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Continuous assembly of polymer on metal-organic framework (CAP on MOF): a 30 nm thick polymeric gas separation membrane

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Experimental Procedure

Materials: 2-aminoterephthalic acid (NH_2-BDC, 99%), α-bromoisobutyryl bromide (BiBB, 98%), poly(ethylene glycol) dimethacrylate (PEGDMA, 550 Da), copper (II) bromide ($CuBr_2$, 99%) and sodium ascorbate (98%) are purchased from Sigma-Aldrich and used as received. Triethylamine (TEA) and tetrahydrofuran (THF) were dehydrated before use. Tris[2-(dimethylamino)ethyl] amine (Me_6tren) was prepared according to reference.[1]

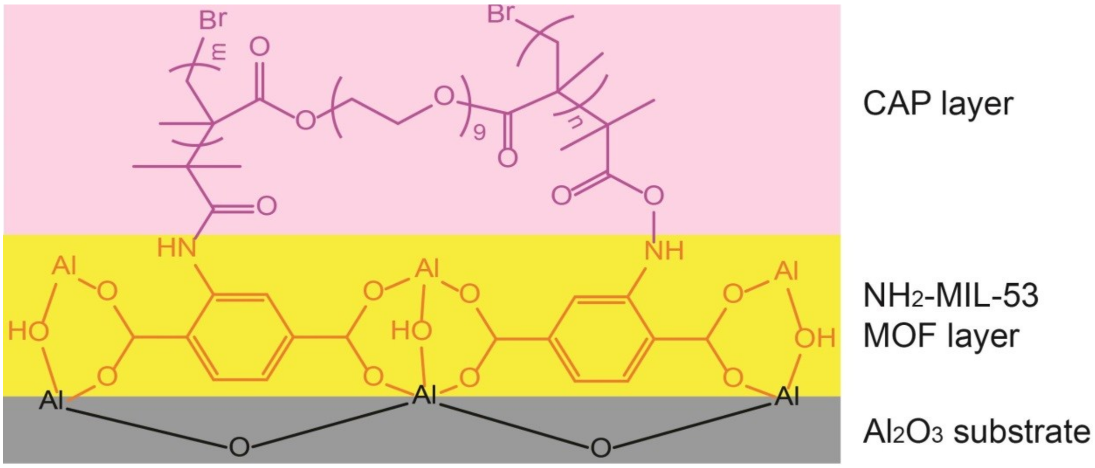
Formation of MOF layer on Anodisc: The MOF layer was prepared via an in-situ reaction between Anodisc (alumina) and 2-aminoterephthalic acid (NH_2-BDC, ligand).[2] In a typical synthesis, NH_2-BDC (140 mg, 0.77 mmol) was dispersed in a glass jar containing 15 mL DI water. An Anodisc (ϕ20 mm with a support ring) was pre-wetted by DI water and placed onto a 27×27 mm glass plate. Then the glass plate supported Anodisc was submerged into the dispersion with care. The glass jar was placed into a Teflon-lined stainless steel autoclave and heated to 120 ^oC for 48 hours, resulting in a yellow coloured MOF/Anodisc membrane. The MOF/Anodic was then sonicated in 10 mL menthol to remove the excess NH_2-BDC and the loosen the MOF crystals. The MOF/Anodisc was dried in vacuum at 60 ^oC overnight before next step. The resulted membrane is named raw MOF/Anodisc (RMA).

Bromide functionalization on MOF/Anodisc: The ATRP initiator site (bromide) was introduced onto the MOF layer by reacting the RMA with α-bromoisobutyryl bromide (BiBB). Specifically, a RMA was submerged into 10 mL anhydrous THF containing 140 µL BiBB and 462 µL triethylamine (TEA) in a glass jar. This jar was then sealed by a plastic cap and Parafilm, and allowed to stand at room temperature for 16 hours. The resulted Br-MOF/Anodisc was rinsed in methanol to remove the excess BiBB, TEA and TEA·HBr salt. The resultant membrane was dried in vacuum at room temperature overnight.

