Electronic Supplementary Material

Remarkable enhancement of gas selectivity on organosilica hybrid membranes using urea-modulated metal-organic framework nanoparticles

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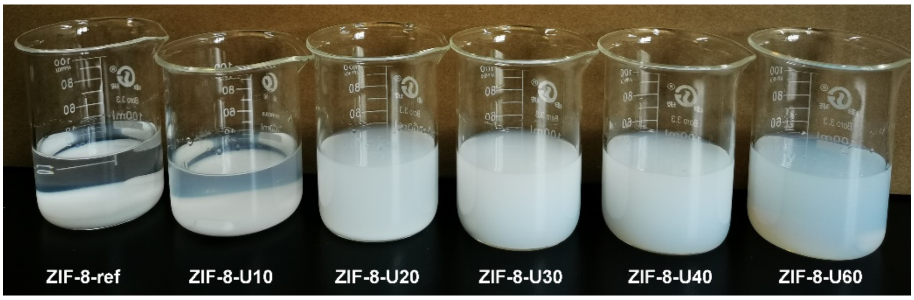

Fig. S1 Digital photographs of ZIF-8 synthetic solutions after aging for 24h.

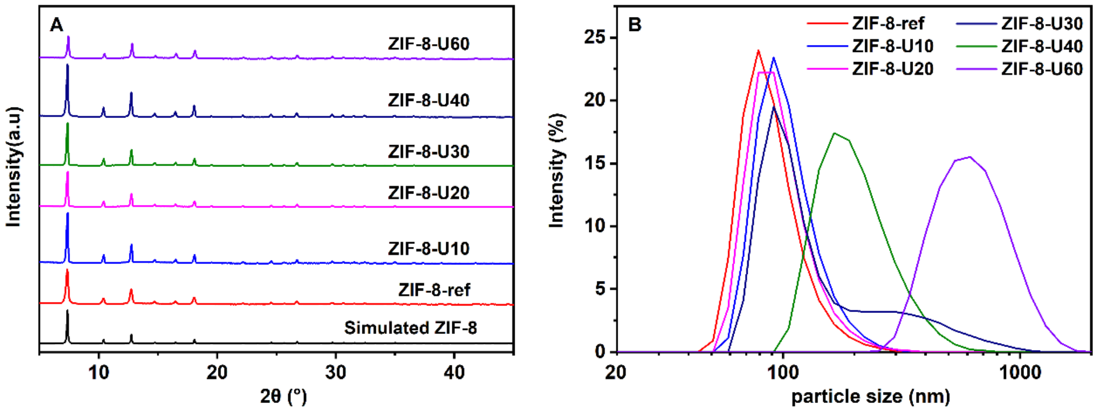

Fig. S2 (A) Powder X-ray ddiffraction analysis and (B) Particle size distribution of as-prepared ZIF-8 nanoparticles.

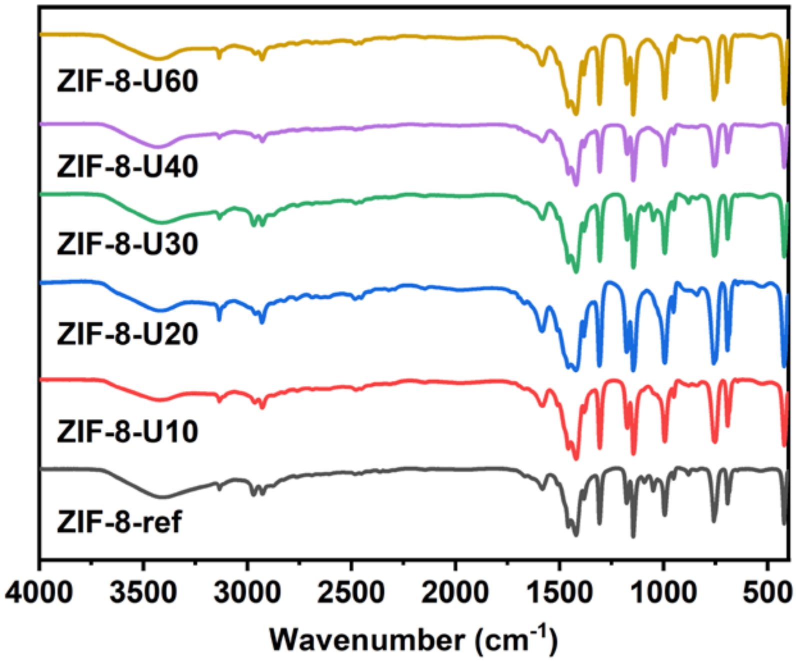

Fig. S3 FT-IR spectra of ZIF-8 nanoparticles.

