Supplementary Information

Unlocking advanced CO_2 separation via scalable and nitrogen-rich MOF-cross-linked polydimethylsiloxane hollow fiber hybrid membrane

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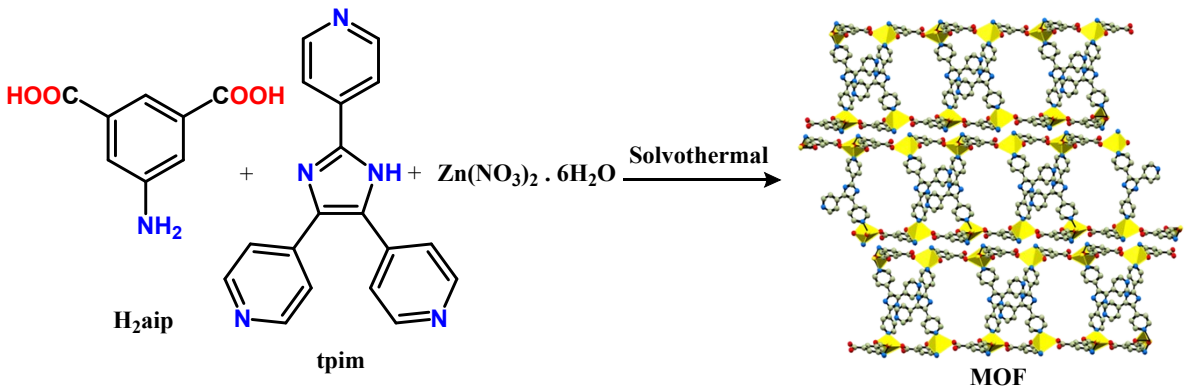

Scheme S1: Synthesis of MOF.

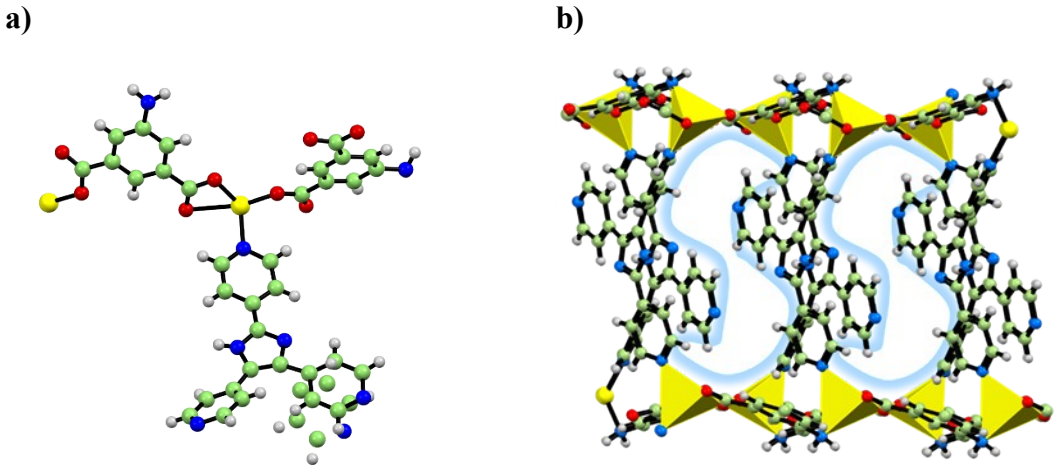

Figure S1: (a) Basic structural unit of MOF (with highly disordered pyridyl arm) (b) S-shaped channels along the 'a' crystallographic axis

