

Solution processable metal-organic frameworks for mixed matrix membranes using porous liquids

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Abstract

The combination of well-defined molecular cavities and chemical functionality makes crystalline porous solids attractive for a great number of technological applications, from catalysis to gas separation. However, in contrast to other widely applied synthetic solids such as polymers, the lack of processability of crystalline extended solids hampers their application. In this work, we demonstrate that highly crystalline porous solids, metal-organic frameworks, can be made solution processable via outer surface functionalization using N-heterocyclic carbene ligands. Selective outer surface functionalization of relatively large nanoparticles (250 nm) of the well-known metal organic framework ZIF-67 allows for the stabilization of processable dispersions exhibiting permanent porosity. The resulting type III porous liquids can either be directly deployed as liquid adsorbents or be co-processed with state-of-the-art polymers to yield highly loaded mixed matrix membranes with excellent mechanical properties and an outstanding performance in the challenging separation of propylene from propane. We anticipate that this approach can be extended to other metal-organic frameworks, and for other applications.

Solution processability is a feature required by many industrial processes, from electronics to the manufacture of membranes. This property has been key to the success of widely applied materials, such as polymers. However, extended solid networks, *i.e.* Metal Organic Frameworks (MOFs), are in general not dispersible and therefore not solution processable.

MOFs are crystalline coordination polymers formed by combining metal nodes or polynuclear clusters and multidentate organic linkers. As a result, pores and cavities with sizes in the range of many molecules of interest are formed with potential applications from catalysis to gas separation.^{1,2} MOF based membranes, either as thin films on porous supports or as Mixed Matrix Membranes (MMMs), are believed to be the future working horse of energy efficient, safe, and reliable separation technologies.³⁻⁶ MMMs, those formed by embedded selective sorbents (MOFs in this case) in a continuous polymer layer present a proper trade-off between the selective host-molecule interactions of MOFs and the mechano-chemical stability and easy processing of polymers. However, agglomeration of the filler during membrane preparation compromises the mechanical properties of the composite and hampers the attainment and application of highly loaded (and therefore highly selective) membranes.⁷

In this spirit, the development of synthetic protocols that would facilitate MOF processability in the liquid phase are highly desired. To achieve this objective, strategies that would allow stable dispersions of MOFs in different solvents are required.⁸ In such stable dispersions,^{9,10} the MOF has to preserve most of its inner porosity empty upon solvation so that the density of the solid phase does not become higher than that of the liquid phase. At the same time, particle-particle interactions have to be prevented to avoid agglomeration. Here, we report a successful approach towards the stabilization of MOF dispersions in non-polar solvents. Outer surface modification of ZIF-67 nanoparticles using two different N-heterocyclic carbenes (NHCs) (1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene (IMes) and 1,3-bis(2,4,6-diisopropylphenyl)imidazole-2-ylidene) (IDip) produce very stable dispersions of relatively large ZIF-67 nanoparticles when using comparatively large solvent molecules such as cyclohexane, cyclooctane and mesitylene. The resulting porous liquids can either be directly applied as liquid adsorbents or co-processed with polymers to form highly loaded mixed matrix membranes with outstanding separation performance.

Outer surface functionalization of ZIF-67

ZIF-67 particles with an average size of 264 ± 54 nm (**Supplementary Figure 1**) were synthesized following the protocol described in the **Methods**. Grafting of the outer surface with organic molecules is well known to prevent particle aggregation.¹¹ In our case, we decided to use NHC based surface

modifiers due to their high reactivity towards unsaturated metal sites¹²⁻¹⁴ and their chemical similarity with the imidazole linker used in ZIF materials. The carbenes IMes and IDip (**Figure 1c**) were attached to the MOFs outer surface by stirring ZIF-67 nanocrystals in a mesitylene solution of the carbene ligand inside a glove box (more details in **Methods**).

Fig. 1 | Comparison between pristine and modified ZIF-67. **a**, ZIF-67 in mesitylene after stirring. **b**, ZIF-67 functionalized with IDip in mesitylene. **c**, Lewis formula of 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IDip) and 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene (IMes). **d**, ¹H NMR spectra of pristine ZIF-67 and after modification with carbenes in D₂SO₄/DMSO-*d*₆. Carbene peaks are highlighted with an asterisk (*). **e**, Nitrogen adsorption isotherms on ZIF-67, ZIF-67-IDip and ZIF-67-IMes, measured at -195.8 °C.

ZIF-67, which is non-dispersible in mesitylene, turns to a colloidal dispersion after 12 h of treatment at room temperature (**Figure 1a, b**). Powder X-ray diffraction (PXRD) patterns of ZIF-67 and ZIF-67-IDip functionalized with different ratios (**Supplementary Figure 2 and Supplementary Figure 3 for ZIF-67-IMes**) demonstrate that the integrity of the MOF crystals is preserved upon surface functionalization. In view of these results, a 5 wt.% ratio of carbene, which is adequate for the functional coating of the particles, was selected. Further particle characterization was performed by Scanning Electron Microscopy (SEM) (**Supplementary Figure 1**). Surface functionalization does not seem to etch the ZIF surface. The resulting solutions from ZIF under acidic conditions were analyzed by ¹H NMR spectroscopy (**Figure 1d**). The ¹H NMR spectrum of ZIF-67-IDip showed peaks at 0.84-0.94, 2.04, 7.38 and 8.21 ppm that can be attributed to the CH-(CH₃)₂ methyl, CH-(CH₃)₂ methine, para-CH, and im-H protons of IDip, respectively. Similarly, the ¹H NMR spectrum of ZIF-67-IMes showed peaks that are consistent with the free carbene. X-ray photoelectron spectroscopy (XPS) (**Supplementary Figure 4**) demonstrates that Co maintains the same oxidation state (Co(II)), with binding energies for Co_{2p3/2} 780.8 eV and 781.0 eV for pristine and modified samples respectively.¹⁵⁻¹⁷ The calculated increase in C/Co and C/N atomic ratios further confirms the successful modification of the ZIF-67 surface (**Supplementary Table 1**). In addition, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) (**Supplementary Figures 5, 6**) shows the bending and stretching modes of the 2-methylimidazole ring below 1500 cm⁻¹ in the fingerprint region.¹⁸ Bands between 2700 cm⁻¹ and 3200 cm⁻¹ correspond to the C-H modes of the linker.¹⁹ More precisely, the C-H stretching mode of the aliphatic chain can be assigned to a wavenumber of 2929 cm⁻¹ and the C-H stretching mode of the aromatic ring to the band at 3135 cm⁻¹.¹⁸ Considering the penetration depth of ATR-FTIR, we speculate that metal ion terminated outer surfaces are the preferred anchoring point and become saturated with increasing carbene amount, which would indeed result in a decrease of the aromatic C-H abundance and an increase in the surface aliphatic C-H stretchings (especially in case of IDip). In order