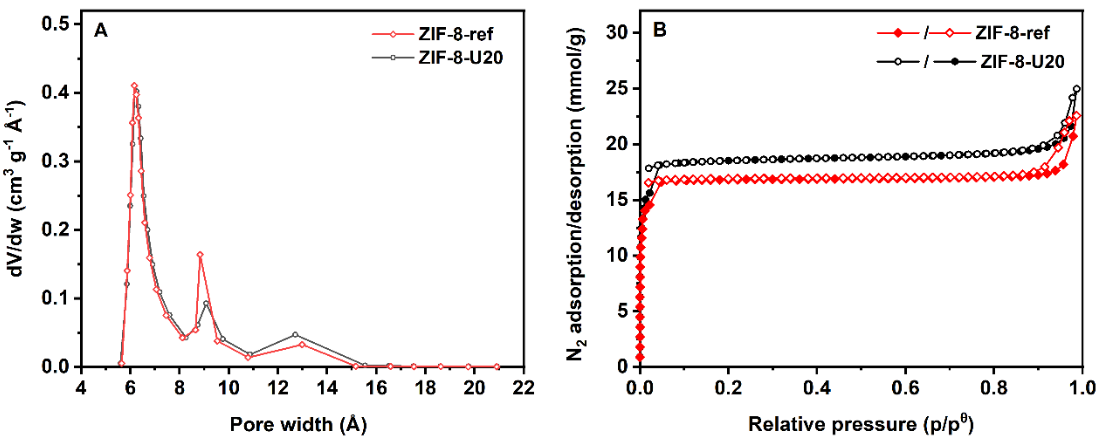

Fig. S4 (A) Pore size distribution curves of ZIF-8-ref and ZIF-8-U20, and (B) N_2 adsorption (solid)/desorption (hollow) isotherms of ZIF-8-ref and ZIF-8-U20 at 77 K.

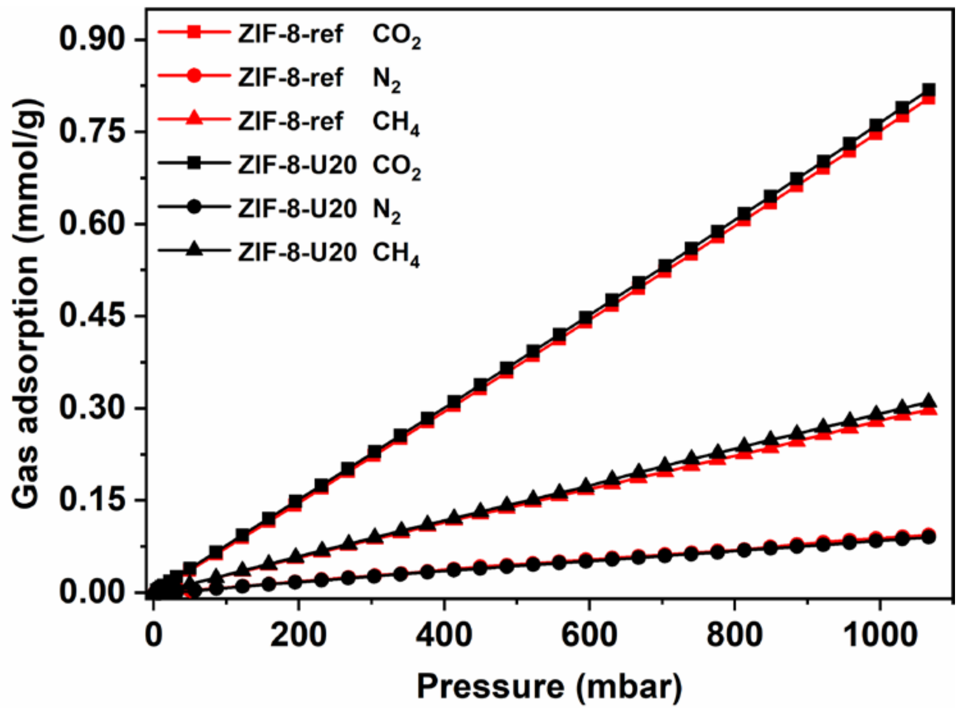

Fig. S5 N_2, CO_2 and CH_4 adsorption isotherms of ZIF-8-ref and ZIF-8-U20 powders at 25°C.

