Phase Control of ZIF-7 Nanoparticles via Mechanochemical Synthesis – Supplementary Information

Materials

Zinc oxide nanopowders (ZnO <100nm particle size), zinc acetate dihydrate (Zn(Ac).2H₂O), cobalt oxide (CoO), benzimidazole (bIm), 5,6-dimethylbenzimidazole (bIm-Dm), and ammonium nitrate (NH₄NO₃) were obtained from Sigma-Aldrich. 5-aminobenzimidazole (blm- NH_2) purchased from Oakwood Chemicals. Methanol, was chloroform and dimethylformamide were obtained from Merck. The polyimide 6FDA-DAM (Mw ~ 370000) was supplied by Akron Polymer Sytems. All the chemicals were used without further purification. Carbon dioxide, nitrogen, methane, propane and propylene gas cylinders were supplied by Coregas.

Methods

Synthesis of ZIF-7 particles by ball milling

For the synthesis of ZIF-7 particles, ZnO by itself, or as a mixture with zinc acetate as a catalyst was used as a zinc metal node source, while benzimidazole was used as the ligand source. CoO was also used as a cobalt metal node source when synthesising ZIF-9, which is a variation of ZIF-7. 5,6-dimethylbenzimidazole (bIm-Dm), and 5-aminobenzimidazole (bIm-NH₂) were also used as an alternative ligand source in the attempt to synthesise functionalised variation of ZIF-7. A variety of catalysts such as ammonium nitrate and triethanolamine were also used in some syntheses. In general, for all samples, 2mmol of metal node source were used together with 4 mmol of ligand source to synthesise different variations of ZIF-7. For the catalyst, 0.19mmol of NH₄NO₃ was added for all syntheses using ammonium nitrate as a catalyst. For all catalysts using zinc acetate as a catalyst, the zinc oxide amount was adjusted such that 99% of the zinc source (1.98mol) comes from ZnO while the remaining 1 % (0.02mol) comes from zinc acetate dihydrate. When triethanolamine was used as a catalyst, only 0.01g of triethanolamine was used per batch. 4g of 3mm diameter and 12g of 5mm diameter ZrO₂

grinding balls were used for all synthesis of ZIF-7. The balls, precursors and catalysts were measured into the 20mL ZrO₂ grinding bowl before being tightly sealed with a silicone seal ring. In the cobalt variation of ZIF-7 (ZIF-9), a special cap with gas flows quick fit was used to introduce inert gas such as Argon, to ensure the synthesis is performed under an inert gas atmosphere. The mechanochemical synthesis was performed at a speed of 800 rpm for 1 hour, before leaving to cool for 30 minutes. The resulting particles were washed with methanol 2-3 times before being used for characterisation or membrane synthesis. For the synthesis of ZIF-7 variations (cobalt and functionalised ZIF-7), ammonium nitrate was consistently used as a catalyst with a solvent amount of 200 μ L for DMF (phase I formation) and 150 μ L H₂O (phase III formation) as earlier results show the best XRD peaks formed at this condition for the different phases.

Synthesis of ZIF-7 membranes

In the formation of the 6FDA-DAM-based membrane, the polymer percentage in the solventpolymer mixture was retained at 7.7 wt%. The ZIF-7 filler was first dispersed in chloroform for at least 12 hours before the addition of 6FDA-DAM. Occasional ultrasonication was also performed using an ultrasonic bath during the 12-hour filler dispersion period. This step is essential to ensure better dispersion of fillers and reduced chances of agglomeration before the addition of the polymer of choice. After filler dispersion, 3 wt% of the full amount of 6FDA-DAM (7.7 wt%) was added to the dispersed filler chloroform solution and left to stir for 24 hours. This step is important as a priming step, to ensure full dissolution and dispersion of 6FDA-DAM polymer while having good contact with the fillers. Occasional ultrasonication was also performed using an ultrasonic bath during these 24 hours to ensure efficient dispersion and reduced agglomeration. After this period, the remaining amount of 6FDA-DAM was added slowly to reduce the formation of agglomerates and then left to be stirred overnight. The highly viscous 6FDA-DAM-filler solution was then sonicated for 20-30 minutes to remove any remaining trapped air in the solution. The solution was then cast on a glass slide using a doctor blade at a height of 500 µm. The glass slide was then immediately covered in a solventsaturated enclosed container and left to slowly evaporate overnight. The resulting membrane was then slowly peeled off and activated in a vacuum oven at 100°C for 24 hours before use.

