Gas Separating Metal-Organic Framework Membrane Films on Large Area 3D-Printed Tubular Ceramic Scaffolds

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Abstract

Polycrystalline metal-organic framework (MOF) membrane films prepared on ceramic supports can separate gases with high energy efficiency. They generally exhibit very high permeance and selectivity but suffer from cost issues through the required ceramic supports. Increasing the area and reducing the ceramic component to a minimum could be a strategy to enabling neat membrane of MOFs. In a rapid prototyping approach using 3D-printed porous scaffolds with a double helical channel geometry, we dramatically increase the active membrane area-to-volume ratio. Following stereolithographic printing and de-binding of a ceramic slurry, an adapted sintering protocol was employed to sinter commercially available alumina slurries into porous scaffolds. The 3D-printed scaffolds were optimized at a porosity of 40%, with satisfying mechanical stability. Furthermore, synthetic procedures yielding omnidirectional, homogeneous coatings on the outside and inside of the tubular scaffolds were developed. Membrane films of ZIF-8 and HKUST-1 covering a huge 50 cm² membrane area were produced in this way by applying a counter-diffusion methodology. Gas separation performance was evaluated for H₂, CO₂, N₂ and CH₄ in single-gas measurements and on their binary gas mixtures.
1. Introduction
Membrane technology is largely inspired by biological membranes that transport proteins, gases, water and many more molecules through the body of living species.[1] In terms of technical membrane applications most basic membrane concepts use non-flexible inorganic membranes, or flexible polymeric membranes, but these are – compared to biological membranes – very simple systems.[2] Although these membranes are still miles away from the complexity of biological systems[3], they offer tremendous energy saving potentials in chemical separations.[4] As a disruptive key separation technology, membranes offer solutions to climate protection by capturing carbon[5] as well as establishing a CO\textsubscript{2} economy[6]. They can be used for resource efficient and energy saving chemical separations to decarbonize the chemical industry, for instance through methane valorisation[7] and by replacing energy intensive distillation plants in the production of high value chemicals[4]. By additive manufacturing technology, such as stereolithographic 3D printing, the complexity of membrane scaffolds can be strongly increased through computer-aided designs (CAD) and validated through fluid dynamics models.[8] In many cases, such designs cannot be achieved by conventional ceramic manufacturing technology[9]. That 3D-printing has a tremendous potential also for membrane science is a widely accepted fact[10] and thus, has found cautious first applications in polymeric membrane systems[11] or as structured substrates[12] mainly for use in water purification, or for devices to coat tubular membranes[13].

Metal-Organic Frameworks (MOFs) are crystalline hybrid materials with permanent porosity that are synthesized following reticular chemistry.[14] They consist of metal ions or metal-oxo clusters interconnected by the big toolbox of organic ligands. On 3D-printed bodies, they have been applied as non-continuous films[15], as particles inside a polymer[16], both applied as adsorptive just to demonstrate MOF growth[17]. However, thus far, they still await utilization in complex geometric systems with a challenging application such as membrane separation. In this study, we present porous α-Al\textsubscript{2}O\textsubscript{3} membrane scaffolds with high surface areas per total volume of the ceramic support by bio inspired double-helical channels and with an outer ribbon structure.[18,19] The costs of ceramic 3D printing are not drastically higher than conventional ceramic manufacturing, as most of the costs come from high temperature treatments.[18] Inspired by porous 3D-printed ceramic scaffolds, where the porosity is introduced through the sintering process to produce biomimetically designing cancellous bone scaffolds[19] we 3D-printed porous scaffolds with grains of about 100 nm that yield porosity suitable for membrane separation with low gas pressure drop and high mechanical stability. To prove the concept of 3D-printed membrane scaffolds we prepared \( \mu \)m—thick membrane films of gas sieving, porous framework materials as gas separation layers[20], namely the metal-organic frameworks ZIF-8 (zeolitic imidazolate framework 8)[21] and HKUST-1 (Hong Kong University of Science and Technology 1)[22]. Previous concepts, such as counter-diffusion and in-situ synthesis, where the substrate acts as a
reservoir for one of the MOF-building species\textsuperscript{[20,23,24]} are used to guide the synthetic preparation of the films; these had to be further improved to yield a 360° continuous coating of the complex 3D-printed scaffold. Usually, synthetic conditions for tubular MOF or COF (Covalent Organic Frameworks; porous crystalline organic frameworks) membranes must only yield a good synthetic procedure for vertical growth, as the tubes with straight channels are placed lengthwise vertically into a Teflon-lined autoclave.\textsuperscript{[25,26]} Now, the challenge in the synthetic procedure was to find conditions that allows efficiently and reliably intergrown, homogenous MOF membranes in contorted, round channels with and counter gravity. Furthermore, the scale of our membrane area has been increased by a factor of \(\sim 20\) compared to our typical ceramic membrane supports discs (sold through Fraunhofer IKTS, \(\varnothing=18\) mm; previous work\textsuperscript{[27,28]}). This is a respectably large area to coat, which puts high standard requirement to our syntheses: reproducible synthetic conditions to yield defect free membrane films.