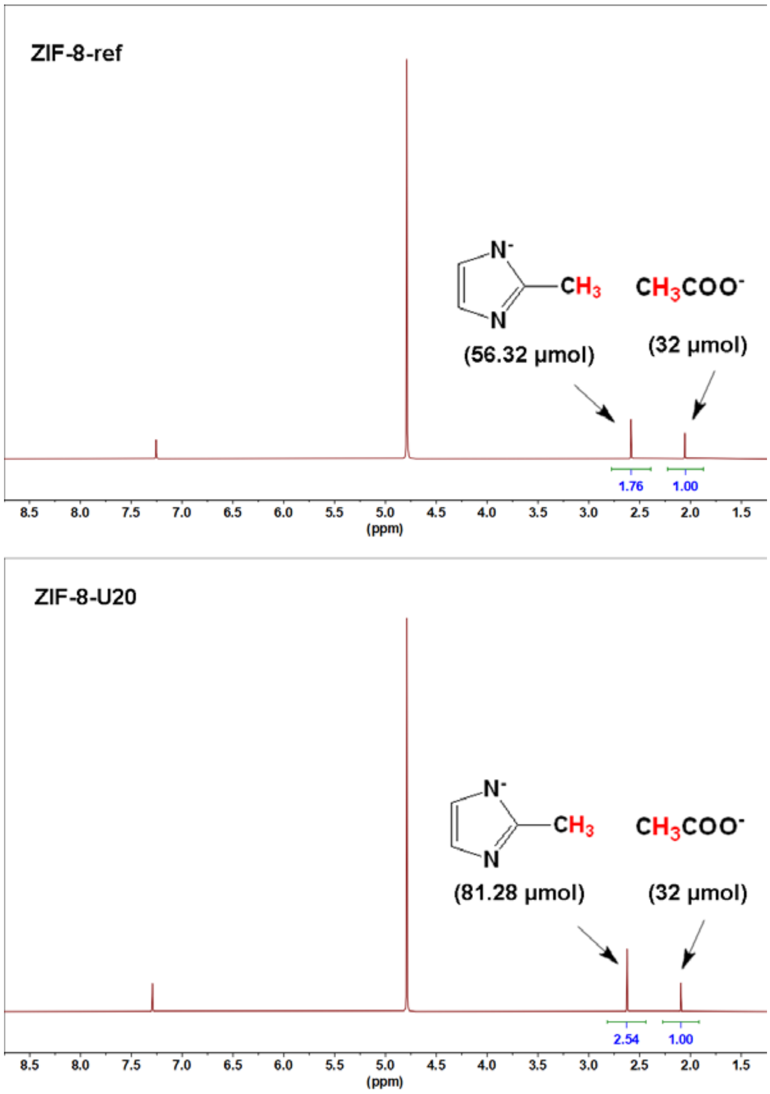

Fig. S6 Dissolution/^{1}H nuclear magnetic resonance spectra of ZIF-8-ref (6.5 mg) and ZIF-8-U20 (9.5 mg).

Table S1 Molar ratios of Zn to mIm in ZIF-8-U20 and ZIF-8-ref.

	n_{mIm} (μmol/mg)	n_{Zn} (μmol/mg)	n_{mIm}/n_{Zn}
ZIF-8-U20	8.556	4.764	1.796
ZIF-8-ref	8.665	4.716	1.837

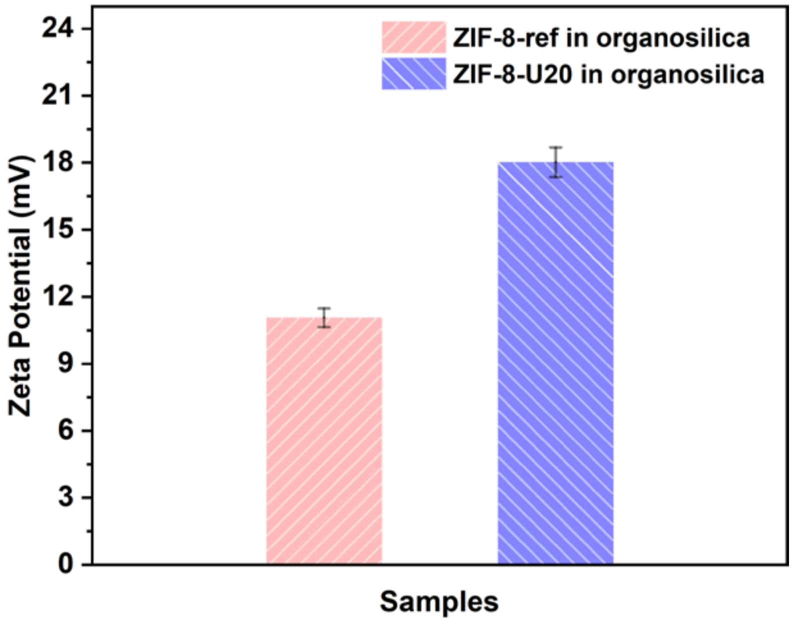

Fig. S7 Zeta potential of ZIF-8-U20 and ZIF-8-ref dispersed in organosilica polymer sol (ZIF-8-U20 or ZIF-8-ref/organosilica = 1/1 wt./wt.).