Membrane gas permeation test



Figure S 1: Flow diagram of gas permeation rig

All pure gas membrane permeation tests were performed in a variable feed pressure and constant volume permeation system as shown in Figure S 1. The membranes will be secured in the gas permeation module before tests. The membranes will be held under vacuum for approximately 5 minutes before being exposed to selected gas on the feed side at a selected pressure varying between 1-3 bars. The permeate side of the membrane (including the buffer tank) was left in a vacuum before the start of the gas permeation test. The pressure of the feed and permeate side of the membrane will be measured at intervals of 1s-5s, and the steady rate of pressure increase on the permeate side is calculated. The effective membrane area for each test was also recorded.

The permeation coefficient was calculated using the following equation:

$$P = \frac{273.15 \times 10^{10} \quad V \times L \quad dp}{760 \times A \times T \quad P_0 \times 76 / \frac{dt}{14.7}}$$

dp

Where P is the permeation coefficient in barrer(1 barrer=1 × 10⁻¹⁰ cm³ (STP) cm cm⁻² s⁻¹ cm Hg⁻¹), A is the effective area of the membrane (cm²), T is the absolute temperature (K), V is the dead-volume of the permeate side (cm³), L is the membrane thickness (cm), P_0 is the feed

pressure (psi), and dt is the steady rate of pressure increase in the permeate side (mm Hg s⁻¹). All permeation values and error bars were obtained from multiple measurements of the samples.

The ideal selectivity for different gas pairs was calculated using the following equation:

$$\alpha = \frac{P_A}{P_B}$$

Where P_A and P_B are the permeation coefficient of pure gas A and B respectively

Characterisation

SEM samples were prepared by mounting them onto an Aluminium SEM sample stub using carbon tape. Particulate samples were dispersed onto a silicon wafer before being secured onto the SEM sample stub. The samples and the stub were dried in the oven overnight at 70°C under a vacuum to remove any residual solvents. The samples will be thinly coated with platinum for morphological analysis (FE-SEM) (ca 15nm thickness) or carbon for Energy Dispersive Spectroscopy analysis (SEM-EDS) (ca 30 nm thickness) using Quorum Q150T high-resolution sputter coater. Scanning Electron Microscopy was performed either using JEOL JSM-7001F or JEOL JSM-7100F for Field Emission Scanning Electron Microscopy (FE-SEM). All SEM analyses for morphological analysis were performed under secondary electron imaging mode at 5kV and a working distance of 10mm. Point Energy Dispersive Spectroscopy (SEM-EDS) were performed using JEOL JSM-7100F at 20kV.

Fourier-Transform Infrared (FT-IR) spectra were obtained using Nicolet 6700 by Thermo Scientific equipped with a diamond attenuated total reflection (ATR) objective. All spectra were collected between 600cm⁻¹ to 4000cm⁻¹.

Room temperature x-ray diffraction measurements were carried out under ambient conditions with Rigaku Miniflex 600 Benchtop X-Ray Diffractometer and a Cu K_{α} (λ = 1.5406 Å) radiation source. Samples in particle or small solid form are ground using a pestle and mortar before being dispersed onto a zero-background holder. Membrane or film samples were cut into squares with the size of ca. 2cm x 2cm before being secured onto a zero-background holder using a blue tac on the edge of the holder. The secured samples were then mounted onto the sample stage for X-Ray diffraction measurements. The 2 θ range was 5° to 50°, with a step size of 0.03° and a 1.5°/min scan speed. The collected XRD data were transformed into xy data format using PowDLL software (N. Kourkoumelis, ICDD Annual Spring Meetings (ed. Lisa O'Neill), Powder Diffraction, 28 (2013) 137-48) before being analysed using excel. Literature comparison CIF data were obtained from the Cambridge Crystallography Data Centre (CCDC). The CIF data were processed using Mercury software obtained from CCDC, and the XRD data were extracted in xy data type format. The single

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crystal XRD for the different ZIF-7 phases can be found elsewhere, and was used as comparison to the as-synthesised ZIF-7 using ball mill in this work (ZIF-7-I¹ ZIF-7-III²). Rietveld refinement was performed using these single crystal data via GSAS-II software. Refined data can be found in Figure S 14.

