Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Molecular insight into CO_2/N_2 separation of 2D-COF supported ionic liquid membrane

Kuiyuan Zhang[a,#], Lixia Zhou[b,#], Zichang Wang[a], Haiyang Li[a], Youguo Yan[a], Jun Zhang[a,*]

[a] School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao 266000, People's Republic of China

[b] College of Science, China University of Petroleum, Qingdao 266000, People's Republic of China

Corresponding author:

E-mail address: zhangjun.upc@gmail.com (Jun Zhang).

[#] These authors contributed equally to this work.

1. Force field parameters

1.1 The Lennard-Jones (LJ) parameters and charges for [BMIM][BF_4]

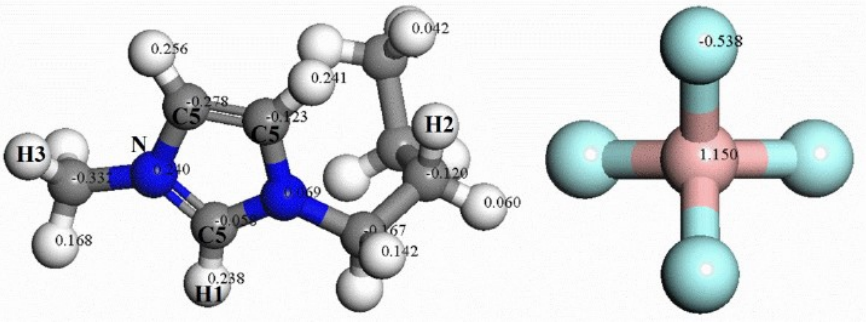

Fig. S1 Partial atomic charges on the $[BMIM]^+$ and $[BF_4]^-$. Atoms are labelled for the bonded-term parameters.

Table S1 LJ parameters of [BMIM][BF_4] employed in this work

Element	N	C5	C3	C2	H1	H2	H3	B	F
ε (kcal/mol)	0.170	0.086	0.011	0.011	0.015	0.0157	0.0157	0.095	0.061
σ (Å)	3.250	3.400	3.400	3.400	2.450	2.650	2.500	3.581	3.118

1.2 The Lennard-Jones (LJ) parameters and charges for gas molecules

Table S2 Partial atomic charges and Lennard-Jones parameters for gas molecules

	CO_2		N_2	
	C	O	N	Center of Mass
ε (kcal/mol)	0.0559	0.160	0.0728	0
σ (Å)	2.757	2.565	3.318	0
q / |e|	0.6512	-0.3256	-0.4084	0.8096

1.3 The Lennard-Jones (LJ) parameters and charges for gas molecules COF membrane and helium sheet

Table S3 Lennard-Jones parameters for COF membrane and helium sheet

Element	C1	O	C2	H	N	HN	He
ε(kcal/mol)	0.0700	0.2280	0.0700	0.0300	0.1700	0.0300	0.0203
σ (Å)	3.5500	2.8598	3.5500	2.4200	3.2500	2.4200	2.600

2. Calculation method for the interaction between the anion and cation

The potential energy was calculated as the sum of the non-bonded interaction, Van der Walls (VDW) and Coulomb interaction, using the following equation:

$$V = \sum_j 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_j \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

i indexes are cations (anions) and j indexes are the membrane's atoms. The first term is

the VDW interaction considering Lenard-Jones (LJ) potential and the second term corresponds to the Coulomb force interaction. And we averaged this interaction energy.

3.The permeability of COF membrane without coated IL.

