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Nanofiller-tuned microporous polymer molecular sieves for energy and environmental processes†

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Microporous polymers with molecular sieving properties are promising for a wide range of applications in gas storage, molecular separations, catalysis, and energy storage. In this study, we report highly permeable and selective molecular sieves fabricated from crosslinked polymers of intrinsic microporosity (PIMs) incorporated with highly dispersed nanoscale fillers, including nonporous inorganic nanoparticles and microporous metal-organic framework (MOF) nanocrystals. We demonstrate that the combination of covalent crosslinking of microporous polymers via controlled thermal oxidation and tunable incorporation of nanofillers results in high-performance membranes with substantially enhanced permeability and molecular sieving selectivity, as demonstrated in separation of gas molecules, for example, air separation (O2/N2), CO2 separation from natural gas (CH4) or flue gas (CO2/N2), and H2 separation from N2 and CH4. After ageing over two years, these nanofiller-tuned molecular sieves became more selective and less permeable but maintained permeability levels that are still two orders of magnitude higher than conventional gas separation membranes.

Introduction

Molecular separations are important for energy, environmental and chemical process industries, such as air separation, natural gas purification, H2 recovery and purification, carbon dioxide capture, desalination of water, and chemical separations in oil refinery processes. These processes have large benefits for society but also present environmental challenges that require cost and energy efficient technological solutions. Conventional separation processes, such as distillation or solvent scrubbing, require a lot of energy input to liquefy gases (cryogenic distillation for air separation), or evaporate liquids (thermal desalination of water, amine scrubbing, or distillation in oil refining processes) since these separations involve phase changes. Membrane separation is a promising alternative technology to these energy-intensive molecular separations. Both gases and liquids can be pressurized and fed to membranes that allow the selective separation of molecules in a single phase, avoiding the energy input for distillation or evaporation. Thus membrane separation processes, with high permeability and selectivity are more attractive for these molecular-scale separations owing to their high energy efficiency, low environmental impact, and compact units with small footprint.1

Commercial molecular separation membranes are dominated by polymeric materials, the molecular transport in which follows the solution-diffusion mechanism, and where the permeability coefficient \( P \) is a product of solubility \( S \) and diffusion coefficient \( D \), \( P = S \times D \). The selectivity of different species \( A \) over \( B \), is defined by the ratio of their permeability, \( \alpha_{AB} = \frac{P_A}{P_B} = \frac{S_A/S_B}{D_A/D_B} \), where \( S_A/S_B \) is the solubility selectivity and \( D_A/D_B \) is the diffusivity selectivity. However, conventional selective polymeric membranes present considerably low gas permeability and an inherent trade-off between permeability and selectivity exists, known as upper bound.2–7 This upper bound was explained theoretically by Freeman,4 who also predicted two strategies to enhance both the permeability and selectivity of polymeric membrane materials: (i) improving the solubility selectivity \( (S_A/S_B)^5 \) or (ii) increasing the stiffness of polymer chains while maintaining large interchain spacing, such as thermally rearranged (TR) polymers,6–7 and polymers of intrinsic microporosity (PIMs).8–16

PIMs polymers are a class of polymers with rigid and contorted backbone structure.8–16 The chemical structure of a representative PIM-1 is shown in Fig. 1a. In the solid state, rigid polymer chains (as visualized in Fig. 1b) cannot pack...
efficiently, forming interconnected cavities behaving like micro pores. The pore structure in PIMs molecular sieves can be visualized as the hour-glass shaped interconnected cavities, as shown in Fig. 1c. The molecule-sized pores and intermolecular interactions allow high solubility of gas molecules, particularly condensable gases, while the bottlenecks or gates interconnecting pores behave as sieves for separating gas molecules with different sizes. Owing to the unique pore structure, these polymeric molecular sieves achieve both higher permeability and higher selectivity. Further structural modifications of PIMs include substituting side functional groups that may introduce stronger intermolecular forces (i.e. hydrogen bonding) or design of more rigid polymer backbone structure, producing more selective or permeable molecular sieves.

Mixed matrix membranes (MMMs), formed by incorporating molecular sieves or nanoscale fillers into polymer matrices, have also attracted significant interest. When the size of fillers in the polymer matrix is reduced to nanoscale, i.e. approximate to that of polymer chains, the properties of nanocomposite materials are strongly dependent on the interface between the polymer and fillers, where the local polymer chain mobility and conformation and their interactions vary significantly. Novel microporous materials, such as metal-organic frameworks (MOFs), with well-defined pores as shown in Fig. 1d, have been demonstrated as building blocks for molecular-sieving membranes, or as fillers in
MMs. Whilst often beneficial to membrane performance, the structure-property relationships of MMMs is complicated to predict, with diffusion and adsorption parameters varying from the bulk polymeric phase, to the interface with the fillers and potentially the internal surfaces of fillers.

PIM-1 polymer-based mixed matrix membranes have been prepared by solution mixing of PIM-1 polymer with various fillers including nonporous fillers and microporous materials, such as PIM-1/silica, PIM-1/ZIF-8, PIM-1/cages, PIM-1/POSS, PIM-1/MOFs, and PIM-1/porous aromatic frameworks (PAFs). In all of these studies, addition of fillers enhanced gas permeability of resulting composite membranes to certain extents, however the selectivity remained relatively unchanged (e.g. CO$_2$/CH$_4$ selectivity at 10-15) and far below the desirable level for practical gas separation technology, for example, CO$_2$/CH$_4$ selectivity at 30-40 for natural gas purification. PIM-1 polymer, the dominant phase in these composite membranes, limits the baseline of performance in gas separation. Novel approaches to production of molecular sieves and nanocomposites with both high permeability and high molecular selectivity are desirable for applications of the fast-growing class of microporous polymers including PIMs, for example, in membrane separations.

Recently, we reported that linear PIM-1 polymer can be transformed to a new class of highly crosslinked, insoluble, infusible, and microporous polymer networks (TOX-PIMs) via thermo-oxidative crosslinking, demonstrating control of membrane molecular sieving properties through control of the reaction kinetics. Such processing leads to membrane materials with excellent selectivity (e.g. CO$_2$/CH$_4$ up to 70) but with an unsurprising loss in overall gas permeability (e.g. CO$_2$ permeability at 1000 Barrer). Since many microporous polymeric materials are subject to ageing that further reduces permeability, in this work, we sought to improve the control of gas permeability in thermo-oxidatively crosslinked TOX-PIM materials by incorporating nanoscale fillers. The resulting nanofiller-tuned crosslinked polymer molecular sieves show an excellent selectivity and maintain the permeability at a significant level, despite the effects of ageing.

Results

Approach

Our strategy of fabricating crosslinked nanocomposite membranes is visualized in Fig. 1e. Nanofillers are incorporated in rigid PIM polymer matrices and then exposed to controlled thermal oxidative crosslinking in the presence of trace amount of oxygen at suitable temperatures (350-450°C). The thermal-oxidation and crosslinking reactions transform linear polymer chains to highly crosslinked, infusible, and insoluble networks where the size and shape selectivity ($D_v/D_n$) of gas molecules is enhanced in the polymer phase while maintaining high solubility ($S$) and solubility selectivity ($S_v/S_n$). On the other hand, nanofillers, regardless of their internal porosity, disrupt the packing of polymer chains and introduce extra free volume and defects at the interface owing to their high external surface area, consequently enhancing the absolute value of gas diffusivity ($D$) compared to pure polymer networks. Therefore, the combination of enhanced rigidity in polymer networks and nanofillers in composite membranes offers high permeability and sufficiently high selectivity for gas separation.

