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ZIF-62 glass foam self-supported membranes to address CH_4/N_2 separations

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Membranes with ultrahigh permeance and practical selectivity could greatly decrease the cost of difficult industrial gas separations, such as CH₄/N₂ separation. Advanced membranes made from porous materials, such as metal-organic frameworks, can achieve a good gas separation performance, although they are typically formed on support layers or mixed with polymeric matrices, placing limitations on gas permeance. Here an amorphous glass foam, agfZIF-62, wherein a, g and f denote amorphous, glass and foam, respectively, was synthesized by a polymer-thermal-decomposition-assisted melting strategy, starting from a crystalline zeolitic imidazolate framework, ZIF-62. The thermal decomposition of incorporated low-molecular-weight polyethyleneimine evolves CO₂, NH₃ and H₂O gases, creating a large number and variety of pores. This greatly increases pore interconnectivity but maintains the crystalline ZIF-62 ultramicropores, allowing ultrahigh gas permeance and good selectivity. A self-supported circular a_{of}ZIF-62 with a thickness of $200-330 \,\mu\text{m}$ and area of 8.55 cm² was used for membrane separation. The membranes perform well, showing a CH₄ permeance of 30,000-50,000 gas permeance units, approximately two orders of magnitude higher than that of other reported membranes, with good CH_4/N_2 selectivity (4–6).

Gas or vapour separation is one of the most important and largest-volume chemical separation processes and is currently dominated by thermal distillation, which is energy intensive¹⁻³. Compared with competing separation technologies, the membrane separation process has some inherent advantages such as high energy efficiency, excellent reliability and a small footprint⁴⁻⁶. Conventional polymeric membranes frequently exhibit a trade-off behaviour between permeance or permeability and selectivity. Conversely, membranes based on ordered/porous materials with a high degree of tunability^{3,7-9}, such as metal–organic frameworks (MOFs)^{1,10-12}, covalent organic

frameworks¹³, zeolites^{14,15}, polymers of intrinsic microporosity^{16,17} and ordered microporous polymers^{5,18,19}, are poised to drastically enhance gas permeance, while maintaining high selectivity, and have the potential to improve the economics of difficult industrial separations²⁰. MOFs have characteristically adjustable pore diameters/apertures even at the ultramicroporous range, tunable porosity, structural versatility and extensive application prospects as pure MOFs or composite thin films^{20–22}. Such a degree of structural diversity and properties is highly desirable to develop gas separation membranes with ultrahigh permeance and practical selectivity^{20,23–25}, which is anticipated

¹State Key Laboratory of Separation Membranes and Membrane Processes, Tiangong University, Tianjin, China. ²Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE) and Technology Development Cell (TechCell), Mohammed VI Polytechnic University, Ben Guerir, Morocco. ³Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK. ⁴Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang, China. ⁵State Key Laboratory of Engines, School of Mechanical Engineering, Tianjin University, Tianjin, China. ⁶National Industry-Education Platform of Energy Storage, Tianjin University, Tianjin, China. ⁷These authors contributed equally: Zibo Yang, Youssef Belmabkhout, Lauren N. McHugh. ^Ce-mail: qiaozhihua@tiangong.edu.cn; michael.guiver@outlook.com; zhongchongli@tiangong.edu.cn to greatly decrease the cost of industrial gas separation^{26,27}. Nevertheless, self-supported porous materials in the form of membranes for gas separation are difficult to achieve²⁸, particularly for crystalline MOFs. MOF membranes are currently formed either on supports or mixed with polymeric matrices, both of which prevent large improvements in gas permeance. MOF glasses are a relatively new discovery, which are typically formed by melt-quenching crystalline MOFs. They retain the short-range inorganic-organic connectivity of their crystalline analogues, but lack long-range ordered connectivity^{29,30}. MOF glasses have been explored for various applications such as energy storage, gas separation and pollution control³¹⁻³⁴. MOF glasses, in the form of self-supported porous membranes, have been reported for conventional gas separations³⁴. They retain the ultramicropores of crystalline MOFs, but their long-range disorder is linked to discontinuous pores and low gas permeance, thus limiting their applicability for difficult gas separations, such as CH₄/N₂. Separately, current foams show continuous meso-pores or macropores produced by pore-inducing agents, but these large pore sizes are much larger than gas molecules, and are thus unsuitable for separation³⁵⁻³⁸. Accordingly, we hypothesize that self-supported membranes combining the advantages of ultramicroporous MOF glass and foam are an effective strategy to greatly improve membrane gas permeance, while maintaining high selectivity. For this purpose, we target the ultramicroporous ZIF-62, a zeolitic imidazolate framework (ZIF) that has been used to produce MOF glass, to prepare a type of glass foam.