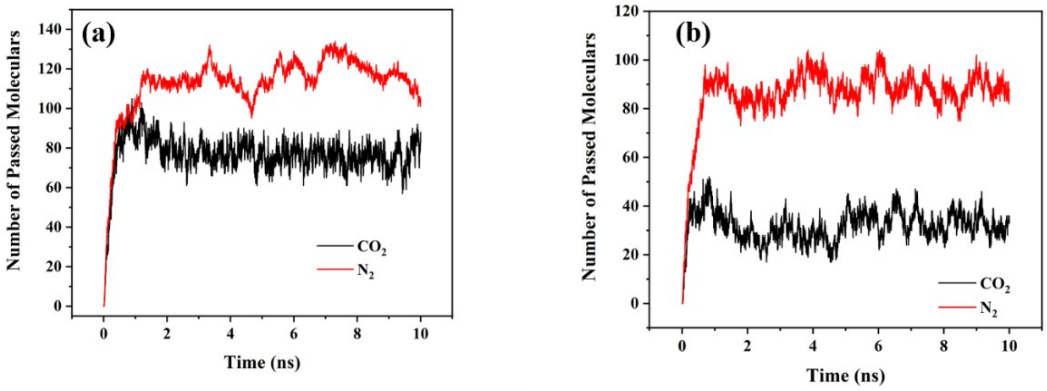

Fig. S2. The number of passed gas (CO_2/N_2) molecules through COF membrane without IL. (a) tetralayers (b) hexalayers

4. The point density distribution diagram of CO_2 passing through the pore.

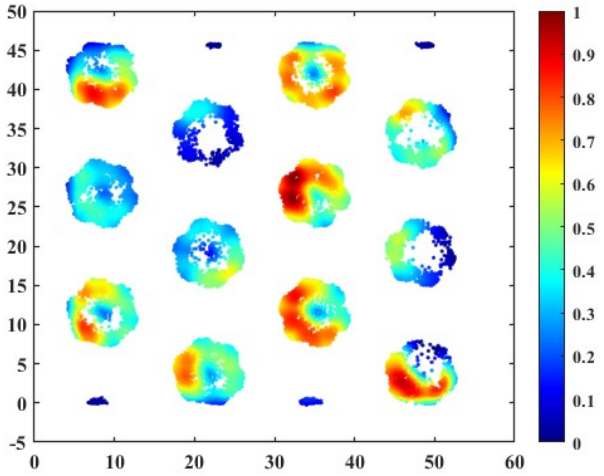

Fig. S3. The point density distribution diagram of CO_2 passing through the pore of bilayers membranes with 8 thick IL

5. The point density distribution diagram of CO_2 dissolved into the ionic liquid.

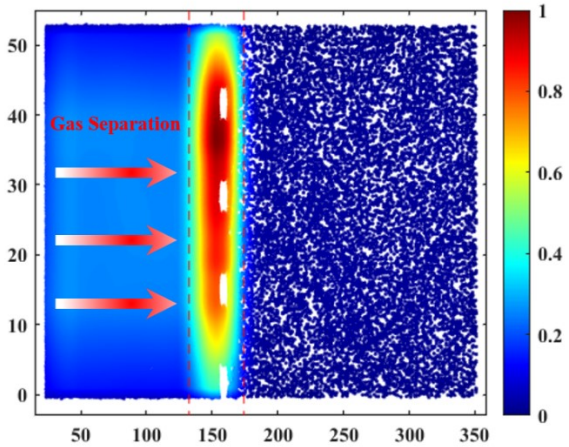

Fig. S4. The point density distribution diagram of CO_2 dissolved into the ionic liquid.

6. Side view of the distribution $[BF_4]^-$ in the pores of bilayers membrane.

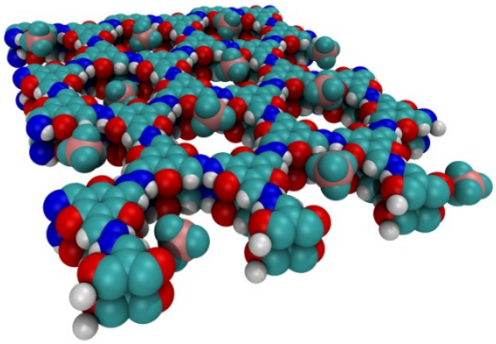

Fig. S5 Side view of the equilibration configuration that the anions partially enter the pore.