Fabrication and characterisation of nanocomposite membranes

Polymer nanocomposite membranes were prepared using the solution mixing and casting method (Supplementary methods, ESI). PIM-1 polymer was synthesized following the chemistry invented by Budd and McKeown (Figure S1). Nanoparticles were dispersed as colloids in chloroform and thoroughly mixed with PIM-1 polymer dissolved in chloroform giving a colloidal mixture, following our previously reported approach. In this study, two representative types of nanofillets were used: porous ZIF-8 nanocrystals (primary size of 70-100 nm, Fig.1f) and nonporous inorganic nanoparticles (fumed silica, primary size of 12 nm). ZIF-8 was selected as a prototypical porous MOF owing to its easy synthesis in the form of nanoparticles, well-defined micropore structure, and high thermal stability. Silica was chosen as archetypal nonporous filler for polymer systems. After casting and slowly evaporating the solvent, we obtained self-standing, optically transparent and mechanically flexible polymer films (Fig. S2, ESI). These PIM nanocomposite films were further exposed to thermal-oxidative crosslinking reactions, following the same protocol reported in our previous work. In this study, the thermal-oxidative crosslinking processing was performed by heating the polymer films at 385°C under continuous vacuum (1 mbar) in a vacuum oven. Afterwards, crosslinked polymer and nanocomposite films became mainly insoluble both in traditional solvents for PIM-1, such as chloroform (see Fig. S2, ESI), tetrahydrofuran or dichloromethane, and non-solvents (acetone, N-methyl-2-pyrroldione, dimethylformamide, toluene, or alcohols). These crosslinked polymer films show certain degree of swelling in chloroform, confirming their polymeric nature. The optical transparency confirms the high degree of dispersion of small nanoparticles without formation of large particles or agglomeration, which would result in significant scattering of light and loss in transparency. Our high-magnification scanning electron microscopy (SEM) images of nanocomposite membranes, including PIM-1/ZIF-8 (Fig. 1g), PIM-1/SiO$_2$ nanocomposites (Fig. 1j) clearly show that the nanofil ers are well dispersed in the polymer, but we also observed the presence of mesopores in the polymer phase or around the nanoparticles. More SEM images are shown in Figs. S3-5 (ESI). Furthermore, SEM-EDX analyses (Figs. S6 and S7, ESI) confirmed the high dispersion of nanofillets in the crosslinked polymer matrices. Similar morphologies can be observed in other composites of PIM-1/nano-silica, PIM-1/ZIF-8, or PIM-1/cages crystals, where heterogeneous interfaces exist. The soluble fractions in most crosslinked samples are below 5 wt% and are of low molecular weight (Fig. S8, ESI) indicating that a minimal degradation of the polymer occurs during the thermo-oxidative process. SEM images confirmed that the thermal treatment leads to densification of mesopores at the interfaces between polymer and nanofillets, as shown in Fig. 2h.
and 2k, though mesopores can still be observed. Thermal-oxidative degradations of PIM-1 polymer nanocomposites were confirmed in thermogravimetric analyzer (Fig. S9, ESI), where the temperature and heating rate, concentration and flow rate of purging gas, and heat transfer could be well controlled. Therefore, the extent of thermal-oxidative crosslinking of polymer films could be carefully tailored by controlling the reaction kinetics.

We used X-ray photoemission spectroscopy (XPS) to probe the chemical bonding states in the surface of polymer films. The high-resolution XPS spectra of O1s, N1s, and C1s of PIM-1 and TOX-PIM-1 films are given in Fig. S10 (ESI). The major difference is the observation of a higher shoulder peak at binding energies of 531.68 eV in O1s spectra, and a new broad weak peak at 288.78 eV in C1s spectra, both of which are associated with the O-C=O bonds owing to presence of residual oxidized groups in the TOX-PIM-1 film. The FTIR spectra of our TOX-PIM-1 and nanocomposite films (Fig. S11 and S12, ESI) confirmed the presence of residual oxidised groups such as C=O and O-H groups, a clear evidence of oxidation. The nitrile (C≡N) groups are relatively stable and peaks associated with imine groups (C= N) are not observable. These changes of chemical bonding correspond to the thermal oxidation of PIM-1 polymer, with several possible initiation sites for chain reactions and crosslinking (Fig. S13, ESI).

It is well known that nanoparticles dispersed in the polymer matrix serve as spacers for polymer chains, so that the polymer phases in polymer-nanoparticle composites are equivalent to thin films. Here, the loose packing in composite membranes is also reflected by lower thermal conductivity (Fig. S14, ESI). We also studied the mechanical properties of nanocomposite films with stress-strain measurements (Table S1, ESI) and nanoindentation tests (Table S2, ESI). These crosslinked polymer nanocomposites show a certain degree of decay in mechanical properties, compared to TOX-PIM-1 film. Nevertheless, these nanocomposite films are still mechanically resilient and can be bended or handled for subsequent high-pressure gas permeation tests.

For nanocomposites incorporated with MOF nanofillers, XRD analysis (Fig. S15, ESI) confirmed the high crystallinity of ZIF-8 nanoparticles in the polymer matrix after annealing at moderate temperatures (<200°C). However, thermal processing at relatively higher temperature over an extended period induced partial degradation of ZIF-8, as reflected by the broadening and lower peaks in XRD patterns of nanocomposite membranes or ZIF-8 nanocrystals alone (Fig. S16, ESI). The partial oxidative degradation of ZIF-8 may be related to the removal of methyl groups. Since those partially degraded ZIF-8 nanoparticles still retain their size (Fig. S17, ESI) and serve as spacers in nanocomposites, the physical effects of such degradation on the polymer network are not significant.

Gas sorption properties

The solubility of various gases in polymer membranes were probed with a series of gas sorption measurements. In our previous work, we found that thermal-oxidatively crosslinked PIM-1 polymer films show an interesting gate-opening phenomena in nitrogen adsorption at low temperature of 77 K. Therefore, N2 adsorption at 77 K is not effective to probe the pore structure of microporous polymers, due to the kinetically-limited diffusion of large N2 molecules. In contrast, for PIM-1 thin films or open ZIF-8 framework (Fig. 2a), the sorption of nitrogen was not diffusion-limited. Polymer nanocomposite films annealed at moderate temperatures (120°C) showed enhanced N2 sorption at a low pressure stage, similar to that of PIM-1 thin films (300 nm).