Fabrication and characterization of a_{gf} ZIF-62

A glass foam, a_{sf}ZIF-62, wherein a, g and f denote amorphous, glass and foam, respectively, was synthesized by a polymer-thermaldecomposition-assisted melting strategy, starting from crystalline ultramicroporous ZIF-62 made from zinc tetrahedra and mixed ligands $(Zn((Im)_{2-x}(bIm)_x); Im, imidazolate, C_3H_3N_2^-; bIm, benzimidazolate,$ $C_7H_5N_2^{-}$). To obtain pure $a_{gf}ZIF-62$, a low-molecular-weight (M_w) polyethyleneimine (PEI; M_w , 300) was selected to ensure its complete thermal decomposition. The advantages and purpose of the introduced PEI are threefold. First, similar to conventional foam formation processes, the evolved gases (CO₂, NH₃ and H₂O) from PEI decomposition create a large number of pores in the glass, increasing the number of pores and the pore continuity and producing a MOF glass foam. Second, to obtain a pure MOF glass membrane, the molecular weight of PEI is low, only ~300, which ensures its complete decomposition and avoids carbonization. Third, the decomposition temperature of PEI is lower than that of ZIF-62, which decreases and facilitates the melting temperature of ZIF-62. The low molecular weight of PEI ensures that the decomposition of PEI initiates prior to ZIF-62 melting, and it continues to decompose during the melt phase of ZIF-62. The prepared a_{gf}ZIF-62 displays complementary structural advantages of both MOF glasses and foams, hence allowing for ultrahigh gas permeance as well as good selectivity. First, like MOF glasses³⁹⁻⁴¹, a_{af}ZIF-62 in the form of a self-supported membrane, maintains ultramicropores and eliminates the need for transport-limiting support substrates. Second, a_{gf} ZIF-62 displays a foam structure having a large number of pores in the glass, which largely increases the pore interconnectivity of the glass.

Crystalline ZIF-62 was prepared using a literature procedure⁴², and its purity was confirmed by powder X-ray diffraction (Supplementary Figs. 1 and 2 and Supplementary Tables 1 and 2). Figure 1a shows the fabrication procedure for a_{gf}ZIF-62. PEI was first mixed with the presynthesized ZIF-62 (Fig. 1a, left panel). The PEI–ZIF-62 mixture (ZIF-62^P; Supplementary Fig. 3) was then pressed into a single circular pellet with a diameter of 4 cm under a pressure of 10 MPa, and was heat treated at different temperatures under an Ar atmosphere. At temperatures higher than 160 °C, PEI starts to decompose and ZIF-62 begins to melt (Fig. 1a, middle panel and Supplementary Fig. 4). Finally, a_{gf}ZIF-62 was obtained when the temperature was reduced to the room temperature. Figure 1a (right panel) shows an image of an a_{gf}ZIF-62 self-supported circular membrane. Characterization by

X-ray diffraction patterns, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, elemental analysis and nuclear magnetic resonance spectroscopy (NMR) confirm that a_{gf} ZIF-62 and the a_{g} ZIF-62 that is obtained from crystalline ZIF-62 (refs. 33,43–46) are elementally pure and that a_{gf} ZIF-62 does not contain PEI residue (Supplementary Figs. 5 and 6 and Supplementary Table 3).

After heat treatment, a_{ef}ZIF-62 transforms from the crystalline state to the amorphous state, showing a structure with short-range order, but long-range disorder. This is confirmed by total scattering measurements on the samples, and the resultant pair distribution functions using appropriate data corrections for the structure factors (Fig. 1b,c and Supplementary Fig. 7). The broad diffuse scattering in the X-ray diffraction patterns of a_{af}ZIF-62 also indicates an amorphous material (Supplementary Fig. 5). The pore size distribution of a_{ct}ZIF-62 determined by positron annihilation lifetime spectroscopy (PALS) analyses is shown in Fig. 1d, indicating that a_{ef}ZIF-62 maintains its ultramicroporosity. Pore size distributions for $a_{\alpha f}$ ZIF-62 based on the N₂ adsorption isotherms (Fig. 1e) indicate that the a_{sf}ZIF-62 contains meso-pores. In addition, the local structure of a_{gf}ZIF-62 was probed by X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS; Fig. 1f,g). The peaks in Fig. 1f are almost the same in a_{gf} ZIF-62 and a_{g} ZIF-62, but the intensity of the peak at ~1.53 Å in Fig. 1g has a slight change, confirming that the local environment of Zn^{2+} ions is different in the $a_{gf}ZIF-62$ (Supplementary Table 4). Based on high-resolution transmission electron microscopy (TEM) images for the samples prepared by ultrathin sectioning without ball milling (Fig. 1h-j), agfZIF-62 displays good pore continuity. A pellet of circular a_{st}ZIF-62 having an area of ~8.55 cm² was divided into nine parts, each of which showed a similar uniform morphology (Supplementary Fig. 8). In addition, to verify the extent of damage by electrons to glass materials undergoing TEM analyses, we carried out a high-resolution TEM examination of the ZIF-62 materials at different magnifications; the images of a_{gf}ZIF-62 and a_gZIF-62 are shown in Supplementary Figs. 9 and 10, respectively. At different magnifications, we did not observe any sign of damage by the electron beam at 200 kV accelerating voltage, indicating a higher stability of the glass materials than that of ZIF-62 crystal.