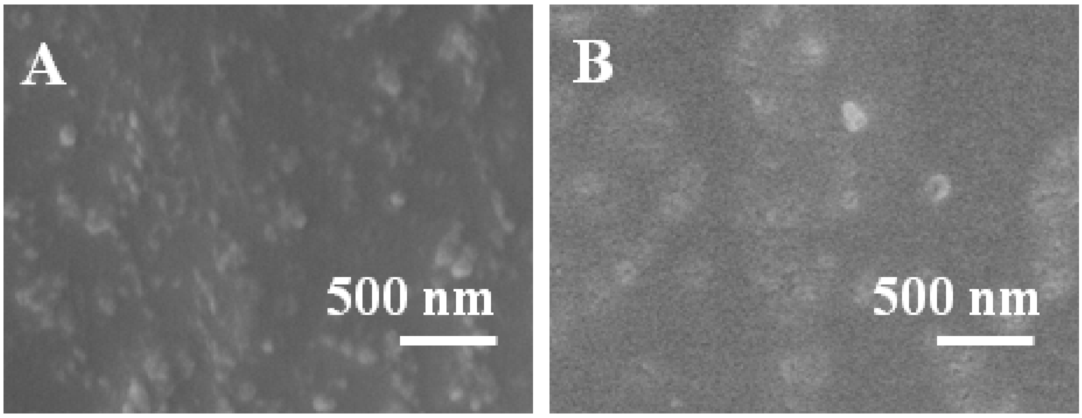

Fig. S8 SEM images of the surface view of the as-prepared ZIF-8/organosilica membranes: (A) M1/1 and (B) M1/1-ref.

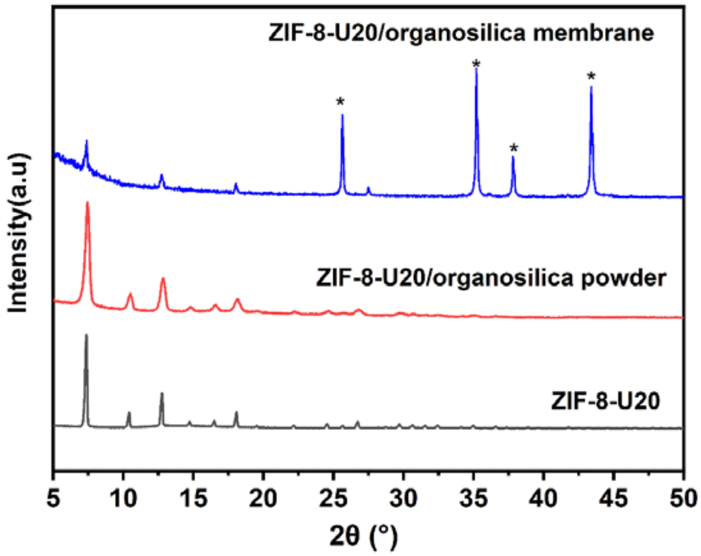

Fig. S9 XRD patterns of the as-made ZIF-8-U20, ZIF-8-U20/organosilica powders and ZIF-8-U20/organosilica membrane on Al_2O_3 support. * labels the peaks from Al_2O_3.

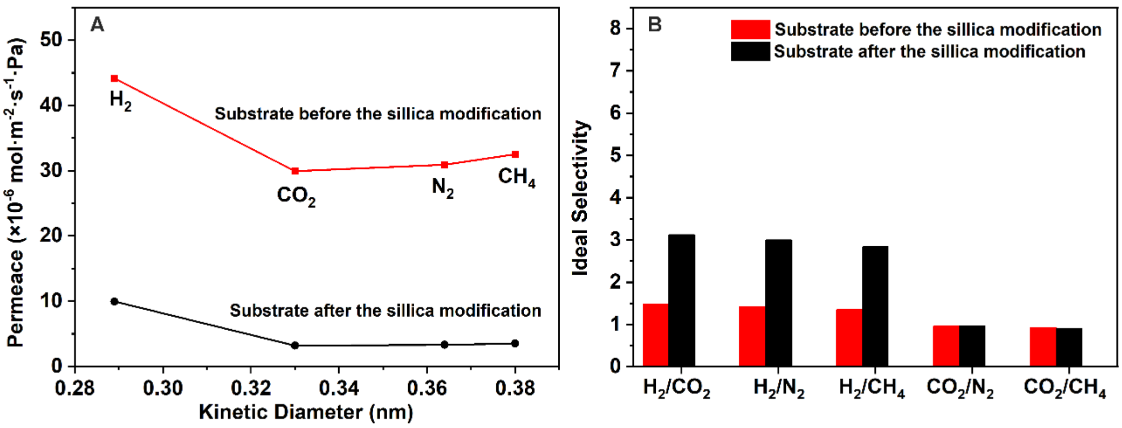

Fig. S10 The gas permeation properties of the tubular ceramic substrate and colloidal silica modified substrate at 25°C.