Fig. 2b confirms the microporosity of crystalline ZIF-8, and the broad size distribution of micropores in PIM-1 and composites. These N2 adsorption isotherms confirm that nanofiller-spaced polymer chains are loosely-packed and behave equivalently to thin films (surface area ~800 m2 g−1). In contrast, crosslinked composite membranes show restricted sorption at low pressure (Fig. 2c), while the total quantity of adsorption at 1 bar does not significantly change. From a thermodynamic perspective, the polymer at low temperature of 77 K behaves as a ‘frozen’ state with lower segment mobility. Gas sorption isotherms of CO2, CH4 and N2 at 273 K (Fig. 2d) confirm that the gas solubility in thermal-oxidatively crosslinked nanocomposites is maintained at the same level as those unmodified samples. Pore size distributions derived from CO2 sorption isotherms at 273 K based on non-local density functional theory (NLDFT) method (Fig. S19, ESI) indicates subtle modifications of ultramicropores (<7 Å). These adsorption isotherms confirm our hypothesis that thermal-oxidative crosslinking does not seriously diminish the fractional free volume (FFV); instead, the crosslinking primarily changes the size of gates and channels connecting free volume elements in the polymer phase, which result in significant changes in kinetics of gas diffusion.
Gas transport properties

Gas transport properties of polymer and nanocomposite films were measured with H\textsubscript{2} (2.89 Å), CO\textsubscript{2} (3.3 Å), O\textsubscript{2} (3.46 Å), N\textsubscript{2} (3.64 Å), and CH\textsubscript{4} (3.82 Å) at 22°C using a time-lag apparatus described in detail elsewhere.\textsuperscript{58} Fig. 3a presents the gas permeability versus kinetic diameter of gas molecules for representative polymer films, showing their remarkable molecular sieving functions. As shown in Fig. 3a, the PIM-1 membrane is initially highly permeable, but after thermal oxidative crosslinking modification the resulting TOX-PIM-1 films maintain a relatively good permeability to small gas molecules such as H\textsubscript{2} and CO\textsubscript{2}, while blocking large molecules. Compared to pure TOX-PIM-1 membranes, the gas permeabilities of crosslinked nanocomposite membranes containing silica and ZIF-8 nanoparticles are enhanced while the ideal gas selectivity decreases, both of which correlate with the volume fraction of fillers, as shown in Fig. 3d and 3e. For example, with the loading of silica nanoparticles increases from 1wt% to 20 wt%, the CO\textsubscript{2} permeability is enhanced from ~1200 Barrer to ~2615 Barrer, with an evident loss of the CO\textsubscript{2}/CH\textsubscript{4} selectivity from ~64 to ~33. For crosslinked nanocomposites with ZIF-8 fillers increasing from 5wt% to 20 wt%, the CO\textsubscript{2} permeability further increases from 2745 Barrer to ~2615 Barrer, with an evident loss of the CO\textsubscript{2}/N\textsubscript{2} selectivity from ~88 to ~30. Therefore, the increase of permeability is attributed to enhanced diffusivity (Fig. 2d).

**Fig. 3.** Gas transport properties. (a) Gas permeability (at 295 K) versus the kinetic diameter of gas molecules. (b) Solubility (at 295 K) versus the critical temperature of gas molecules. (c) Diffusivity (at 295 K) versus the square of effective diameter of gas molecules. (d) Gas permeability, (e) ideal selectivity, (f) solubility, (g) selectivity, (h) diffusion coefficient, (i) diffusivity selectivity, as a function of the volume fraction of nanofiller in thermal-oxidatively crosslinked PIM-1 nanocomposite films. TOX-PIM-1 and nanocomposite films were oxidatively crosslinked at 385°C for 24 h under vacuum (1 mbar). Data of nonporous nanosilica (solid symbols) and porous ZIF-8 (open symbols) at different loadings are plotted together in (d-i). TOX-PIM-1/ZIF-8 nanocomposites with loading of ZIF-8 nanocrystals at 5, 10, and 20wt%, respectively. TOX-PIM-1/SiO\textsubscript{2} nanocomposites with loading of silica nanoparticles at 1, 2, 5, 10, and 20 wt%, respectively. The volume fractions are derived based on weight loadings and densities of the polymer and nanofillers. Lines in (a-c), (d), and (e) are added to guide eyes.
With the increasing loading of nanofillers regardless of their internal porosity, the solubility selectivity ($S_{\text{H}_2}/S_{\text{N}_2}$) remained relatively constant (i.e. $\text{CO}_2$/CH$_4$ about 4.0) while the diffusivity selectivity ($D_{\text{H}_2}/D_{\text{N}_2}$) decreased, for example, diffusivity selectivity of $\text{CO}_2$/CH$_4$ dropped from 19 to 7 (Fig. 3). It is well known that gas diffusivity in molecular sieves could change over multiple magnitudes depending on the shape and geometry of pore apertures (Fig. S20, ESI). Previous work has shown that nanofillers disrupt the packing of rigid polymer chains and physically change the microstructure and free volume elements of polymer phase.\textsuperscript{26} Here, the enhanced diffusion and compromised selectivity at high loading of nanofillers is due to a combination of molecular sieving in polymer phase and enhanced diffusion through interfacial defects.

The effects of nanofillers and thermal processing are more evident when we compare the gas transport properties with the Robeson’s upper bound (Fig. 4). For composite membranes containing nonporous nanofillers such as fumed silica nanoparticles, the gas permeability is enhanced while the ideal selectivity is compromised as a function of silica loadings. Such observations agree well with previous study on PIM-1/silica composites.\textsuperscript{48} In the instances of PIM-1/ZIF-8 composites, the gas permeability was also enhanced while the changes in ideal selectivity varied for different gas pairs. The permeability of $\text{H}_2$ increases significantly with the loading of ZIF-8, while the corresponding gas selectivity to large gas molecules show slight increase, e.g. $\text{H}_2$/N$_2$ from 14 to 18, H$_2$/CH$_4$ from 12 to 15. Similarly, $\text{O}_2$ permeability shows a remarkable enhancement from ~1000 to ~1500 Barrer while the $\text{O}_2$/N$_2$ selectivity increases from 4 to 5. Compared to nanocomposites containing nonporous nanosilica filler, the samples with ZIF-8 show relatively higher selectivity. The gas transport properties of these nanocomposite membranes are similar to previous studies\textsuperscript{48-50}, and are determined by a number of factors: (i) the increase of free volume in loosely packed polymer due to disruption of nanoparticles and alcohol-swelling treatment, (ii) microcavities and defects at the interface between polymer and nanoparticle, and (iii) rapid diffusion through the porous fillers, all of which could enhance the gas diffusivity and consequently permeability of the composite films.

![Graphs showing gas transport properties](image-url)

**Fig. 4.** Upper bound plots of selectivity versus permeability for important gas pairs of $\text{H}_2$/N$_2$, $\text{O}_2$/N$_2$, $\text{CO}_2$/N$_2$, and $\text{CO}_2$/CH$_4$. Robeson upper bound reported in 1991 and 2008 are plotted.\textsuperscript{25} Open squares: PIM-1 in literature; solid triangles: other PIMs in literature\textsuperscript{15-17, 20-22}. Solid squares (black): unmodified PIM-1; Solid squares (red): TOX-PIM-1 membranes. Blue open circles: PIM-1/SiO$_2$ composites; Blue solid circles: TOX-PIM-1/SiO$_2$; Red open diamonds: PIM-1/ZIF-8; Red solid diamonds: TOX-PIM-1/ZIF-8. Gas transport properties were measured from pure gas permeation at 4 bar and room temperature of 22°C. PIM-1 and PIM-1 based nanocomposite films were annealed at 120°C for 24 h. PIM-1/SiO$_2$ nanocomposites with loading of SiO$_2$ nanoparticles (primary particle size 12 nm) at 1, 2, 5, 10, 20, 30, 40 wt%, respectively. TOX-PIM-1/ZIF-8 and TOX-PIM-1/SiO$_2$ nanocomposite films were oxidatively crosslinked at 385°C for 24 h under vacuum (1 mbar). Note: individual data points for each nanocomposite loading may be cross-referenced from Fig. 3.
For our TOX-PIM-1 composite films after crosslinking, the selectivities of all gas pairs are enhanced to a very promising level, at a slight trade-off of permeability. For composites exposed to the same processing history as TOX-PIM-1 polymer films, incorporating nanofillers into crosslinked PIM-1 network enhances the permeability while the ideal selectivity of gas pairs decreases as a function of the volume fractions of nanofillers. These nanocomposites are still far more selective than non-crosslinked nanocomposites. Such significant enhancement of gas selectivity along with the combination of high permeability allows the overall gas separation performance of these nanocomposites to surpass the Robeson upper bound for a range of gas pairs (such as CO$_2$/CH$_4$, O$_2$/N$_2$, H$_2$/N$_2$ and H$_2$/CH$_4$).