to demonstrate this hypothesis, we performed similar functionalization experiments using ZIF-8 instead of ZIF-67. While the latter documented to expose abundant uncoordinated Co(II) atoms on its outer surface, the former is usually linker terminated.²⁰ In good agreement with our theory, stable dispersions of ZIF-8 could not be obtained upon carbene treatment. Altogether, these results confirm the targeted functionalization of the outer surface of ZIF-67 and highlight the importance of surface termination modes for MOF surface chemistry. Introducing additional Zn(II) atoms to the surface of ZIF-8 by dispersing MOF particles in a solution of zinc nitrate in methanol led to a Zn terminated ZIF-8 that could be further functionalized with IDip to form stable colloidal suspensions (**Supplementary Figure 7-9**). These results confirm the crucial role played by surface unsaturated metal ions.

Adsorption isotherms of C₃H₆ and C₃H₈ as well as N₂ and CH₄, of ZIF-67 and ZIF-67-IDip are compared in **Figure 1e** and **Supplementary Figures 10, 11**. The N₂ uptake of 447 cm³g⁻¹ found for the pristine ZIF-67 is similar to the literature value.²¹ The similarity of the isotherms attests to no significant changes for the modified particles. Adsorption isotherms of propane, propylene (**Supplementary Figure 10**), CH₄ and CO₂ (**Supplementary Figure 11**) are also similar for both the functionalized and unfunctionalized ZIFs, demonstrating that outer surface functionalization hardly affects the adsorptive behavior of ZIF-67.

Fig 2. | Linker substitution energies. **a**, IDip and IMes adsorption after removing an imidazole linker on the metal site of (100), **b**, of (110) surfaces of ZIF-67. The numbers reported in the picture are linker substitution energies by the respective NHC on ZIF-67 (**bold**) and ZIF-8 (*italic*) in eV. The colors used to represent C within MOF, C within carbenes, N, H, and Co are brown, green, blue, off-white, and orange, respectively.

To analyze the interaction of NHCs with the ZIF surfaces, we calculated the adsorption energies of IDip and IMes on the Co(Zn) sites of ZIF-67(ZIF-8) (**Supplementary Table 2**). The experimentally prepared particles have dodecahedral rhombohedral shape and thus (110) is the dominantly present facet (**Supplementary Figure 1** and **Figure 3**). Additionally, we considered the (100) slab as its surface energy is only 0.07 Jm⁻² higher than that of (110) slab. Both the (100) and (110) linker terminated surfaces of ZIF-67 expose on each side of the slab four dangling imidazoles. To preserve the electroneutrality of the system, on each side of the slab two of these imidazoles were protonated. Thus, both the (100) and (110) ZIF slabs we modeled have two dangling imidazoles and two dangling imidazoles exposed on each side. The energy for substituting a dangling imidazole by IDip and IMes, E_{sub} , was evaluated using Eq. 1:

$$E_{sub} = E[ZIF-IM+NHC] + E[IM] - E[ZIF] - E[NHC] \quad (\text{Eq. 1})$$

In this equation, ZIF slab can be either the (100) or (110) slabs of ZIF-67. $E[ZIF-IM+NHC]$ is the energy of the slab with one imidazole linker substituted by an NHC, $E[NHC]$ is the energy of the gas phase IDip or IMes, and $E[IM]$ is the energy of neutral imidazole linker in the gas phase. The substitution of imidazole by NHCs is exothermic on both (100) and (110) surfaces of ZIF-67 (**Supplementary Table 3** and **Figure 2**) and is therefore feasible. Importantly, the binding energy of the dangling imidazole on both the (100) and (110) slabs is very similar to that in the monometallic $Co(imidazolate)_2(imidazole)_2$ (**Supplementary Table 2**), indicating minor impact of the slab geometry on the imidazole binding. To understand the resistance to etching of surface functionalized ZIF-67, we calculated the surface energies in the presence of the NHCs. Minute deviations in surface energies of IDip and IMes functionalized ZIF slabs from that of pristine surface energies (**Supplementary Table 4**) support the experimental observations that attaching NHCs does not damage the ZIF particles.

