Post-synthetic Ti Exchanged UiO-66 Metal-Organic Frameworks that Deliver Exceptional Gas Permeability in Mixed Matrix Membranes

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Gas separation membranes are one of the lowest energy technologies available for the separation of carbon dioxide from flue gas. Key to handling the immense scale of this separation is maximised membrane permeability at sufficient selectivity for CO2 over N2. For the first time it is revealed that metals can be post-synthetically exchanged in MOFs to drastically enhance gas transport performance in membranes. Ti-exchanged UiO-66 MOFs have been found to triple the gas permeability without a loss in selectivity due to several effects that include increased affinity for CO2 and stronger interactions between the polymer matrix and the Ti-MOFs. As a result, it is also shown that MOFs optimized in previous works for batch-wise adsorption applications can be applied to membranes, which have lower demands on material quantities. These membranes exhibit exceptional CO2 permeability enhancement of as much as 153% when compared to the non-exchanged UiO-66 mixed-matrix controls, which places them well above the Robeson upper bound at just a 5 wt.% loading. The fact that maximum permeability enhancement occurs at such low loadings, significantly less than the optimum for other MMMs, is a major advantage in large-scale application due to the more attainable quantities of MOF needed.

Combustion of coal accounts for 41% of electricity generation globally, contributing 8270 million tonnes to annual anthropogenic carbon dioxide emissions1,2. As a consequence; technologies that can isolate carbon dioxide from the exhaust stream are relevant (known as post-combustion capture, PCC). One of the key challenges for prospective carbon capture technologies is the energy required to operate the process. Batch-wise technologies that rely on temperature, pressure or vacuum swing processes to regenerate materials employed for carbon dioxide capture can require significant proportions of the power plant’s produced energy for this operation1. As a consequence, continuous processes that offer lower energy demands are attractive for further investigation.

Membranes are prospective alternatives that operate through the transport of gases at varying rates through the thin selective membrane layer. In this case, carbon dioxide can pass through the membrane layer significantly faster than nitrogen, the predominant gas in the flue stream. Assessments for the required operating performances of gas separation membranes in PCC setting are that a membrane must have a selectivity for CO2 over N2 of at least 20 to sufficiently concentrate the product for sequestration or utilisation, and, having attained this, operate with maximum CO2 permeability due to the diminishing savings in energy costs at higher selectivities, and the sheer scale of the task at hand3–5. The most readily processible membranes are polymer-based systems, yet, as originally described by Robeson and explained by Freeman6–8, there is a trade-off between these two target attributes of permeability and selectivity, largely as a result of the limited control attainable between the number and size of pores within polymer films.

Within this set of materials, polymers of intrinsic microporosity (PIMs) are attractive candidates9–11. Since their inception in the early 2000s, PIMs have found applications ranging from separating gases and liquids12 to polymer resists13. Consisting of contorted spirobisindane and dioxane units, PIM-1 exhibits both high selectivity and permeability for the CO2/N2 gas pair11,14. Additionally, the nitrile groups in PIM-1 can be functionalised to tailor membrane properties to suit application requirements11,15–18.
Recently, we showed that the porous additive PAF-1 can be used to intercalate with the side chains of the polymer, stopping physical aging within the membrane\(^9\). A promising approach for improving polymeric membranes is to add filler particles, forming mixed matrix membranes (MMMs)\(^{20–22}\). Inorganic fillers such as SiO\(_2\)\(^{23–25}\) or TiO\(_2\)\(^{26–29}\) have been widely explored, and depending on particle agglomeration, can drastically enhance gas transport and separation properties of MMMs. However, owing to the additional gas transport pathways through the pores of porous materials, the incorporation of porous materials into polymer matrices can improve gas transport and separation properties better than their non-porous analogues (Figure 1)\(^{30–32}\). Unfortunately, high particle content is usually required to generate optimal separation enhancement, which impacts application costs and can compromise mechanical durability of the composite.

