Supplementary Information

for

CO_2/N_2 separation properties of polyimide-based composite membranes comprising UiO-66 with various functionalities

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Table S1 Elemental Analysis of UiO-66 and its derivative

Sample	C (%)	H (%)	N (%)	Br (%)[a]
UiO-66	29.75	2.121	0.899	-
UiO-66-NH_2	28.76	2.833	3.845	-
UiO-66-Br	22.93	1.772	0.259	9.262
UiO-66-$(OH)_2$	28.77	1.811	1.834	-

[a] Estimated from EDX analysis (Figure S1)

Table S2 Theoretical amount of UiO-66 and its derivative[(a)]

Sample[(b)]	M_w (g/mol)	Zr (%)	C (%)	H (%)	O (%)	N (%)	Br (%)
UiO-66	1664.1	32.89	34.64	1.695	30.77	0	0
UiO-66-NH_2	1712.1	31.96	33.67	1.413	28.03	4.91	0
UiO-66-Br	2137.4	25.61	26.97	1.037	23.95	0	22.43
UiO-66-$(OH)_2$	1856.0	29.48	31.06	1.520	37.93	0	0

[(a)] Due to the potential presence of residual solvents or water in MOF, it is possible that the deviation between experimental and theoretical value can be observed. Nevertheless, the trend in C(%), H(%), N(%) are generally consistent across all UiO-66 framework.

[(b)] Molecular formula: $Zr_6C_{48}H_{28}O_{32}$ (UiO-66); $Zr_6C_{48}H_{24}O_{30}N_6$ (UiO-66-NH_2); $Zr_6C_{48}H_{22}O_{32}Br_6$ (UiO-66-Br); $Zr_6C_{48}H_{28}O_{44}$ (UiO-66-$(OH)_2$)

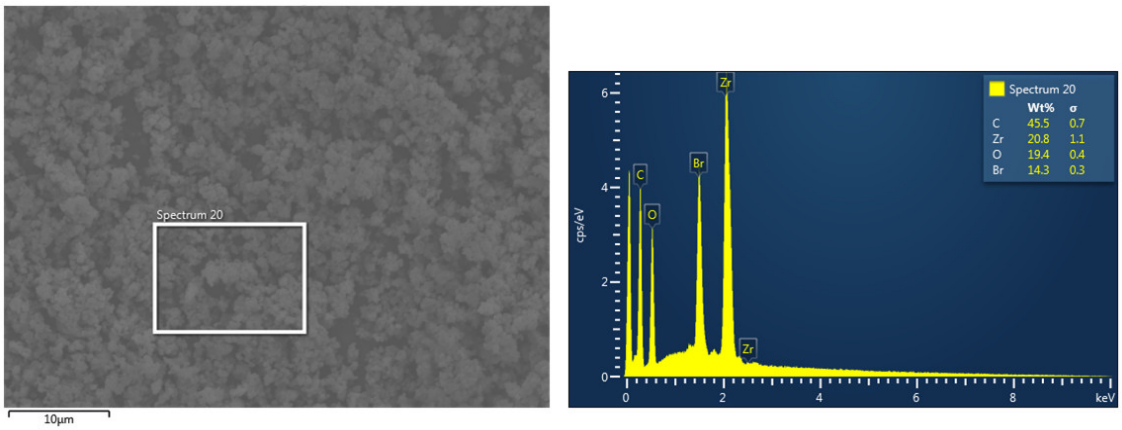

Figure S1 EDX analysis of UiO-66-Br

Table S3 Fitting Parameters for CO_2 and N_2 for UiO-66 and its derivative at 25 °C

Unit of P = bar; Unit of q = mmol/g

$$q = \frac{q_{sat} bp}{1 + bp}$$

Sample	*gas*	q_{sat} *(bar)*	*b* (bar^{-1})	R^2 value
UiO-66	CO_2	6.119	0.2734	1
	N_2	6.119	0.01543	0.992
UiO-66-NH_2	CO_2	5.376	0.359	0.9998
	N_2	5.376	0.01673	0.964
UiO-66-Br	CO_2	3.302	0.837	0.9998
	N_2	3.302	0.03773	0.9972
UiO-66-$(OH)_2$	CO_2	2.151	1.040	0.9996
	N_2	2.151	0.0271	0.9889

