₂/CO₂ separation performance of MMMs via Robeson upper bound (2008)^[40];**
 6 **details are shown in Table S5^[41, 60]**

7 As discussed in the introduction section, the main challenge for MMMs for H₂/CO₂
 8 separation is the high adsorption and solubility of CO₂ in MMMs, which results in
 9 lower H₂/CO₂ selectivity compared to other gas pairs that requires high CO₂
 10 permeability, such as CO₂/CH₄. This work provides new strategy to achieve H₂/CO₂
 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
 13 negative effect on the separation.

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 H₂ molecules from CO₂ molecules, thus suggesting the diffusion
 19 control H₂ permeation and adsorption prevention of CO₂ permeation^[18]. 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 NH₂-HKUST-1-30%/PEI mainly occupying the
 23 permeable channels, resulting in decreased permeability for both H₂ and CO₂. In
 24 addition, the small NH₂-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 -NH₂ groups (Table 1 and Figure S4). Firstly,
 27 the activation energy of permeation (E_p) of the small H₂ molecules is lower than that
 28 of the big CO₂ molecules, resulting in high H₂/CO₂ selectivity of the membranes.
 29 Secondly, the decreased ΔH_S (H₂ and CO₂) of NH₂-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)	ΔH_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

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