In stark contrast to ZIF-67, ZIF-8 prefers to remain imidazole terminated in the presence of NHCs, as imidazole substitution is endothermic on both its (100) and (110) surfaces, (**Figure 2** and **Supplementary Table 3**). To understand this difference between ZIF-67 and ZIF-8, we decomposed the adsorption energies into deformation and interaction energies.²² ZIF-8 is more rigid than ZIF-67 as inferred from the higher deformation energies upon NHC adsorption (**Supplementary Table 5**). Furthermore, interaction energy of NHCs with Co is stronger than that of imidazole by ~ 1.5 eV, while for ZIF-8 interaction of NHCs with Zn decreases below 1 eV (**Supplementary Table 5**), which is also reflected in the smaller bond length of NHC-Co than NHC-Zn (**Supplementary Table 6**). Therefore, in comparison to ZIF-67, both higher rigidity of slabs and weaker interaction of NHCs with Zn in ZIF-8 preserve linker termination of the surfaces upon exposure to IDip and IMes.

ZIF-67 based porous liquids

James *et al.* proposed in 2007 three different types of porous liquids: type I²³⁻²⁸ corresponds to an empty host that creates a neat porous liquid, Type II contains dissolved empty host molecules,^{29,30} and Type III dispersed microporous framework materials.²³ To the best of our knowledge, the only example of a porous liquid based on a pristine MOF (Type III) consists of a stable dispersion of methanol surrounded ZIF-8 particles in an ionic liquid.^{9,10,31}

In our case, the outer surface functionalized ZIF-67 particles are ideal candidates to act as pore generators in porous liquids. Given the crystallographic pore-aperture size of ZIF-67 (3.4 Å) and the nature of the carbene modifiers, we chose apolar organic solvents sufficiently large as to ensure that the porosity of the ZIF would remain unoccupied upon dispersion. We successfully prepared stable dispersions of functionalized ZIF-67 in cyclohexane, cyclooctane, and mesitylene. The dynamic viscosity of 1, 2, 3, 4, 5 and 6 wt. % suspensions of ZIF-67-IDip was investigated. The measurements,

summarized in **Supplementary Figure 12**, show a clear trend towards non-Newtonian behavior with strongly increasing viscosity at low shear rates. By increasing the concentration, the dynamic viscosity (determined as a function of the shear rate) increases at low shear rates drastically from 0.16 Pa·s to about 22 Pa·s and at high shear rates from 0.004 Pa·s to 0.011 Pa·s. The non-Newtonian behavior can be derived from the non-linear dependency of the viscosity with the shear rate, showing a shear thinning behavior.³²

Fig. 3 | Gas adsorption and breakthrough curves of C₃H₆/CH₄ mixture on porous liquid. Error bars were obtained from three independent measurements. **a**, CO₂ adsorption isotherms expressed in mmol of CO₂ adsorbed per gram obtained for mesitylene and ZIF-67-IDip 6 wt.%. **b**, CO₂ adsorption isotherms expressed in mmol of CO₂ adsorbed per gram of ZIF-67 obtained for ZIF-67 and ZIF-67-IDip 6 wt.%. **c**, C₃H₆ adsorption isotherms expressed in mmol of C₃H₆ adsorbed per gram obtained for ZIF-67 and ZIF-67-IDip 6 wt.%. **d**, C₃H₆ adsorption isotherms expressed in mmol of C₃H₆ adsorbed per gram of ZIF-67 obtained for mesitylene and ZIF-67-IDip 6 wt.%. **e**, Breakthrough curves obtained using ZIF-67-IDip@mesitylene as porous liquid. **f**, Breakthrough curves obtained using ZIF-67-IDip@methanol as sorption material.

In order to prove that a material is porous, gas sorption isotherms are typically measured. When the material is a liquid, this becomes less straightforward. To measure CO₂, C₃H₆ and C₃H₈ adsorption isotherms on ZIF-67-IDip@mesitylene, we employed a homemade high vacuum line (**Supplementary Figure 13**), where activation via freeze-thaw pumping and dosing steps were performed manually. The porous liquid with a 6 wt.% loading of ZIF was chosen as a model system. All the gases are somewhat soluble in mesitylene, hence the “adsorption” isotherm of pure mesitylene was collected as blank. The amount of gas adsorbed per gram of ZIF-67 is equal in both cases, whether present as activated powder or as pore generator within a liquid (**Figure 3 a, c** and **Supplementary Figure 14** for propane uptake data). The amount of gas that ZIF-67 can uptake (**Figures 3 a, b, c, d** and **Supplementary Figure 14**) is far above the amount of gas that mesitylene can accommodate. As a result, gas uptake increases in the porous liquid.

For the sake of studying ZIF-67-IDip@mesitylene in an actual application in an adsorption process, we designed and tested a breakthrough setup with a “liquid sorbent bed”. In our experiments, an equimolar gas mixture of methane and propylene was bubbled into a designed column filled with ZIF-67-IDip@mesitylene porous liquid (**Supplementary Figure 15**). During breakthrough with a porous liquid, the gas would both be adsorbed by ZIF-67 and dissolve in the solvent. Since CH₄ and C₃H₆ are not well soluble in mesitylene (**Figure 3 e, f**), the MOF filler is solely responsible for the difference in breakthrough times. When the experiment was conducted with only mesitylene in the column, propylene breaks through the membrane 2.5 minutes after methane (**Figure 3 e**, dashed curves). However, having the column loaded with ZIF-67-IDip@mesitylene porous liquid (**Figure 3 e**, solid curves) increased significantly the difference between breakthrough times of methane and propylene,

with propylene breaking through 8.43 minutes after methane. Addition of methanol to fill the MOF pores resulted in a complete loss of selectivity, further demonstrating that ZIF porosity is responsible for the increase in C₃H₆ retention time (**Figure 3f**).

Solution processability allows the manufacture of highly loaded Mixed Matrix Membranes.