Table S4 Fitting Parameters for CO_2 and N_2 for UiO-66 and its derivative at 35 °C

Unit of P = bar; Unit of q = mmol/g

$$q = \frac{q_{sat} bp}{1 + bp}$$

Sample	*gas*	q_{sat} *(bar)*	*b* (bar^{-1})	R^2 value
UiO-66	CO_2	5.404	0.2357	0.9998
	N_2	5.404	0.01432	0.9894
UiO-66-NH_2	CO_2	5.528	0.2526	0.9996
	N_2	5.528	0.01228	0.9818
UiO-66-Br	CO_2	3.405	0.5721	0.9995
	N_2	3.405	0.02908	0.9947
UiO-66-$(OH)_2$	CO_2	2.065	0.7765	0.9994
	N_2	2.065	0.02145	0.9800

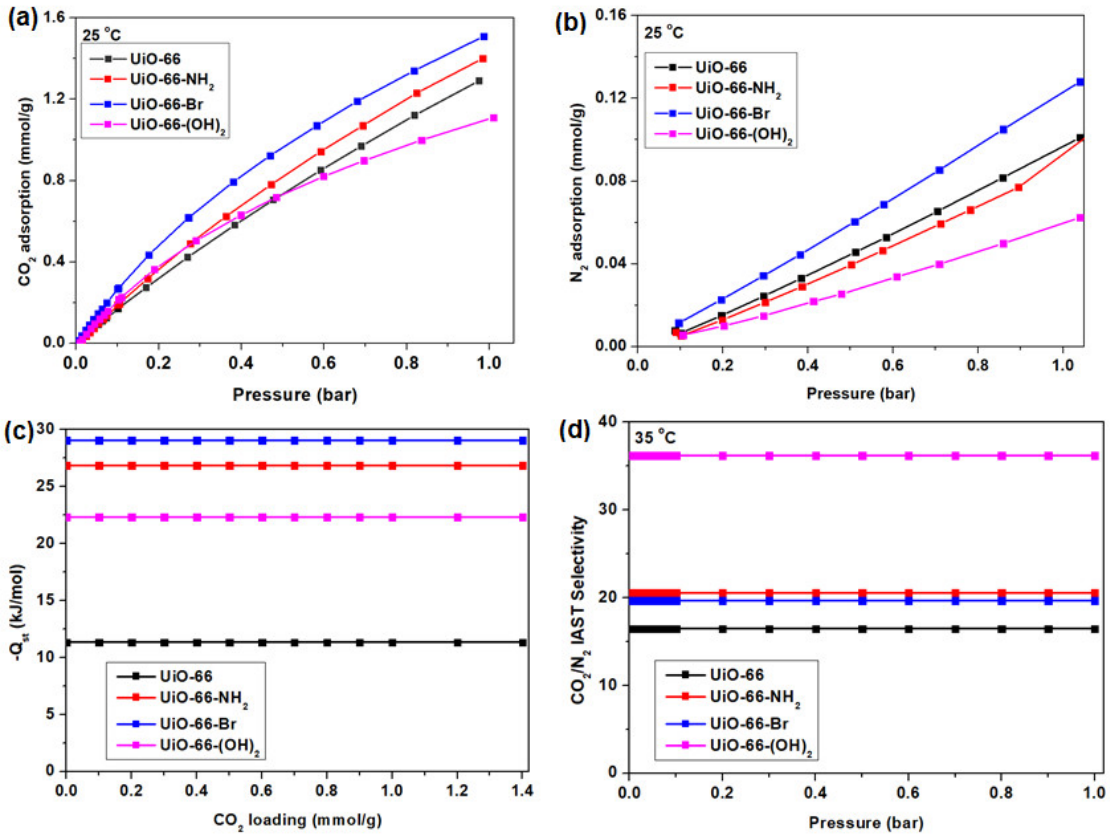

Figure S2 (a) CO_2 adsorption at 25 °C; **(b)** N_2 adsorption at 25 °C; **(c)** Isosteric heat of adsorption of CO_2 and **(d)** CO_2/N_2 IAST selectivity (feed mixture of CO_2/N_2 = 20/80) of for UiO-66, UiO-66-NH_2, UiO-66-Br and UiO-66-$(OH)_2$