Figure 2a depicts the effect of the PEI decomposition process on the formation of a_{ef}ZIF-62. As shown in Fig. 2a (left panel), PEI crosslinks with ZIF-62 by hydrogen bonding, as confirmed by FTIR analyses (Supplementary Fig. 5). Pure PEI begins to decompose at ~160 °C, and completely decomposes by ~370 °C (Supplementary Fig. 4). Figure 2a (left middle panel) shows that the decomposition of PEI occurs prior to the melting of ZIF-62, which is a crucial step in the preparation of a_{gf} ZIF-62. As shown in Fig. 2b, the melting temperature (T_m) of ZIF-62^P is 378 °C, lower than that of conventional ZIF-62 (414 °C). We believe this may be ascribed to the decomposition of PEI adsorbing a substantial amount of heat (Supplementary Fig. 11), facilitating the melting process of ZIF-62. This was verified by differential scanning calorimetry (DSC) analysis of ZIF-62 samples containing different amounts of PEI (Supplementary Fig. 12), as well as by thermomechanical analysis (Supplementary Fig. 13). PEI decomposes to evolve three low-molecular-weight gases (NH₃, CO₂ and H₂O), as shown in Fig. 2a (right middle panel), confirmed by thermogravimetric and mass spectroscopy (TGA-MS) analyses, shown in Fig. 2c-e. TGA-MS analyses also show that the gases are released predominantly in the cooling process for ZIF-62^P, opposite to the heating process for pure PEI (Supplementary Fig. 14), indicating that the melting process of ZIF-62 delays the release of the gases evolved from PEI. As in conventional foam formation, the evolved gases create a large number of pores in the glass, which is confirmed by the increased pore continuity and porosity compared to agZIF-62 (Fig. 2f,g and Supplementary Figs. 15 and 16). This is clearly reflected by the relative pore size distributions of the a_gZIF-62 and a_{gf}ZIF-62 obtained by PALS analyses (Fig. 2f), the kinetic CO₂ gas adsorption isotherms of a_{cf}ZIF-62 and a_{cf}ZIF-62 under



Fig. 1 | **Preparation and characterization of a_{gt}ZIF-62. a**, Preparation process of a_{gt} ZIF-62. Low-molecular-weight PEI is mixed with ZIF-62 to form ZIF-62^P (left). ZIF-62^P is pelletized under a pressure of 10 MPa, and then heat treated (middle). When the temperature is higher than 160 °C, the PEI begins to decompose and ZIF-62 begins to melt. The a_{gt} ZIF-62 is formed (right). **b**, X-ray scattering factors (*s*) for a_{gt} ZIF-62 determined from total scattering data recorded at beamline 115-1 of the Diamond Light Source; *q* is the scattering vector. **c**, Pair distribution function (*G*) for a_{gt} ZIF-62, obtained via Fourier transform of the total scattering data shown in **b**; *r* is the radius of the radial distribution function

of the atom. **d**, Pore size distributions for a_{gf} ZIF-62 based on PALS analyses. **e**, Pore size distributions for a_{gf} ZIF-62 based on density functional theory fitting of the N₂ adsorption isotherms at 77 K. **f**, Normalized XANES spectra of a_{gf} ZIF-62 and a_g ZIF-62. The curves of Zn foil and ZnO are provided as comparisons, representing the valences of Zn⁰ and Zn²⁺, respectively. **g**, Fourier transformed (FT) k^3 -weighted x(k) function of the EXAFS spectra; k is the wave vector, x is the EXAFS function, and R_a is the mean radial distance between the central atom and other atoms. The standard curves of Zn foil and ZnO are exhibited to confirm the presence of different peaks. **h–j**, High-resolution TEM images of a_{gf} ZIF-62.

low constant pressure (Fig. 2g) and the high-pressure CO₂ adsorption isotherms (Supplementary Fig. 16). It is evident that the CO₂ uptake equilibrium for a_{gf} ZIF-62 is much faster than that of a_g ZIF-62, and its adsorption capacity is also higher, which signifies that gas diffusion in the a_{gf} ZIF-62 is much faster than in the a_g ZIF-62. This indicates that the pore continuity of a_{gf} ZIF-62 is much better than that of the a_g ZIF-62, and also that the porosity of the a_{gf} ZIF-62 is higher than that of the a_g ZIF-62. The pore diameters of a_{gf} ZIF-62 and a_g ZIF-62 are the same, both 6.3 Å. These pores substantially increase the pore continuity of a_{gf} ZIF-62, relative to that of a_g ZIF-62, as confirmed by the high-resolution TEM comparison shown in Supplementary Fig. 17. We compare the a_g ZIF-62 and a_{gf} ZIF-62 in Supplementary Tables 5 and 6 in detail. The increased pore continuity of a_{gf} ZIF-62 remains in the ultramicroporous range, having minimal change as compared to a_g ZIF-62 (Supplementary Tables 5 and 6). Moreover, the pore structures of the mechanochemically synthesized and solvothermally synthesized a_{gf} ZIF-62 are similar (Supplementary Fig. 18 and Supplementary Tables 5 and 7). Figure 2a (right panel) shows the sketch structure of a_{gf} ZIF-62. The a_{gf} ZIF-62 formation process is also confirmed by the evolution of scanning electron microscopy (SEM) images (Supplementary Fig. 19).