2. Preparation of ZIF-8 and HKUST-1 Membranes on 3D-printed Scaffolds

2.1 Preparation of Porous Alumina Scaffolds from Commercially Available Slurry

The ceramic scaffolds were prepared using a commercial alumina slurry (LithaLox 360) adapted to the employed stereolithographic printing platform (CeraFab Multi 2M30) for printing green bodies. The debinding steps were conducted according to the handling manual instruction, but sintering steps had to be varied to retain defined porosity in the scaffolds with enough sintered particles to achieve the desired mechanical performance. For the detailed procedures please refer to the SI. The scaffolds were designed in Autodesk Inventor (the .stl format data is available in the SI). The 3D-printed cylindrical tube’s outer dimension is 3.45 cm long with a 2 cm cylinder diameter, but two helical channels and the additional outer ribbon structure increase the active membrane area drastically. The two channels offer combined \(\sim 26\) cm², while the outer ribbons structure offers \(\sim 24\) cm² membrane area, resulting in overall \(\sim 50\) cm² membrane area. Comparing to a conventional ceramic tube, at the same length, the double helical tube design yields a membrane area x4 larger. However, literature examples usually work with only 1 cm long tubes with 0.65 cm inner diameter on the lab scale\textsuperscript{[29]}. The double-helical design offers an increased membrane area by a factor of x2 on a length of only 3.45 cm compared to previously used tubular scaffolds of 5 cm length, with an 0.85 cm inner diameter from our own work\textsuperscript{[26]}. With this complex structured membrane substrate and significantly higher membrane area, synthesizing a defect free membrane becomes highly challenging. Nevertheless, we succeeded to coat these substrates and demonstrate gas separation MOF membranes in geometrically complex tubular scaffolds.

2.1 Synthetic Strategy to Coat ZIF-8 and HKUST-1 on 3D-printed Scaffolds

To reproducibly control the growth of MOF coatings, training substrates (smaller scale substrates) were printed and prepared to perform initial coating experiments (Figure 1a,b). Once the synthetic procedures showed X-ray diffraction (XRD) patterns of ZIF-8 on all sides (counter-gravity, vertical, with
gravity; Figure 1c), we transferred the synthetic procedure to a larger membrane training substrate and further to the actual membrane scaffold (Figure 1a). The largest membrane substrate shown in Figure 1a had persistent layer adhesion problems, demonstrating the delamination limit, serving as an outlook substrate. There are several challenges that needed to be overcome: (i) uniform crystal seed formation, (ii) uniform intergrowth of the MOF crystallites to form a continuous film and (iii) controlled termination of the deposition reaction. The challenge (i) originates mainly from complex geometries for the synthetical coating. In order to produce defect free MOFs the chemicals need to be pre-distributed for crystal seed formation. Therefore, we used a pre-coating with amino-propyl triethoxysilane (APTES) and further adapted counter-diffusion techniques for an in-situ synthesis in Teflon-lined autoclaves. Here, the α-Al2O3 scaffold is immersed prior to synthesis in the metal precursor solution.