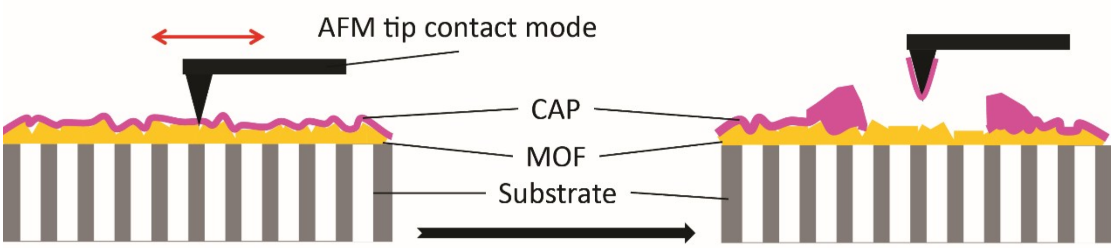
Coating of ultra-thin polymer layer on MOF/Anodisc: The ultra-thin polymer layer was coated *via* the ATRP of poly(ethylene glycol) dimethacrylate (PEGDMA, 550 Da, as the macro-crosslinker). In a normal procedure, PEGDMA (330 mg, 0.6 mmol for PMA-A; 660 mg, 1.2 mmol for PMA-B; 990 mg, 1.8 mmol for PMA-C, and 1320 mg, 2.4 mmol for PMA-D), $CuBr_2$ (2.2 mg, 0.01 mmol), Tris[2-(dimethylamino)ethyl] amine (Me_6Tren, 2.66 µL, 0.01 mmol) and sodium ascorbate (6 mg, 0.03 mmol) were dissolved in 10 mL DI-water. The Br-MOF/Anodisc membrane was placed into this solution and kept at room temperature under static conditions for 16 hours. After the reaction, the membrane was rinsed in DI-water and dried in vacuum at room temperature overnight before gas separation measurements.

Characterizations: *Scanning electron microscope* (SEM) images were acquired using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini Sputter Coater prior to imaging. *Transmission electron microscopy* (TEM) and *energy-dispersive X-ray spectroscopy* (EDX) mapping are carried out on a FEI Tecnai F20 TEM equipped with an EDAX TEAM™ EDS System. *X-ray diffraction* (XRD) patterns of the samples were recorded on a Bruker D8 Advance instrument with Cu Kα radiation (40 kV, 40 mA) and a nickel filter, and the samples were exposed at a scanning rate of 2θ = 0.020 $°\cdot s^{-1}$ in the range of 3-70°. *Atomic force microscopy* (AFM) scanning and scratching were conducted on an Asylum Research MFP3D using a silicon tip. *X-ray photoelectron spectroscopy* (XPS) data was acquired using a VG ESCALAB220i-XL spectrometer equipped with a hemispherical analyser. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 220 W (22 mA and 10kV). Survey (wide) and high resolution (narrow) scans were taken at analyser pass energies of 100 eV and 20 eV, respectively. A low energy flood gun was used to compensate the surface charging effect. *Thermogravimetric analysis* (TGA) was performed on a TGA/SDTA851e, Mettler Toledo in air with heating rate of 10 ^oC min^{-1}. The gas adsorption isotherms were recorded on an ASAP 2050 Xtended Pressure Sorption Analyzer, Micromeritics at 0 ^oC. All the samples were degassed at 85 ^oC prior to measurement.