Metal Organic Frameworks (MOFs) are metal atoms or clusters connected periodically to one another by organic linker units. Their regular pores, lined with under-coordinated, polarising metal atoms, are ripe for selective gas transport. Additionally, record breaking internal surface areas, which are in well-interconnected porous architectures, offer rapid gas transport pathways; and are known to improve the gas permeability and selectivity of polymer membranes. Sivaniah and co-workers reported that the inclusion of 30 wt.% ZIF-8 nanoparticles into Matrimid\(^8\), a commercially available polyimide, can enhance gas permeability with negligible losses in selectivity through the increase in free volume of polymer with ZIF-8 loading and the free diffusion of gas through the cages of ZIF-8\(^33\). Musselman and co-workers incorporated 50 wt.% ZIF-8 in Matrimid\(^8\), and improved the ideal gas selectivities of such nanocomposites, at the expense of gas permeabilities; demonstrating a transition from a polymer-driven to a MOF controlled gas transport process\(^8\). Yang and Chung demonstrated that ZIF-8/polybenzimidazole nanocomposites exhibited remarkably high mixed gas selectivities at high temperatures, and the presence of CO and water did not impact H\(_2\)/CO\(_2\) separation\(^9\). These recent works show that MOF-loaded MMMs improve gas permeabilities via the provision of open gas transport channels, formation of additional free volume elements at the interface between polymer and nanoparticle, and through high loadings of MOF that provide a direct pathway for gas transport.

A possible route to further improve the gas transport properties of MOF-loaded MMMs is to utilise enhanced gas uptakes of MOFs with functionalised linkers\(^8\). We have expanded this investigation to also examine the effect of metal exchange\(^8\). Recently, it was reported that one of the few water and high temperature stable MOFs, the Zr-based UiO-66, can be post-synthetically exchanged with titanium\(^9\). In our previous work, the smaller Ti atom was found to shrink the pores within the framework, which, in concert with the improved size-to-charge ratio of Ti\(^{IV}\) for polarising CO\(_2\), delivered drastically enhanced adsorption capacity\(^9\). Additionally, the exchanged “Ti\(_x\)UiO-66”, where ‘x’ is the metal exchange incubation period (days), maintains UiO-66’s very high thermal and chemical stability\(^9\) as well as its structural stability through water adsorption/desorption cycles\(^9\).

Described herein is the systematic post-synthetic transmetallation of Ti\(^{IV}\) ions into the Zr UiO-66 framework to deliver remarkable increases in separation performance, placing the resulting mixed matrix membranes well above the Robeson upper bound\(^7\). The rate of membrane aging was also reduced. Preparation and characterisation of the films as a function of MOF loading and Ti-exchange period allowed for the factors behind the exceptional performance to be deduced.

**Results**

As hypothesised, addition of the Ti\(_x\)UiO-66 into PIM-1 resulted in a drastic increase in CO\(_2\) permeability, with the greatest measured result (Ti\(_5\), 5 wt.%, 13500 Barrer) 274% higher than that of the pristine PIM-1 membrane (denoted as 0 wt.% loading in Figure 2). This permeability is also 153% higher than the corresponding native UiO-66 mixed matrix membrane (5340 Barrer), confirming the titanium exchange further improved separation performance. Membranes containing Ti exchanged UiO-66 exhibit a rapid increase in permeability at low loadings, which offers a competitive advantage over other reported MMMs\(^{23–25,42,43}\) that exhibited maximum permeability when loadings approached 50 wt.%. The large increase in permeability effect can be isolated as being particular to Ti-substitution. Ideal selectivities were unaffected by the level of titanium exchange and also MOF loading levels (Table S3\(^{24}\)). The higher gas adsorption and stronger CO\(_2\) affinity in Ti-exchanged MOFs (Table 1) did not influence the level of selective gas transport.

The polymer-MOF interactions were interrogated with DSC analysis (Figure 3), which showed that Ti\(_x\)UiO-66 membranes had higher peak decomposition temperatures than the similarly loaded native UiO-66 membranes (Figures S17, S18\(^\dagger\)). The increased decomposition temperature of Ti\(_x\)UiO-66 membrane suggests that the Ti exchange of UiO-66 affects the MOF’s exterior surface, resulting in a stronger polymer-MOF interaction and increased thermal stability.

![Figure 1](image-url) **Figure 1** | Ti-exchange of UiO-66 MOF increases the interaction with PIM-1 polymer, leading to a drastic increase in CO\(_2\) permeability in comparison to a UiO-66 PIM-1 membrane.