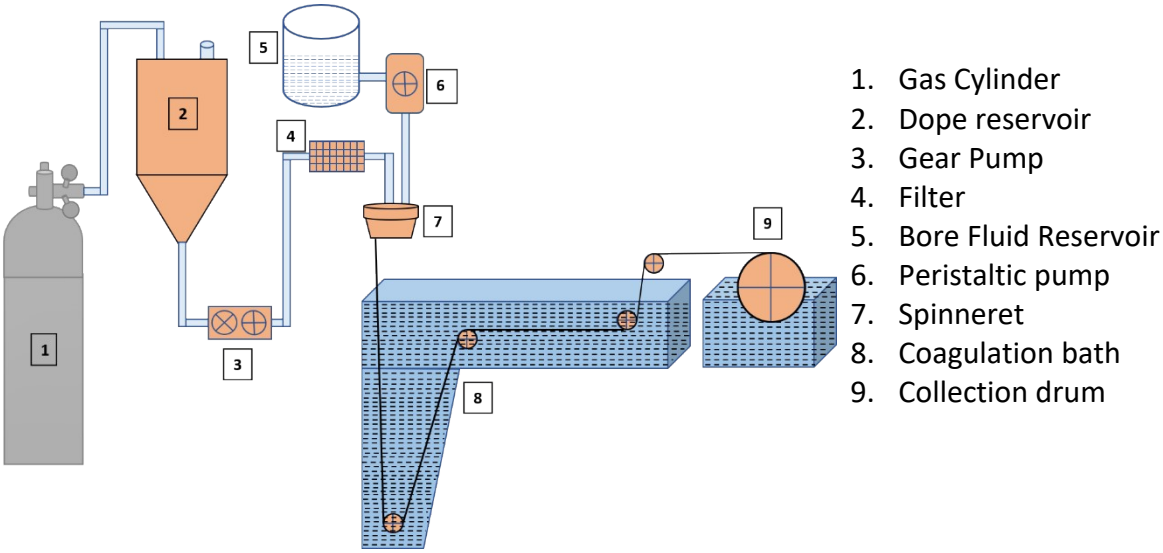

Figure S2: Hollow fiber spinning unit.

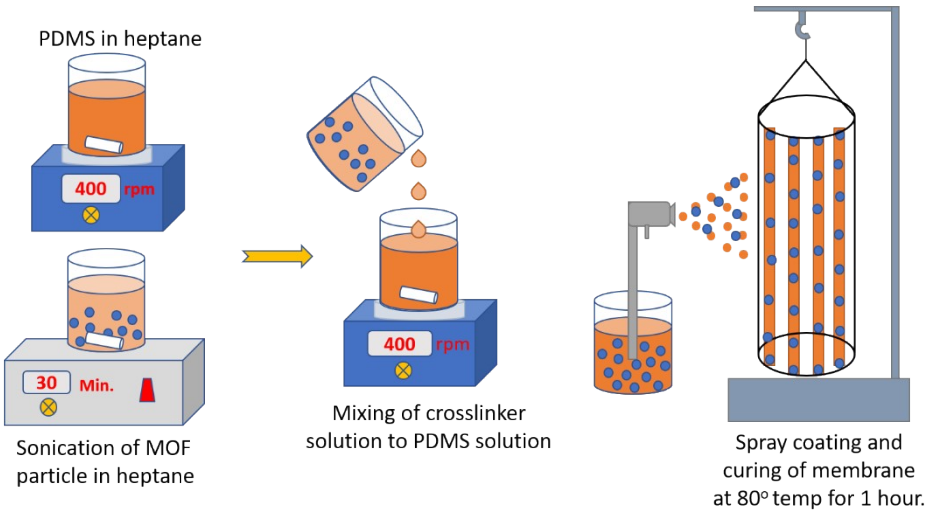

Figure S3: Hollow fiber membrane spray coating process.

S1. Procedure to separate MOF-PDMS coating film from the support:

In the hybrid membrane, MOF-PDMS formed the top coating layer and the PSf is a polymeric porous hollow fiber support. To characterize the film better, a freestanding MOF-PDMS film is necessary to separate from the support. First, the hollow fibers were cut and made like a flat film by applying gentle pressure. Now these films were dipped into the DMF so they started to float upon the surface of the DMF and support polymer PSf gradually started to dissolve. This resulted in transparent to translucent floating freestanding films of MOF-PDMS. The freestanding film was deposited upon a silicon wafer support and dried overnight at room temperature. These films were again dipped in DMF two times to completely remove the traces of support polymer. Finally, the film upon the silicon wafer support dried at 60 ^{0}C in a hot air oven. This method for the removal of freestanding methods is reported previously.[1]