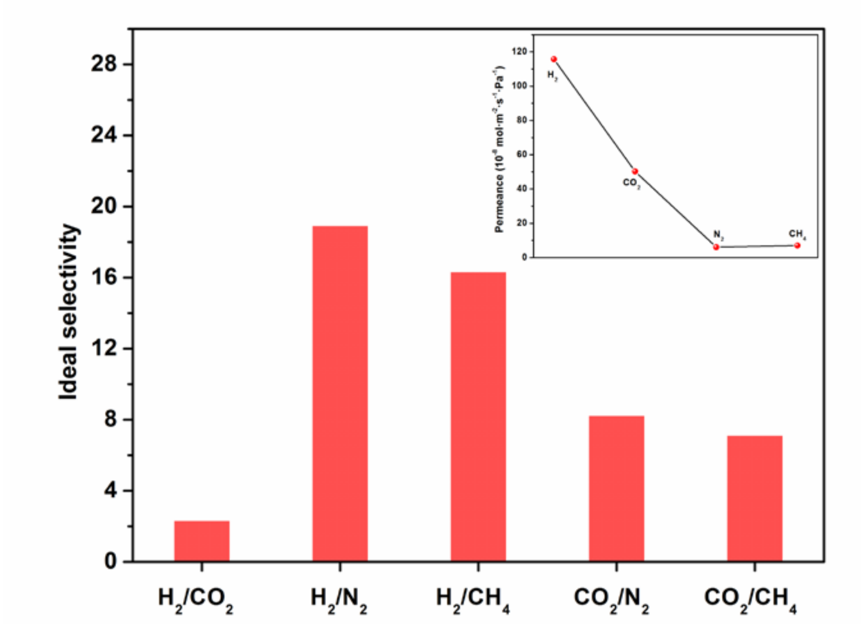

Fig. S11 Gas permeation properties of the pure organosilica membrane at 25°C.

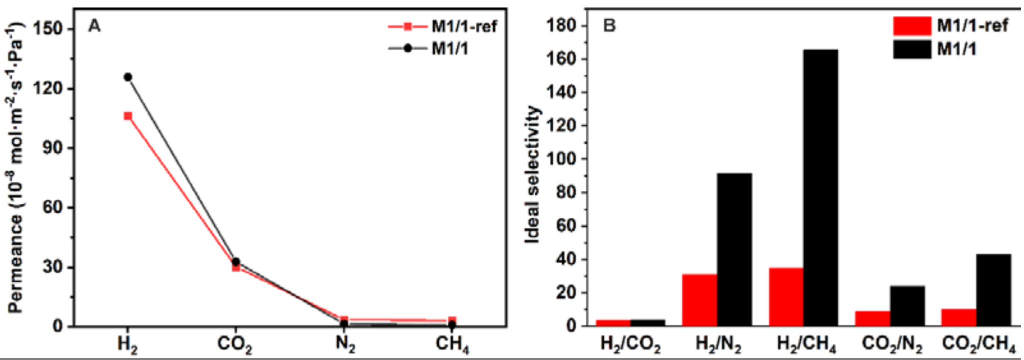

Fig. S12 (A) Single gas permeance of H_2, N_2, CO_2 and CH_4 through the as-prepared ZIF-8/organosilica membranes: M1/1 and M1/1-ref. (B) The ideal separation factors for the corresponding gas pairs. Permeance was measured at Δp = 0.2 MPa and T = 25°C.

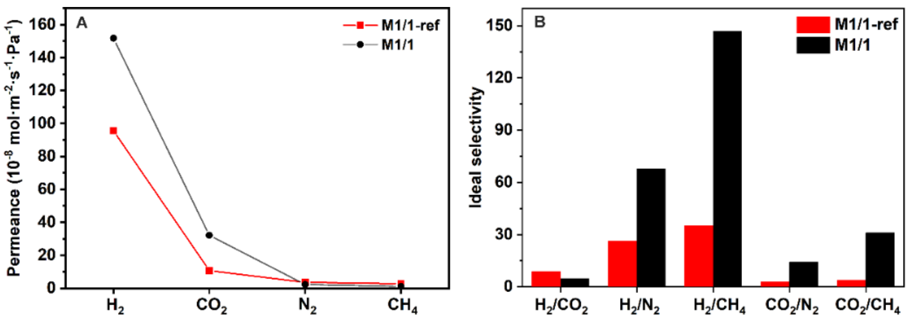

Fig. S13 (A) Single gas permeance of H_2, N_2, CO_2 and CH_4 through the as-prepared ZIF-8/ organosilica membranes: M1/1 and M1/1-ref. (B) The ideal separation factors for the corresponding gas pairs. Permeance was measured at Δp = 0.2 MPa and T = 150 °C.