![Diagram](https://doi.org/10.26434/chemrxiv-2023-5rn0w ORCID: https://orcid.org/0000-0002-5866-1106 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0)
The metal-precursor remains in the porous ceramic and is placed into a Teflon lined autoclave containing a solution with only the linker. Thereby, the scaffold acts as a reservoir (c.f. Figure 1 d), transporting Me$^{2+}$ to the interface between solvent (linker solution) and ceramic, forming a homogeneous seed layer. However, it must be mentioned that the gravitational effects on these large area ceramics cannot be fully ruled out, even when using counter-diffusion synthesis (c.f. Figure 1c).

Challenge (iii) is directly solved by the reservoir effect of the scaffold. Here, a big influence is gravity. If the synthesis takes place without the controlled Me$^{2+}$ distribution through the reservoir effect, particles will form in large quantities. Gravity leads to rapid sedimentation of particles (which also happens here, but to seemingly smaller extent), resulting in uncontrollable growth. Further, challenge (iii) is solved, because the Me$^{2+}$ precursor is provided with a defined quantity, while the linkers are provided in excess quantities. The diffusion-controlled release allows to grow omnidirectional and reproducible films. This interplay is crucial to form a 360° continuous membrane film inside the double-helical channels (Figure 1d). The successful growth of the film is then proven with X-ray diffraction, which revealed ZIF-8 related patterns on the flat face of the scaffold and the curved lateral outer spirals (Figure 1e).

Figure 2 a) Photograph of HKUST-1 coated 3D-printed ceramic training scaffold that was sawn open to do µXRD line scans (black dashed lines) on the top part. The handling with during sawing has led to loss of HKUST-1, resulting in some white spots (compare Figure S2). Inside the channels, white particles from the sawn α-Al$_2$O$_3$ have gathered. b) Horizontal µXRD line scan along the horizontal line shown in a). c) Vertical µXRD line scan following the vertical line shown in a). It is clearly visible by eye, but also from the µXRD line scans that the HKUST-1 has grown inside the tubular scaffold, but not in the microporous ceramic itself.
Through microarea XRD measurements (µXRD), patterns on the cross-section of the coated scaffolds could be collected with high spatial resolution. These measurements revealed that MOF material did not form in the pores between the α-Al₂O₃ grains. The MOF-membrane grew only as a film on top of the ceramic, the inside of the tubular channels and on the outer ribbon structure, as revealed by µXRD. The collected µXRDs show exclusively alumina signal, or some smaller amounts of residual linker molecules in the micropore volume of the scaffold’s “bulk”, while clear patterns corresponding to ZIF-8 are detected in the helical channels.

In Figure 2a, an image of a saw-open HKUST-1 membrane on a membrane training substrate is given with its corresponding horizontal and vertical µXRD line scans in Figure 2b,c. The line scans and the blue colour of HKUST-1 give a clear picture of the surface growth of the membrane film. Through the handling and sawing of the substrate, the layer detached partly. The complicated handling of these membrane tubes without destruction of the membrane coatings remains.

### 2.2 MOF membrane layer formation

The selected MOFs, ZIF-8 and HKUST-1 are both suitable networks for gas separation, while the molecular sieving effect is much stronger for the ZIF-8 lattice due to their crystallographic confinement. ZIF-8 crystallizes in the space group I\textunderline{4}3\textunderline{m} with a zeolite LTA topology, using bidentate 2-methylimidazole linkers. However, ZIF-8 has shown to be a very flexible MOF due to the imidazole linkers.\cite{28,30} HKUST-1 crystallizes in the space group Fm\textunderline{3}m and is build up very rigidly through the tridentate trimesic acid.\cite{31} In ZIF-8, the metal centres are single ions, while two copper sides in HKUST-1 form a paddle wheel moiety as secondary building unit. The average pore opening diameter of ZIF-8 is 3.4 Å, while the average pore opening diameter in HKUST-1 are 4 and 6.9 Å.\cite{24,32} The lattice of ZIF-8 interconnects 11 Å pore cages through the windows of 3.4 Å. In HKUST-1, three different sized cages are found with 5, 11 and 14 Å diameter.\cite{26,32}