To demonstrate that the successful formation of stable dispersions of a MOF in a liquid goes beyond the formation of porous liquids, we studied the advantages of solution processability for the preparation of MOF-polymer composites. To this end, dispersions of ZIF-67-IDip were blended with the state-of-the-art polymer 6FDA-DAM and our newly developed copolymer 6FDA-DHTM-Durene (**Supplementary Figure 16**), in the shape of mixed-matrix membranes.

Primarily we aimed to fabricate mixed-matrix membranes with MOF loadings varying from 20 to 50 wt.% in 6FDA-DAM polymer. Using ZIF-67-IDip we achieved filler loadings up to 47.5 wt.% in 6FDA-DAM (**Supplementary Figures 17, 18 and Supplementary Figures 19, 20 for the membranes with ZIF-8**), while maintaining excellent physical resistance. The ability to increase the MOF loading while preventing agglomeration offers the opportunity to greatly improve separation performance.³³

Composite membranes fabricated with similar amounts of unfunctionalized ZIF-67 were too brittle as to be handled. We observed that the membranes fabricated using unfunctionalized ZIF-67 maintain good physical resistance at relatively low MOF loadings, further increasing the concentration of filler to circa 34.5 wt.% results in very brittle membranes that nearly disintegrate upon mechanical punching (*vide infra*). The microscopic and macroscopic pictures of the resulting membranes are shown in **Figure 4a, b, and e**. Cross-section SEM images of 34.5 wt.% unfunctionalized ZIF-67 and 47.5 wt.% ZIF-67-IDip in 6FDA-DAM polymer membranes with different magnification (**Figure 4a, b and Supplementary Figure 21**) demonstrate clear differences between the two fillers. While unfunctionalized ZIF-67 seems to hardly interact with the 6FDA-DAM and to cluster (**Figure 4a**), the ZIF-67-IDip based membrane shows a much better adhesion and filler dispersion (**Figure 4b**). This observation was further confirmed by Focused Ion Beam SEM (FIB-SEM) analysis (**See Supplementary Video**). Even at loadings as high as 47.5 wt.%, no agglomeration or sedimentation of ZIF-67-IDip nanocrystals was observed (**Supplementary Figure 21**).

Fig. 4 | Physical characterization of membranes. **a-d**, Cross-sectional SEM images of ZIF-67/6FDA-DAM and ZIF-67-IDip/6FDA-DAM MMMs containing 34.5 wt.% ZIF-67 in 6FDA-DAM (**a**), 47.5 wt.% ZIF-67-IDip in 6FDA-DAM (**b**), 34.2 wt.% ZIF-67 in 6FDA-DHTM-Durene (**c**), and 43.1 wt.% ZIF-67-IDip in 6FDA-DHTM-Durene (**d**). **e**, Photographs of MMMs containing 34.5 wt.% ZIF-67 in 6FDA-DAM (**top**), and 47.5 wt.% ZIF-67-IDip in 6FDA-DAM (middle and bottom), the degree of fragility are apparent after being mechanical punched. **f-g**, C₃H₆ (**f**) and C₃H₈ (**g**) adsorption isotherms of ZIF-67-IDip powder, 43.1 wt.% ZIF-67-IDip in 6FDA-DHTM-Durene membranes and pure 6FDA-DHTM-Durene membrane measured at 35 °C, respectively.

We validated this unprecedented enhancement in MOF-polymer interface compatibility *via* IDip functionalization using another polymer matrix, namely 6FDA-DHTM-Durene (2:8) (see **Methods**). This polymer displays a higher selectivity C_3H_6/C_3H_8 selectivity than 6FDA-DAM at the expense of permeability. In this spirit, we fabricated mixed-matrix membranes with various MOF loadings in 6FDA-DHTM-Durene (**Supplementary Figures 22, 23 and Supplementary Figures 24, 25 for the membranes with ZIF-8**). Using ZIF-67-IDip and 6FDA-DHTM-Durene, we were able to achieve a 43.1 wt.% filler loading, slightly lower than that of 6FDA-DAM probably because of the lower molecular weight of the former (Mw= 187 kDa) compared to the latter (Mw=330 kDa). Cross-section SEM images of 34.2 wt.% unfunctionalized ZIF-67 and 43.1 wt.% ZIF-67-IDip in 6FDA-DHTM-Durene MMMs at different magnification (**Figure 4c, d and Supplementary Figure 26**) show again a more homogeneous filler dispersion throughout the composite (**Figure 4d**) for the functionalized ZIF. To complete the study, we further fabricated MMMs using the two polymers and ZIF-8 and ZIF-8-IDip, obtaining similar better compatibilities (**Supplementary Figures 27, 28**).

Adsorption isotherms of C_3H_6 and C_3H_8 of different MMMs are compared with neat polymers and powder samples in **Figure 4f, g and Supplementary Figures 29-32**. Incorporation of ZIF-67 or ZIF-67-IDip in the polymer significantly increases C_3H_6 adsorption (**Figure 4f and Supplementary Figure 29a**), but barely increases C_3H_8 adsorption compared to the pure polymer (**Figure 4g and Supplementary Figure 29b**). As previously reported, in case of most ZIFs, gas molecules with size larger than the pore aperture of the MOF (3.3 Å for ZIF-67) can diffuse into the framework. This adjustable pore aperture in ZIF-67 is attributed to the flexible/elastic behavior of 2-Methylimidazole ligands³⁴. In contrast to powder samples, mixed-matrix membranes based on both polymers exhibited only an increase in C_3H_6 adsorption capacity but not in C_3H_8 when compared to the pure polymer. Since powder X-ray diffraction (PXRD) (**Supplementary Figures 33-40**) and ATR-FTIR (**Supplementary Figures 41-48**) analyses confirmed that the structural integrity of the MOF is retained upon polymer blending, we attribute the observed change in adsorptive capacity to hindrance of mobility of the imidazole linkers in close contact with the polymer matrix.