7. The point density distribution diagram of $[BF4]^-$ in pores

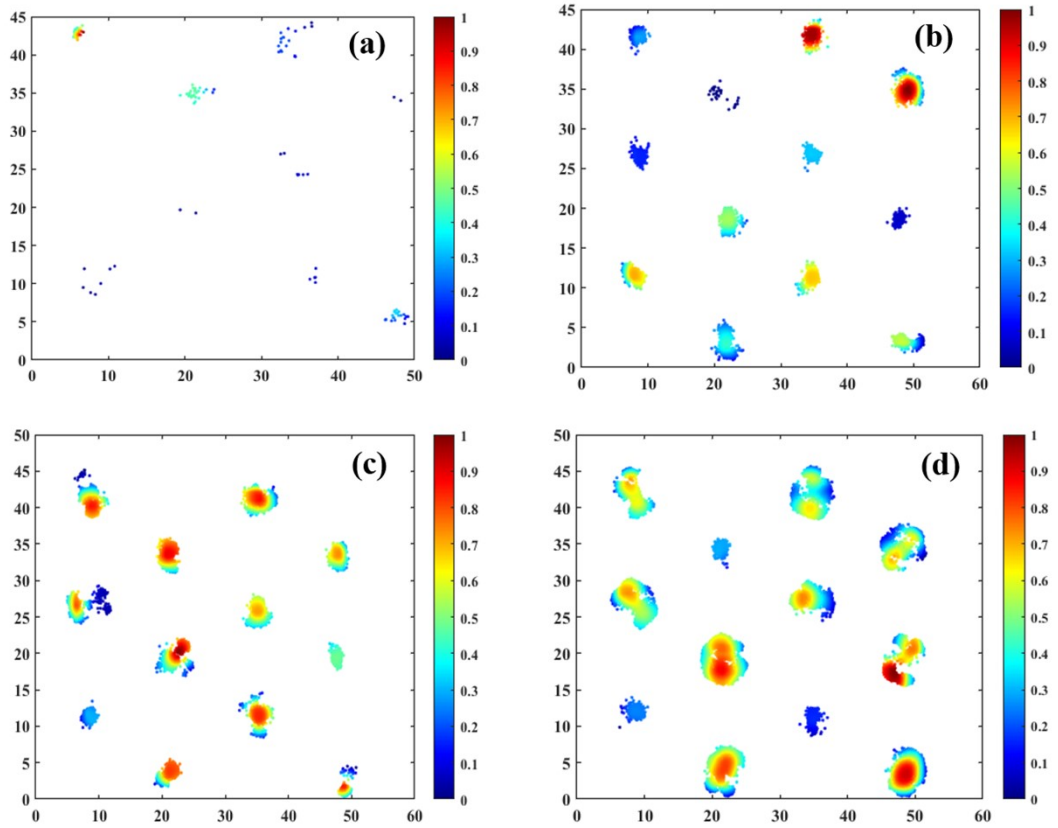

Fig. S6. The point density distribution diagram of $[BF_4]^-$ in pores of different layer membranes. (a) monolayer, (b) bilayers, (c) tetralayers, (d) hexalayers.

8. The equilibration configuration of bilayers COF membranes coated with 4 Å and 8 Å thick IL.

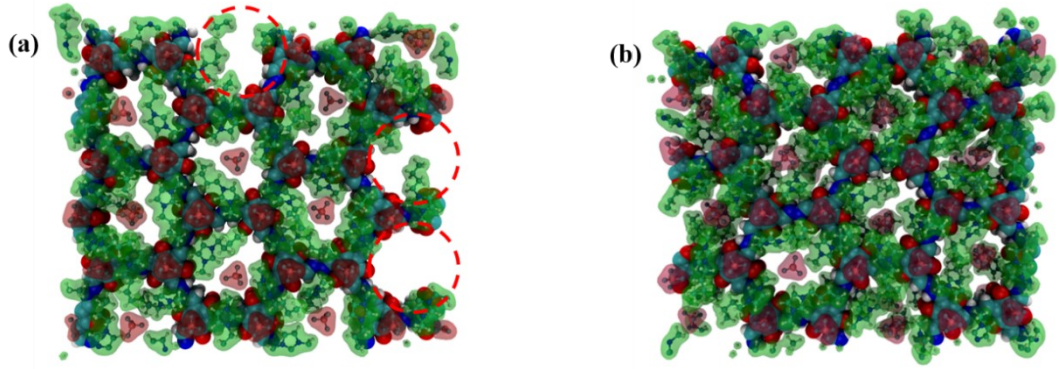

Fig. S7. The top view of bilayers COF membrane with different thick IL ([BMIM][BF4]). (a) The thickness is 4 Å. (b) The thickness is 8 Å. The IL was displayed as stick and ball model. The cations are highlighted with a green edge and the anions with a red edge.