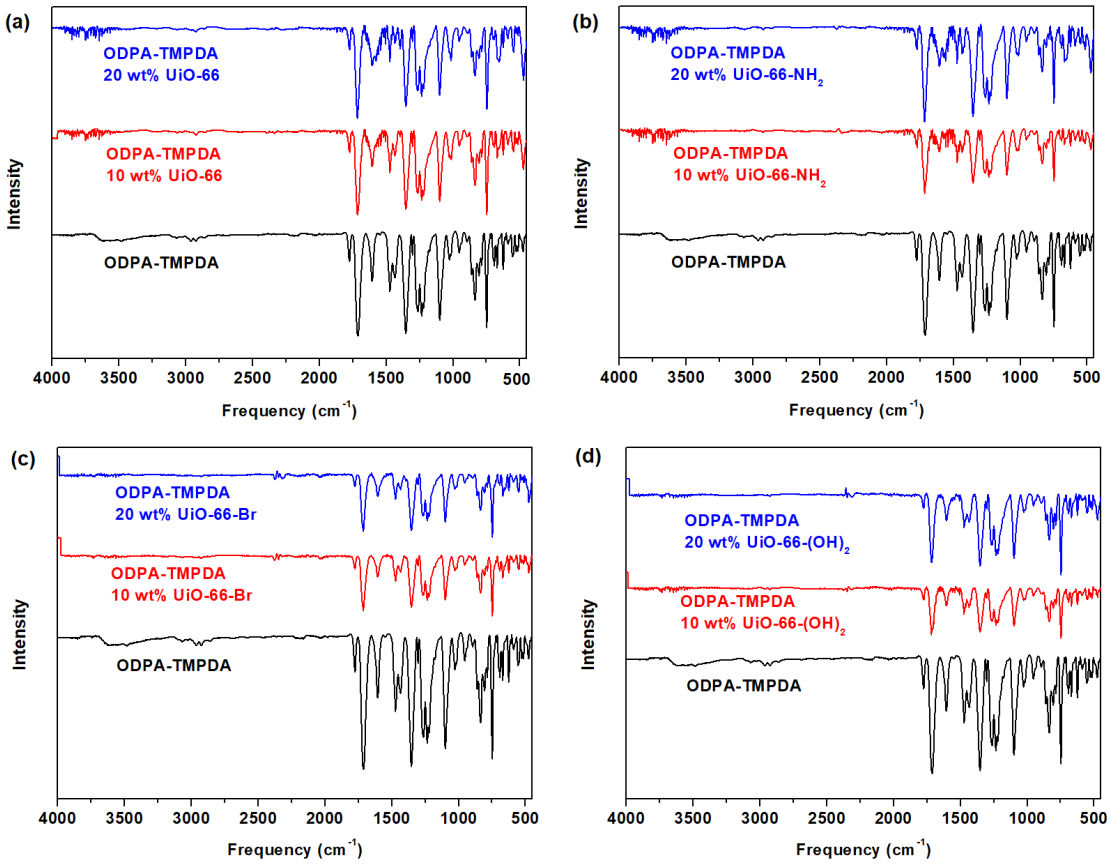

Figure S3 FT-IR spectrum of mixed-matrix membrane

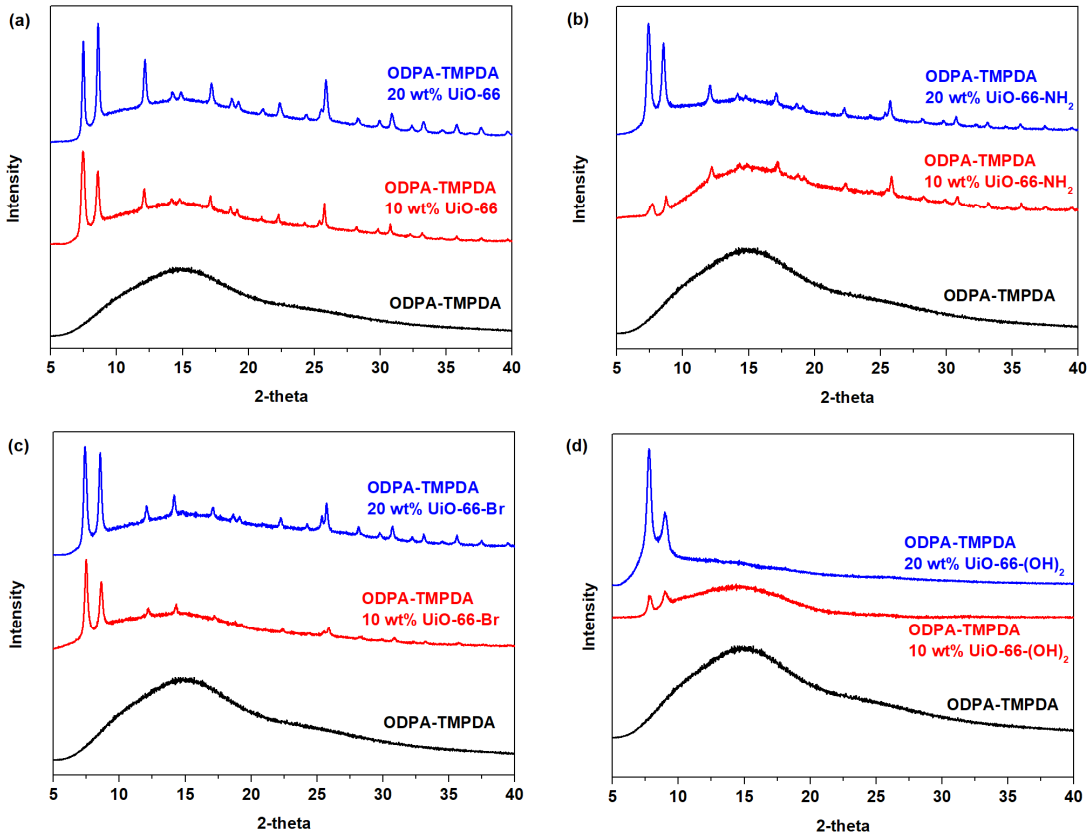

Figure S4 XRD analysis of mixed-matrix membrane

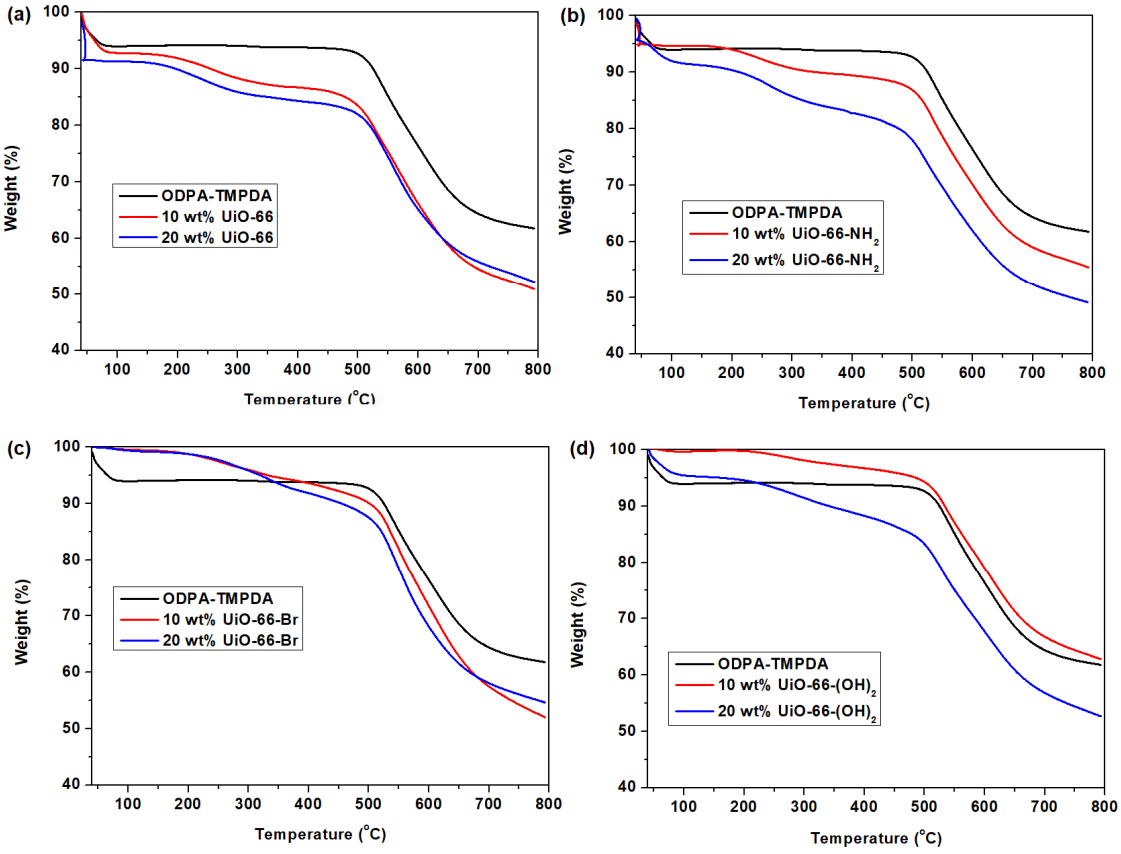

Figure S5 TGA analysis of mixed-matrix membrane

Table S5 Fitting Parameters for CO_2 and N_2 for polymeric and mixed-matrix membranes at 35 °C