The separation performance of ZIF-67/6FDA-DAM and ZIF-67-IDip/6FDA-DAM membranes was evaluated in the separation of C_3H_6/C_3H_8 mixtures at 35 °C. In good agreement with the literature,^{35,36} both C_3H_6 permeability and C_3H_6/C_3H_8 selectivity increase gradually upon increasing filler loading (**Figure 5a**). At a relatively low MOF loading (≤ 34 wt.%), MMMs using unfunctionalized ZIF-67 deliver a slightly higher separation factor while higher permeances are observed for the ZIF-67-IDip at similar loadings (**Figure 5a**). The similar intrinsic sorption properties of ZIF-67 and its IDip functionalized counterpart (**Supplementary Figure 11**) cannot account for these differences in separation performance, which are therefore attributed to the better imbedding of the ZIF-67-IDip in the polymer

matrix, that may prevent polymer rigidification around the MOF particles. Such rigidification is well known⁶ to slightly enhance separation factor at the expenses of permeability. However, a remarkable difference can be found when gas mixtures are evaluated. C₃H₆/C₃H₈ selectivity of pure 6FDA-DAM and ZIF-67/6FDA-DAM membranes are significantly deteriorated compared with ZIF-67-IDip/6FDA-DAM membranes (**Figure 5a**). The mixed-gas C₃H₆/C₃H₈ selectivity of 6FDA-DAM and ZIF-67/6FDA-DAM membranes are diminished by 44.6% and 43.6%, whereas in case of ZIF-67-IDip/6FDA-DAM only a 23.8 % loss is observed, even at similar MOF loading (□34 wt.%), (**Supplementary Table 7**). The detrimental effect in mixed-gas separation is normally assigned to competitive sorption of C₃H₆ and C₃H₈ in both the polymer and the MOFs and to the similar condensabilities of these two gases^{35,36}. However, the differences observed between functionalized and unfunctionalized ZIF-67 suggest that polymer swelling also plays a very important role: the excellent filler-polymer interfacing in ZIF-67-IDip/6FDA-DAM membranes greatly reduces polymer swelling. As a result, when comparing performance in mixed gas separation of ZIF-67-IDip/6FDA-DAM with that of the bare 6FDA-DAM polymer, enhancements in C₃H₆/C₃H₈ selectivity and C₃H₆ permeability of 153.6% and 324.1%, for membranes containing a 47.5 wt.% of filler are observed (**Figure 5a and Supplementary Table 7**). Under similar condition, ZIF-67/6FDA-DAM membranes with filler loadings of 34.5 wt.% (the maximum achievable) showed increases of 82.1% and 88.5% in selectivity and permeability.

Fig. 5 | Gas permeation properties. **a,b**, Single- and mixed-gas C₃H₆ permeability and C₃H₆/C₃H₈ selectivity of ZIF-67/6FDA-DAM and ZIF-67-IDip/6FDA-DAM (**a**), and ZIF-67/6FDA-DHTM-Durene and ZIF-67-IDip/6FDA-DHTM-Durene (**b**) membranes with various MOF loading by wt.%. Filled and half-filled symbols indicate gas separation data obtained from single and mixed-gas permeation measurements, respectively. Pure gas permeation was conducted under 2 bar, and mixed-gas feed condition was C₃H₆/C₃H₈ : 50/50, 4 bar, at 35 °C. Solid and dashed lines for eye guide and indicate the enhancements in C₃H₆ permeability and C₃H₆/C₃H₈ selectivity compared with polymer (black circle) by adding ZIF-67 or ZIF-67-IDip. The black line is a guide to the eye and is used only to indicate a general trade-off between permeability and selectivity in reported polymer-based membranes. **c**, A direct comparison of C₃H₆ permeability and C₃H₆/C₃H₈ selectivity enhancement under mixed-gas for 6FDA-/MOF-based MMMs in the literature with the results in this study using 47.5 wt.% ZIF-67-IDip/6FDA-DAM (circle), 43.1 wt.% ZIF-67-IDip/6FDA-DHTM-Durene (diamond), 38.6 wt.% ZIF-8-Zn-IDip/6FDA-DAM (hexagon), and 36.7 wt.% ZIF-8-Zn-IDip/6FDA-DHTM-Durene (pentagon) membranes, respectively. **d**, Plot of C₃H₆ permeability and C₃H₆/C₃H₈ selectivity under mixed-gas provides a recent literature review of polymer/MOF-based MMMs, the black dash line indicates the mixed-gas upper bound for state-of-the-art polymer membranes. **e**, Solubility and diffusivity of C₃H₆ and C₃H₈, and **f**, Sorption and diffusion selectivity of C₃H₆/C₃H₈ in 6FDA-DAM, 6FDA-DHTM-Durene, 34.5 wt.% ZIF-67/6FDA-DAM, 47.5 wt.% ZIF-67-IDip/6FDA-DAM, 34.2 wt.% ZIF-67/6FDA-DHTM-Durene and 43.1 wt.% ZIF-67-IDip/6FDA-DHTM-Durene membranes, respectively.

Encouraged by the separation performance of ZIF-67-IDip/6FDA-DAM membranes, we further explored the separation performances of ZIF-67-IDip/6FDA-DHTM-Durene membranes along with ZIF-

67/6FDA-DHTM-Durene membranes (**Figure 5b** and **Supplementary Tables 8, 12**). Remarkably, mixed-gas C_3H_6/C_3H_8 selectivity and permeability enhancements of 255.1% and 259.6% are achieved for 43.1 wt.% ZIF-67-IDip/6FDA-DHTM-Durene as compared to 6FDA-DHTM-Durene membranes. Similar effects were observed for ZIF-8 based composites (**Supplementary Figures 49, 50** and **Supplementary Tables 9, 10**, for adsorption isotherms see **Supplementary Figures 51, 52**).