Gas separation *tests*: For single gas tests, a constant pressure variable volume (CPVV) apparatus designed and built in-house was used to measure the flow rate of individual gases (CO_2 and N_2). The permeate flow rate was measured with a digital flowmeter (ADM2000, Agilent Technologies) for PMA-B and PMA-C, and bubble flow meter for RMA and PMA-A due to the very high flow rate. The membranes were tested at 35 ^oC and gas pressure drop of 100 kPa. The mixed gas separation performance was measured with helium as the sweeping gas on the permeate side. The gas pressure drop was kept at 100 kPa with the upstream flow rate of 50 mL min^{-1}. The gas flow rates at the permeate side were determined by a digital flowmeter (ADM2000, Agilent Technologies) and a gas chromatography (CP-3800, Varian). All the membrane properties presented are the average of at least three membranes.



Scheme S1 The illustration of the chemical bindings of CAP on MOF membranes.



Scheme. S2 An AFM scratching experiment was carried out to investigate the thickness and chemical compound of the top layer. This scheme tells how AFM scratching works. It has been reported that the Young's modules of the MIL-53 type crystal can be as high as 94.7 Gpa,[3] while the cross-linked PEG has much lower value of ~0.1 Gpa.[4] Owing to such a significant mechanical property difference, it is possible to use a physical force to scratch the soft nano-scale PEG layer off the rigid MOF layer. As shown in scheme, the AFM was adjusted to the contact mode and 0.47 Gpa was applied on the tip to scratch the polymeric layer off. After the scratching, the MOF crystals exposed and some polymeric film is attached on the AFM tip.