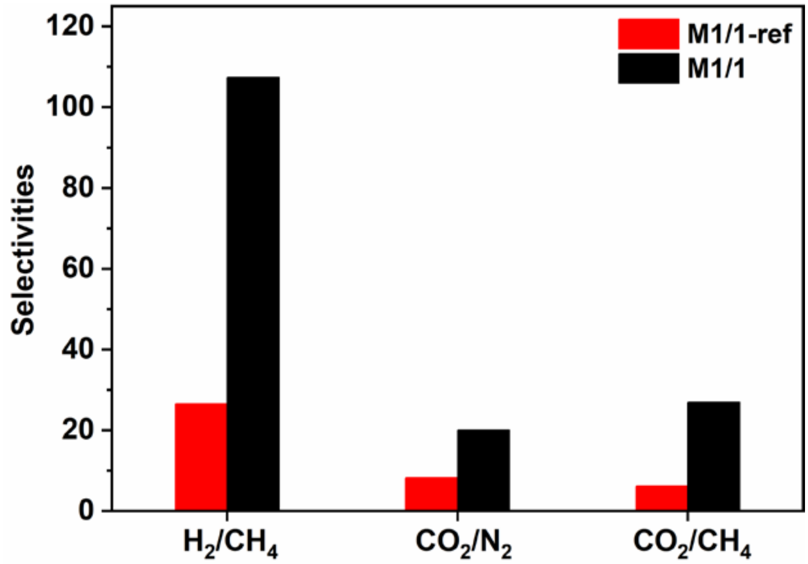

Fig. S14 Selectivities of H_2/CH_4, CO_2/N_2, and CO_2/CH_4 gas mixtures through the ZIF-8/organosilica membranes: M1/1 and M1/1-ref. Permeation was measured at Δp = 0.2 MPa and T = 25 °C.

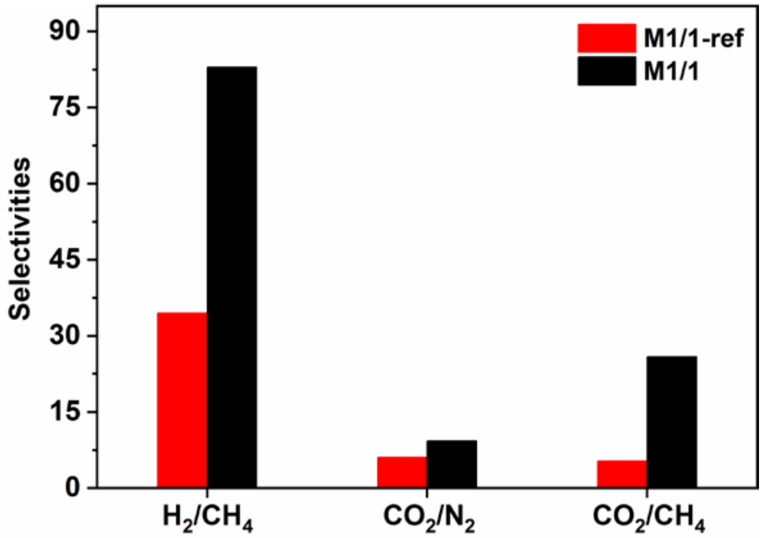

Fig. S15 Selectivities of H_2/CH_4, CO_2/N_2, and CO_2/CH_4 gas mixtures through the ZIF-8/organosilica membranes: M1/1 and M1/1-ref. Permeation was measured at Δp = 0.2 MPa and T = 150 °C.

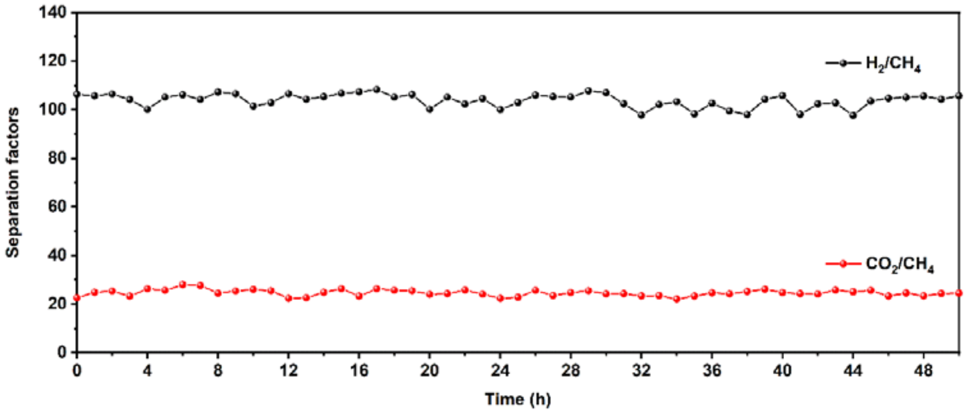

Fig. S16 Long-term separation performance of M1/1 membrane for an equimolar H_2/CH_4 or CO_2/CH_4 mixtures at room temperature and 0.2 MPa.

