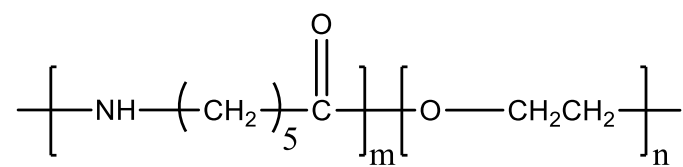


## **Supporting Information**

### **Mixed matrix membranes based on metal-organic frameworks with tunable pore size for CO<sub>2</sub> separation**

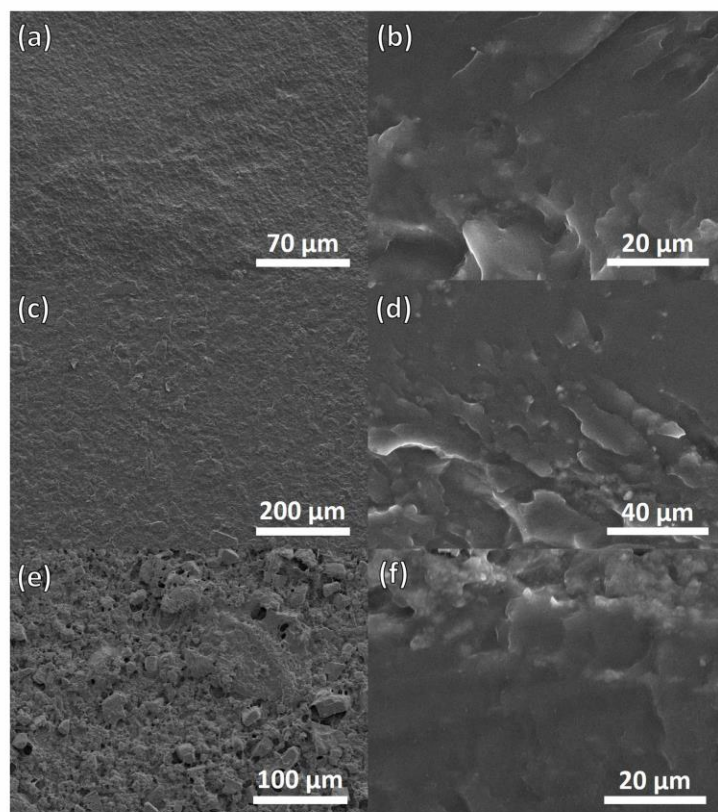
Lili Fan, Zixi Kang,\* Yuting Shen, Sasa Wang, Haoru Zhao, Hanyi Sun, Xueting Hu, Haixiang Sun, Rongming, Wang and Daofeng Sun\*



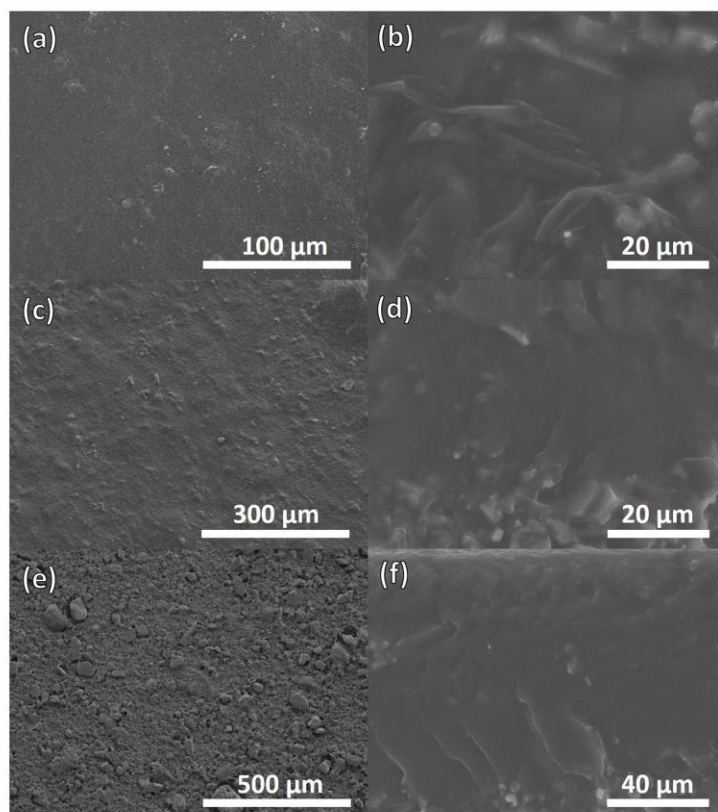
**Figure S1** The structural formula of the polymer Pebax used in this work.