Mixed gas transport properties

We also confirmed the enhanced gas permeability and excellent selectivity of thermal-oxidative crosslinked nanocomposite films in mixed gas permeation, with initially equimolar CO$_2$/CH$_4$ mixture, as shown in Fig. 5a-b. For high free volume glassy polymers, CO$_2$ and other condensable gases adsorbed in the polymer can increase the overall free volume and polymer chain segment mobility, termed as plasticization, which tends to result in lower selectivity at high CO$_2$ partial pressure. At high pressure, the competing sorption of CO$_2$ and CH$_4$ further compromised the gas selectivity. Here, these thermo-oxidatively crosslinked networks show lower gas selectivity at high pressure, which are sufficiently selective for gas separation. The fractions of CH$_4$ in the permeates through these selective films are below 5 vol.% (CO$_2$ purity above 95 vol.%) (Fig. 5c), whereas it is as high 15 vol.% for unmodified PIM-1 polymer membranes. The CO$_2$/CH$_4$ selectivity for commercial membranes (e.g. cellulose acetate) is about 20-30 below 10 bar and decreases to about 10-15 at higher pressure of 30 bar. Here,

![Fig. 5. Mixed gas transport properties and aging behaviour. (a) Gas permeability versus the fugacity of CO$_2$ in feeding gas, (b) selectivity CO$_2$/CH$_4$ versus fugacity of CO$_2$ in feeding gas mixture, and (c) permeate concentrations for separation of CO$_2$/CH$_4$ (50/50 vol.% gas mixture. (d) Upper bound plot showing the gas transport properties of polymer films during ageing for two years. Commercial polymers are included for comparison: cellulose acetate (CA); polycarbonate (PC); Matrimid® 5218 polyimide (Pi); polyetherimide (PEI); polyphenyleneoxide (PPO); polysulfone (PSF), polystyrene (PS), cited from reference.]

Fig. 5a-b
our membranes give higher selectivity at low pressure, therefore they produce similar gas purity, yet they are far more permeable than commercial membranes.

**Ageing behaviour**

Physical ageing, resulting in gas permeability reduction over time, is a critical issue that limits the industrial applications of membranes fabricated from glassy polymers. Such physical ageing is especially severe for high-free-volume polymers.\(^{51}\) PIMs membranes also suffer from the physical ageing because entangled polymer chains still tend to conform and pack tightly over time. Various approaches have been investigated, such as chemical crosslinking,\(^{62-63}\) and incorporation of additives such as porous aromatic frameworks.\(^{53-54}\) Our recent work showed that TOX-PIM-1 networks still suffer from ageing to some extent, with gas permeability rapidly decreases in 30 days but then slowly stabilized over time.\(^{55}\) In this study, the aged crosslinked nanocomposites and TOX-PIM-1 still show loss in permeability, but the gas permeability and selectivity are maintained at a remarkably high level after ageing over two years (Fig. S21, ESI), as compared with the upper bound in Fig. 5d. Interestingly, the selectivity of smaller gas molecules to large ones increased to remarkably high level. For example, the H\(_2\) permeability decreased to 1250 Barrer, while the H\(_2\)/CH\(_4\) selectivity increased from ~100 to 350 after ageing. These two-years-aged nanocomposites are still relatively more permeable and less selective compared to aged TOX-PIM-1 films. Furthermore, these aged polymer films maintain high permeability levels that are still two orders of magnitude higher than conventional polymer materials used for gas separation membranes, as presented in Fig. 5d. These data confirm that the thermal-oxidative crosslinking is an effective approach to enhance the rigidity and restrict the pore collapse in microporous polymeric networks.

**Discussion**

Although this study is focused on the crosslinked microporous PIM polymer network incorporated with nanofillers, we also investigated thermo-oxidation at intermediate temperature (i.e. 300°C), which induced oxidative degradation instead of crosslinking. Oxidative degradation also results in changes in physical and chemical properties, e.g. densification of polymer/filler interface (Fig. 1i), loss of ZIF-8 crystallinity (Figs. S15 and S16, ESI), lower molecular weight (Fig. S18, ESI), and diffusion-restricted gas sorption (Fig. S19, ESI). These changes are related to the heterogeneous structure of nanocomposites where thermal oxidative degradation is prone to happen owing to disrupted polymer thin film and enhanced O\(_2\) diffusion. The restricted diffusion as observed in gas sorption may be related to local denser molecular packing, and intermolecular interactions in the oxidized polymer matrix, e.g. hydrogen bonding between oxidized polymer chains which would enhance the local rigidity of polymer chains.\(^{55, 64}\) In addition, for those degraded PIM-1/ZIF-8 composites, the polymer-nanofiller interfaces are more complex, e.g. oxidation of polymer, degradation of ZIF-8, and interactions between them, for example, hydrogen bonding may form between oxidized groups in polymer segments (C=O) with imidazole (N-H) groups at the boundary of ZIF-8. These complex interactions induced by thermal oxidation would lead to significant changes in the pore structure and gas transport properties. This also indicates that it is possible to combine MOF nanofillers with polymers with well defined surface chemistry and interactions at the interfaces.

A further discussion is on the difference between porous MOFs fillers and inorganic nanoparticles. Owing to the high internal porosity of MOFs and low density, a very small amount of MOF filler (less than 20 wt%) could give sufficient high interfacial areas that drastically change the gas transport properties. Compared to inorganic nanoparticles, MOF fillers are relatively vulnerable to degradation owing to the organic nature, yet their porous structure and functionalities along with tuneable interfacial interactions with polymers would still make them favourable candidates for composites.

One of the important features of polymer nanocomposites is the large surface area of interfaces between nanofillers and polymers. For unmodified PIM-1 and the nanofillers used in this study, their interactions lacks strong forces such as hydrogen bonding or covalent interactions, therefore the interface is mainly dominated by physical dispersion and altered chain mobility and packing. Increasing the volume fraction of nanofillers could significantly increase the interfacial area which controls the properties of nanocomposites including gas diffusion. Still the synergistic combination of covalent crosslinking of polymer phases with enhanced molecular sieving selectivity and enhanced diffusivity at interfaces introduced by dispersed nanoparticles lead to the overall enhanced permeability and sufficiently high selectivity that do not exist for covalently crosslinked polymer alone.

In this study we probed the structure of thick polymer nanocomposite films by gas adsorption and diffusion, whereas thin films would be used practically for membrane separation applications. The gas transport properties in thin film membranes would be different, particularly the ageing behaviour. Previously we have successfully demonstrated that crosslinking is also effective for PIM-1 thin films (~100 nm) coated on inorganic substrates, research on thermally crosslinked thin film membranes is in progress and will be reported in future.