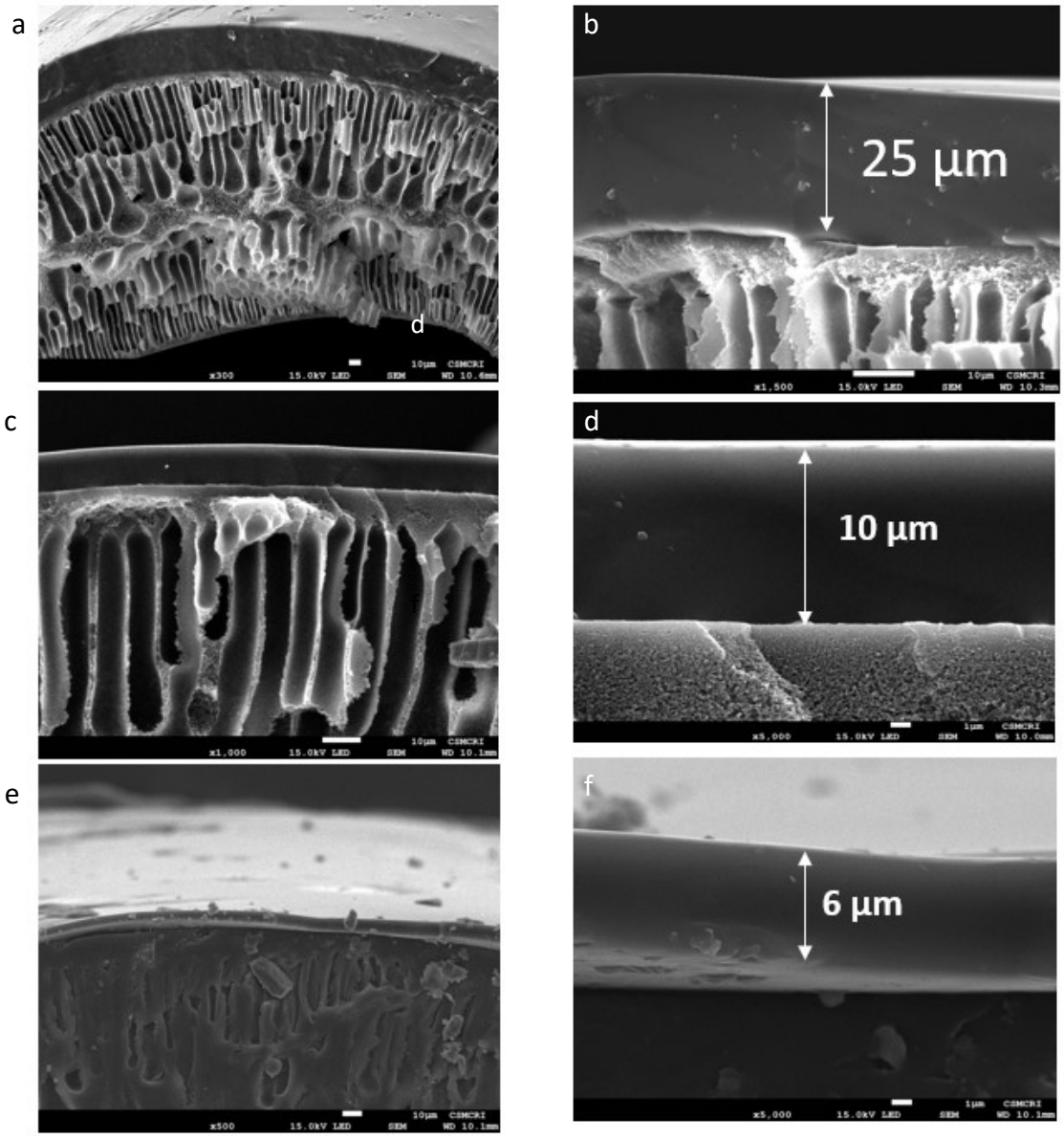

Figure S4: SEM cross-section images of 25% (a,b), 10% (c,d), and 5% (e,f) PDMS solution coating and their effective coating layer thickness respectively.