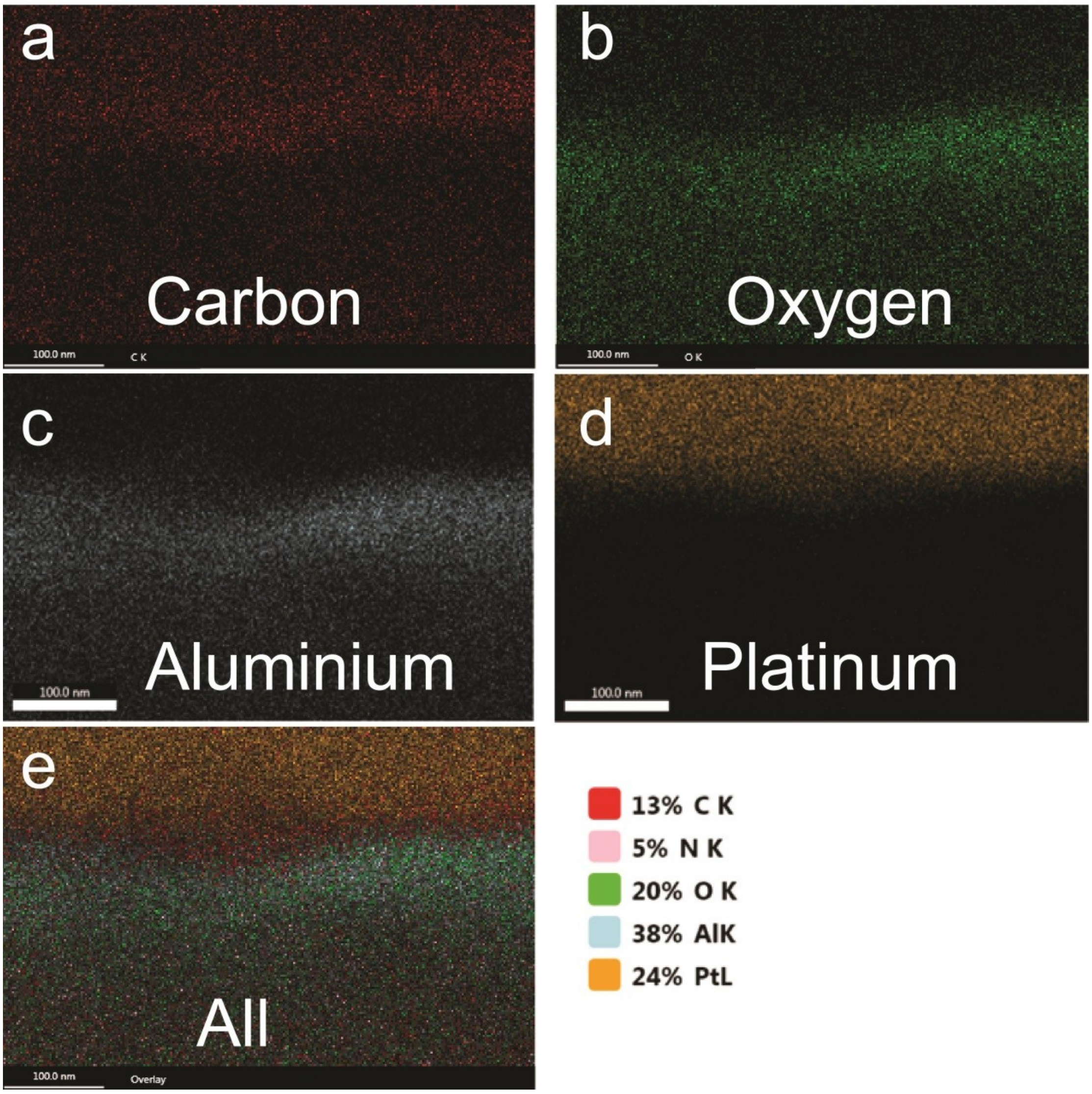


Fig. S1 (a-d) The EDX mapping of single elements: a) Carbon; b) Oxygen; c) Aluminium; d) Platinum. e) The overlay of all elements, the atomic percentage of each element from this image is listed on the right.