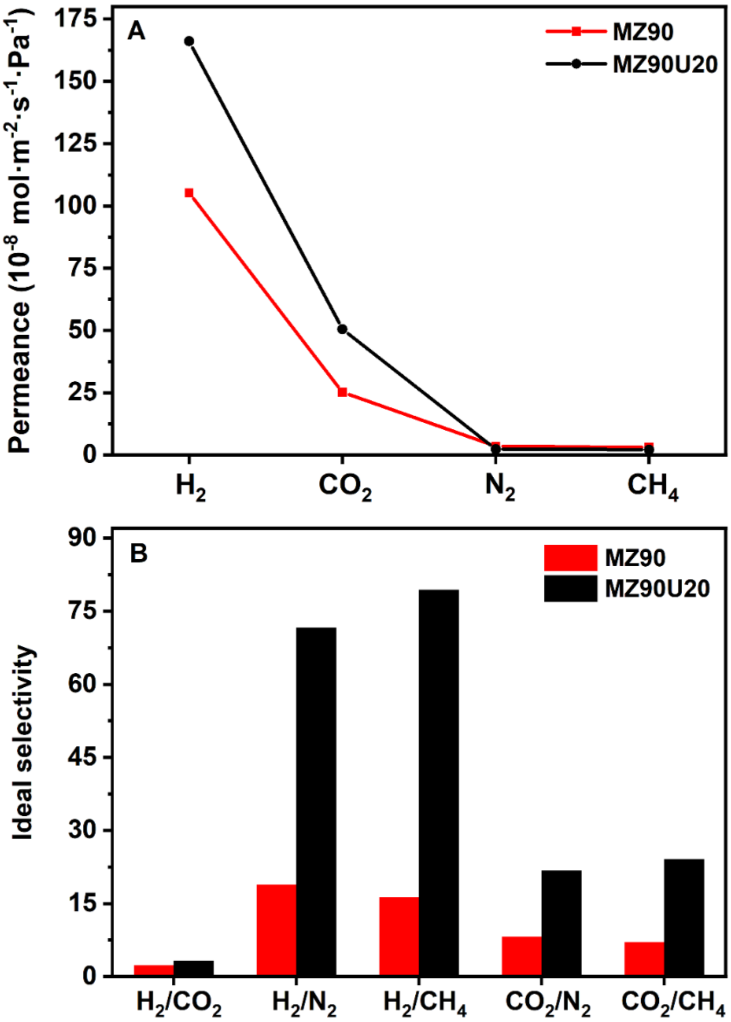

Fig. S17 Single gas permeance of H_2, N_2, CO_2 and CH_4 through the as-prepared ZIF-90/organosilica membranes: MZ90 (A) and MZ90U20 (B) The ideal selectivity for the corresponding gas pairs. Permeation was measured at $\Delta p = 0.2$ MPa and T = 25 °C**.**

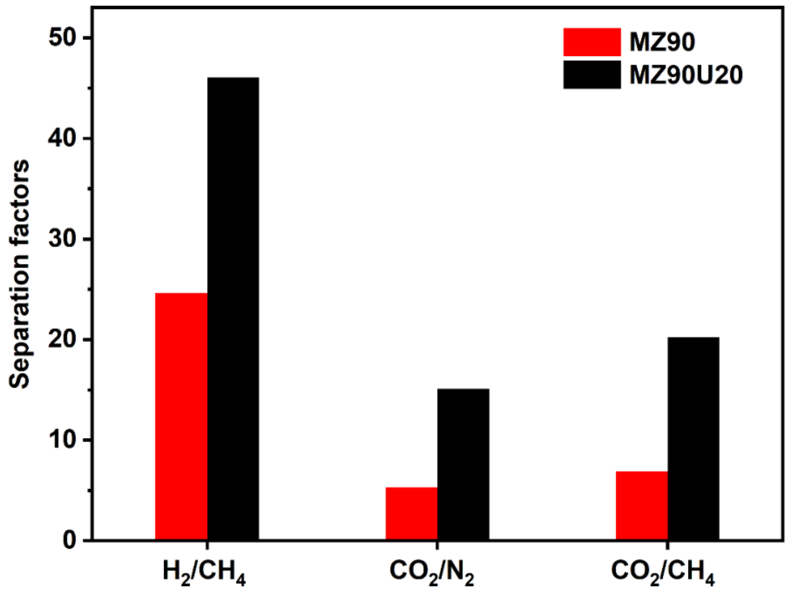

Fig. S18 Separation factors of H_2/CH_4, CO_2/CH_4 and CO_2/N_2 gas mixtures through the MZ90 and MZ90U20 membranes. Permeation was measured at Δp = 0.2 MPa and T = 25 °C.

