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

Two-Dimensional Diamine-Linked Covalent Organic Frameworks for CO_2/N_2 Capture and Separation: Theoretical Modeling and Simulations

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Supporting Information

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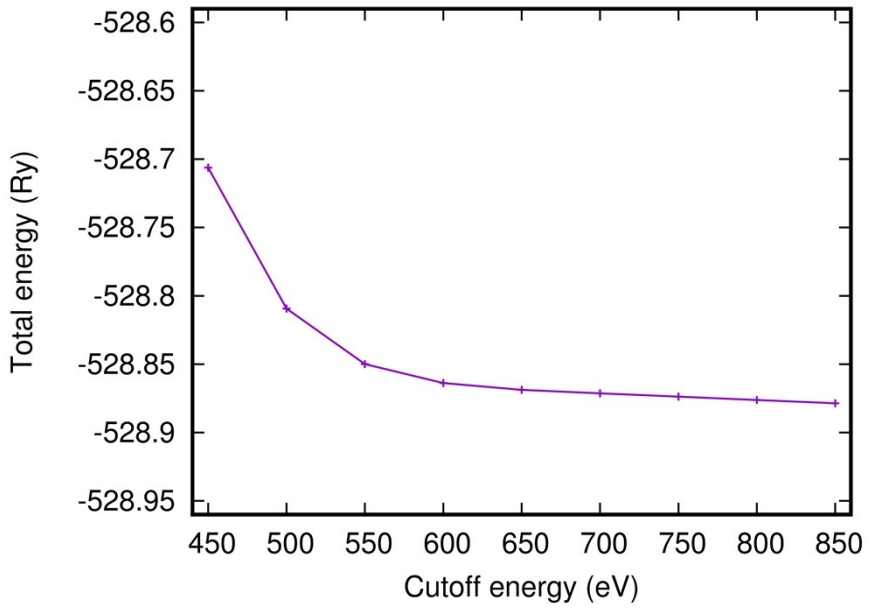

Fig. S1. Total energy of IPB-1H tested against various cutoff energies. The energy convergence was achieved and a cutoff energy of 700 eV was considered as the best choice in term of computational efficiency

Table S1. Total energy of IPB-1H tested against various Monkhorst–Pack k-point grids

k-point grids	Total Energy (Ry)
1 × 1 × 1	-528.87167360
2 × 2 × 1	-528.87133963
3 × 3 × 1	-528.87133880
4 × 4 × 1	-528.87133921
5 × 5 × 1	-528.87134026
6 × 6 × 1	-528.87133921
7 × 7 × 1	-528.87133750

*By considering the energy fluctuation, the k-point grids of 5 × 5 × 1 was considered as the best choice in term of computational efficiency.

Table S2. Structural comparison of IPB-1H between PBE and PBE0 functionals (GGA and hybrid correlation methods, respectively)

Geometry Parameters	PBE	PBE0
Cm – Hz	1.12 Å	1.11 Å
Nf – Nf	1.40 Å	1.39 Å
Cm – Nf	1.46 Å	1.45 Å
Cb – Cm	1.52 Å	1.51 Å
Cb – Ch	1.41 Å	1.40 Å
Ch – Hb	1.10 Å	1.09 Å
Nf – Hn	1.03 Å	1.02 Å
Cb – Ch – Cb	121.00°	120.97°
Ch – Cb – Ch	118.97°	119.05°
Cb – Cm – Nf	110.97°	111.23°
Ch – Cb – Cm	120.53°	120.39°
Cb – Ch – Hb	119.39°	118.63°
Cm – Nf – Hn	110.71°	111.32°
Cm – Nf – Nf	118.30°	118.19°
Hb – Ch – Cb – Ch	179.14°	179.09°
Ch – Cb – Ch – Cb	0.57°	0.34°
Cm – Nf – Nf – Cm	46.41°	46.55°
Hn – Nf – Nf – Hn	150.35°	148.00°
Hz – Cm – Nf – Hn	179.53°	179.69°
Hy – Cm – Nf – Hn	62.84°	63.40°

*Both functionals produced a similar molecular geometry. The unit cell of IPB-1H and its partial atomic labeling are given by the following figure.