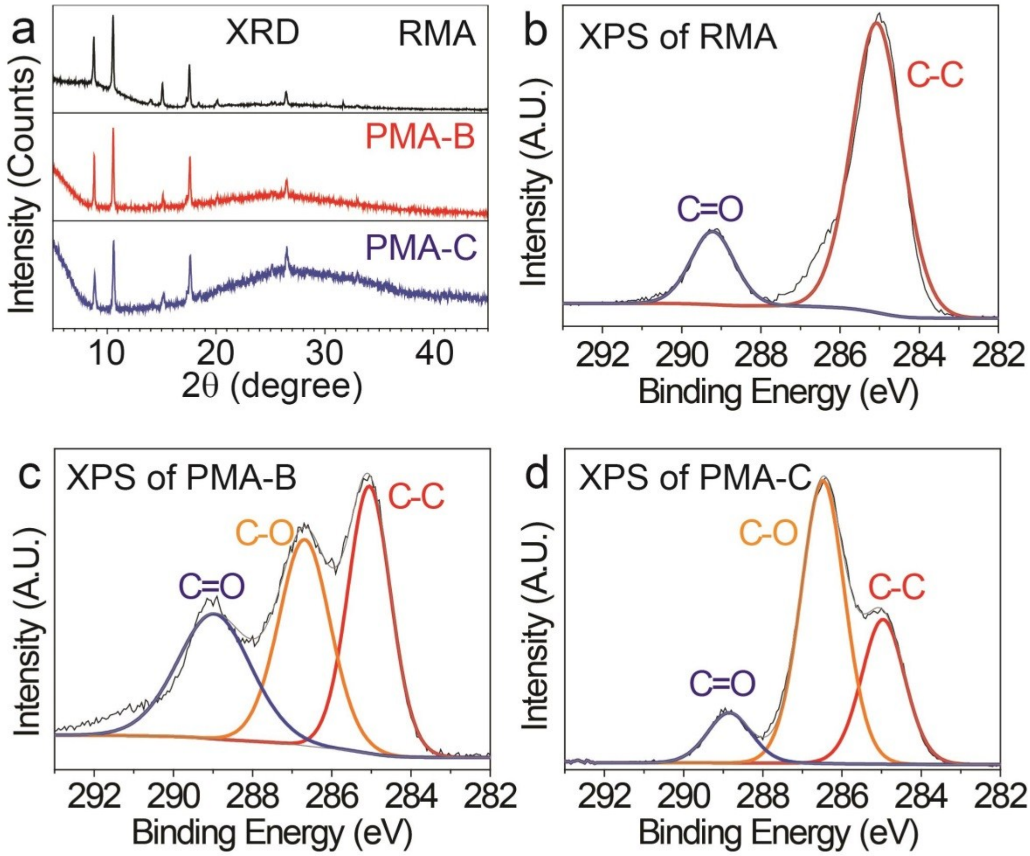


Fig. S2 Spectrum characterizations of membranes. a) The reflective XRD spectrum of RMA (black), PMA-B (red) and PMA-C (blue). b-d) The C1s XPS spectrum for RMA (b), PMA-B (c) and PMA-C (d).

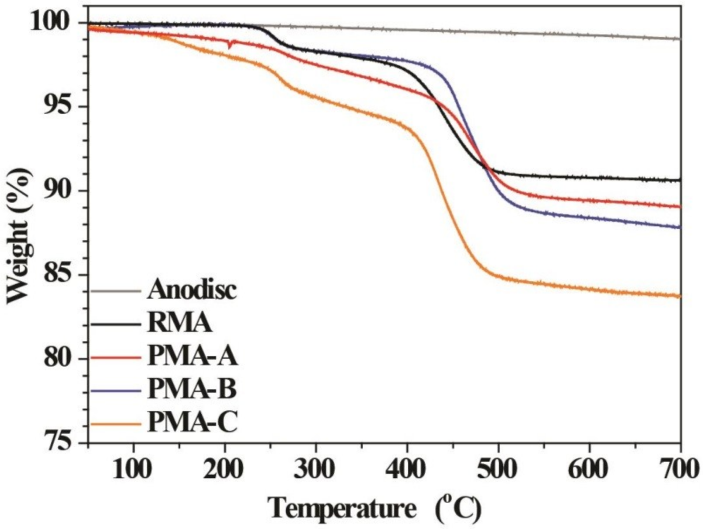


Fig. S3 The thermogravimetric analysis (TGA) curves of bare Anodisc (grey), raw MOF/Anodisc (RMA: black), Polymer/MOF architecture (PMA-A: red, PMA-B blue and PMA-C orange respectively). The curves were recorded in air stream.

Table S1 The summary of TGA results. The MOF content is calculated based on the NH_2-MIL-53 chemical formula $Al(OH)(OOC\text{-}C_6H_6\text{-}NH_2\text{-}COO)$[5,6] ($F_w$ = 226.14), assuming all the MOF was transformed to Al_2O_3 (F_w = 101.96), meaning 22.6 % weight remained for MOF part. The polymer content is calculated by deducting the weight loss contributed by MOF, and polymer was totally burnt after thermal treatment. The weight loss contributed by bare Anodisc is deducted in all cases.

Sample	Weight remained (%)	MOF content (%)	Polymer content (%)	Polymer/MOF ratio
Anodisc	0.9901	0	0	—
RMA	0.9069	10.7	0	0
PMA-A	0.8909	10.5	1.84	0.175
PMA-B	0.8781	10.4	3.25	0.314
PMA-C	0.8372	9.88	7.76	0.785