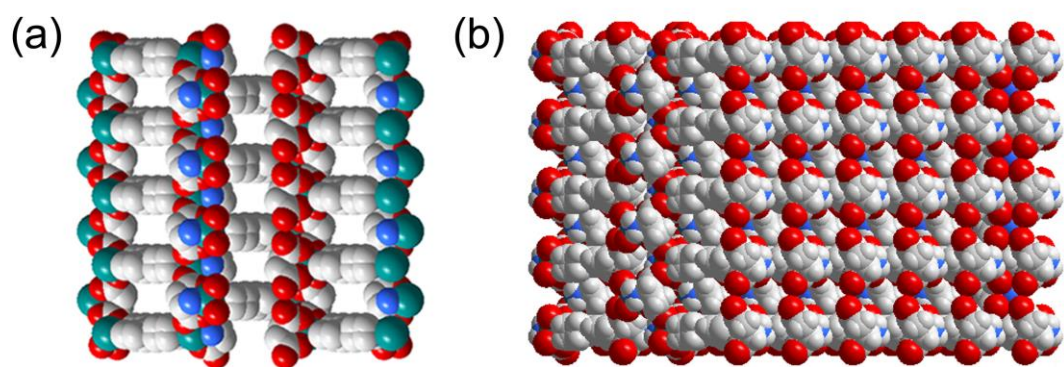
**Figure S2** Optical image of the pure polymer Pebax membrane.



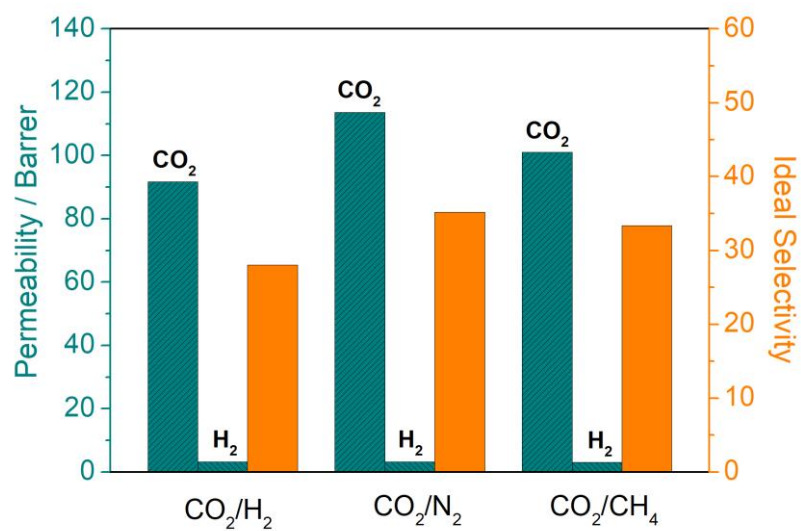
**Figure S3** Top view and cross-section SEM images of (a) (b) Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax-10, (c) (d) Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax-20 and (e) (f) Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax-30.



**Figure S4** Top view and cross-section SEM images of (a) (b) Ni<sub>2</sub>(L-asp)<sub>2</sub>pz@Pebax-10, (c) (d) Ni<sub>2</sub>(L-asp)<sub>2</sub>pz@Pebax-20 and (e) (f) Ni<sub>2</sub>(L-asp)<sub>2</sub>pz@Pebax-30.



**Figure S5** 3D structure of  $\text{Ni}_2(\text{L-asp})_2\text{bipy}$  (Ni cyan, C gray, N blue and O red;) viewed along (a)  $[0\ 1\ 0]$  and (b)  $[1\ 1\ 0]$ .



**Figure S6** The binary gas mixture (CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>) permeability and corresponding selectivity of Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax-20 membrane.

**Table S1** Pure component CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> permeation properties of Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax membranes measured at 1 atm pressure and 25 °C.