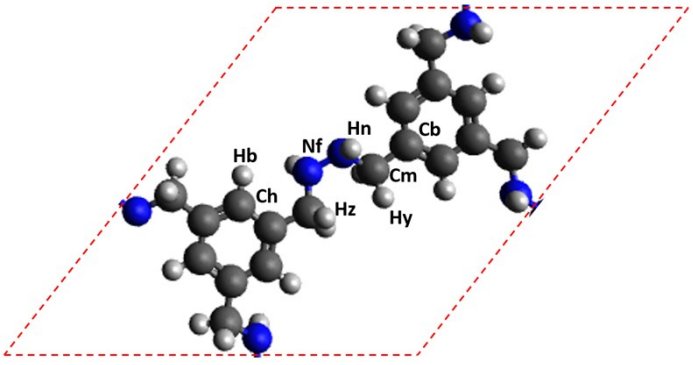

Table S3. Atomic charges of 2D-COFs used for MD simulations

IPB-1H		IPB-2H	
Atom Type*	**Charge (e)**	**Atom Type***	**Charge (e)**
Nf	−0.1250	Nf	−0.1426
Hn	0.0986	Hn	0.1039
Cm	0.0052	Cm	0.0160
Hz	0.0168	Hm	0.0277
Hy	0.0301	Hb	0.0300
Hb	0.0236	Cb	0.0100
Cb	0.0026	Ch	−0.0497
Ch	−0.0519	Cn	0.0380
		Cp	−0.0590
		Hp	0.0285

*Atom type (labeling) description is shown in Fig. 2 of the main text

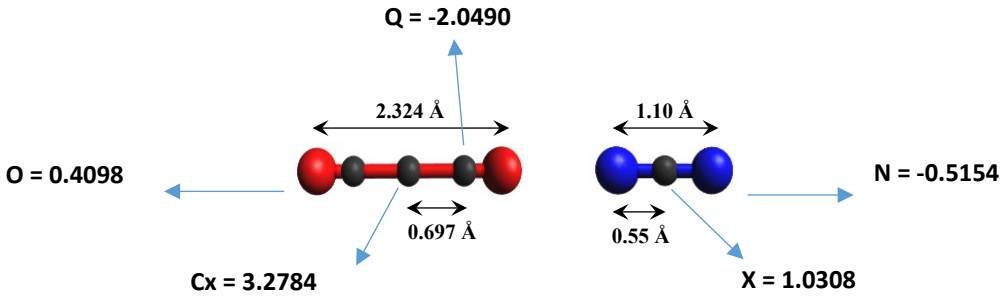

Fig. S2. Molecular representation of CO_2 and N_2 molecules with atom labeling and corresponding charges (e). Cx is the symbol of carbon atom, and Q is a point charge representing the C–O bond of CO_2 molecule. X is a point charge representing the N–N bond of the N_2 molecule