Fig. 2 | **Formation route and mechanism of a**_{gf}**ZIF-62. a**, Effect of the PEI decomposition process on the formation of a_{gf}**ZIF-62. b**, DSC patterns of ZIF-62 and ZIF-62^P. The red line shows that the melting temperature (T_m) of ZIF-62^P is 378 °C, which is lower than that of ZIF-62 ($T_m = 414$ °C), represented by the black line. There is an endotherm (Endo) evident in the range of 150–250 °C for each of the curves, which is consistent with solvent (N,N-dimethylformamide) release³⁵.

The endotherm observed on the red curve, in the temperature range of 265–378 °C, corresponds to decomposition of PEI and melting of ZIF-62. **c**–**e**, TGA-MS of a ZIF-62^P pellet during the cooling process shows that NH₃, H₂O and CO₂ are evolved, due to PEI decomposition. **f**, Pore size distributions of a_{gf}ZIF-62 and a_gZIF-62 determined by PALS. **g**, Kinetic CO₂ gas adsorption measurements by time-dependent CO₂ uptake profiles at 273 K at a pressure of 5 torr.

STP) $cm^{-2} s^{-1} cmHg^{-1}$, permeability (in barrers, where 1 barrer =

Fabrication and characterization of $a_{\rm gr} ZIF\text{-}62$ membranes

The prepared circular a_{gf} ZIF-62 was directly used for membrane gas separation. Figure 3 shows circular a_{gf} ZIF-62 membranes with a diameter of 3.3 cm, which were prepared with thicknesses of 200–330 µm (Fig. 3a and Supplementary Figs. 20–26). Figure 3b,c and Supplementary Fig. 27 indicate that the a_{gf} ZIF-62 membrane presents a uniform and defect-free SEM surface and cross-section, and a homogeneous atomic force microscopy phase distribution and laser scanning confocal microscope distribution over an entire membrane area. Micrographs of the a_{gf} ZIF-62 membrane under parallel and cross-polarized light (Supplementary Fig. 28) show optical isotropy, confirming the absence of a grain boundary⁴⁴, deemed to facilitate gas permeation³¹.

Gas separation performance of a_{gf}ZIF-62 membranes

Next, we demonstrate the utility of the membranes for CH_4/N_2 separation, which is one of the most important, but also one of the most difficult, gas separations²⁰, mainly due to the close similarities in kinetic diameter and other physical-chemical characteristics of the gases⁴⁷. Permeance (in gas permeance units (GPU), where 1 GPU = 10^{-6} cm³(at

10⁻¹⁰ cm³(at STP) cm cm⁻² s⁻¹ cmHg⁻¹) and selectivity are three important parameters for gas separation membranes. The separation performance of the membranes was measured by the constant pressure method using a laboratory-made test device, shown in Supplementary Figs. 29-31. The gas was passed through the membrane test cell to obtain the gas permeance, and the selectivity was obtained from the CH₄ permeance divided by the N₂ permeance. The gas permeability, obtained from the gas permeance multiplied by the membrane thickness, is almost the same as that obtained by a laboratory-made instrument based on the constant-volume/variable-pressure time-lag method (Supplementary Fig. 31). The active area of the membrane test cell was 4.91 cm². Figure 4a and Supplementary Tables 8a and 9 show the single gas CH_4/N_2 separation performance of the a_{gf} ZIF-62 membranes. These membranes show a favourable compromise between permeability and selectivity. An ultrahigh CH₄ permeance of 30,000-50,000 GPU and permeability of $\sim 1.0 \times 10^7$ barrer, along with a high CH₄/N₂ selectivity of 4-6, were obtained. This performance was further confirmed by mixed gas CH₄/N₂ measurements (Supplementary Table 8b) showing almost the same separation performance of the agfZIF-62 membranes as in the single gas performance. Moreover, the performance of a_{of}ZIF-62

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Fig. 3 | **Characterization of a**_{gf}**ZIF-62 membranes with different thicknesses. a**, Photographic image and thickness of membranes with a diameter of 3.3 cm (ruler in centimetres). **b**,**c**, Atomic force microscopy phase image (**b**) and laser scanning confocal microscope image (**c**). The uniform yellowish-brown colour of **b** signifies that the membrane surface is in the same phase state. The uniform green colour of **c** signifies that the membrane surface is smooth. Three individual membranes of each type were tested. The membrane thickness is taken as the average value of the three membranes which are presented as mean values \pm s.d. Supplementary Figs. 20–26 provide detailed information about evaluating membrane thickness.