Unit of P = bar; Unit of q = mmol/g

$$q = \frac{q_{sat} bp}{1 + bp}$$

Sample	*gas*	q_{sat} *(bar)*	*b* (bar^{-1})	R^2 value
ODPA-TMPDA	CO_2	1.444	0.9832	0.9996
	N_2	1.017	0.02502	0.9862
20 wt% UiO-66	CO_2	1.611	0.6785	0.9999
	N_2	0.5807	0.04649	0.9778
20 wt% UiO-66-NH_2	CO_2	1.446	0.6945	0.9999
	N_2	0.1717	0.1365	0.9869
20 wt% UiO-66-Br	CO_2	1.381	0.7766	0.9999
	N_2	1.471	0.01143	0.9451
20 wt% UiO-66-$(OH)_2$	CO_2	1.373	0.8565	0.9998
	N_2	4.263	0.005002	0.9847

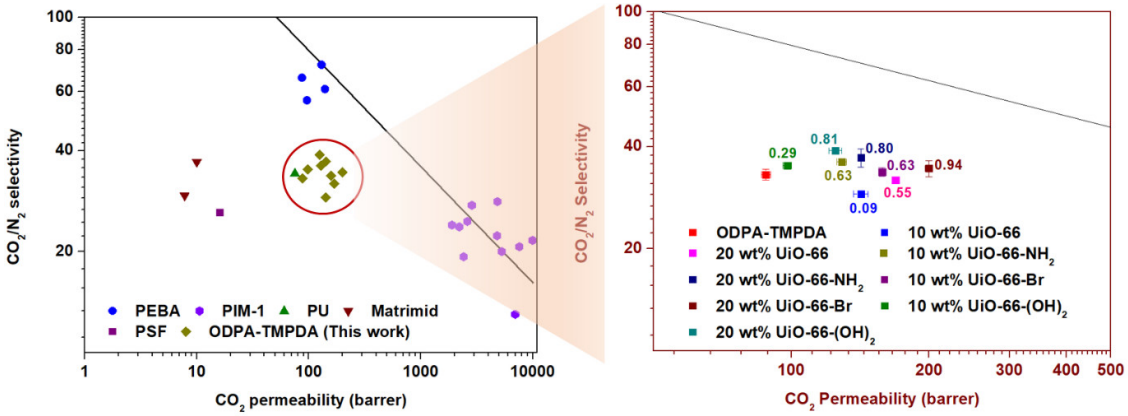

Figure S6 Comparison of the gas permeation data with the upper bound limit for CO_2/N_2 constructed in 2008. The numerical number indicated in the figure illustrate the value of F_{index} as described in Section 2.4.5. The data used in this plot is provided in **Table 4**.