9. The calculation details for PMF profile

In order to probe forces governing the gas transport across an anion-gated pore, the potential of mean forces (PMFs) for gas molecules were studied (free energy). The PMFs were determined in umbrella sampling (US) calculations. The reaction

coordinate was partitioned into 19 windows of 1 Å widths. Confinement potentials were introduced in the form of harmonic restraints with a force constant of k=1 kcal/(mol·Å^2), and each window was run for 2 ns. The weighted histogram analysis method (WHAM) was used to reconstruct the PMF.

10. The preparation of different thicknesses of IL film in the COF membrane surface.

Three IL boxes with area of 45.72 Å × 53.08 Å and different thicknesses of 4 Å, 8 Å, 12 Å and 16 Å were constructed based on the IL bulk density. Corresponding, 32, 64, 96 and 128 IL pairs were contained in these boxes, respectively. Then the IL boxes were putted onto the COF membrane. Next, the coated IL was heated to 500 K in 1 ns firstly, then insulated for 1 ns, and cooled to 298 K in 1 ns finally. After annealing, the equilibrium configurations could be obtained.

11. The gas permeability and solubility of COF-SILM.

Table S4. The CO2 permeability of membrane with different layer numbers coated 8 Å thickness IL. (10^{6}GPU)

Layers / Permeability / Time	1	2	4	6
1	**5.136**	**2.317**	**1.358**	**1.019**
2	**5.329**	**2.132**	**1.448**	**0.945**
3	**5.097**	**2.247**	**1.321**	**1.057**

Table S5. The N2 permeability of membrane with different layer numbers coated 8 Å thickness IL. (10^{6}GPU)

Layers / Permeability / Time	1	2	4	6
1	**0.745**	**0.145**	**0.036**	**0.024**
2	**0.712**	**0.101**	**0.040**	**0.027**
3	**0.794**	**0.174**	**0.037**	**0.022**

Table S6. The CO2 permeability of membrane with different layer numbers without IL. (10^6GPU)

Layers / Permeability / Time	2	4	6
1	**9.661**	**7.823**	**3.872**
2	**9.892**	**7.274**	**4.317**
3	**9.021**	**7.736**	**4.093**

Table S7. The N2 permeability of membrane with different layer numbers without IL. (10^6GPU)

Layers / Permeability / Time	2	4	6
1	**9.962**	**9.973**	**7.735**
2	**10.332**	**9.684**	**7.511**
3	**10.112**	**9.752**	**7.512**

Table S8. The CO2 permeability of the bilayer COF membrane with different thickness of IL. (10^6GPU)

Thickness / Permeability / Time	4	8	12	16
1	**3.607**	**2.317**	**1.467**	**0.753**
2	**3.739**	**2.132**	**1.371**	**0.796**
3	**3.712**	**2.247**	**1.410**	**0.739**

Table S9. The N2 permeability of the bilayer COF membrane with different thickness of IL (10^6GPU)

Thickness / Permeability / Time	4	8	12	16
1	**2.920**	**0.145**	**0.051**	**0.024**
2	**3.058**	**0.101**	**0.039**	**0.029**
3	**3.197**	**0.174**	**0.064**	**0.021**

Table S10. The number of CO2 molecules absorbed in different thick IL

Thickness / Number / Time	4	8	12	16
1	**41**	**67**	**80**	**94**
2	**38**	**58**	**75**	**92**
3	**36**	**50**	**83**	**95**

Table S11. The number of N2 molecules absorbed in different thick IL

Thickness / Number / Time	4	8	12	16
1	**10**	**12**	**15**	**18**
2	**9**	**11**	**14**	**17**
3	**9**	**12**	**14**	**17**