membranes synthesized by different methods is consistent (Supplementary Fig. 32). The ultrahigh gas permeance of the a_{sf}ZIF-62 membranes is primarily supported by following the experimental evidence. First, based on the high-resolution TEM analyses (Supplementary Figs. 8 and 17), the a_{gf}ZIF-62 membrane shows good pore continuity, which has a large positive influence on the gas permeance. Second, based on the pore size distribution of the a_g ZIF-62 and a_{gf} ZIF-62 membranes obtained by CO₂ and N₂ adsorption isotherms, respectively, both membranes have micropores and meso-pores, but do not have macropores. The micropore content of a_{af} ZIF-62 is substantially higher than that of a_{r} ZIF-62, while there is no obvious difference in the meso-pores between a_gZIF-62 and a_{gf}ZIF-62 (Supplementary Fig. 15 and Supplementary Tables 5 and 6). In addition, the gas transport mechanism of CH₄ in the a_{rf}ZIF-62 membrane is preferential-adsorption/surface-diffusion, because there are strong preferential affinity interactions with CH₄, which facilitate its selective transport, allowing us to address one of the most difficult gas separations: CH_4 separation from the CH_4/N_2 mixed gas. This is primarily due to the retention of ultramicropores and the preferential van der Waals interactions of CH₄ with the open metal sites⁴⁸ of the unsaturated Zn^{2+} ions in $a_{gf}ZIF-62$ (confirmed by the EXAFS results reported in Supplementary Table 4) due to the larger polarizability of CH_4 compared with N_2 (ref. 49), as confirmed by CH_4 and N₂ adsorption-desorption isotherms (Supplementary Fig. 33). Besides CH₄, the open metal sites in the membranes also show preferential π bond interactions with C₂H₄, C₃H₆, *n*-C₄H₈ and *i*-C₄H₈ (ref. 50) and preferential van der Waals interactions with O₂ to enable selective facilitated transport of these gases⁵¹, while they cannot readily adsorb N₂. Then, the gas transport model of the gases (besides N₂) across the pores is governed by surface diffusion, while that of N₂ is free diffusion. By stark contrast, the a_gZIF-62 membrane exhibits very low gas permeance, showing a CH₄ permeance of only 36.3 GPU with a slight CH₄/N₂ selectivity of 1.1 (Supplementary Table 8a), mainly attributed to poor pore continuity and low porosity.

In contrast with other membranes containing PEI, the role of PEI here is twofold. The evolution of gas molecules from PEI decomposition greatly increases the pore continuity, by creating foam pores



Fig. 4 | **CH**₄/**N**₂ **separation performance of a**_{gf}**ZIF-62 membranes. a**, Pure gas permeance and selectivity of a_{gf}ZIF-62 membranes with different thicknesses. The *x*-axis values of three bar charts correspond to the thickness of three different membranes, and the *y*-axis values correspond to the pure CH₄ permeance of the three different membranes. The error bars represent the standard deviation of three samples (*n* = 3), and data are presented as mean values ± s.d. **b**, Comparison of the gas separation performance of the a_{gf}ZIF-62 membranes with other reported membranes with high performance values. The highest permeance among the membranes from the literature that are being compared is <10³ GPU. Data including identities and reference citations for the membranes shown are listed in Supplementary Table 10.

and through-channels as well as open metal sites. The a_{af}ZIF-62 membranes display the best CH_4/N_2 separation performance, showing high CH₄ permeance, approximately two orders of magnitude higher than those of other reported membranes, with high CH_4/N_2 selectivity. As shown in Supplementary Fig. 34, the a_{gf}ZIF-62 membrane also shows much higher permeances for other gases, with different gas selectivities depending on the affinity of the pore structure with the gases. High-permeance membranes allow one to greatly decrease the membrane area, and hence, reduce the cost of the process, providing some inherent advantages when compared with competing separation technologies such as absorption that have properties such as high energy consumption and cost. The reported permeances of supported and self-supported membranes are relatively low, due to resistance limitations of the support layer or poor pore continuity. Figure 4b and Supplementary Table 10 compare the CH₄/N₂ separation performance of a_{st}ZIF-62 membranes with other high-performing membranes reported in the literature. While very few of these membranes show a higher gas selectivity^{52,53}, their gas permeance is less than 1 GPU, which is about four orders of magnitude lower than that of a_{gf} ZIF-62. Thus, substantially larger membrane areas for real gas separation will greatly increase the cost of the membrane process.

For evaluating the stability of the a_{gf} ZIF-62 membrane, a series of measurements were conducted. The gas separation performance of a 265-µm-thick membrane was compared using dry and humidified CH₄/N₂ mixed gas (50/50 by volume) for 24 h. Supplementary Figs. 35 and 36 show no obvious changes in membrane permeance and selectivity. After immersion in water for 72 h and drying in a vacuum

drying oven for 12 h, the performance remains stable, as shown in Supplementary Fig. 37. Then, the thermal stability of a 265-µm-thick membrane was evaluated after a thermal treatment (100–400 °C) for 60 min. As shown in Supplementary Fig. 38, the membrane performance is quite stable following treatment below 200 °C, but after treatment temperatures of 300–400 °C it substantially decreases, mainly because of a glass transition process similar to that of an a_g ZIF-62 glass membrane. Moreover, the effect of temperature on the CH₄/N₂ separation performance of a 265-µm-thick membrane was investigated. With an increase in temperature from 25 °C to 60 °C, the membrane permeance slightly increases, and the selectivity slightly decreases, as shown in Supplementary Fig. 39.