In Figure 3a,b,d,e exemplary scanning electron microscopy (SEM) images of the coatings from training membrane substrates are given. The discussed MOF structures are shown in Figure 3c,f. The pictures are taken from vertical growth direction, to get an average thickness value. While counter gravity coatings might yield thinner, and coatings that face gravity accumulate thicker membrane films, the thickness measured for the coatings shown here was assumed to be the average thickness of the membranes. From the top view SEM micrographs, it is visible that both, HKUST-1 and ZIF-8 assemble homogeneous polycrystalline membrane films without any voids or point defects. HKUST-1 shows its typical octahedral crystal habitus, while ZIF-8 shows the characteristic. The cross-sectional SEM analysis reveals the continuously intergrown polycrystalline films with maximum thicknesses of 7 µm for ZIF-8 and about 5 µm for HKUST-1. Further the SEM analysis proves the growth takes place on top of the α-Al₂O₃ scaffold and not inside the porous scaffold again, which is highly beneficial for the membrane.
performance. In Figure 3a, and more clearly in Figure 3d, when looking closely, the layers of the 3D printer structure with periodicity of ~10 µm size can be seen (slightly contrasted lines from bottom left to top right).

![Figure 3](https://example.com/figure3.jpg)

**Figure 3** a) The top-view of the ZIF-8 membrane showing a defect free, intergrown, rhombic dodecahedral ZIF-8 film. b) The cross-sectional SEM image of the ZIF-8 membrane layer with variations in thickness from 4-7 µm. c) the unit cell of ZIF-8 with N= green, C=black, Zn tetrahedra = grey, H = white, CCDC# 1429243. d) The top view of the HKUST-1 membrane showing a defect free, well intergrown HKUST-1 film with octahedral morphology. e) Cross-section of the HKUST-1 film with about 5 µm thickness. f) The unit cell of HKUST-1 with Cu = blue, O = red, C = black, H = white, CCDC# 112954.

### 3. Mechanical Analysis and Porosity of the 3D-printed Scaffolds

The porosity of the 3D-printed scaffold after the successful sintering process has been evaluated by Hg-porosimetry. The sintered α-Al₂O₃ scaffolds shows a Hg accessible volume of 160 mm³/g from 5 MPa on and thereby a rest porosity of 40% (Figure 4a), which is comparable to the commercially available membranes supplied to many MOF-membrane scientists by Fraunhofer IKTS. The cumulative pore volume V_c was measured and provides the median pore diameter D, which is then shown in the differential pore volume dV/logD to be about 150-200 nm (Figure 4b). The pore size distribution from dV/logD is very narrow.
Figure 4 a) The Volume of the 3D-printed scaffolds in mm$^3$ g$^{-1}$ after sintering and the remaining porosity of 40 % versus the pressure. b) The cumulative pore volume $V_c$ in mm$^3$ g$^{-1}$ and the differential pore volume $dV/d\log D$ in mm$^3$ g$^{-1}$, $D$ versus the pore diameter. It is clearly visible that the pore size distribution is narrow and the pore size is 150-200 nm. c) The mechanical testing in a 4-point bending test (Weibull-likelihood method) shows the cumulative failure probability versus the effective stress for a horizontally printed bar. d) The mechanical testing in a 4-point bending test (Weibull-likelihood method) shows the cumulative failure probability versus the effective stress for a vertically printed bar. The vertically printed bar is a lot weaker than the horizontally printed one and the data is less reliable, because a lot of samples failed before testing and the sample size is low leading to an inaccurate confidence calculation.