Membrane	Permeability (Barrer)				Selectivity		
	CO <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Pebax	55.85	32.11	1.39	1.56	1.729	40.18	35.81
Ni <sub>2</sub> (L-asp) <sub>2</sub> bipy@Pebax-10	107.5	5.427	4.571	5.004	19.81	23.52	21.48
Ni <sub>2</sub> (L-asp) <sub>2</sub> bipy@Pebax-20	120.2	3.656	3.052	3.243	32.88	39.38	37.06
Ni <sub>2</sub> (L-asp) <sub>2</sub> bipy@Pebax-30	82.31	2.72	1.571	2.353	30.26	52.39	34.98



**Table S2** Pure component H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> permeation properties of Ni<sub>2</sub>(L-asp)<sub>2</sub>pz@Pebax membranes measured at 1 atm pressure and 25 °C.

Membrane	Permeability (Barrer)				Selectivity		
	CO <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
Pebax	55.85	32.11	1.39	1.56	1.729	40.18	35.81
Ni <sub>2</sub> (L-asp) <sub>2</sub> pz@Pebax-10	46.10	4.603	2.487	3.820	10.01	18.54	12.07
Ni <sub>2</sub> (L-asp) <sub>2</sub> pz@Pebax-20	89.66	2.896	3.105	3.875	30.96	28.88	23.14
Ni <sub>2</sub> (L-asp) <sub>2</sub> pz@Pebax-30	80.83	2.478	2.662	3.431	32.62	30.36	23.56

**Table S3** Binary gas mixture (CO<sub>2</sub>/H<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>) permeation properties of Ni<sub>2</sub>(L-asp)<sub>2</sub>bipy@Pebax-20 membrane measured at 1 atm pressure and 25 °C.

Membrane	Permeability (Barrer)						Selectivity		
	CO <sub>2</sub> /H <sub>2</sub>		CO <sub>2</sub> /N <sub>2</sub>		CO <sub>2</sub> /CH <sub>4</sub>		CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
	CO <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>			
Ni <sub>2</sub> (L-asp) <sub>2</sub> bipy@Pebax-20	91.7	3.27	113.6	3.23	101.0	3.03	28.04	35.17	33.33

**Table S4** Comparison of gas separation performance of this work with those of reported MOF based MMMs.

membrane	Temp	Pressure (bar)	Loading	CO <sub>2</sub> permeability	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	reference
Pebax-1657/4A Zeolite	25	24.5	10%	97	-	54	26.5	[1]
Pebax-1657/4A Zeolite	25	24.5	30%	155.8	-	12.9	7.9	[1]
Pebax-1657/GTA	25	4	80%	1200	29	51	9	[2]
IL-Pebax-1657/ZIF-8	30	2	8%	261	10	71	36	[3]
Pebax/PDA/ZIF-8-15 (dry)	25	1	15%	220.06	-	56.14	-	[4]
Pebax/PDA/ZIF-8-15 (humidified)	25	1	15%	267.74	-	62.65	-	[4]
MWCNTs/Pebax	30	10	5%	265.15	6.4	58.5	-	[5]
MWCNTs/Crosslinked Pebax	30	10	5%	17.47	2.4	84.5	-	[5]
[bmim][Tf2N]/ZIF-8/Pebax 1657	25	1	15%	104.9	10	83.9	34.7	[6]
UiO-66-PEBA (humid)	25	3	10%	139.7	-	61.1	-	[7]
UiO-66-PEBA-NH2 (humid)	25	3	10%	130.2	-	72.2	-	[7]
ZIF-7/Pebax-1657	25	3.75	22%	111	-	97	30	[8]
Pebax-1657/PEG50	30	0.6	50%	151	10.8	47	15.5	[9]
Pebax-1657/PEG-DME	30	0.3	50%	606	15.1	43	-	[10]
Pebax/CuBTC/PEG-ran-PPG (PEG-ran-PPG ) /20% (CuBTC)	30	15	32.76%	1163.8	-	-	32.7	[11]
(Pebax 1657)/SAPO-34	35	7	50%	338	9	54	18	[12]
Pebax	25	1	-	50.5	6.38	79.5	16.7	<b>This work</b>
Ni <sub>2</sub> (L-asp) <sub>2</sub> bipy@Pebax-20	25	1	20%	120.2	32.88	39.38	37.06	<b>This work</b>

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