Thermogravimetric analysis (TGA) was carried out using a METTLER TOLEDO TGA/DSC 1 STARe System. The sample was heated from 25°C to 900 °C at a rate of 10 °C min⁻¹ under flowing air (20 mL/min).

ICP-OES were analysed on a Thermo iCAP PRO XP. Samples were dissolved in concentrated nitric acid before test.

Adsorption isotherms were measured using Micromeritrics TriStar II 3020. Samples were degassed overnight under a high vacuum before adsorption analysis. BET surface area was calculated using N₂ isotherms at 77K at a relative pressure (P/P₀) range of between 0.05 and 0.15. N₂ isotherms at 77K were performed between relative pressure of 0.001 to 0.95 through one adsorption-desorption cycle. CO₂ and N₂ isotherms at 273K were performed from high vacuum up to 130 kPa through one adsorption-desorption cycle. Samples were degassed between different adsorption tests.

(S1- a) Effect of solvent ratio towards ZIF-7 phase formation

We also continue to study the effect of mixed solvent between DMF and H₂O to see its effects on the phase transition of ZIF-7 mechanochemical synthesis. This is as the formation of ZIF-7 from ZnO and benzimidazole results in a small formation of H₂O as a by-product. The amount of H₂O as a by-product could create a mixed solvent environment within the ball mill when DMF is used as the main solvent, which could lead to the behaviour seen in Figure 1c in the main text. However, as can be seen in Figure S3, the initial formation of ZIF-7 at a lower H₂O percentage of 5% is consistently ZIF-7-I, regardless of the type of catalyst. ZIF-7-III was also formed for both catalysts when the H₂O content exceeds 15%. However, at 10% H₂O, it can be seen that although a mixed phase of ZIF-7-I and ZIF-7-III can be seen for both catalysts, the zinc acetate catalyst contains a considerably larger amount of ZIF-7-III as compared to NH₄NO₃ catalyst. Although the amount of H₂O initially present in the zinc acetate catalyst (as zinc acetate was used in a dihydrate form) may play a role in this behaviour, the amount of zinc acetate used was very small and account for less than 1% of the possible H₂O contributed towards the overall reaction. Thus, it can be said that the usage of NH₄NO₃ can withstand a higher H₂O percentage loading in a mixed solvent environment to form a better pure ZIF-7-I. This makes NH₄NO₃ a better catalyst choice for the mechanochemical synthesis of ZIF-7-I in a humid environment due to its robustness in withstanding additional H_2O molecules. However, this does also show that the water content in a mixed solvent does not directly explain the behaviour seen in Figure 1c, and thus a much different mechanism involving NH₄⁺ from the NH₄NO₃ catalyst in the reaction must have occurred to have resulted in the unique phase formation behaviour.

(S1 – b) FTIR in detail analysis

In the smaller wavenumber region below 800cm⁻¹, at around 650cm⁻¹ a peak can be seen for all samples of ball-milled and solvothermal ZIF-7, which represents the C-C-C in-plane bending. An additional peak at around 665cm⁻¹ which represents a C-C-C out of plane bending can be seen for solvothermal ZIF-7, but not in ball-milled ZIF-7. The peaks in the region between 700cm⁻¹ to 950cm⁻¹ represent the C-H out of plane bending, which is similar across all three samples except for an extra peak at around 755cm⁻¹ for ZIF-7-III, which follows closely with reported literature.³ The bands at 1005 cm⁻¹ represent a C-C-C trigonal bending, and the bands between 1050cm⁻¹ to 1200cm⁻¹ which represent C-H in-plane bending are also almost similar across the three samples. The peaks responsible for C-C stretching at 1240cm⁻¹, C-H in-plane stretching at 1275cm⁻¹, C-N stretching between 1300cm⁻¹ to 1365cm⁻¹ and C=C stretching of benzene ring between 1390cm⁻¹ to 1650cm⁻¹ were also present in all samples except for the peaks at 1390cm⁻¹ and 1405cm⁻¹ that could be seen in solvothermal ZIF-7-I, but could not be seen in ball-milled ZIF-7-I. A peak for C=N at 1675cm⁻¹ was also seen only in the solvothermal sample but not in any of the ball-milled ZIF-7 samples. The extra peak at 1785cm⁻¹ that only exists only for ZIF-7-III synthesised via ball mill is also consistent with the literature, at which this peak represents the N-H in-plane bending and C-C-C out of plane bending that can only be seen for ZIF-7-III.³

(S1 – c) Other ZIF-7 particle analysis and characterisations

The adsorption of solvothermal ZIF-7 (ZIF-7-S) and mechanochemical ZIF-7 (ZIF-7-I and ZIF-7-III) were tested at both liquid N2 temperatures (N2 adsorption 77K, for BET) and ice temperature (CO2 and N2 adsorption 273K, for adsorption behaviour). The adsorption plot can be found in Figure S 4.