Table S4. ILJ parameters used for 2D-COFs – CO_2/N_2 MD simulations

Interacting Molecules	IPB-1H				IPB-2H			
	Pair	ε (meV)	r_0 (Å)	β	Pair	ε (meV)	r_0 (Å)	β
$CO_2 - CO_2$	Cx – Cx	3.416	3.317	9.00	Cx – Cx	3.416	3.317	9.00
	O – O	5.519	3.653	9.00	O – O	5.519	3.653	9.00
	Cx – O	5.340	3.363	8.50	Cx – O	5.340	3.363	8.50
$N_2 - N_2$	N – N	3.526	3.770	9.00	N – N	3.526	3.770	9.00
$N_2 - CO_2$	N – Cx	3.400	3.548	9.00	N – Cx	3.400	3.548	9.00
	N – O	4.500	3.699	9.00	N – O	4.500	3.699	9.00
COFs – CO_2	Ch – Cx	3.686	3.613	7.00	Ch – Cx	3.686	3.613	7.00
	Cb – Cx	3.686	3.613	7.00	Cb – Cx	3.686	3.613	7.00
	Cm – Cx	3.868	3.553	7.00	Cm – Cx	3.868	3.553	7.00
	Nf – Cx	4.130	3.525	7.00	Nf – Cx	4.130	3.525	7.00
	Hb – Cx	2.120	3.178	7.00	Hb – Cx	2.120	3.178	7.00
	Hn – Cx	2.120	3.178	7.00	Hn – Cx	2.120	3.178	7.00
	Hy – Cx	2.120	3.178	7.00	Hm – Cx	2.120	3.178	7.00
	Hz – Cx	2.120	3.178	7.00	Hp – Cx	2.120	3.178	7.00
	Ch – O	4.994	3.752	7.00	Ch – O	4.994	3.752	7.00
	Cb – O	4.994	3.752	7.00	Cb – O	4.994	3.752	7.00
	Cm – O	5.131	3.702	7.00	Cm – O	5.131	3.702	7.00
	Nf – O	5.424	3.679	7.00	Nf – O	5.424	3.679	7.00
	Hb – O	2.354	3.410	7.00	Hb – O	2.354	3.410	7.00
	Hn – O	2.354	3.410	7.00	Hn – O	2.354	3.410	7.00
	Hy – O	2.354	3.410	7.00	Hm – O	2.354	3.410	7.00
	Hz – O	2.354	3.410	7.00	Hp – O	2.354	3.410	7.00
					Cp – Cx	3.686	3.613	7.00
					Cn – Cx	3.686	3.613	7.00
					Cn – O	4.994	3.752	7.00
					Cp – O	4.994	3.752	7.00
COFs – N_2	Ch – N	4.090	3.796	7.50	Ch – N	4.090	3.796	7.50
	Cb – N	4.090	3.796	7.50	Cb – N	4.090	3.796	7.50
	Cm – N	4.181	3.745	7.50	Cm – N	4.181	3.745	7.50
	Nf – N	4.409	3.723	7.50	Nf – N	4.409	3.723	7.50
	Hb – N	1.844	3.477	7.50	Hb – N	1.844	3.477	7.50
	Hn – N	1.844	3.477	7.50	Hn – N	1.844	3.477	7.50
	Hy – N	1.844	3.477	7.50	Hm – N	1.844	3.477	7.50
	Hz – N	1.844	3.477	7.50	Hp – N	1.844	3.477	7.50
					Cn – N	4.090	3.796	7.50
					Cp – N	4.090	3.796	7.50

Table S5. Amount of gas molecules and the corresponding pressure in the simulation box of CO_2/N_2 gaseous mixtures at 353 K

Pressure (atm)	Total Molecules	CO_2 (Molecules)	N_2 (Molecules)
1.00	26	13	13
1.80	48	24	24
2.54	66	33	33
3.18	84	42	42
4.00	106	53	53
4.62	122	61	61
5.47	144	72	72