In a broad context, our work improves the fundamental understanding on molecular transport in the new class of PIMs polymers and nanocomposites. Since PIMs and other microporous polymers have been demonstrated as of great potential for applications, such as gas storage, adsorbents, sensors, catalyst supports, separators for batteries, membranes for gas separation and organic solvent nanofiltration, and hydrocarbons separation for oil refinery processes, we expect that our approach of controlled thermal processing and nanocomposites could be extended to fabrication and processing of the rapid-growing large family of microporous polymers including PIMs and functional nanocomposites for a wide range of applications.
Conclusions

In summary, we demonstrate an approach to the design of polymer molecular sieves fabricated from thermo-oxidatively crosslinked PIM-1 polymer networks incorporated with nonporous inorganic nanoparticles or microporous MOF nanocrystals. Thermal oxidative crosslinking of the PIM-1 polymer phase substantially enhances the gas selectivity of nanocomposites while the gas permeability remains at a remarkably high level. Incorporations of nanoscale fillers, either porous or nonporous, in the crosslinked PIM-1 polymer networks introduce extra channels and heterogeneous interfaces for enhanced diffusion of gas molecules while the gas solubility remains constant, consequently enhancing the overall gas permeability while maintaining sufficiently high selectivity. These highly permeable and selective nanocomposites are promising for a wide range of industrially important molecular separations in energy and environmental processes, such as removal of CO₂ from natural gas, shale gas purification, biogas purification, air separation, hydrogen separation and recovery, and other molecular-level separations. Our report, with two-year ageing studies, also indicates the importance of enhancing permeability in this high-free-volume glassy polymer through nanofiller additions. We expect that our approach and findings would have broad scientific implications on understanding the structure and molecular transport phenomena in novel microporous polymeric molecular sieves and polymer nanocomposites, for a broad range of applications beyond gas separations.

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Electronic Supplementary Information (ESI) for

Nanofiller-tuned microporous polymer molecular sieves for energy and environmental processes

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Experimental methods

Synthesis of polymer. The PIM-1 polymer was synthesised following the method invented by Budd and McKeown,1 from polycondensation reaction of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethylspirobisindane (TTSBI, Alfa Aesar) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, Matrix Scientific) in the presence of K2CO3 (Aldrich) in anhydrous dimethylformamide. After the mixture has been stirred at 60°C for about 48 h, the polymer was purified by dissolving in chloroform and re-precipitation from methanol, filtered and dried in vacuum oven at 110°C for overnight. The molecular weight of purified polymer was determined from gel permeation chromatography (GPC), giving an average molecular weight of Mn = 80,000 to 100,000 dalton and a polydispersity (PDI) of 2.0.

Preparation of films. Thick dense polymer films were prepared by solution casting of polymer solution in chloroform. Non-dissolved particles were removed by filtration through PTFE filters or by centrifugation. Polymer solutions were casted on clean glass substrate in a glove box. After the solvent has been slowly evaporated at room temperature in two days, the dry free-standing films were obtained and exposed to methanol soaking for overnight and dried in air. After, the films were dried in a vacuum oven at 120°C for 24 h.

Fabrication of nanocomposite films. Nanocomposite films were prepared from the colloidal solution of polymer/nanoparticle mixture following our previous approach.3 Two types of nanoparticles were used as fillers: (1) porous zeolitic imidazolate framework (ZIF-8) nanocrystals with diameter of 60-100 nm were synthesized by rapid reaction of zinc nitrate hexahydrate [Zn(NO3)2·6H2O] and 2-methylimidazole (C4H6N2) in methanol following Cravillon et al.,3 (2) nonporous inorganic silica nanoparticles (aggregation size of 200-300 nm) with an average primary particle size of 12 nm (99.8% trace metals basis, Sigma Aldrich). The nanoparticles were dispersed in chloroform and then mixed with PIM-1 polymer solution and thoroughly stirred for two days. After, the mixture was bubbled with pure N2 to slowly evaporate excess solvent, and then the homogeneous and viscous solutions were casted to form nanocomposite films, following the same protocol of solution casting and post treatment as pure polymer films.

Thermal treatment. The polymer films were exposed to thermal treatment under controlled atmosphere in a high-temperature vacuum oven (Heraeus, 20-400°C). The vacuum oven was modified allowing operation in
controlled vacuum or purging mode. The pressure was monitored continuously by pressure transmitters (Keller Ltd, UK). A series of experiments were performed by heating the polymer films at different temperature under continuous controlled vacuum (1 mbar). Flat polymer films were placed on the plate in the vacuum oven and heated under vacuum at 120°C for 3 h, then heated to final temperature at 10^6°C min\(^{-1}\). Then the samples were maintained at the temperature for extended time up to 24 h. Thermal-oxidative crosslinking (degradation) of polymer films were also performed in a thermogravimetric analyser (TGA) in well-controlled atmosphere. A batch of dense polymer films (~5 mg, dimension of 3x3 mm) were heated at 120°C for 1 h under continuous flow of purging gas to remove moisture and residual gases, then heated at 10^6°C min\(^{-1}\) to varied temperature (up to 385°C), then kept at 385°C for 2 h. Throughout, the purge gas was certified O\(_2\)/Argon mixture (200 ppm O\(_2\), balance argon, BOC).

**Characterization methods.** Scanning electron microscopy (SEM) was performed using a Hitachi S5500 microscope. The polymer films were fractured in liquid nitrogen and coated with a thin layer of gold (2-3 nm). Gel permeation chromatography (GPC) calibrated with polystyrene standards was used to quantify the molecular weight. The crosslinked polymer films were soaked in chloroform with weight fraction of insoluble gel quantified, while the molecular weight of soluble fraction was measured by GPC. FTIR analysis was carried out using the Bruker Tensor 27 Infrared Spectrometer, equipped with an attenuated total reflectance (ATR) cell. XRD patterns were collected with a Bruker D8 X-ray diffractometer operated at 40 mA and 40 kV using Cu Kα radiation with a step of 0.02°/sec. X-ray photoemission spectra were measured \textit{ex situ}, with an X-ray photoemission spectroscopy (ESCALAB 250Xi, Optoelectronics group, Cavendish Laboratory). The polymer films were evacuated under vacuum of 10\(^{-10}\) mbar for one hour prior to moving to the chamber for measurement. High-resolution spectra of O1s, C1s, and N1s were acquired first prior to survey spectra. The C-C peak at 284.8 eV was used as a charge correction reference. Tensile tests of polymer films were carried out at a home-made stretcher machine. The films (length of ~20 mm and width of ~2 mm) were stretched for 0.02 mm in each step with a relaxation time of 30 s, giving an apparent strain rate of ~4×10\(^{-5}\) s\(^{-1}\). The average value of Young’s modulus, the tensile strength at break and elongation with a relaxation time of 30 s, giving an apparent strain rate of ~4×10\(^{-5}\) s\(^{-1}\). Tensile tests of polymer films were performed at ambient temperature using a sharp Berkovich tip in the continuous stiffness measurement (CSM) mode on an MTS NanoIndenter® XP (MTS Corp., Eden Prairie, MN). The indenter axes were aligned normal to the membrane planes. The average values of the Young’s modulus (E) and the hardness (H) were extracted from the force-displacement \(P-h\) curves over depths of 100–1000 nm, with a series of 20 measurements at different locations.

**Gas sorption.** Low-pressure gas sorption was performed with Micromeritics ASAP 2020 with pressure up to 1 bar. Dense polymer films (~0.1 g) with thickness of ~50 μm were cut into small pieces and degassed at 120 °C under high vacuum(<10\(^{-6}\) bar) prior to the gas sorption measurement. Nitrogen adsorption-desorption isotherms were measured at 77 K. Gas sorption isotherms of N\(_2\), CO\(_2\) and CH\(_4\) were also measured at 273 K.