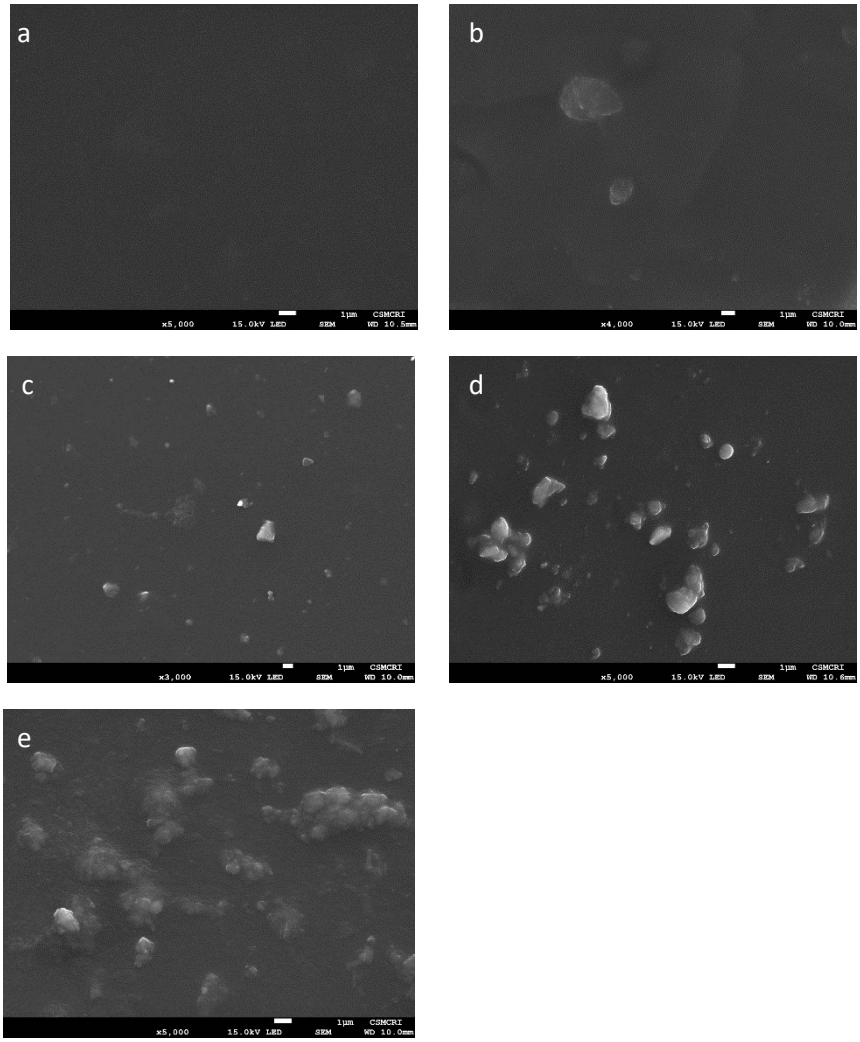

Figure S5: Top surface SEM images of membrane samples, (a) PDMS, (b) 0.5-MOF-PDMS, (c) 1-MOF-PDMS, (d) 2-MOF-PDMS, (e) 4-MOF-PDMS.