Sample	ZIF-7-S	ZIF-7-I	ZIF-7-III
BET Surface Area, m²/g	693.06 ± 81.08	112.56 ± 0.73	17.96 ± 0.25

ZIF-7-III consistently shows the lowest BET and adsorption behaviour as it has a 2D planar structure and is reported to be denser than ZIF-zni and consequently should have much lower adsorption. Despite ZIF-7-I having a smaller BET pore size than ZIF-7-S, ZIF-7-I shows a higher CO2 adsorption amount than ZIF-7-S, which may indicate better interaction of CO2 with ZIF-7-I over ZIF-7-S. The BET behaviour for all samples shows a type II isotherm, which is reasonable as the particles formed are very small and thus aggregate much closer together during drying, developing small mesopore-like intergrain leading towards capillary condensation as seen for type-II isotherm. The BET for ZIF-7-I, however, shows a possible multilayer pore distribution with N2 hysteresis at the second step, which means that the particles might be packed much more closely, forming some intergrain with pore closely similar to N2 kinetic diameter.

A quick analysis was also performed to understand the possibility of contamination from the mechanochemical container and balls during synthesis. Two methods were used to analyse the possible contamination of zirconium, as zirconium balls and bowls were used – SEM-EDS and ICP.

Analysis through SEM-EDS was unable to detect any zirconium residue in any of the ZIF-7 synthesised, both through solvothermal and mechanochemical routes. As seen in Figure S 5, clear peaks for Zn can be observed, which are from the metal nodes of the ZIF-7 particles. Silicon peaks were also observed due to the deep electron penetration depth at high voltage, as well as the microscopic nature of the ZIF-7 particles. No zirconium peaks can be detected in all samples. The particles look bigger than reported in Figure 2 in the main manuscript and are combined in these SEM-EDS images for two main reasons – higher voltage for SEM-EDS and aggregation. Significant aggregated ZIF-7 particles must be selected for SEM-EDS analysis due to the deeper electron penetration depth to have a better signal. However, the morphology image has lower surface resolution at higher voltage, causing the grain boundaries to be less clear, making the aggregate look like a larger rough particle, which morphologically is not the case.

Sample	Zr:Zn ratio measured by ICP		
ZIF-7-S	0:1		
ZIF-7-I	0.0009:1		
ZIF-7-III	0.0047:1		

An analysis using ICP however detected a miniscule amount of zirconium for mechanochemically synthesised ZIF-7 as can be seen in Table 6. However, the amount of contamination is relatively small and thus may explain the absence from detection via the SEM-EDS analysis.

(S1 – d) ZIF-7 variations characterisation analysis

Further characterisation was performed on these ZIF-7 variations, with a focus on the samples with successful crystallinity (Co-ZIF-7 and ZIF-7-NH₂). The SEM images from Figure S 8 show that the variations formed using DMF as solvent (a and b) have consistently formed a more irregular shape, while the H₂O solvent variation (c and d) forms a flatter sheet-like shape with some irregular-shaped particles mixed in between. This is reasonably consistent with the previous observation of our main series of ZIF-7 synthesis, which also shows irregular shapes and planar-like shapes when DMF and H₂O are used as solvents respectively. This further indicates that the solvent choice impacts not only the crystallinity but also the morphology of the resultant crystal, at which for the case of ZIF-7, DMF forms a more irregular or spherical-like shape and H₂O as solvent was also shown here to demonstrate that using H₂O as solvent is still capable of synthesising sheet-like ZIF-7, even when the particles lose crystallinity (sheet-like amorphous material) which may be of interest for researchers in the area of amorphous materials.