**Gas permeation.** Pure gas permeation was carried out using a constant volume apparatus following the time-lag method, with feed pressure at 4 bar and temperature of 22°C. Detailed information can be found in our recent study.\(^2\) Mixed gas permeation was performed in another membrane permeation apparatus using constant flow method. The membrane was exposed to certified feed gas mixtures (BOC, UK) of CO\(_2\)/CH\(_4\) (50/50 vol.%.) and CO\(_2\)/N\(_2\) (50/50 vol.%.) with pressure up to 35 bar at room temperature (22°C), with a stage cut (ratio of flow rates of permeate to feed) less than 1 %. The gas compositions were analyzed by a gas chromatograph (GC-2014, Shimadzu).

**Thermal conductivity.** The thermal conductivity of samples was measured using a hot disk thermal constants analyzer, at 25°C and atmospheric pressure. An encapsulated Ni-spiral sensor is sandwiched between two pieces of flat thick discs (thickness of 2 mm, diameter of 20 mm, solution-casted using the same solution for preparation of dense membranes). The output of power is 0.05 W and measurement time is 5 seconds. The final thermal conductivity was averaged from 4-6 measurements. Pure PIM-1 polymer, ZIF-8 pellet, and PIM-1/ZIF-8 nanocomposites were measured. ZIF-8 nanocrystals were dried at 120°C under vacuum and pelletized.
Fig. S1. Synthesis of PIM-1 polymer and ZIF-8. TTSBI: 5,5′,6,6′-tetrahydroxy-3,3′,3′,3′-tetramethylspirobisindane; TTFPN: 2,3,5,6-tetrafluoroterephthalonitrile; Solvent was dimethylformamide. ZIF-8 nanocrystals were synthesized by rapid reaction of zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O, Alfa Aesar] and 2-methylimidazole [C$_4$H$_6$N$_2$, Sigma-Aldrich] in methanol following Cravillon et al.$^3$ The detailed procedure of washing and processing can be found in our previous study.$^2$
Fig. S2. Photos of polymer films. (a) Polymer solution and mixture of polymer and nanoparticles. (b) PIM-1 and nanocomposite films after solvent being evaporated and further exposure to annealing at 120°C for 24 h. (c) Films after thermal oxidative crosslinking treatment, and (d) films became insoluble in chloroform solvent. TOX-PIM-1, TOX-PIM-1/SiO₂ and TOX-PIM-1/ZIF-8 were prepared by thermal oxidation at 385°C for 24 h under vacuum (1 mbar). Loadings of SiO₂ nanoparticles and ZIF-8 nanocrystals in composite membranes are 20 wt%.
Fig. S3. Cross-sectional SEM images. (a, c) PIM-1/ZIF-8 (20 wt%), (b) PIM-1/nanosilica (20 wt%), and (d) thermal-oxidatively crosslinked PIM-1/ZIF-8 nanocomposite films (20 wt%), without observable microscopic voids.
Fig. S4. Cross-sectional SEM images of PIM-1 polymer films incorporated with ZIF-8 nanocrystals. (a-b) 5wt%, (c-d) 10wt%, (e-f) 20wt%. (a, c, e) PIM-1/ZIF-8, (b, d, f) TOX-PIM-1/ZIF-8. The thermal oxidative crosslinking was performed by curing the polymer composite films at 385°C for 24 h under vacuum (1 mbar).
Fig. S5. SEM images of cross-sections of PIM-1/SiO₂ and TOX-PIM-1/SiO₂ nanocomposite films. (a-b) 1wt%, (c-d) 2wt%, (e-f) 5wt%, (g-h) 10 wt%, (i-j) 20wt%, (k-l) 30wt%. (a, c, e, g, i, k) PIM-1/SiO₂ annealed at 120°C for 24 h. (b, d, f, h, j, l) TOX-PIM-1/SiO₂ composites, thermal-oxidatively crosslinked at 385°C for 24 h under vacuum (1 mbar). Scale bar in all panels: 200 nm.
Fig. S6. SEM-EDX of cross-section of TOX-PIM-1/SiO2 nanocomposite films. (a) SEM, (b) EDX spectra, and element mapping of (c) carbon, (d) nitrogen, (e) oxygen, and (f) silicon.
Fig. S7. SEM-EDX of cross-section of TOX-PIM-1/ZIF-8 nanocomposite films. (a) SEM, (b) EDX spectra, and element mapping of (c) carbon, (d) nitrogen, (e) oxygen, and (f) zinc.
Fig. S8. Molecular weight distribution. The composite films after thermal oxidative crosslinking at 385°C for 24 h was dissolved in chloroform and the soluble fraction was measured in GPC. The weight percentage of soluble fraction is lower than 5 wt%.
Fig. S9. Thermal oxidative pyrolysis of polymer films. (a), PIM-1/ZIF-8 nanocomposite membranes, pure PIM-1 and ZIF-8 are included. (b) PIM-1/SiO$_2$ nanocomposite membranes. (c) Photos of membranes after thermal-oxidative degradation/crosslinking. The samples were purged at 120°C for 1 h under 200 ppm O$_2$ in argon, then heated to 385°C at 10°C/min, then maintained at 385°C for 60 min. Note that the degree of oxidation/crosslinking is lower than those films treated in vacuum oven for gas permeation tests.
Fig. S10. Probing the chemical bonding. (a-c) X-ray photoemission spectroscopy (XPS) spectra of PIM-1 and TOX-PIM-1 polymer films. (a) O1s, (b) N1s, and (c) C1s. Circles: raw spectrum. Lines: deconvoluted peaks, backgrounds, and sum. The PIM-1 film was annealed at 120°C for 24 h. The TOX-PIM-1 film was prepared by heating at 385°C under continuous vacuum (1 mbar) for 24 h. The major difference in O1s spectra is the observation of a higher shoulder peak at binding energies of 531.68 eV, associated with the O-C=O bonds. In the C1s spectra, the peak of C-O-C bonds (ether linkages) at the binding energy of 286.68 eV became relatively weaker in the TOX-PIM-1 film, in comparison to the corresponding peak in original PIM-1 polymer. Chemical bonds corresponding to aldehyde or ketone group (–C=O) in the range of binding energies of 287-288 eV may also exist, but it is difficult to deconvolute them. A new broad weak peak at 288.78 eV, corresponding to O-C=O bond (e.g. carboxylic acid), is observed in the TOX-PIM-1 film. The primary peaks at binding energy of 284.8 eV, corresponding to the overlap of C-C, C-H and C≡N bonds, do not show significant difference in both PIM-1 and TOX-PIM-1 films. As for the N1s spectra of the polymer films, the primary symmetric peak at binding energy of 399.0 eV is attributed to the aromatic nitrile (C≡N) bonds. The peak became asymmetric in the TOX-PIM-1 film, and deconvolution of the peak gives a broad weak peak at binding energy of 400.4 eV, which we can not assign accurately to specific carbon-nitrogen bonds (e.g. C=N) because NO bonds is also possible owing to the oxidation of nitrile groups.
Fig. S11. FTIR spectra of thermal-oxidatively crosslinked PIM-1 polymer composite films.
Fig. S12. FTIR spectra of PIM-1/ZIF-8 composite membranes annealed at different temperatures. ZIF-8 loading in PIM-1/ZIF-8 nanocomposites is 20 wt%.
Fig. S13. (a) Possible initial reaction sites of thermal oxidative crosslinking of PIM-1, involving hydrogen abstraction from methyl group, or cleaving of methyl group by oxygen resulting in CO$_2$ release and a radical site for crosslinking. The thermal crosslinking may also involve intermediate steps such as oxidation and further decarboxylation. Thermal-oxidation is proposed to occur at the large less-selective pores where oxygen molecules diffuse through preferentially. (b) A possible crosslinking pathway through the methyl groups on the spiro-sites. Residual oxidized groups are not shown here. It should be noted that although the oxidative crosslinking mechanism is still not clear, it would not significantly alter the novelty of using the technique to crosslink the polymer nanocomposite membranes incorporated with nanofillers to achieve enhanced diffusion.
The thermal conductivity of PIM-1 polymer is about 0.23 W m\(^{-1}\) K\(^{-1}\), which is in the normal range of conventional polymers (0.1-0.3 W m\(^{-1}\) K\(^{-1}\)). Therefore, the heat transfer properties during thermal treatment of PIM-1 membranes should be similar to that of conventional polymers. The thermal conductivity of ZIF-8 is not known in the literature. Here, ZIF-8 nanocrystals were dried at 120°C under vacuum and pelletized giving an apparent value of 0.19 W m\(^{-1}\) K\(^{-1}\) at 295 K, which is likely an underestimation of the intrinsic value due to the presence of voids between the crystals. The thermal conductivity of MOF-5 single crystal gives an intrinsic low value of ~0.3 W m\(^{-1}\) K\(^{-1}\) at 300 K\(^5\).