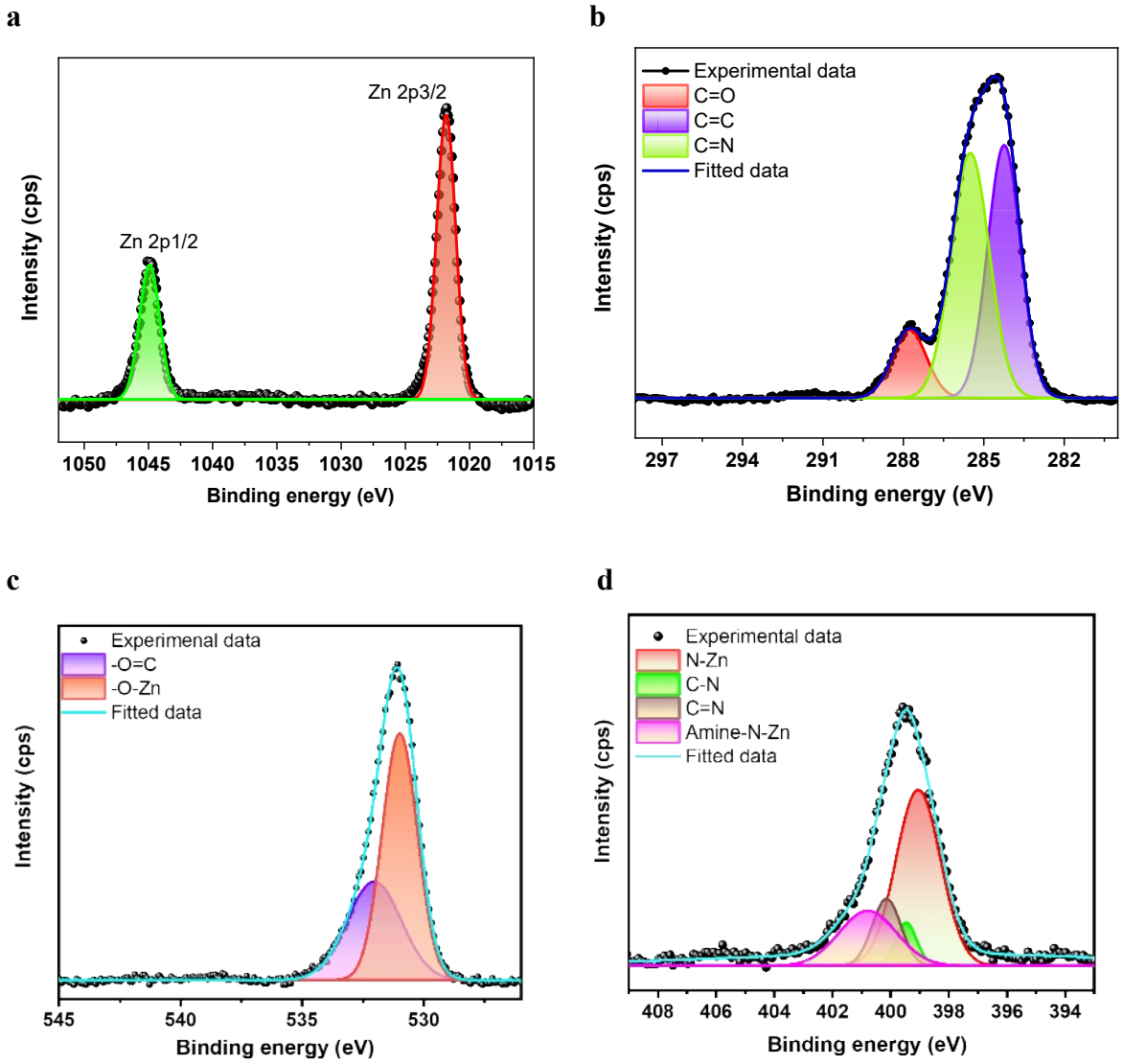

Figure S6: XPS spectra of (a) Zn 2p (b) C1s, (c) O1s, (d) N1s for MOF particle.

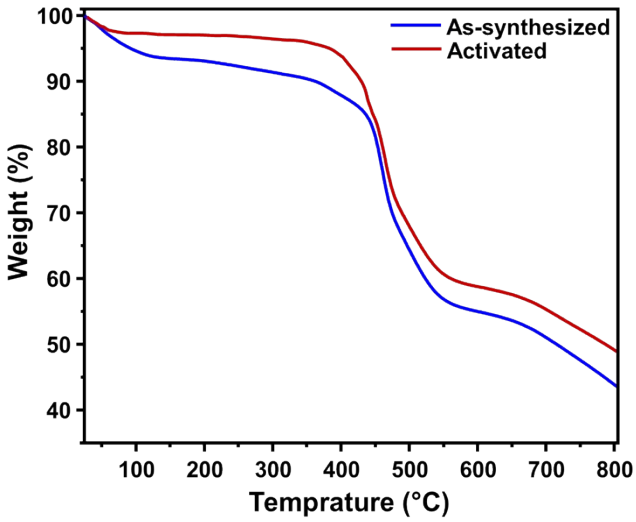

Figure S7: TGA curve of the as-synthesized and activated MOF material.