A thermal analysis was also performed on the ZIF-7 variations, specifically on the crystalline variations. As can be seen from Figure S 9, Co-ZIF-7 synthesised by a ball mill has a much lower thermal stability in the air, as it starts to decompose at a comparatively low temperature of around 300°C when compared to the previously synthesised ZIF-7 (decomposition temperature of more than 500°C). This decomposition temperature is also lower than other ZIF-9 decomposition temperatures reported in the literature.⁴ ZIF-7-NH₂ also has some slight drop in weight at a lower temperature, which may be resulted from desolvation, before having a decomposition-related drop in weight at around 400°C. However, this indicates that despite having a much lower decomposition temperature as compared to normal ZIF-7, these

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ZIF-7 variations should still be applicable in some high-temperature applications, for up to 300°C, which is a reasonable range for a wide variety of applications including catalysis and gas separation.

An FTIR analysis was also performed on the ZIF-7 variations, as can be seen, in Figure S 10. Co-ZIF-7 variations can be seen to have very similar bonding interaction to ZIF-7-III, irrespective of the solvent used. Extra peaks at 755cm⁻¹ (C-H out of plane bending) and 1785cm⁻¹ (N-H in-plane bending and C-C-C out of plane bending) were seen for both Co-ZIF-7 synthesised by ball mill, which is indicative of bonding similar to ZIF-7-III as opposed to ZIF-7-I.³ This may be another demonstration that the presence of H₂O as solvent allows for a morphological change in the Co-ZIF-7 structure, without significantly changing the crystal structure and bonding behaviour of the crystal.

The ZIF-7-NH₂ however have a very different FTIR behaviour when compared to any of the normal ZIF-7 phases. The ZIF-7-NH₂ variations all demonstrated similar C-C-C in-plane bending similar to the normal ZIF-7 structure at 650cm⁻¹. The peaks between 700cm⁻¹ to 950cm⁻¹, which indicates C-H bending, were also shifted when compared to normal ZIF-7, with the ZIF-7-NH₂ having peaks at 767cm⁻¹, 806cm⁻¹, 831cm⁻¹, and 954cm⁻¹ respectively. The peak at 1005cm⁻¹, which represents the C-C-C trigonal bending was also seen in ZIF-7-NH₂, which is consistent with normal ZIF-7. There were also shifts in most peaks between 1090cm⁻¹ to 1275cm⁻¹, which mostly indicates C-H in-plane bending, with the peak at 1240cm⁻¹ (C-C stretching), at which this peak is consistent throughout both ZIF-7-NH₂ and normal ZIF-7 samples. There was also slight shifting between 1300cm⁻¹ to 1370cm⁻¹ (C-N stretching), some shifting and new peaks between 1380cm⁻¹ to 1620cm⁻¹ (C=C stretching of benzene ring), and some peaks between 1580cm⁻¹ to 1650cm⁻¹, which indicates N-H bending. All of these differences can be explained due to the addition of an amino group to one of the C atoms in the structure, thus changing most C-H and C-N bending behaviours (due to the addition of NH₂ replacing H in one of the C) and the aromatic ring bending energies. Not much change was seen for all C-C-C in-plane and trigonal bending. New peaks associated with amines were also introduced. Both of the ZIF-7-NH₂ structure also shows multiple peaks between 3000cm⁻¹ to 3500cm⁻¹, which indicates the existence of multiple different N-H stretching, indicating that the amine group is actively interacting with the structure. These many interactions of the

amino group within the structure or with the precursors may also be the reason why it fails to form a crystalline structure via the normal solvothermal route.

(S1 – e) ZIF-7 membrane characterisations analysis

The ZIF-7 of different phases were then applied in a gas separation membrane to study the gas separation improvement capability of these ZIF-7 as fillers. ZIF-7 synthesised through the solvothermal route can improve both CO₂/N₂ and CO₂/CH₄ selectivity when applied as a mixed matrix membrane.^{5–7} In this work, ZIF-7 synthesised via ball milling will be dispersed in the 6FDA-DAM polymer as the group of 6FDA-based polymers have been consistently shown to be a good polymer for gas-based separation and have been successfully implemented by our group for other types of ZIF fillers.^{8–11} A ZIF-7 loading of 20% was chosen and fixed as according to another research in the literature, the selectivity of ZIF-7-based mixed matrix membrane starts to drop above 20% loading, which may be due to aggregation when the particle concentration is too high.⁷