For the mechanical analysis, two different printing directions were chosen – one vertical and one horizontal - and consecutively tested them. Therefore, square shaped rods with a 3 x 4 mm base and a length of 50 mm were printed and sintered the same way as the 3D-printed membrane scaffolds. The data collected for both printing directions is shown in Figure 4c,d. The likelihood of breaking for the horizontally printed scaffolds under a pressure of 47.85 MPa turns out to be 63.21 % for a sample set of 12 rods, while the vertically printed scaffold breaks at the same likelihood at about 16.31 MPa for a set of 3 (low sample size). However, the vertically printed samples were very brittle, and the number of attempts diminished quickly prior to testing. These results help to determine possible improvements to the 3D printing, such as layer heights, to get a better vertical adhesion of the print layers for future
works. Values of porous Al₂O₃ membranes supports prepared at IKTS are in the range of 60-80 MPa, derived from the same measurement method. Nevertheless, these values strongly depend on pore size, manufacturing process and used raw materials.

4. Evaluating the Membrane Performance

4.1 Construction of the membrane permeator

The membrane geometry combines two helical channels inside a tubular membrane scaffold, which increases the active membrane area significantly. In Figure 5a images of the CAD model are given, as well as the printed ceramic scaffold. After successful MOF coating (see Figure 1, Figure 2), to assure a perfect sealing with the Viton® O-rings in the permeator, glass rings prepared from flat glass sheets were glued to the top and the bottom of the substrate using UV resin, as shown in Figure 5b. The permeator is designed as a flange that gets sealed by an acryl butadiene rubber O-Ring 32.00 x 4.00 mm with 70 shore hardness (inner diameter x thickness) and hold by 4 M3 screws. The glued-on glass plates, and thus the membrane sides, are sealed with another 16.00 x 2.00 mm acryl butadiene rubber O-Ring with 70 shore hardness. This allowed a very controlled gas inlet on both sides of tubular membrane with directed gas flow through the channels. The permeator (Figure 5c,d) was designed to fit the exact geometry after sintering of the scaffold, which showed slight variations.

![Figure 5 a) The CAD construction of the double-helical support for the 3D-printed ceramic scaffolds. b) The ceramic scaffold with glass rings glued to it from top and bottom side to provide a smooth surface for gas-tight O-Ring sealing. c) A photograph of the HKUST-1 coated tubular membrane. d) CAD construction of the resin 3D-printed permeator that is applied using additive manufacturing with Swagel!k® fittings.](https://doi.org/10.26434/chemrxiv-2023-5rn0w ORCID: https://orcid.org/0000-0002-5866-1106 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0)
Since the sintering is essentially “incomplete” on purpose to yield a porous ceramic scaffold, the size had to be measured by hand and the permeator had to be fitted to the outcome of the sintering. The permeator was printed on a Formlabs Form 2 stereolithography resin printer using standard white draft resin supplied by Formlabs. We supply the .stl data in the SI, but for reproducible results a correct fitting to the scaffold that is obtained in the readers’ lab is recommended. The Swagelok fittings were screwed in the 3D-printed device after drilling a thread for them. To obtain a gas tight fitting of the threads they were additionally sealed by UV glue. Detailed building instructions are given in the SI. The permeator with an HKUST-1 membrane can be seen in the photograph in Figure 5c together with a schematic from Autodesk Inventor in Figure 5d.

4.2 Gas Permeation Experiments

Gas permeation was performed on the MOF coated, 3D-printed ceramic membrane tubes using the Wicke-Kallenbach principle. The measurement is performed with single gases and binary gas mixtures in 1:1 ratio under ambient conditions without overpressure and at room temperature. The membranes were activated at 80 °C over night in an N₂ gas stream prior to use to remove residual guest molecules. The measurement of the bare 3D-printed ceramic tube did not show any separation of gas species in the Knudsen regime and the flux through the membrane walls was 100% of the introduced gas flux, because of the large membrane area and high porosity of the 3D-printed ceramic.