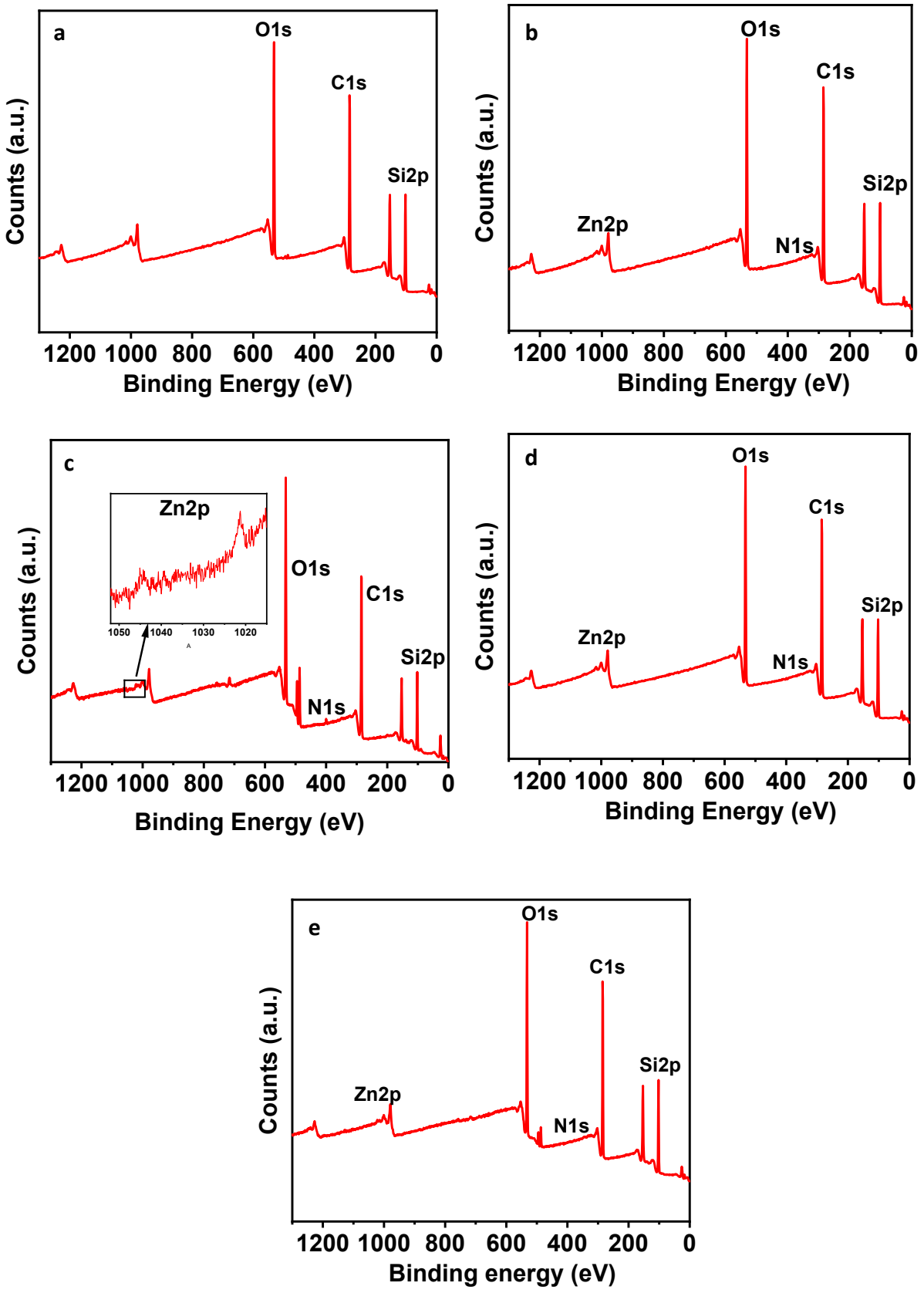

Figure S8: XPS survey spectra of (a) Neat PDMS (b) 0.5-MOF-PDMS, (c) 1-MOF-PDMS, (d) 2-MOF-PDMS, and (e) 4-MOF-PDMS membrane sample.