![Figure 2](image-url) **Figure 2** | CO\(_2\) Permeability of PIM-1 Ti\(_x\)UiO-66 mixed matrix membranes. Permeability measurement recorded with a pressure differential of 2 Bar, at 298 K and within +/- 5% deviation. (esi-10\(^\dagger\)). Lines are drawn to guide the eye.
This increased polymer-MOF interaction was confirmed by viscosity measurements of the 5 wt.% membrane casting solutions (Figure 4) that showed solution viscosity decreases with increasing Ti exchange.

Changes in viscosity can be used to identify the various interactions in composite materials. There are three main interactions that can lead to a lowering of viscosity:

(a) reduction of polymer entanglement by surface absorption to the additive
(b) increase in free volume
(c) confinement with the additive’s pores

The significant drop in viscosity with the addition of UiO-66 may be assigned to the increased free volume as confirmed by density measurements (Figure S20). Further drops for Ti5 and Ti15 samples must come from (a) surface absorption as their free volume was actually lower (Figure S20), and (c) confinement identical in all MOF additions due to their isomorphism. As a consequence this directly confirms that Ti-transmetallation delivers a stronger MOF-polymer interaction. Interaction of PIM-1’s nucleophillic groups occurs with exposed TiIV/ZrIV metal sites, which increases with the loss of crystallinity caused by Ti substitution (Figure S12).

SEM images of PIM-1 Ti5UiO-66 membranes (Figure 5) exhibit surface topologies similar to previously reported mixed matrix membranes, characteristic of particle interaction at the polymer interface. Images also reveal agglomeration of Ti5 UiO-66 MOF at higher loadings, which increases effective particle size.

The different CO2 permeability, solubility and diffusivity values in Table 2 can be attributed to the different PIM-1 synthesis protocol adopted in this work. The depressed solubility coefficients in MOF-loaded membranes increase with Ti-incorporation. As predicted by Cohen and Turnbull’s Free Volume theory, the permeability enhancement was largely generated by the increase in diffusivity coefficient (Table 2, right).

Notably, the titanium exchange in the Ti5UiO-66 (5 wt.%) membrane significantly improved both the solubility (+23%) and diffusivity coefficients (+106%) over the corresponding native UiO-66 membrane.

As depicted in Figure 6, the permeability trends measured across the series of mixed matrix membranes are best described as the result of an additive effect between several competing factors. Permeability enhancements are assigned to the effects of increased CO2 sorption and diffusion in MOFs (a–b, at low loadings) and higher free volume within PIM-1 (c). Losses in permeability relate to lower CO2 MOF diffusion and PIM-1 fractional free volume (b, high loadings) and also the lower MOF crystallinity in Ti-substituted MOFs (d). Permeability enhancement factors a, b and c are accentuated by the Ti MOF substitution compared to the Zr MOF counterparts, accounting for the drastic increase in CO2 permeability with Ti-substitution in MOFs. The lower CO2 permeability in high loading Ti-substituted MOF membranes compared to PIM-1 controls is related to the lower crystallinity resulting from Ti-substitution in the Zr-MOF UiO-66.

CO2 sorption (a) was found to increase as shown in Table 1, dropping away with increased Ti loading. This aligns with values previously reported. CO2 diffusivity (b) was by far the strongest effect, accounting for the beneficial enhancement of CO2 permeability. Diffusivity increased by a factor of four in Ti substituted MOF samples and by a factor of 2 in the Zr analogues. Free volume in PIM-1 (c) is affected by the well known increase in polymer free volume (Figure S9) upon nanoparticle addition, which is eventually decreased with strong polymer-MOF interactions occurring. These interactions are witnessed in the stabilisation of membranes during DSC (Figure S18) when Ti is introduced, the reduction of viscosity of PIM-1 Ti5 UiO-66 solutions with increasing Ti (Figure S26), and the lower level of MOF agglomeration in SEM (Figures S21–S25). The

Table 1 | Brunauer-Emmett-Teller (BET) and Langmuir surface area

| Ti5UiO-66 | BET surface Areaa, m2/g | Langmuir surface areaa, m2/g | CO2 adsorptionb, mmol/g (STP) |
|-----------|--------------------------|-----------------------------|-------------------------------|
| TiO-66    | 1263                     | 1471                        | 2.53                          |
| Ti5UiO-66 | 1263                     | 1482                        | 2.83                          |
| Ti10UiO-66| 1359                     | 1535                        | 3.06                          |
| Ti15UiO-66| 1328                     | 1487                        | 3.07                          |
| Ti10UiO-66| 1249                     | 1448                        | 2.83                          |

*a calculations based on N2 isotherm data measured at 77 K.
*b maximum CO2 adsorption measured at 273 K and 1.2 Bar.