We investigated the porosity of the a_{gf} ZIF-62 before and after annealing for some time above the glass transition temperature (T_{g}), which indicated that the porosity of the a_{gf} ZIF-62 is stable at 25 °C (Supplementary Figs. 35–37), but is not persistent after annealing above T_{g} . Based on comparisons of density (Supplementary Fig. 40), high-resolution TEM images (Supplementary Figs. 17 and 41), CH₄/ N₂ adsorption isotherms (Supplementary Figs. 33 and 42) and gas separation performances (Supplementary Fig. 38), we observe that the a_{gf} ZIF-62 samples before and after annealing at 350 °C are different. Based on comparisons of high-resolution TEM images and CH₄/N₂ adsorption isotherms, the a_{gf} ZIF-62 after annealing at 350 °C for 6 h is similar to conventional a_{gf} ZIF-62, which is mainly due to the disappearance of PEI through decomposition. The densities of the a_{gf} ZIF-62 and a_{gf} ZIF-62 obtained by a He pycnometry test are 1.5764 g cm⁻³ and 1.5156 g cm⁻³, respectively.

 O_2/N_2 separation is industrially important, primarily for N_2 production, but also for O_2 enrichment. Our membranes show high O_2 permeability (-7.6 × 10⁶ barrer) and O_2 permeance (-38,000 GPU), values that are approximately three orders of magnitude higher than for other reported membranes, and the O_2/N_2 selectivity (-3) is well above the 2015 upper bound (Supplementary Fig. 34b).

Outlook

In summary, using the polymer-thermal-decomposition-assisted melting strategy methodology, we report the simple preparation of a type of glass foam, a_{gt}ZIF-62, combining the structural advantages of MOF glass and foam. This study provides a practical approach for the preparation of self-supported high-performance membranes. Future efforts will focus on achieving other large-area ultrathin self-supported MOF glass membranes based on their self-supported characteristics, or by using MOF glasses as a continuous phase. Other porous materials with specific gas transport properties will be used as the dispersion phase in mixed matrix glass membranes to achieve the separation of target gas mixtures.

Online content

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Methods

Mechanosynthesis of ZIF-62

ZIF-62 was synthesized according to a previous report with slight modifications. All the reagents, Zn(OH)₂ (3.976 g), Zn(OAc)₂·2H₂O (2.195 g), imidazole (5.95 g), benzimidazole (1.50 g) and DMF (5 ml), were added into a 100 ml stainless steel grinding mill, along with grinding balls (15 with a diameter of 10 mm and 15 with a diameter of 6 mm). This experimental composition was selected following a series of attempts shown in Supplementary Table 1. The ball mill jar was sealed and shaken at 300 Hz for 60 minutes on a QM-3SP04L mixer mill. The powder was extracted from the jar and was washed using the following procedure54,55: The powders were filtered and washed three times with DMF (30 ml) and once with dichloromethane (DCM; 30 ml) and then placed in an oven at 60 °C to dry overnight. A vield of 7.59 g of ZIF-62 crystal was obtained. The mechanochemical method is a common method for porous material preparation, having the advantages of a short synthesis time, mild synthesis conditions and high yield, and is beneficial to the fabrication of glass membranes for industrial applications.

Fabrication procedure of agZIF-62 membrane

The ZIF-62 pellet was fabricated as follows. A certain volume of methanol (-150 μ l) was dropped onto ZIF-62 powder (300 mg) in an agate mortar, and the mixture was ground thoroughly. Next, the powder was transferred into a pellet mould with a diameter of 4 cm and spread uniformly. In the pelletization process, the applied pressure was 10 MPa (4.0 tonnes), which was maintained for 30 s, and then the pressure was released slowly to prevent fracturing. The resulting ZIF-62 pellet was placed on a glass slide, heated to 440 °C at a rate of 3 °C min⁻¹ and held for 20 min before being allowed to cool to room temperature under an Ar atmosphere. An a_gZIF-62 membrane was obtained.

Fabrication procedure of a_{gf} ZIF-62 membrane

First, the pellet containing PEI and ZIF-62 was prepared and denoted as the ZIF-62^P pellet. The fabrication procedure for the ZIF-62^P pellet was similar to that of the ZIF-62 pellet, except for the addition of a methanolic PEI solution for the grinding process. The PEI-methanol solution (5.0 wt%) was prepared by stirring PEI (0.5 g) in anhydrous methanol (9.5 g) for 2 h. A certain quantity of 5.0 wt% PEI solution was dropped into different quantities of ZIF-62 powder (300 mg, 400 mg and 500 mg) placed in an agate mortar, and the mixture was ground thoroughly. Next, the powder was transferred into a pellet mould with a diameter of 4 cm and spread uniformly. The pelletization process was identical to the previous description. Then, ZIF-62^P pellets with different thicknesses were obtained and placed on a glass slide, heated to 440 °C at a rate of 3 °C min⁻¹ and held for 20 min before being allowed to cool to room temperature under an Ar atmosphere. Finally, a_{of}ZIF-62 membranes were obtained. To explore the influence of PEI content, different loadings of PEI with 0 wt%, 1.72 wt%, 3.38 wt% and 4.99 wt% were prepared according to the same procedure described previously.