Single gas and mixed gas permeances $\Gamma_{ij}$ and a comparison of the ideal $\alpha_{\text{ideal}}$ and real selectivities $\alpha_{\text{real}} = \Gamma_i / \Gamma_j$ of the gases through the ZIF-8 and HKUST-1 membrane films are given in Figure 6. The measured gases species in single gas permeation were H₂, CO₂, N₂, and CH₄, whereas the measured gas pairs in mixed-gas permeation were H₂/CO₂, H₂/N₂, H₂/CH₄, CH₄/N₂ and CO₂/CH₄. A collection of all permeation data in a table can be found in Table S4-S17.

Expectedly, permeance of H₂ is the highest of all gases through both membranes. For the ZIF-8 membrane (see Figure 6 a-c), the single gas measurements, with $\Gamma_{H₂} = 2.48 \cdot 10^{-7}$ (mol/s · m² · Pa) show the ideal selectivity $\alpha_{\text{ideal}}$ of 11.8, 15.6 and 24.6 for H₂/CO₂, H₂/N₂, H₂/CH₄, respectively. In the mixed gas measurements, the selectivity $\alpha_{\text{real}}$ is 11.3, 12.9 and 21.6, for H₂/CO₂, H₂/N₂ and H₂/CH₄. The slightly lower performance is a usually observed result, as single gas measurements – other than mixed gas – do not take competitive gas diffusion into account. This is different for the CO₂/N₂ and CO₂/CH₄ measurements, which show $\alpha_{\text{ideal}}$ of 1.3 and 2.1, while $\alpha_{\text{real}}$ gives values of 1.9 and 2.3 slightly higher because of competitive diffusion mechanisms.

A similar trend is observed for HKUST-1, $\alpha_{\text{ideal}}$ and $\alpha_{\text{real}}$, but with overall lower values than those of ZIF-8, due to larger pores and channels. The ideal H₂ permeance for HKUST-1 is measured to be $\Gamma_{H₂} = \ldots$
The $\alpha_{\text{ideal}}$ of HKUST-1 are 2.7, 3.7, 6.4, 1.3, 2.3 for $\text{H}_2/\text{CO}_2$, $\text{H}_2/\text{N}_2$, $\text{H}_2/\text{CH}_4$, $\text{CO}_2/\text{N}_2$ and $\text{CO}_2/\text{CH}_4$, respectively. The corresponding $\alpha_{\text{real}}$ values are 2.2, 4.3, 6.2, 1.6, 1.9.

Figure 6 Permeation data for the gas pairs: $\text{H}_2/\text{CO}_2$, $\text{H}_2/\text{N}_2$, $\text{H}_2/\text{CH}_4$, $\text{CO}_2/\text{CH}_4$. a) ZIF-8 single gas characterization and ideal selectivity. b) ZIF-8 mixed gas measurements and real selectivity. c) Comparison of real and ideal gas selectivity for the ZIF-8 layer. d) HKUST-1 single gas characterization and ideal selectivity. e) HKUST-1 mixed gas measurements and real selectivity. f) Comparison of real and ideal gas selectivity for the HKUST-1 layer.

The lower selectivity values for HKUST-1 originate in the differences of the average pore opening diameter differences between ZIF-8 (3.4 Å) and HKUST-1 (6.9 Å), which expectedly yield a better flux through the HKUST-1 membranes (even though the layer is thicker, c.f. Figure 3), but a lower molecular sieving capability.

The molecular sieving cut-off is given in Figure 7. Plotting the single gas permeances against the kinetic diameter of the gas species allows to visualize the quality of the molecular sieving properties of the membranes. Figure 7 a) shows the clear molecular sieving cut-off for ZIF-8 between hydrogen and CO$_2$ and even stronger for N$_2$ and CH$_4$ in the permeance (c.f. Figure 6). The molecular sieving cut-off is much stronger if the pore opening diameter is smaller, which is the case for ZIF-8 in comparison to HKUST-1. For HKUST-1, the molecular sieving cut-off is plotted on the same scale as for ZIF-8 in Figure 7 b). The logarithmic scale in both cases helps to visualize the difference. HKUST-1 cannot show a strong molecular sieving cut-off in the range of the kinetic diameters of the used gases, which are $\text{H}_2 = 2.89$ Å, $\text{CO}_2 = 3.3$ Å, $\text{N}_2 = 3.64$ Å, $\text{CH}_4$ 3.8 Å.
Figure 7 Molecular sieving plots of logarithmic single gas permeance against kinetic diameter for a) the ZIF-8 film on the 3D-printed ceramic tube and b) for the HKUST-1 membrane on the 3D-printed ceramic tube.