Figure 3 | DSC analysis of the PIM-1 Ti5UiO-66 membranes. Arrow highlights the trend in peak decomposition.

Figure 4 | Viscosity of Aged PIM-1 Ti5UiO-66 (5 wt.%) membrane casting solutions (Table S6). Arrow highlights trend in viscosity. Line drawn to guide the eye.
enhanced exposure and reactivity of Ti-exchanged SBUs is a likely
ccontributor to this strengthened polymer-MOF interaction. MOF crystallinity clearly diminishes with the level of Ti substitution,
as seen in broadening PXRD peaks (Figure S12). This is in
agreement with our previous findings and leads to fewer ordered
gas transport pathways through the MOF.

Taken together, the factors measured within this present study
reveal that the mechanism responsible for the remarkable gas trans-
port properties recorded is an additive combination of several struc-
tural and chemical changes that are as a result of both the loading of
MOFs into the PIM-1 polymer membrane, and the titanium substi-
tution within the MOF additives.

Another factor affecting the industrial application of membranes
is their useable lifetime. Inclusion of Ti₅UiO-66 (5 wt.%) nanopar-
ticles resulted in a significant increase in gas permeability, and also
decreased the rate of relative permeability loss in the PIM-1 mem-
branes over time (Figure 7). Notably, CO₂/N₂ ideal selectivity increased (α = 20 to 24) in both membranes over the course of
membrane aging. Loading of 5 wt.% Ti₅UiO-66 also improved the
PIM-1’s mechanical properties under 2 Bar of gas pressure, not
exhibiting any instance of mechanical failure under testing condi-
tions for 63 days, compared to pristine PIM-1’s consistent membrane
fracture after 24 days of aging. This indicated improved mechanical
stability in the MOF composite membranes.

Discussion
This work reports the study of the gas permeation performance
of mixed matrix membranes developed specifically for improving CO₂/
N₂ separation performance for the application of carbon capture and
sequestration. The hypothesised amalgamation of PIM-1, a polymer
already near the Robeson upper bound, and a previously demon-
strated MOF of high CO₂ affinity, Ti-exchanged UiO-66, generated a
significant increase in membrane CO₂ permeability (13500 Barrer,
+274%). This improvement was achieved without selectivity loss,
exceeding the CO₂/N₂ Robeson Upper bound (Figure 8) and the
separation performance of a number of other high performance
mixed matrix membranes. This study highlights the potential advan-
tages of matching materials and tuning the surface of nanoparticles
in polymeric mixed matrix membranes. The strong interaction
between Ti₅UiO-66’s exposed metal centres to PIM-1 polymer has
significant effects on the formation of interfacial free volume, gen-
erating a significant increase in permeability at the optimal loading of
5 wt.%, a loading significantly lower than peak performance of other
MMM’s (40–60%). This study also provides a validation for research

Table 2 | Permeability (P), Solubility (S) and Diffusivity (D) Coefficients

| Membrane       | P (CO₂) (Barrer) | S (1 atm, 298 K) cm⁻³(STP)/cm²atm | D x10⁶ cm²s⁻¹ |
|----------------|-----------------|----------------------------------|--------------|
| PIM-1          | 3620            | 41.8                             | 0.07         |
| PIM-1 UiO-66 5 wt.% | 5340            | 26.2                             | 0.16         |
| PIM-1 Ti₅UiO-66 5 wt.% | 13540          | 32.3                             | 0.32         |

Diffusivity coefficients were calculated from Permeability data and Solubility coefficients (1 atm). Dual mode sorption parameters were derived from CO₂ sorption measurements (Refer ESI15).
involving transmetallation of MOFs as a route to further improve mixed matrix membrane performance.