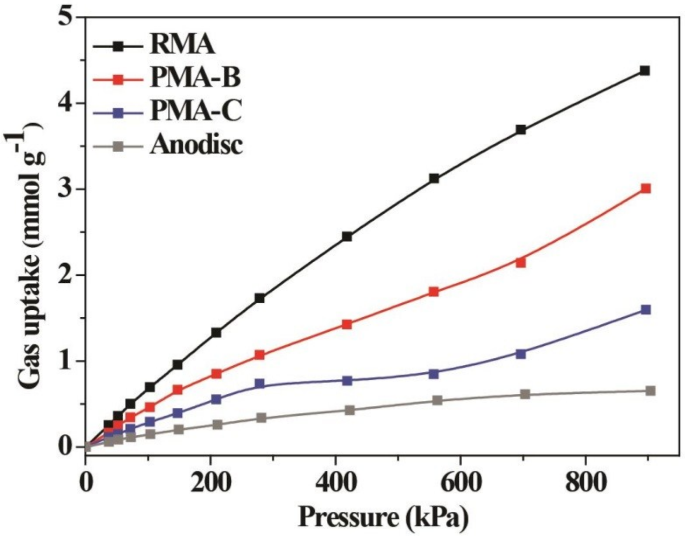


Fig. S4 CO_2 adsorption isotherms for indicated membranes. The measurement was carried out in ice bath.

Table S2. Additional CO_2/N_2 gas separation performance of PMA-B, PMA-C and PMA-D.

Entry	Mixed gas measurement [a]			Single gas measurement		
	N_2 Permeance [GPU, STP]	CO_2 Permeance [GPU, STP]	CO_2/N_2 selectivity	N_2 Permeance [GPU, STP]	CO_2 Permeance [GPU, STP]	CO_2/N_2 selectivity
PMA-B	190 ± 20	2,600 ± 210	14 ± 2	90 ± 8	3,000 ± 320	34 ± 3
PMA-C	7.6 ± 0.5	300 ± 20	40 ± 2	8.0 ± 0.4	310 ± 30	37 ± 2
PMA-D				5.6	220	39

[a] Mixed gas performance was measured using 10/90 mol% CO_2/N_2 at 35 ^{o}C with pressure difference of 100 kPa.

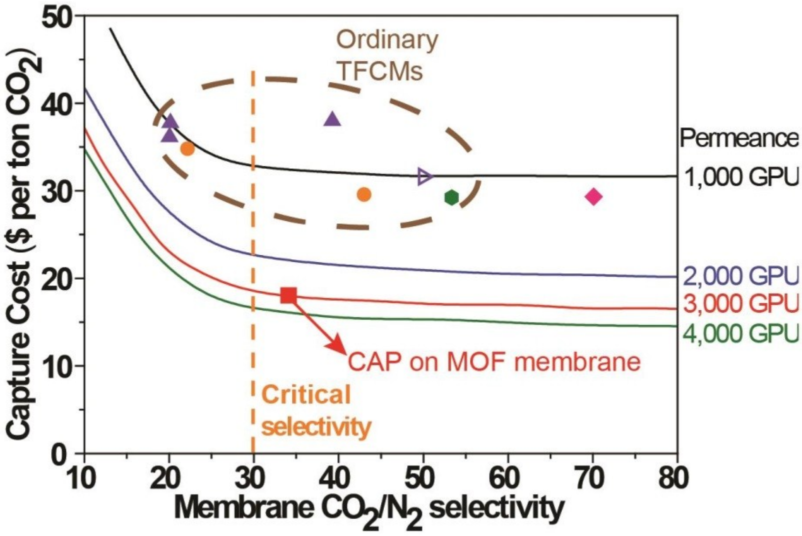


Fig. S5 The comparison of CO_2 capture cost among different types of high permeance CO_2/N_2 separation membranes. The symbols refer to the membranes presented in Fig. 3 and Table 2 in the main text. The economic evaluation is reported by Merkel et al. [7] There is a critical selectivity of 30 for CO_2/N_2 separations. Further increasing selectivity above 30 has little *benefit,* thus in such cases the membrane permeance should be emphasized. The presented PMA-B membrane has a selectivity of 34, which is higher than the benchmark value. According to this evaluation, the CAP on MOF membrane (red square) has the lowest CO_2 capture cost in comparison with currently documented TFCMs despite some of those membranes possessing higher selectivity.

Table S3 Post-combustion CO_2 captures cost of 3,000 GPU membranes with various CO_2/N_2 selectivity.