5. A critical discussion

The membrane performance data collected is in good agreement with values reported in literature\cite{23,24,28,34} and we took the first steps towards 3D-printed ceramic membrane scaffolds for the scalable coating with MOF membranes. Obviously, the membranes cannot compete with the best ever reported ZIF-8\cite{35} or HKUST-1\cite{36} membranes, but the proof of concept for complex geometrical membrane systems based on additive manufactured ceramic scaffolds has been made. In all honesty, there is still space for improvement, especially in the perfectness of the two membranes layers, which cannot be totally excluded to have defects on such a large scale of 50 cm². The defects are certainly the factors that hamper the membranes performance which could be much better with both, the outer membrane layer and the inner membrane layer in the tubes being fully functional. Even though we did not reach state-of-the-art thin films thicknesses of only a few 100 nm that have been reported in

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literature\cite{37}, we were able to demonstrate membrane preparation on \~{}50 cm² area (inner tubes and outer ribbons) under gravity-optimized conditions that show promising separation values. We could improve the synthetic conditions to an efficient level over the course of the work. To the best of our knowledge, we synthesized and measured here the largest area coatings of supported MOF membranes on ceramic surface in the current state of literature. In the future, more complex geometries and fluid dynamic optimized membranes could be printed and applied, cutting the costs of ceramic manufacture by increasing the membrane surface area drastically.

6. Conclusion
Membrane technology has been inspired by nature and biological membranes but has not reached high complexity nor functionality. Through ceramic 3D-printing and additive manufacturing we introduce a higher degree of complexity and proof that this technology can be used as a promising and versatile tool for research in the MOF membrane field by increasing the active membrane area in complex geometries. We combined rapid prototyping of double-helical 3D-printed ceramic scaffolds from stereolithographic printing, and the corresponding SLA printing of the permeation setup with additive manufacturing, ceramic sintering techniques and synthesis know-how. Through a fabrication approach using 3D-printed training substrates we developed a simple 360° omnidirectional coating technique that was used to grow membrane films of ZIF-8 and HKUST-1. We characterized the ceramic scaffolds mechanically and measured (printing direction depended) mechanical strength at about 47.85 MPa (horizontal) and 19.87 MPa (vertical). Hg-intrusion of the scaffold measured a narrow pore size distribution of 150-200 nm and an overall porosity of 40%. We were then able to proof our successful ZIF-8 and HKUST-1 membrane film coatings on the outside of the ceramic scaffolds and on the walls of the internal double-helical channels through µXRD and SEM. Membrane permeation shows successful formation of gas separation layers of ZIF-8 and HKUST-1 and yielded membrane flux and selectivity comparable to literature data. We were able to demonstrate the largest MOF membrane coatings of about 50 cm² for gas separation applications to date.

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Author Contributions Statement

A.Kn. and L.W. conceived the project idea, for which A.Kn created a workflow concept, conceived the computer aided designs and builds, set up the devices and measurements and validated the membranes. A.Kn. and L.W. managed the project. S.R. deindented and sintered the membranes, synthesized the MOF materials, visualized and wrote parts of the draft, set up the measurements. R.S. did all XRD and SEM preparation and analysis, visualized and reviewed the manuscript. A.Kn., A.K. and O.S. measured the membranes, validated the mechanical analysis. J.B.S. 3D-printed all ceramic substrates. A.Kn. and L.W., visualized and revised the draft. A.Kn., L.W., J.J.V., D.G., R.W., I.V. supervised work and acquired funding. R.W. took care of the Hg-porosimetry and mechanical measurements. All authors commented on the manuscript.

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