The Maxwell equation was used to predict the effective thermal conductivity of nanocomposite membranes \(k_{\text{eff}}\) using the as measured apparent data:

\[
k_{\text{eff}} = k_c \left[ \frac{k_d + 2k_c - 2\phi (k_c - k_d)}{k_d + 2k_c + \phi (k_c - k_d)} \right]
\]

Where \(k_c\) and \(k_d\) are the thermal conductivity of continuous phase (polymer) and dispersed phase (fillers), respectively. \(\phi\) is the volume fraction of fillers. The experimental thermal conductivity of nanocomposite membranes is lower than the prediction of Maxwell equation, which is due to the presence of voids and cavities at the interface (not considered in the model).
Fig. S15. X-ray diffraction of PIM-1/ZIF-8 membranes. (A) PIM-1/ZIF-8 nanocomposite with different loadings of ZIF-8 nanocrystals, samples annealed at 120°C for 24 h; (B), PIM-1/ZIF-8 nanocomposite with ZIF-8 loading of 20wt%, thermally treated at different temperatures under vacuum (1 mbar).
Fig. S16. XRD patterns of ZIF-8 nanoparticles exposed to heat treatment at varied temperatures under vacuum (1 mbar).
Fig. S17. SEM images of ZIF-8 nanoparticles. (a) annealed 300°C for 24 h under vacuum (1 mbar); (b) annealed at 300°C for 48 h under vacuum (1 mbar); (c) annealed at 350°C for 24 h under vacuum (1 mbar); (d) annealed at 385°C for 24 h under vacuum (1 mbar). Scale bar: 500 nm. In extreme instance, the ZIF-8 nanocrystals heated at 300°C for prolonged period of 48 h under vacuum became irregular shaped and lose crystallinity completely.
Fig. S18. Molecular weight distribution of the soluble fraction of composite films after thermal treatment at various temperatures. The control PIM-1 polymer films are also included. Nanocomposite membranes containing ZIF-8 heated at intermediate temperature of 300°C for 48 h under vacuum (1 mbar) was still completely soluble in chloroform but lower molecular weight and degradation of ZIF-8 were observed, while pure PIM-1 polymer films heated at 300°C was thermally stable.
Fig. S19. (a) N₂ adsorption-desorption isotherms of PIM-1 polymer films at 77 K. Squares: PIM-1 thin film (300 nm) dried at 120°C under vacuum; Blue circles: thick dense PIM-1 films (~50 μm) annealed at 120°C under vacuum; Uptriangles: thick dense PIM-1 film annealed at 300°C for 48 h under vacuum. Downtriangles: thick dense PIM-1 film annealed at 385°C for 24 h under vacuum. (b) PIM-1/ZIF-8 nanocomposite films. ZIF-8 loading at 20 wt%. Squares: annealed at 120°C for 24 h; Uptriangles: annealed at 300°C for 48 h under vacuum. Circles: crosslinked at 385°C for 24 h under vacuum. (c) CO₂ sorption of PIM-1/ZIF-8 nanocomposites treated at various temperatures, and (d) derived pore size distribution. All samples were degassed at 120°C under high vacuum prior to gas sorption measurements.
Fig. S20. Influence of pore size on the diffusion coefficient of gas molecules in porous materials. Redrawn from reference.\textsuperscript{6}
Fig. S21. Gas transport properties of (a-b) TOX-PIM-1 and (c-d) TOX-PIM-1/ZIF-8 nanocomposites (ZIF-8 loading at 5wt%) upon physical aging over two years. These membranes were exposed to vacuum between gas permeation tests. The samples were prepared by thermal oxidative crosslinking at 385°C for 24 h under vacuum (1 mbar).
Table S1. Mechanical properties. The data were derived from stress-strain profiles of PIM-1, thermal oxidatively crosslinked PIM-1 and composite films.

| Samples                  | Tensile strength at break (MPa) | Elongation Strain at break (%) | Young’s modulus (GPa) |
|--------------------------|---------------------------------|--------------------------------|-----------------------|
| PIM-1                    | 47.5±2.3                        | 14.3                           | 1.43±0.15             |
| TOX-PIM-1/385°C 1 mbar 24 h | 54.8±2.7                        | 4.4                            | 1.72±0.05             |
| TOX-PIM-1/SiO₂ 1wt% 385°C 1 mbar 24 h | 38                             | 2.4                            | 1.90                   |
| TOX-PIM-1/SiO₂ 2wt% 385°C 1 mbar 24 h | 35                             | 2.3                            | 1.60                   |
| TOX-PIM-1/SiO₂ 5wt% 385°C 1 mbar 24 h | 21                             | 1.4                            | 1.55                   |
| TOX-PIM-1/ZIF 8 10wt% 385°C 1 mbar 24 h | 15                             | 1.0                            | 1.50                   |
| TOX-PIM-1/ZIF 8 5wt% 385°C 1 mbar 24 h | 23                             | 1.6                            | 1.51                   |
| TOX-PIM-1/ZIF 8 10wt% 385°C 1 mbar 24 h | 19                             | 1.4                            | 1.39                   |
| TOX-PIM-1/ZIF 8 20wt% 385°C 1 mbar 24 h | 16                             | 1.3                            | 1.33                   |

Table S2. Young’s modulus and Hardness derived from nanoindentation measurement.

| Sample                  | Young’s modulus E (GPa) | Hardness H (MPa) |
|--------------------------|-------------------------|------------------|
| PIM-1 120°C 24 h         | 1.876±0.029             | 149±4.0          |
| TOX-PIM-1 385°C 1 mbar 24 h | 1.885±0.039             | 188±3.0          |
| PIM-1/ZIF-8 20wt% 120°C 24 h | 1.954±0.075             | 159±13.0         |
| TOX-PIM-1/ZIF-8 20wt% 385°C 1 mbar 24 h | 1.732±0.027             | 158±4.0          |

Table S3. Representative gas transport properties of thermally crosslinked PIM polymer nanocomposite membranes. Crosslinked membranes were thermally oxidized at 385°C under vacuum (1 mbar) for 24 h.