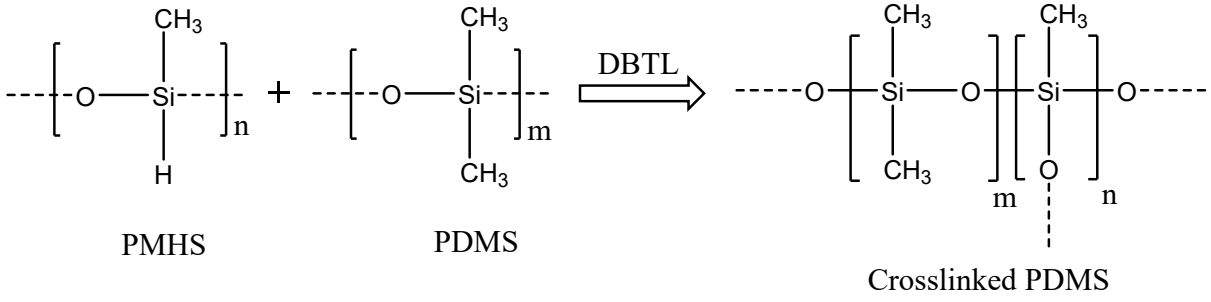

Figure S9: Crosslinking reaction of Pre-polymer PDMS with cross-linker PMHS in the presence of DBTL catalyst.

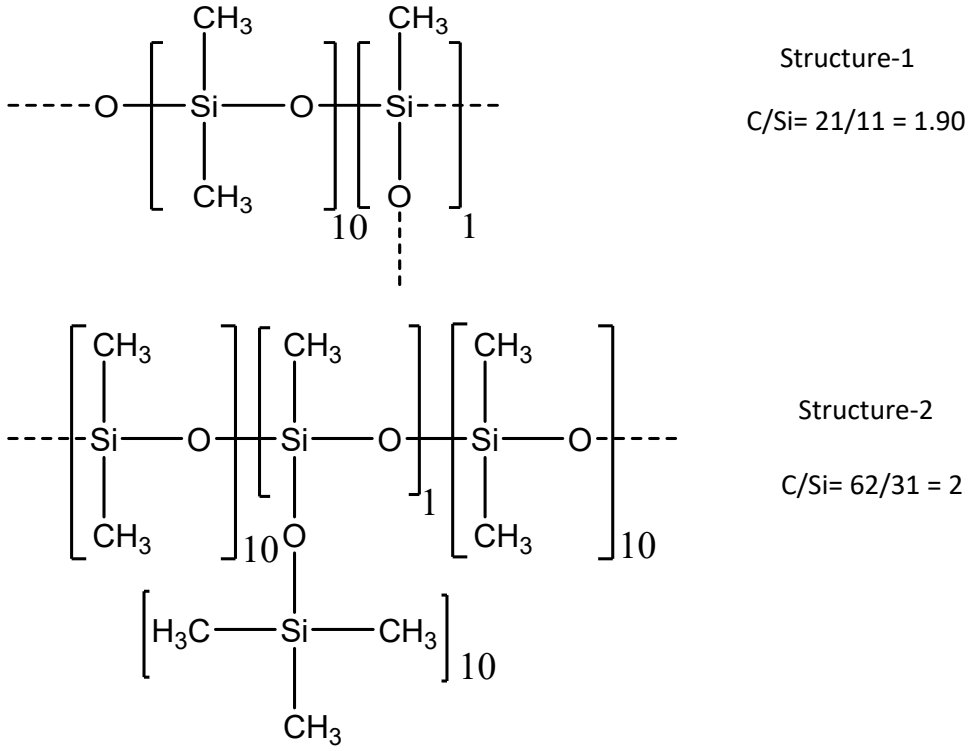

Figure S10: Chemical structure of crosslinked PDMS. Structure-1 corresponds to 1-MOF-PDMS membrane structure with C/Si ration = 1.9. Structure-2 corresponds to 0.5-MOF-PDMS and 2-MOF-PDMS membrane structures with a C/Si ratio = 2.