For a comparison, we synthesized ZIF-62, $a_gZIF-62$ and $a_{gf}ZIF-62$ following a solvothermal literature method⁵⁶. Their pore structures were evaluated using CO₂ as an adsorbent for obtaining the adsorption–desorption isotherms and PALS results, which are given in Supplementary Fig. 18 and Supplementary Tables 5 and 7. Although the gas capacity of solvothermally synthesized ZIF-62 are larger than those of the mechanochemically synthesized ZIF-62, amorphous $a_gZIF-62$ and $a_{gf}ZIF-62$ synthesized by both methods are similar in terms of gas capacity, pore diameter and free volume and also show the same gas separation performance (Supplementary Figs. 18 and 32 and Supplementary Tables 5 and 7). Furthermore, the CO₂ adsorption capacity and pore diameters of the $a_gZIF-62$ are almost the same as those reported in the literature⁵⁷. All the ZIF-62, $a_gZIF-62$ and $a_{gf}ZIF-62$ samples described in our work are mechanochemically synthesized (except where noted).

Characterization

Powder X-ray diffraction data $(2\theta = 3^{\circ} \text{ to } 50^{\circ}, \text{ where } \theta \text{ is the angle}$ between the incident X-ray and the crystal plane) were recorded on a Bruker D2 PHASER X-ray diffractometer equipped with graphite monochromatized Cu K radiation (wavelength, $\lambda = 1.54056 \text{ Å}$) at 30 kV and 10 mA. The step size was 0.02°, with 10 s per step.

TGA was performed on a Netzsch 209 F3 Tarsus at a heating rate of 5 °C min⁻¹ from 30 to 500 °C with an Ar flow rate of 100 ml min⁻¹. The DSC curve was obtained on a NETZSCH instrument. The samples were placed in a ceramic crucible situated on a sample holder, and then heated for two scan cycles. Briefly, the samples were heated at 5 °C min⁻¹ from 30 °C to 500 °C in scan 1. Then, a heat treatment the same as scan 1 was carried out for the samples after they were cooled at 20 °C min⁻¹. The process was undertaken in an Ar atmosphere.

The T_m is the temperature at which the slope of scan 1 changes at around the melting point. The slope is a first-order derivative obtained by using the measurement software (Proteus v.6.1) to judge the temperature at the beginning and end of the endotherm.

TGA was performed on Netzsch STA449F3 with parallel online MS analysis (Bruker, QMS403C) at a heating rate of 3 °C min⁻¹ from 20 to 440 °C and holding for 20 min, following a cooling procedure with a rate of 5 °C min⁻¹ from 440 °C to 30 °C. The process was undertaken in an Ar atmosphere with a flow rate of 100 ml min⁻¹.

Attenuated total reflection FTIR measurements were performed on a Bruker TENSOR II.

Solution proton NMR (¹H-NMR) spectra of digested samples (about 10 mg in a mixture of DCl (20%)/D₂O (0.2 ml) and DMSO-d₆ (0.8 ml)) were performed on a Bruker AVANCE 400M at 298 K. Chemical shifts were referenced to the residual solvent proton signals of DMSO-d₆. The spectra were processed with the MestreNova Suite⁵⁸.

Permeance (*R*), permeability (*P*) and selectivity (α) are three important parameters of gas separation membranes. Single gas and mixed gas (50:50 by volume) permeance of the membranes were measured by laboratory-made test equipment reported in the literature⁵⁹, which is depicted in Supplementary Fig. 30. The permeance and permeability of a membrane are calculated by equations (1) and (2):

$$R_i = \frac{Q_i}{A \times \Delta p_i} \tag{1}$$

$$P_i = \frac{Q_i \times \delta}{A \times \Delta p_i} \tag{2}$$

where R_i is the gas permeance of the *i* component in gas permeance units, P_i is the gas permeability of the *i* component in barrers, Q_i is the molar flow rate of the *i* component (in cubic centimetres at STP per second), δ is the thickness of the membrane (in micrometres), *A* is the membrane area (in square centimetres) and Δp_i is the pressure difference across the membrane (in pascals).

Single or mixed gas selectivity of the membrane is calculated by the division of two different gas permeance values, as shown in equation (3):

$$\alpha = \frac{R_i}{R_j} \tag{3}$$

The CH₄ and N₂ adsorption properties of a_g ZIF-62 and a_{gf} ZIF-62 at pressures up to 1 bar were measured volumetrically using a Micromeritics ASAP-2020 instrument, and the experimental isotherm data for CH₄ and N₂ (measured at 298 K) were fitted using the Langmuir–Freundlich model. The solubility coefficient (*S*) of a single gas in a membrane sample can be expressed by equation (4):

$$S = \frac{C}{p} \tag{4}$$

where C (cubic centimetres at STP per cubic centimetre of membrane) is the concentration for the adsorbed component, and p (centimetres of Hg) is the adsorbate gas pressure at equilibrium. The diffusion coefficient (D) is calculated from the relationship between the permeability (P) and solubility coefficient (S) using equation (S):

$$D = \frac{P}{S} \tag{5}$$

X-ray total scattering data of selected a_g ZIF-62 materials and their crystalline parent frameworks were collected with an incoming beam energy of 70 keV at the 13w beamline at Shanghai Synchrotron Radiation Facility. The *G*(*r*) and *s*(*q*) values were calculated using routines from the DiffPy-CMI library. With the aim to observe the differences, three ZIF-62-based materials (ZIF-62, a_g ZIF-62 and a_{gr} ZIF-62) were studied.