**Methods**

**Synthesis of PIM-1.** The synthesis of PIM-1 polymer is based on a rapid polycondensation reaction of 2,3,5,6-Tetrafluoroterephthalonitrile (TFTPN) (12.5 mmol) and 4,4,6,6-tetramethyl-1,1-spirobisindane (TTSBI) (12.7 mmol) in the presence of excess anhydrous K$_2$CO$_3$ (38.8 mmol), however a previously unreported solvent mixture of DMAc (25 mL) and CS$_2$ (12.5 mL) was used$^{30,31,32}$. The reaction mixture (under inert atmosphere) was refluxed using a dean stark trap at 165 °C for an hour. The reaction solution was decanted into stirred MeOH to precipitate the polymer. The product was then dissolved in CHCl$_3$ and recrystallized from MeOH before being dried by vacuum filtration.

**Synthesis of UiO-66.** UiO-66 was prepared as previously reported$^{39,54}$. Equimolar quantities (43 mmol) of zirconium tetrachloride and 1,4-benzenedicarboxylic acid were reacted in the presence of a large excess (684 mmol) of benzoic acid in a DMF:H$_2$O (1650:83 mL) solvent. The resulting product was washed sequentially with DMF and MeOH before being dried under vacuum at 100 °C.

**Post synthetic exchange of UiO-66 with Ti$^{IV}$.** Titanium exchange of the UiO-66’s zirconium metal centres followed the recently reported method using TiCl$_4$(THF)$_2$ in DMF at 85 °C. The reaction solution was stirred for an hour. The reaction mixture was filtered and the filtrate was decanted into stirred MeOH to precipitate the polymer. The product was then dissolved in CHCl$_3$ and recrystallized from MeOH before being dried by vacuum filtration.

**Membrane Preparation.** Membranes were cast at ambient conditions from ~0.2 g/ ml CHCl$_3$ solutions in 75 mm diameter PTFE dishes, covered in perforated aluminium foil, and vacuum dried (80 °C) overnight before use. Single gas (N$_2$, H$_2$, CH$_4$, and CO$_2$) permeation measurements were undertaken in duplicate on the day following casting to maintain a consistent processing history.$^{11}$

**Characterisation.** NMR spectra ($^1$H and $^13$C) of the PIM-1 used in this study were recorded using a Bruker Av500 and Bruker Av400X, respectively. Gel Permeation Chromatography (GPC) of the PIM-1 Polymer was completed in THF (30 °C flow rate: 1 mL min$^{-1}$) using Waters Alliance e2695 liquid chromatograph equipped with a Waters 2414 differential refractometer. Powder X-Ray Diffraction (PXRD) spectra were collected on a Bruker D8 Advance X-ray Diffractometer, using Cu Kα radiation (40 kV, 40 mA) equipped with a LynxEye silicon strip detector. Samples were scanned over the 2$h$ range 5 to 85° with a step size of 0.02° 2$h$ and a count time of 0.4 seconds per step. Adsorption isotherms of the prepared Titanium exchanged and native UiO-66 were measured using an ASAP 2420 with carbon dioxide (273 K, 298 K) and nitrogen (77 K, 273 K) adsorbates. MOF samples were activated at 120 °C under vacuum overnight prior to analysis. Langmuir and BET surface areas were calculated by curve fitting to equation 1, as reported. Viscosity measurements were made using a Schott AV350 Viscometer (standard ASTM D445) using a 52610/I Scanning Calorimeter. Samples were encapsulated in aluminium pans and heated from 25 °C to 500 °C at 10°C/min. Pycnometry measurements were made using an AccuPyc Pycnometer (He) to determine the relative density, and by extension, free volume present in the prepared Ti$_x$UiO-66 PIM-1 membranes. A Philips XL30 Field Emission Scanning Electron Microscope (FESEM) with an accelerating voltage of 5 kV was used for imaging the cross sectional surface of membrane samples (Figure S21-25). Cross-section surfaces were prepared by fracturing membranes in liquid nitrogen and mounting to SEM stubs using carbon tape, before sputter coating with gold. Membrane solubility coefficients were calculated from High-pressure Sorption (Setaram PCT Pro) measurements. Dual-mode sorption parameters were calculated by curve fitting to equation 1, as reported.$^{10}$ Viscoelasticity measurements were made using a SCHOTT AV350 Viscometer (standard ASTM D445) using a 52610/I U-tube calibrated with a de-ionised water standard at 20°C.
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