| Sample                  | Volume fraction | Permeability (Barrer) | Selectivity |
|--------------------------|-----------------|-----------------------|-------------|
|                          | Volume fraction | H₂        | CO₂  | O₂  | N₂  | CH₄ | CO₂/N₂ | CO₂/CH₄ | O₂/N₂ | H₂/N₂ | H₂/CH₄ |
| PIM-1                    | 0               | 3361      | 5040 | 1020 | 244 | 288 | 20.6   | 17.5   | 4.2   | 13.8  | 11.7   |
| PIM-1/ZIF-8 5 wt%        | 0.057           | 3778      | 5223 | 1179 | 252 | 309 | 20.7   | 16.9   | 4.7   | 15.0  | 12.2   |
| PIM-1/ZIF-8 10 wt%       | 0.113           | 5005      | 5928 | 1492 | 282 | 351 | 21.0   | 16.9   | 5.3   | 17.7  | 14.2   |
| PIM-1/ZIF-8 20 wt%       | 0.223           | 4977      | 6342 | 1521 | 293 | 426 | 21.7   | 14.9   | 5.2   | 17.0  | 11.7   |
| PIM-1/ZIF-8 30 wt%       | 0.330           | 5456      | 6424 | 1452 | 304 | 370 | 21.1   | 17.4   | 4.8   | 17.9  | 14.8   |
| PIM-1/SiO₂ 1 wt%         | 0.005           | 4068      | 5381 | 1116 | 279 | 335 | 19.3   | 16.1   | 4.0   | 14.6  | 12.1   |
| PIM-1/SiO₂ 2 wt%         | 0.010           | 4175      | 5756 | 1079 | 282 | 346 | 20.4   | 16.6   | 3.8   | 14.8  | 12.1   |
| PIM-1/SiO₂ 5 wt%         | 0.025           | 5385      | 6061 | 1130 | 330 | 427 | 18.3   | 14.2   | 3.4   | 16.3  | 12.6   |
| PIM-1/SiO₂ 10 wt%        | 0.051           | 5614      | 6193 | 1229 | 368 | 447 | 16.8   | 13.9   | 3.3   | 15.3  | 12.6   |
| PIM-1/SiO₂ 20 wt%        | 0.108           | 5715      | 7227 | 1509 | 453 | 628 | 16.0   | 11.5   | 3.3   | 12.6  | 9.1    |
| PIM-1/SiO₂ 30 wt%        | 0.171           | 5500      | 8351 | 1678 | 536 | 754 | 15.6   | 11.1   | 3.1   | 10.3  | 7.3    |
| PIM-1/SiO₂ 40 wt%        | 0.243           | 5544      | 8505 | 1734 | 581 | 830 | 14.6   | 10.2   | 2.9   | 9.5   | 6.7    |
| TOX-PIM-1                | 0               | 1820      | 1104 | 245  | 30  | 16  | 36.6   | 69.2   | 8.1   | 60.4  | 114.1  |
| TOX-PIM-1/SiO₂ 1 wt%     | 0.005           | 1935      | 1198 | 266  | 36  | 19  | 33.0   | 63.5   | 7.3   | 53.4  | 102.6  |
| TOX-PIM-1/SiO₂ 2 wt%     | 0.010           | 2069      | 1552 | 362  | 49  | 25  | 31.7   | 62.4   | 7.4   | 42.2  | 83.1   |
| TOX-PIM-1/SiO₂ 5 wt%     | 0.025           | 2405      | 1824 | 420  | 61  | 33  | 29.8   | 55.0   | 6.9   | 39.3  | 72.6   |
| TOX-PIM-1/SiO₂ 10 wt%    | 0.051           | 2551      | 2352 | 492  | 79  | 56  | 29.7   | 42.3   | 6.2   | 32.2  | 45.9   |
| TOX-PIM-1/SiO₂ 20 wt%    | 0.108           | 2816      | 2615 | 603  | 101 | 80  | 26.0   | 32.5   | 6.0   | 28.0  | 35.0   |
| TOX-PIM-1/ZIF-8 5 wt%    | 0.057           | 3086      | 2745 | 608  | 100 | 73  | 27.5   | 37.6   | 6.1   | 31.0  | 42.2   |
| TOX-PIM-1/ZIF-8 10 wt%   | 0.113           | 3230      | 3199 | 682  | 118 | 104 | 27.1   | 30.7   | 5.8   | 27.4  | 31.0   |
| TOX-PIM-1/ZIF-8 20 wt%   | 0.223           | 3465      | 3944 | 800  | 139 | 147 | 28.3   | 26.8   | 5.7   | 24.9  | 23.6   |

*Volume fraction of the dispersed in the composites is defined as: \( \phi_d = (m_d/\rho_d)/(m_s/\rho_s + m_c/\rho_c) \), where \( m \) and \( \rho \) refer to the mass and density of the continuous phase (polymer) and dispersed phase (filler).
### Table S4. Summary of gas permeability, diffusion coefficient, solubility coefficient, diffusion selectivity and solubility selectivity for thermally crosslinked PIM-1 and nanocomposite membranes.

| Samples | P (Barrer) | D (10^{-8} cm^2 s^{-1}) | S (10^{-2} cm^3 cm^{-3} cmHg^{-1}) | Diffusivity selectivity | Solubility selectivity |
|---------|------------|--------------------------|-----------------------------------|------------------------|------------------------|
|         | CO₂ | N₂ | CH₄ | CO₂ | N₂ | CH₄ | CO₂/N₂ | CO₂/CH₄ | CO₂/N₂ | CO₂/CH₄ |
| TOX-PIM-1 | 1104 | 30 | 16 | 23.6 | 9.2 | 1.2 | 49.0 | 3.8 | 12.1 | 2.6 | 19.2 | 13.0 | 4.1 |
| TOX-PIM-1/SiO₂ 1 wt% | 1198 | 36 | 19 | 24.2 | 10.7 | 1.5 | 49.4 | 3.4 | 12.2 | 2.3 | 15.7 | 14.6 | 4.0 |
| TOX-PIM-1/SiO₂ 2 wt% | 1552 | 49 | 25 | 30.3 | 11.4 | 2.2 | 51.2 | 4.3 | 11.2 | 2.7 | 13.6 | 11.9 | 4.6 |
| TOX-PIM-1/SiO₂ 5 wt% | 1824 | 61 | 33 | 39.2 | 14.7 | 2.9 | 46.5 | 4.2 | 11.3 | 2.7 | 13.3 | 11.2 | 4.1 |
| TOX-PIM-1/SiO₂ 10 wt% | 2352 | 79 | 56 | 47.6 | 21.8 | 4.1 | 49.4 | 3.6 | 13.4 | 2.2 | 11.5 | 13.6 | 3.7 |
| TOX-PIM-1/SiO₂ 20 wt% | 2615 | 101 | 80 | 53.3 | 26.7 | 6.7 | 49.0 | 3.8 | 12.1 | 2.0 | 8.0 | 13.0 | 4.1 |
| TOX-PIM-1/ZIF-8 5 wt% | 2745 | 100 | 73 | 54.5 | 29.3 | 5.9 | 50.3 | 3.4 | 12.3 | 1.9 | 9.2 | 14.8 | 4.1 |
| TOX-PIM-1/ZIF-8 10 wt% | 3199 | 118 | 104 | 63.2 | 37.5 | 7.5 | 50.6 | 3.1 | 13.9 | 1.7 | 8.4 | 16.1 | 3.6 |
| TOX-PIM-1/ZIF-8 20 wt% | 3944 | 139 | 147 | 83.3 | 43.9 | 12.0 | 47.3 | 3.2 | 12.2 | 1.9 | 6.9 | 14.9 | 3.9 |

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