The surface and near-surface bulk morphologies were studied by dual-beam focused ion beam using a ZEISS CrossBeam 550 instrument. SEM was carried out before and after sectioning a ZIF- 62^{P} pellet by the ion beam. A large pellet of ZIF- 62^{P} formed by pressing was mounted in conductive resin and mechanically ground to give a flat surface before sectioning, and a ZIF- 62^{P} fragment was studied by focused ion beam after Au coating using Blatc SCD005. Focused ion beam sectioning was performed at a 30 kV ion gun voltage; rough sectioning, at a current of typically 30 nA; and final polishing, at 1 nA to reveal the microstructure. SEM imaging was carried out at 5 kV and 10 kV electron beam voltages. Additionally, many images were obtained by backscattered electron mode.

High-resolution TEM was acquired using a Jeol JEM-F200 with a Gatan complementary metal-oxide-semiconductor CCD (charge-coupled device) camera. The instrument was operated at 200 kV with a resolution of 0.23 nm. The samples were prepared by ultrathin sectioning without ball milling.

All materials were studied with an Olympus BX51 and Canon A630 polarized light photomicroscope. Pictures of one grain under parallel and crossed-polarized light are shown for a_{gf} ZIF-62. For a a_{gf} ZIF-62 grain, four positions of maximum illumination from four different directions (one every 90°) are obtained. The a_{gf} ZIF-62 grain shows no change in illumination at the four different positions, due to their amorphous and isotropic nature.

The ZIF-62, a_g ZIF-62 and a_{gf} ZIF-62 were studied using an Elementar vario El cube elemental analyser instrument. The samples were dried in a vacuum oven for 12 h at 150 °C.

Pore structural parameter acquisition

The gas adsorption isotherms of CH_4 and N_2 for powders were conducted using a Micromeritics ASAP-2020 instrument. All the powder samples were first immersed in DCM to exchange residual DMF in the pores using the higher polarity of DCM⁶⁰. The DCM-exchanged samples were degassed at 80 °C for 48 h under dynamic vacuum. The gas sorption isotherms of samples for CH_4 and N_2 were performed at 273 K and 298 K.

Low-and-constant-pressure CO_2 adsorption tests of $a_{gf}ZIF-62$ and $a_gZIF-62$ were carried out using a gas sorption analyser (BSD-VVS, Bei Shi De) at 273 K at a pressure of 5 torr following a literature procedure⁶¹, and kinetic CO_2 gas adsorption isotherms were obtained. High-pressure CO_2 adsorption tests of $a_{gf}ZIF-62$ and $a_gZIF-62$ were carried out using a high-pressure gas sorption analyser (BSD-PH, Bei Shi De) at 273 K, and the pressure was in the range of 0–30 bar. All of the samples were degassed at 80 °C for 48 h under dynamic vacuum.

Positron annihilation lifetime spectroscopy

PALS measurements were performed at room temperature using a standard fast-slow coincidence system with a time resolution 210 ps.

The routine MELT4.0 was used for the analysis of positron lifetime spectra. The obtained *ortho*-positronium (*o*-Ps) annihilation lifetime can be transformed through equation (6) based on the Tao–Eldrup free volume model⁶²:

$$\tau_j = 0.5 \operatorname{ns} \left[1 - \frac{r_j}{r_j + \Delta l} + \frac{1}{2\pi} \sin\left(\frac{2\pi r_j}{r_j + \Delta l}\right) \right]^{-1}$$
(6)

where r_j is the average radius of the free volume cavity (in ångströms), Δl is a fitted empirical electron layer thickness ($\Delta l = 1.66$ Å) derived from fitting well-known cavities, τ_j is the lifetime of *o*-Ps in nanoseconds (j = 3 or 4) and the spin-averaged lifetime of the *o*-Ps is 0.5 ns.

The relative fractional free volume (FFV) is obtained according to the Williams–Landel–Ferry equation⁶² shown in equation (7):

$$FFV = \sum_{j} 0.00181 I_{j} V_{f} \left(\frac{4}{3} \pi r_{j}^{3}\right)$$

$$\tag{7}$$

where I_j is the *o*-Ps intensity (in percent), which is used for the estimated pick-off lifetime τ_j (j = 3 or 4). The mean free volume (in cubic ångströms) of pores in the glass membranes are represented by V_f based on the mean free volume radius r_j .

Data availability

The authors declare that all data supporting this study are available within the paper and Supplementary Information. Source data are provided with this paper.

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Author contributions

Z.Y., Z.Q. and S.L. fabricated the membranes and conducted the characterization. C.Z., Z.Q., M.D.G., T.D.B., Y.B., L.N.M., S.L., D.A. and Y.S. helped with experimental design, the membrane formation mechanism and data analyses. Z.Q., Z.Y., C.Z., M.D.G., T.D.B., Y.B. and L.N.M. wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

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