Selectivity	Compared with PMA-B
10	+107 %
15	+61%
20	+27 %
30	+3.3 %
34 (PMA-B)	N/A
54	-5.0 %
80	-8.3 %

Stability of PMA-B

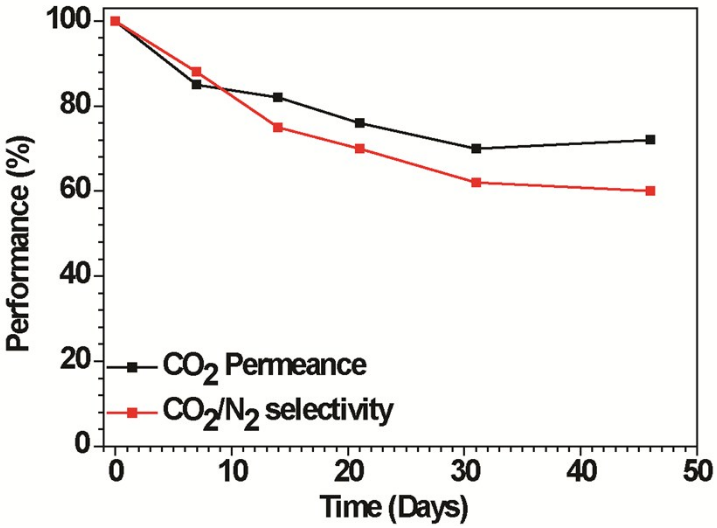


Fig. S6 The study on long-term performance of PMA-B.

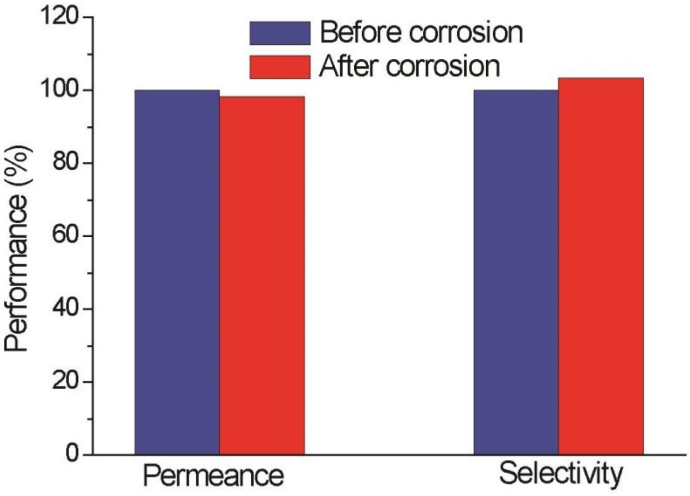


Fig. S7 The study on chemical stability of PMA-B. An industrial evaluation[8] indicates that H_2O, NO_x and SO_x are the major impurities in the post-combustion flue gas, equivalent to a 7.03 µM acid solution. Hence the PMA-B was submerged into a 7 µM HCl solution for 12 hours and dried *in vacuum* to mimic the post-combustion corrosion conditions. The treated membrane showed identical gas separation performance compared to the untreated membrane. This result implies that the PMA-B is chemically stable.

Table S4 Mechanical stabilty of PMA-B.*

Materials	Young's modulus	Suvived pressure (MPa)	Cracked pressure (MPa)
Bulk PEG	105 MPa [4]		
Bulk Al_2O_3	309 GPa [9]		
Anodisc	N/A	<3.1	3.6
PMA-B	N/A	<2.0	2.8

* The compressive stability of Anodisc and PMA-B was measured by directly applying mechanical pressure on the membranes. The integrity of the membrane is checked each time after the compression. The "survived" pressure means the membrane keeps its integrity below the applied pressure, and "cracked" pressure indicates the membrane cracked when the pressure is applied. Generally, the pressure for post-combustion CO_2 capture is less than 0.3 MPa,[7] therefore the PMA-B is mechanically stable under post-combustion conditions.

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