Figure 5c, d and **Supplementary Table 12, 13** show an in depth comparison among C_3H_6/C_3H_8 mixed-gas separation performance for different MOF/6FDA-polyimide composites reported in the literature³⁷⁻⁴² with the results obtained in this study. Permeability and selectivity enhancement factors were calculated based on MOF/6FDA-polyimides membranes separation performances as compared to pure polyimide membranes (**Supplementary Table 12** and **Supplementary Figures 53, 54**). As it can be clearly observed, performance of the membranes here reported far exceeds any other report in the literature. To the best of our knowledge, such simultaneously high selectivity and permeability enhancement has never been achieved for high challenging C_3H_6/C_3H_8 separation. These can be rationalized by recognizing the importance of the MOF-polymer interface and considerably high MOF loadings achievable upon functionalization. Direct application of our best performing membranes leads to 97% pure C_3H_6 from a 50/50 C_3H_6/C_3H_8 mixture for at least 30 days under continuous operation. This opens the door to membrane processes based on two-stage separation schemes where polymer grade propylene at high productivities could be obtained from equimolar propane-propylene mixtures. Although better separation performance has been reported for thin supported MOF membrane films,^{43,44} the straightforward manufacture method, the excellent mechanical properties, reproducibility and stability on stream, make this new family of mixed matrix membranes more attractive from an application point of view.

Deconvolution of the permeability (P_i) into the product of sorption coefficient (solubility, S_i) and diffusion coefficient (diffusivity, D_i) was performed based on the sorption-diffusion model⁴⁵ to gain further insight into the separation mechanism of ZIF-67 and ZIF-67-IDip based membranes. **Figures 5e, f** and **Supplementary Tables 11-14** display the obtained results. As it can be observed, sorption selectivity hardly changes upon MOF incorporation. In sharp contrast, addition of a MOF filler results in much higher diffusion selectivity, which further increases upon ZIF-67 functionalization and that we attribute to the more efficient “gate closing” of the outer linkers resulting from the excellent filler-polymer interaction.

In summary, our findings underline the importance of solution processability in the field of porous crystalline materials. Although we could not achieve high porogen loadings, we anticipate that more viscous solvents may allow for the preparation of highly loaded porous liquids with enhanced separation performance, be it as liquid membranes or operating in adsorption-desorption mode.

Going further, one can think of an application of these liquids in oil diffusion pumps or other industrial separation processes, where combining the properties of MOFs with fluidic systems may lead away from batch to cyclical processes.⁴⁶ In these applications, selection of solvents with very low (or preferably 0) vapor pressures will be highly desired. Last but not least, we demonstrated that solution processability is key to achieve a good blending between MOFs and polymers. We anticipate these findings will further encourage researchers and industry to look at MMMs as an excellent compromise between polymeric and pure MOF membranes. Next to gas separation, we envisage this and similar strategies to enable the application of these materials in other technological applications that require solution processability, from micro and nanopatterning to functional coatings, textiles or catalysis.

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Competing interests

The authors declare no competing financial interests.

Data availability

All data generated and/or analyzed in this study are included in this published article and its supplementary information file, and are also available from the corresponding author (Jorge Gascon) on reasonable request.

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Contributions

J.G. and A.K. conceived and designed the project and managed cooperation between KAUST, LUH and DIK. A.K., L.S., L. G-T. and A.B. were responsible for synthesis of the particles, the functionalization and

several measurements, as in particular: A.K. and L.S. did XRD, SEM and ATR-FTIR. A.B. and S.J.D. were responsible for the adsorption measurements. A.B., L. G-T. and S.D. performed the breakthrough measurements. D.S. and I.W. performed and helped with interpretation of the dynamic viscosity measurements. G.S. performed XPS measurements. L. G-T. performed NMR measurements. Y.L. proposed the use and synthesized the carbenes. S.D. obtained adsorption isotherms on the liquid samples. S.J.D. and M.E. designed mixed-matrix membranes; S.J.D. fabricated and analyzed MMMs, and measured C₃H₆ and C₃H₈ sorption isotherms on MOFs powder, MMMs and polymers. S.J.D. calculated solubility and diffusivity and described the findings of mixed-matrix membranes in the manuscript. M.K. performed membranes permeation tests. I.D.C. synthesized 6FDA-DHTM-Durene polymer. I.D.C. and S.J.D. characterized MMMs using SEM, XRD, TGA and ATR-FTIR. R.A, S.K and L.C performed DFT simulations. A.K., L.S., A.B., J.C., S.J.D., R.A, S.K, L.C and J.G. drafted the paper. All authors contributed to the writing of the manuscript and gave their approval to the final version.

METHODS

Synthesis of ZIF-67

The synthesis parameters were adopted from literature with slight changes.²¹ 7.18 g of Co(NO₃)₂·6H₂O and 16.22 g of 2-methylimidazole were each dissolved in 500 ml MeOH. The metal solution was poured into the linker solution and vigorously stirred afterwards for 12 min, then left standing over night. The particles were collected by centrifugation (10000 rpm, 10 min), washed two times with MeOH and dried overnight (150 °C, 50 mbar).

Particle Functionalization

The ZIF-67 particles were surface functionalized on their outer surfaces (ZIF-67-IMes, ZIF-67-IDip) by dissolving either IMes or IDip in mesitylene and mixing it with ZIF-67. We tested different ratios, however, we empirically found a ratio of 100:5 ZIF:carbene to give reliable results without wasting too much of the carbene. Thus, in a typical synthesis 50 mg of IMes or 50 mg of IDip were added to 1 g of ZIF-67 in 20 ml mesitylene. The mixture was stirred overnight, thereafter the particles were collected by centrifugation (10000 rpm, 10 min), washed two times and dried overnight (80 °C, 50 mbar).