An SEM analysis was performed to understand further the morphology of the as-synthesised ZIF-7 loaded 6FDA-DAM MMM membranes, as seen in Figure S 11. The surface morphology of ZIF-7-I@6FDA-DAM was slightly rougher compared to neat 6FDA-DAM and ZIF-7-III@6FDA-DAM membranes. This observation may be due to the nature of ZIF-7-I being 3D, thus forming a bulge in the matrix. This rough surface was not seen in ZIF-7-III, which may also be due to the planar morphology of ZIF-7-III, allowing it to be oriented in-plane with the membrane, causing a smoother look on the surface. The cross-sectional image of the membranes also shows no significant aggregation of the filler ZIF-7-I and ZIF-7-III within the 6FDA-DAM membranes, which indicates good filler dispersion. The difference in morphology between the cross-sectional images may be due to artefacts caused by liquid N2 freezing during membrane breaking before the SEM study. The different fillers' shapes (3D vs 2D) and arrangements may have induced different brittleness of the membrane. The differences in

the brittleness of the membranes may have contributed to the various artefacts observed across the cross-sectional images.

The 20% ZIF-7-I and ZIF-7-III loaded 6FDA-DAM membranes were first characterised to understand if there were any changes in the physical or chemical properties of the filler or the polymer. These characterisations were all done in comparison to pure 6FDA-DAM. The XRD analysis of the different ZIF-7 loaded 6FDA-DAM membranes from Figure S 12a shows that the ZIF-7 particles were successfully integrated into the membrane. The broader peak seen between 10° to 30° can be attributed to the 6FDA-DAM polymer, while the respective ZIF-7-I and ZIF-7-III peaks can be seen for each of the ZIF-7-I @ 6FDA-DAM and ZIF-7-III @ 6FDA-DAM mixed matrix membranes respectively. The TGA analysis in Figure S 12b also shows that the decomposition of the mixed matrix membranes occurs around 500°C-600°C, which is very close to both the pure 6FDA-DAM polymer and their respective particle's decomposition temperatures. The residual amount of the ZIF-7-I @ 6FDA-DAM and ZIF-7-III @ 6FDA-DAM at the end of the TGA run is also very similar at around 9%, which is a reasonable result when compared to the residual amount of pure 6FDA-DAM (2%), and also considering almost half of the ZIF-7 particle will lose its weight after the end of the TGA run from the previous particle TGA result.

The FTIR analysis in Figure S 12c also demonstrated the successful incorporation of the ZIF-7 particles into the 6FDA-DAM polymeric matrix. All of the peaks from the 6FDA-DAM polymer were retained in all ZIF-7 mixed matrix membrane samples. The additional peaks that were seen other than the 6FDA-DAM peaks in the mixed matrix membrane variations can all be attributed to their respective ZIF-7 variation fillers. A slight peak shift was observed from 914cm⁻¹ in pure 6DA-DAM to 910cm⁻¹ for both ZIF-7 loaded mixed matrix membranes. As the peak in this region is usually attributed to C-H out of plane bending, this may indicate that the ZIF-7 is interacting well with the C-H structure within the 6FDA-DAM polymer.

(S1 – f) Light hydrocarbon separation analysis

Other than the typical CO_2 -based separation, ZIF-7 have also been demonstrated to be a suitable candidate for light hydrocarbon-based separation. Kaptejin et al. have previously demonstrated the gate opening capabilities in ZIF-7 particles, showing that olefins such as propylene and ethylene adsorbs and desorbs at different pressure, making ZIF-7 an

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interesting filler candidate for light hydrocarbon-based separation.¹² We then proceed to test the ZIF-7 loaded mixed matrix membranes with different light hydrocarbon pairs to study this phenomenon in a membrane format as can be seen in Figure S 13. In the case of ethylene/ethane-based separation, only permeance improvement can be seen with no clear selectivity improvement. The ethylene permeance improved from pure 6FDA-DAM with an 11.3% and 55% increase in permeability (barrer) for ZIF-7-I and ZIF-7-III respectively. For propylene/propane-based separation, both the permeance and selectivity were improved. ZIF-7-I improved the propylene permeability and propylene/propane selectivity by 122% and 12.6% respectively, while ZIF-7-III improved the propylene permeability and propylene/propane selectivity by 68.3% and 11.5% respectively.