Table S2 Comparison of gas separation performance of ZIF-8/organosilica membrane with other reported H_2-selective MOF membranes.

Membranes	Substrates	Thickness / μm	H_2 Permeance / ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	H_2 Permeability / barrer	H_2/CH_4 Selectivity
ZIF-7_{22}-8[1]	Al_2O_3 disks	0.45	2.7×10^{-8}	36.45	71
MIL-125-TG[2]	Al_2O_3 disks	2.54	2.05×10^{-7}	1562.1	40.7
ZIF-8[3]	Al_2O_3 tube	5	1.02×10^{-7}	1530	40.1
ZIF-67[4]	Al_2O_3 tube	5	227.5×10^{-9}	3412.5	45.4
ZIF-67[5]	Al_2O_3 disks	3	1.48×10^{-6}	13320	18
ZIF-95[6]	Al_2O_3 disks	0.6	9.65×10^{-7}	1737	64.3
ZIF-94[7]	Al_2O_3 disks	7.1	4.2×10^{-9}	89.46	136
ZIF-62 glass[8]	Al_2O_3 disks	70	1.9×10^{-8}	4156	50
ZIF-11/6FDA-DAM[9]	/	70	1.3×10^{-9}	272.45	32.82
ZIF-8/Matrimid[10]	/	/	/	100.2	79.3
UiO-66-NH_2/PIM-1[11]	/	80-100	$(1.1\text{-}0.9)\times10^{-8}$	2641	25.9
Ni^{2+}-$Ti_3C_2T_x$[12]	Al_2O_3 hollow fiber	2.7	9.52×10^{-8}	771.12	147.17

TMMOS/TEOS[13]	/	0.03	8.3×10^{-7}	74.7	140
APTES/glycidyl-POSS[13]	Al_2O_3 disks	/	1.41×10^{-8}	/	144.86
BTESE/MTES[14]	Al_2O_3 tubes	0.3	4.99×10^{-7}	499.1	73.6
BTESE/POSS[15]	Al_2O_3 disks	/	2.24×10^{-8}	/	109.28
ZIF-8/BTESE[16]	Al_2O_3 tubes	/	1.06×10^{-6}	/	35
M1/1-ref (this work)	Al_2O_3 tubes	0.25	1.08×10^{-6}	810	35.2
M1/1 (this work)	Al_2O_3 tubes	0.25	1.25×10^{-6}	937.5	165.5

Table S3 Comparison of gas separation performance of modified ZIF-8/organosilica membrane with other reported CO_2-selective hybrid membranes.

Membranes	Thickness / µm	CO_2 permeance / ($mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$)	CO_2 permeability / barrer	CO_2/CH_4 Selectivity
ZIF-7_{22}-8[1]	0.45	1.50×10^{-8}	20.25	24.5
ZIF-8/Matrimid[10]	/	/	37.5	25.9
ZIF-8/Pebax-2533[17]	/	/	158.4	27.7
ZIF-8@CNF[18]	/	/	550	36.6
ZIF-8/PIM-1[19]	/	/	9667	13.85
Pebax/ZIF-8[20]	/	/	102.4	23
Pebax/PSS-ZIF[21]	80	2.2×10^{-9}	528	36
ZIF-11/6FDA-DAM[9]	70	1.23×10^{-9}	257.5	31.02
ZIF-11/PSF[22]	/	/	22.14	42.7
ZIF-7-NH_2/Pebax[23]	/	/	96	40
ZIF-301/6FDA-DAM[24]	/	/	891	29.3
UiO-66-NH_2@ICA/ Matrimid[25]	/	/	40.1	64.7
UiO-66-PEI@pSBMA/ 6FDA-ODA[26]	/	/	185.12	60.32
UiO-66-PEI/ 6FDA-ODA[27]	1	9.61×10^{-9}	28.83	56.49
UiO-66-NH_2/PSF[28]	65	2.37×10^{-10}	43	24
MOF-199-NH_2/ 6FDA-ODA[29]	20-40	$(4.43\text{-}2.22)\times10^{-9}$	26.6	59.6
MIL-53-NH_2 /6FDA-DAM[30]		7.37×10^{-9}		28
APTES/glycidyl-POSS[13]	/	2×10^{-8}	/	48.3
	/	9.1×10^{-9}	/	93.8

BTESE/MTES[14]	0.3	3.53×10^{-7}	317.7	32.6
BTESE[31]	0.5	9.5×10^{-8}	142.5	91
BTESE/APTES [32]	0.5	8×10^{-7}	1200	70
MIL-53-NH_2/ BTESE[16]	/	1.44×10^{-7}	/	23.2
M1/1-ref (this work)	0.25	3.07×10^{-7}	230.54	10
M1/1 (this work)	0.25	3.27×10^{-7}	245.13	43

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