Preparation of Porous Liquids

Porous liquids with concentrations from 1 wt. % to 6 wt. % were prepared by dispersing the ZIF-67-carbene particles in mesitylene *via* stirring or sonication. After all characterization was done, the particles could be removed from the solution by centrifugation, washed, dried and were reusable afterwards. The prepared porous liquid were observed to be stable and not showing any sedimentation of MOF particles for at least one year.

Breakthrough experiments

In order to obtain breakthrough curves, a binary equimolar mixture of propylene (1.5 ml min^{-1}) and CH_4 (1.5 ml min^{-1}) was fed into a glass tube filled with 8 ml of ZIF-67-IDip@mesitylene (6 wt.%) porous liquid. The column downstream was continuously monitored using a mass spectrometer. Since the uptake of methane by ZIF-67 (**Supplementary Figure 15**) and also its solubility in mesitylene are low, the moment CH_4 broke through the liquid membrane was considered as $t=0$ (**Figure 3e, f**).

Synthesis of highly loaded Mixed-Matrix Membranes (MMMs)

MOFs nanocrystals (ZIF-67, ZIF-67-IDip, ZIF-8, ZIF-8-Zn-IDip, ZIF-90 and ZIF-90-Zn-IDip) stock solution

To prevent agglomeration, MOFs nanocrystals were not dried before film casting and formation. Concentrations of MOFs nanocrystals in THF solution was determined by drying 1ml of aliquot to find the mass of nanocrystals, and resulting stock solutions were found to be 50~60 mg/ml.

Synthesis of 6FDA-polyimide polymers

6FDA-DHTM-Durene (2:8) copolyimide polymer was prepared by high-temperature one-step polycondensation reaction as following: into a dry Schlenk flask equipped with a nitrogen gas inlet and outlet, 0.581 g (2 mmol) of DHTM and 1.31 g (8 mmol) of Durene were dissolved in 25 mL of freshly distilled *m*-cresol. After complete dissolution, 4.44 g (10 mmol) of 6FDA was added. Prior use, 6FDA was purified once by vacuum sublimation. The temperature was gradually increased up to $190 \text{ }^\circ\text{C}$ and stirred overnight. During reaction period, the water produced by imidization reaction, which was removed with a gentle nitrogen stream. After cooling, the reaction mixture was added to methanol. The resulting fibrous polymer was collected by filtration, redispersed in hot methanol for several hours, then filtered off and dried overnight at $200 \text{ }^\circ\text{C}$ under vacuum to give an off-white solid. The molecular weight (M_w) of the synthesized 6FDA-DHTM-Durene (2:8) copolyimide was found to be $187,600 \text{ g mol}^{-1}$ with a polydispersity index (PDI) of 2.23. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, 500 MHz, δ): 9.37 (0.2H, s); 8.23-8.16 (2H, m); 7.98 (3.2H, m); 7.86 (0.8H, m); 7.42-7.40 (d, 0.8H); 7.33-7.31 (0.8H, d); 7.03-7.01 (0.4H, d); 6.76-6.74 (0.4H, d); 5.66 (0.2H, s); 2.07 (9.6H, s). Polyimide 6FDA-DAM ($M_w = 330 \text{ kDa}$, PDI: 2.48) was purchased from Akron Polymer Systems, Inc.

Membrane Fabrication

General: Membrane fabrication was performed in a glove bag filled with THF vapor in order to prevent a rapid solvent evaporation from the emerging membrane. Prior to gas adsorption and permeation measurements, membranes were thermally treated at $250 \text{ }^\circ\text{C}$ for 20 h under a dynamic vacuum to remove any residual solvent or water in polymers as well as within pores of MOFs.

Pure polyimide dense films

Polyimides (6FDA-DAM or 6FDA-DHTM-Durene) were dried in a vacuum oven at 150 °C overnight before being dissolved in THF. Pure polyimide (6FDA-DAM or 6FDA-DHTM-Durene) membrane with desired thickness (typically 75 μm) was fabricated by dissolving 250 mg of dried polyimide in 3 mL of THF. The solution was mixed on a mechanical shaker overnight to dissolve the polymer. The resulting casting solution was poured in a glass Petri dish on a leveled surface, which was placed in a glove bag pre-saturated with THF vapour for at least 1 h. The film was left in the glove bag overnight to allow the THF solvent to evaporate slowly.

MOF/polyimide mixed-matrix-membrane (MOF = ZIF-67, ZIF-67-IDip, ZIF-8, ZIF-8-Zn-IDip, ZIF-90 or ZIF-90-Zn-IDip and polyimide = 6FDA-DAM, or 6FDA-DHTM-Durene)

MOF/polyimide mixed-matrix-membranes with various MOF nanocrystals loading in a thickness range of 75 - 120 μm were fabricated by dissolving the appropriate amount of polyimides (6FDA-DAM or 6FDA-DHTM-Durene) and MOF nanocrystals in THF solvent.

Polymer solution preparation: A polymer solution was prepared by dissolving 200 mg of dried polyimides (6FDA-DAM or 6FDA-DHTM-Durene) in 2.5 mL of THF by shaking on a mechanical shaker for 3 h at room temperature.

MOF suspension preparation: A required amounts of aliquot from MOF nanocrystals stock solution (e.g. 0.89 mL for 21.1 wt.%, 1.72 mL for 34 wt.% and 3.02 mL for 47.5 wt.% MOF/6FDA-DAM mixed-matrix membranes) was added in a 25 mL glass vial and a required amount of THF was added in order to maintain a total volume of 3 mL.