According to the gate opening effect reported in the literature, the selectivity flow of light hydrocarbon through ZIF-7 should favour the paraffin part (ethane and propane) over the olefin part (ethylene and propylene), but no clear selectivity improvement in that direction was observed. Rather, for the case of propylene/propane, the selectivity was improved favouring propylene flow over propane. The improvement in permeance can be attributed to the high differential pressure during the testing. In this test, the differential pressure across the membrane was set to 2 bars with a vacuum on the permeate side. Although the initial hypothesis is that the gate opening effect could be utilised in some parts of the membrane due to the pressure gradient across the membrane, the pressure used may be too high such that the selectivity change could not be seen and may require further process optimisation in the future. This higher pressure allowing all hydrocarbon to flow through the ZIF-7 pores may be an explanation for the selectivity improvement of propylene/propane but not for ethylene ethane. This is because when all gases can go through the small pores, the interaction of the molecules with the pore walls dominates the selectivity. As ethylene and ethane have much closer properties and sizes as compared to the propane and propylene pair (For example, the kinetic diameter of ethylene and ethane is 4.163Å and 4.443Å respectively while propylene and propane are 4.678Å and 5.118Å respectively).¹³ The larger propylene/propane pair to ethylene/ethane pair may also result in stronger interaction with the wall. This may have affected the separation, thus favouring the smaller and more polar propylene over propane in some cases, while no clear selectivity was seen over the ethylene/ethane pair. However,

this observation is still not conclusive and warrants further research for a more complete view of this phenomenon.

Catalyst	Solvent	Solvent Amount (μL)	ZIF-7 phase	ZnO presence
Triethanolamine	H ₂ O	100	ZIF-7-III	Yes
	DMF	100	ZIF-7-I	Yes
Zinc acetate	H ₂ O	100	ZIF-7-III	Yes
	DMF	50	ZIF-7-I	Yes
	DMF	100	ZIF-7-I	Yes
	DMF	150	ZIF-7-I	Yes
	DMF	200	ZIF-7-I	No
Ammonium nitrate	H ₂ O	50	ZIF-7-III	No
	H ₂ O	100	ZIF-7-III	Yes
	H ₂ O	150	ZIF-7-III	No
	DMF	50	ZIF-7-I	Yes
	DMF	100	ZIF-7-III	No
	DMF	150	ZIF-7-I	No
	DMF	200	ZIF-7-I	No

(S1 – g) Summary of mechanochemical synthesis parameters toward the ZIF-7 phase



Figure S 2: X-ray diffraction analysis of mechanochemically synthesised ZIF-7 for varying H₂O solvent using NH₄NO₃ as a catalyst



Figure S 3: XRD on the effects of H2O percentage in H2O/DMF mixed solvent amount on ZIF-7 synthesised via ball mill with the presence of a)zinc acetate and b)NH4NO3 as a catalyst



Figure S 4: Adsorption performance of ZIF-7 synthesised through solvothermal and mechanochemical synthesis route at 77K and 273K.



Figure S 5: SEM-EDS of a)ZIF-7-S and mechanochemically synthesised b)ZIF-7-I and c)ZIF-7-III.



Figure S 6: XRD analysis on the formation of ZIF-9 with different phase



Figure S 7: XRD analysis on the formation of ZIF-7 with different functionalisation group



Figure S 8: SEM images of ZIF-7 variations synthesised via the ball milling method a)Co-ZIF-7 (DMF solvent), b)Co-ZIF-7 (H2O solvent), c) ZIF-7-NH2 (DMF solvent), d) ZIF-7-NH2 (H2O solvent)



Figure S 9: TGA analysis on ZIF-7 variations



Figure S 10: FTIR analysis of ZIF-7 variations.



Figure S 11: SEM images of solvothermal ZIF-7-S (a,d), mechanochemical ZIF-7-I (b,e) and ZIF-7-III (c,f). a,b,c is the surface images, while d,e, and f are cross-section images.



Figure S 12: Comparison between Pure 6FDA-DAM with 20% ZIF-7-I and 20%ZIF-7-III loaded 6FDA-DAM using a) XRD, b) TGA and c) FTIR.



Figure S 13: Light hydrocarbon-based gas permeation results of ZIF-7 loaded 6FDA-DAM membrane



Figure S 14: Refined PXRD data of a) ZIF-7-I and b) ZIF-7-III, both synthesised via mechanochemical synthesis.

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