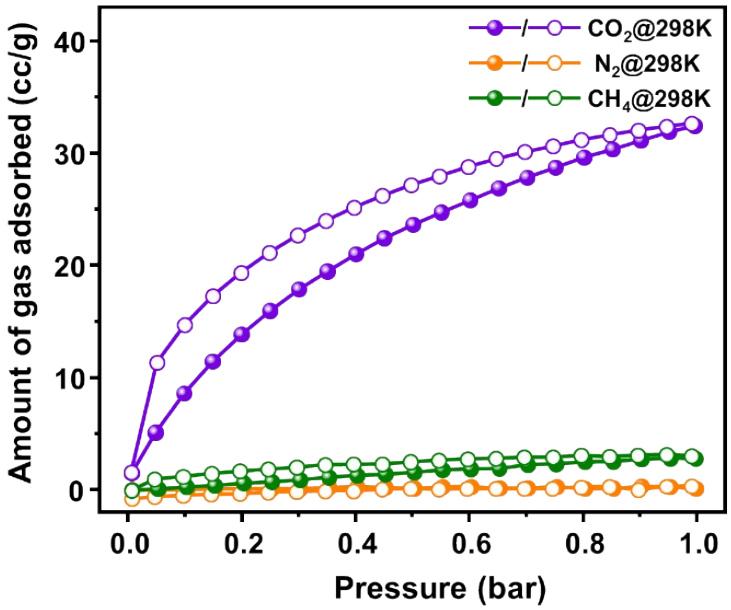

Figure S11: Gas adsorption isotherm of MOF for CO_2, N_2 and CH_4 at 298K.

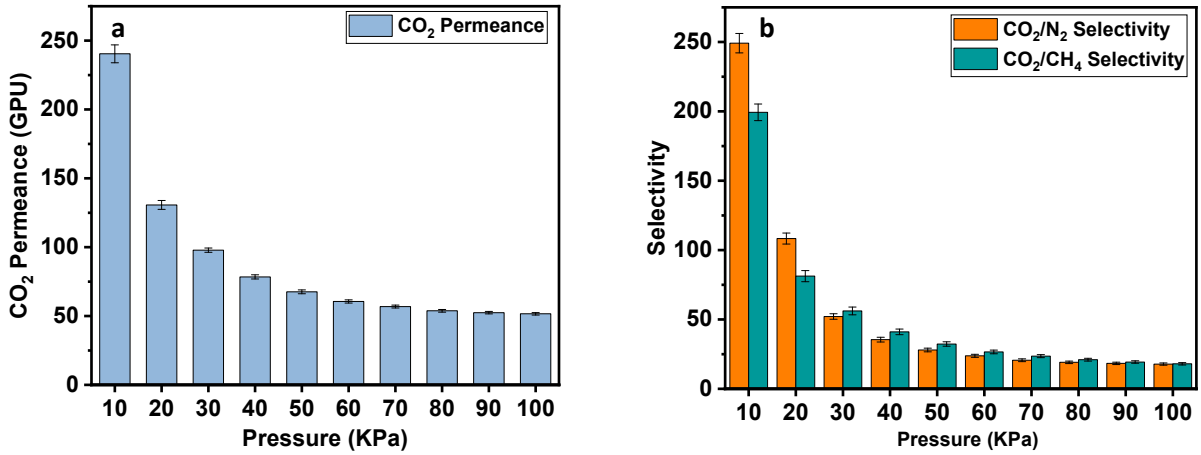

Figure S12: (a) CO_2 permeance of 1-MOF-PDMS membrane, (b) CO_2/N_2 and CO_2/CH_4 selectivity of 1-MOF-PDMS membrane.

Table S1 Crystal data and structure refinement for MOF.

-Identification code	MOF
Empirical formula	$C_{31}H_{14}N_6O_8Zn_2$
Formula weight	729.22
Temperature/K	162.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.017(2)
b/Å	7.6428(9)
c/Å	35.361(5)
α/°	90
β/°	99.594(4)
γ/°	90
Volume/Å^3	4268.2(9)
Z	4
ρ_{calc}g/cm^3	1.135
μ/mm^{-1}	1.168
F(000)	1464.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.008 to 43.93
Index ranges	$-16 \leq h \leq 16$, $-8 \leq k \leq 8$, $-37 \leq l \leq 37$
Reflections collected	51219
Independent reflections	4190 [R_{int} = 0.0897, R_{sigma} = 0.0375]
Data/restraints/parameters	4190/15/493
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0875
Final R indexes [all data]	R_1 = 0.0846, wR_2 = 0.1189
Largest diff. peak/hole / e Å^{-3}	0.71/-0.26

Reference:

1 U. G. Thummar, A. Koradiya, M. Saxena and V. Polisetti, *Desalination*, 2022, **530**, 115650.