To this MOF suspension, 10% of the polymer solution was added and the suspension further stirred for 30 min (priming). After that, the rest of the polymer solution was added to the MOF suspension and stirred 45 min (for ZIF-67 or ZIF-67-IDip), 90 min (for ZIF-8 or ZIF-8-Zn-IDip) and 90 min (for ZIF-90 or ZIF-90-Zn-IDip) at 35 °C. During the time, the viscosity of the mixture was changed significantly. The resulting viscous casting solution was poured in a glass dish (for ZIF-67 or ZIF-67-IDip@polyimide membranes) or Teflon dish (for ZIF-8 or ZIF-8-Zn-IDip@polyimide membranes) and (for ZIF-90 or ZIF-90-Zn-IDip@polyimide membranes) on a leveled surface, which was placed in a glove bag pre-saturated with THF vapour for at least 1 h. The dish was left in the glove bag overnight at room temperature to allow the THF solvent to evaporate slowly. The freestanding membrane was then dried in a vacuum oven at 250 °C for 20 h to remove any residual THF.

Gas adsorption measurements

Low-pressure C₃H₆ and C₃H₈ gas adsorption isotherms and kinetics study between 0 and 760 torr were measured using a Micromeritics ASAP 2020 and Vstar-Quantachrome instrument. Typically, 60-80 mg of MOFs powder, pure polymer membranes, or mixed-matrix membranes were placed into a preweighed glass tube sample holder, and heated at 250 °C for 12 h under a dynamic vacuum. The

mass of the activated sample was then used as the basis for the adsorption measurements. The equilibrium times for MOFs powder and MMMs were 10-15 second and 5-7 seconds, respectively. After an adsorption isotherm was measured, the sample was reactivated at 200 °C for 6 h before measuring a subsequent adsorption isotherm.

Gas permeation measurements

Pure gas permeation measurements:

Gas permeation properties of membrane was conducted using a permeation system that was constructed in-house. The pure gas permeation properties were evaluated by a variable-pressure constant-volume methods at 35 °C and 2 atm for C₃H₆ and C₃H₈. Detailed description of the permeation cell set-up and testing procedure has been described elsewhere. The round membrane was mounted on the permeation cell and masked with adhesive aluminum tape and sealed by epoxy resins. On curing, a small area of membrane remained exposed, and the area of membrane accessible to gas transport was determined using a scanner. The membrane thickness was measured with a depth gauge. The permeation systems was evacuated at 35 °C for 12 h before performing any permeation test. The slope of downstream pressure vs. time (dp/dt) at the steady state condition was used for the calculation of gas permeability with accordance to the below equation:

$$P = \frac{Vl}{p_0ART} \frac{dp}{dt} \times 10^{10} \quad (1)$$

where P refers to the gas permeability of a membrane in Barrer (1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹), V is the volume of downstream chamber (cm³), l is the membrane thickness (cm), p_0 is the upstream pressure (cmHg), A refers to the effective area of membrane (cm²), R is the gas constant (0.278 cm³ cmHg cm⁻³(STP) K⁻¹), T is the operating temperature (K).

The ideal selectivity of gas A to gas B, $\alpha_{A/B}$, was evaluated based on the equation as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

where P_A and P_B denote the permeability of gases A and B, respectively.

Based on the solution-diffusion model, permeability is defined as a product of diffusivity (D) and solubility (S). Thus, ideal permeability selectivity (α_P) is the product of diffusivity selectivity (α_D) and solubility selectivity (α_S):

$$P = D \times S \quad (3)$$

$$\alpha_{A/B} = \alpha_P = \alpha_D \times \alpha_S = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \quad (4)$$

where D_A and D_B are the diffusion coefficients for components A and B, respectively, with a unit of cm²/s, whereas S_A and S_B are the solubility coefficients of components A and B, respectively, with a unit of cm³(STP)/(cm³ cmHg).

The diffusivity coefficient D ($\text{cm}^2 \text{s}^{-1}$) was determined from the time lag method using the following equation:

$$D = \frac{l^2}{6\theta} \quad (5)$$

where l is the membrane thickness and θ is the time lag (s).

The solubility coefficient S ($\text{cm}^3 \text{ (STP)} \text{ cm}^{-3} \text{ cmHg}^{-1}$), was obtained indirectly as the ratio of the permeability to the diffusion coefficient as following equation:

$$S = P/D \quad (6)$$

Mixed gas permeation measurements:

A binary gas $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$: 50/50 mixture was used for mixed-gas permeation tests. The mixed-gas permeation measurement was performed using the modified single-gas permeation equipment integrated with micro-gas chromatography (Agilent 490 Micro-GC). The both pure and mixed-matrix membranes were evaluated at a total mixed gas feed pressure of 4 bar at 35 °C. The stage cut (the flow rate ratio of permeate to feed) was maintained below 1% to avoid concentration polarization on the upstream side of the permeation cell and keep the driving force across the membrane constant throughout the course of the experiment. The gas mixture was allowed to permeate the membrane until a steady-state permeation rate was reached (>5 time lags). The permeate volume was then evacuated and allowed to accumulate under steady-state conditions. The permeate gas was then expanded into an evacuated volume and analyzed with a GC. The mixed gas permeability of component i was measured by following equation

$$P_i = 10^{10} \frac{y_i}{x_i p_0} \frac{V l}{A R T} \frac{d p}{d t} \quad (7)$$

where y and x are the mole fractions in permeate and feed respectively, and the p_0 is the feed pressure of the component i .

The separation factor α was calculated as the ratio of the permeability of two components i and j .

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} \quad (8)$$