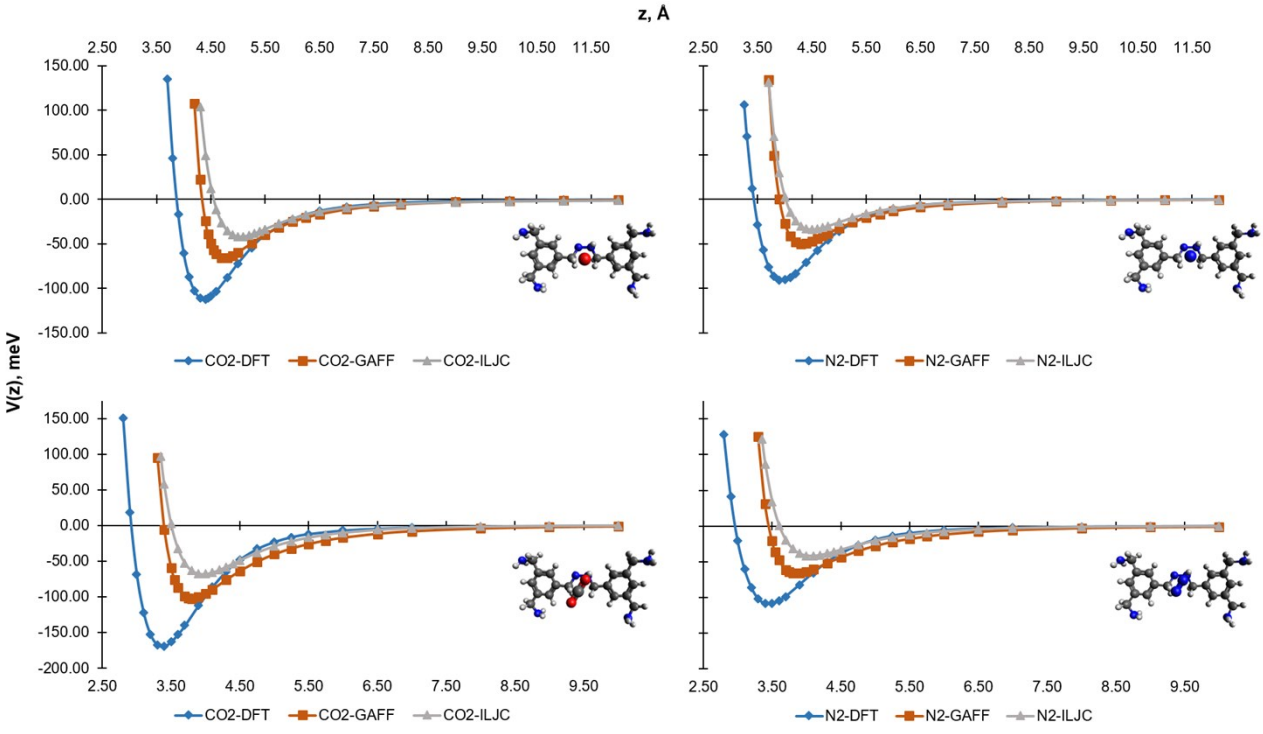

Fig. S3. Adsorption energy profiles of IPB-1H in perpendicular and parallel geometries of gas molecules as a function of z (i.e., distance from the center of the linker)

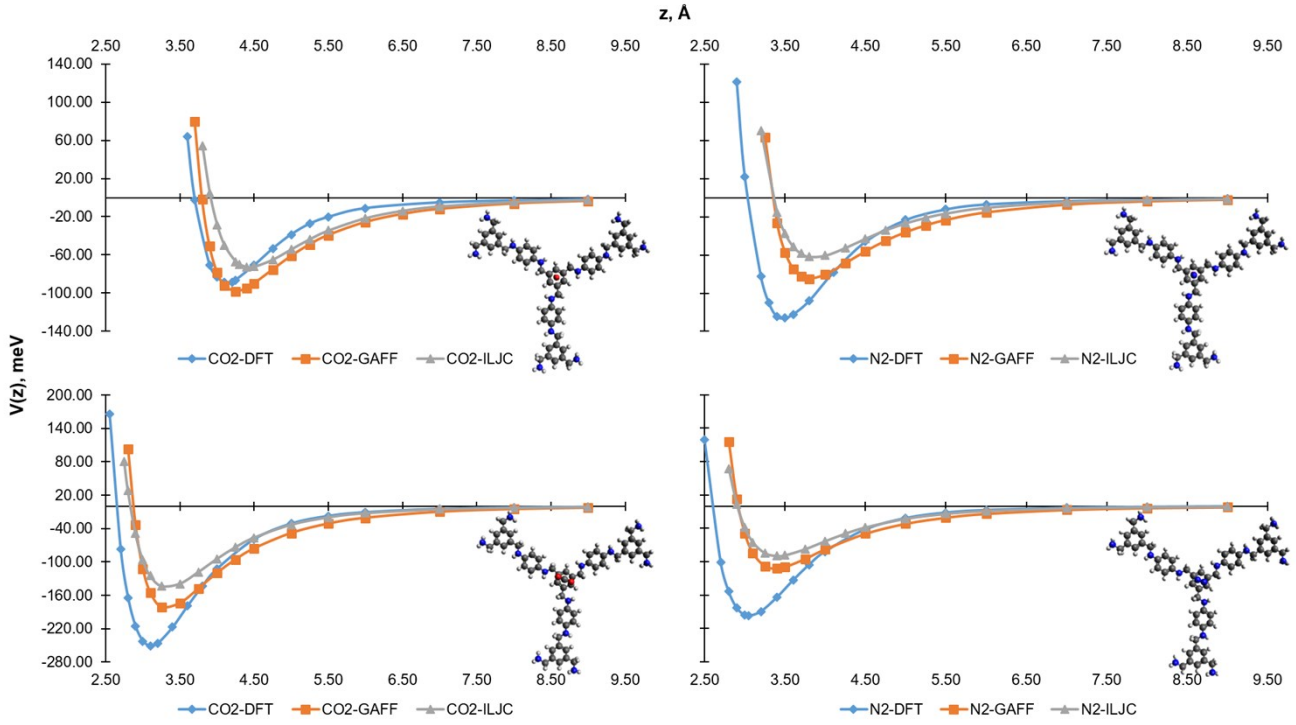

Fig. S4. Adsorption energy profiles of IPB-2H as a function of z (i.e., distance from the building unit)

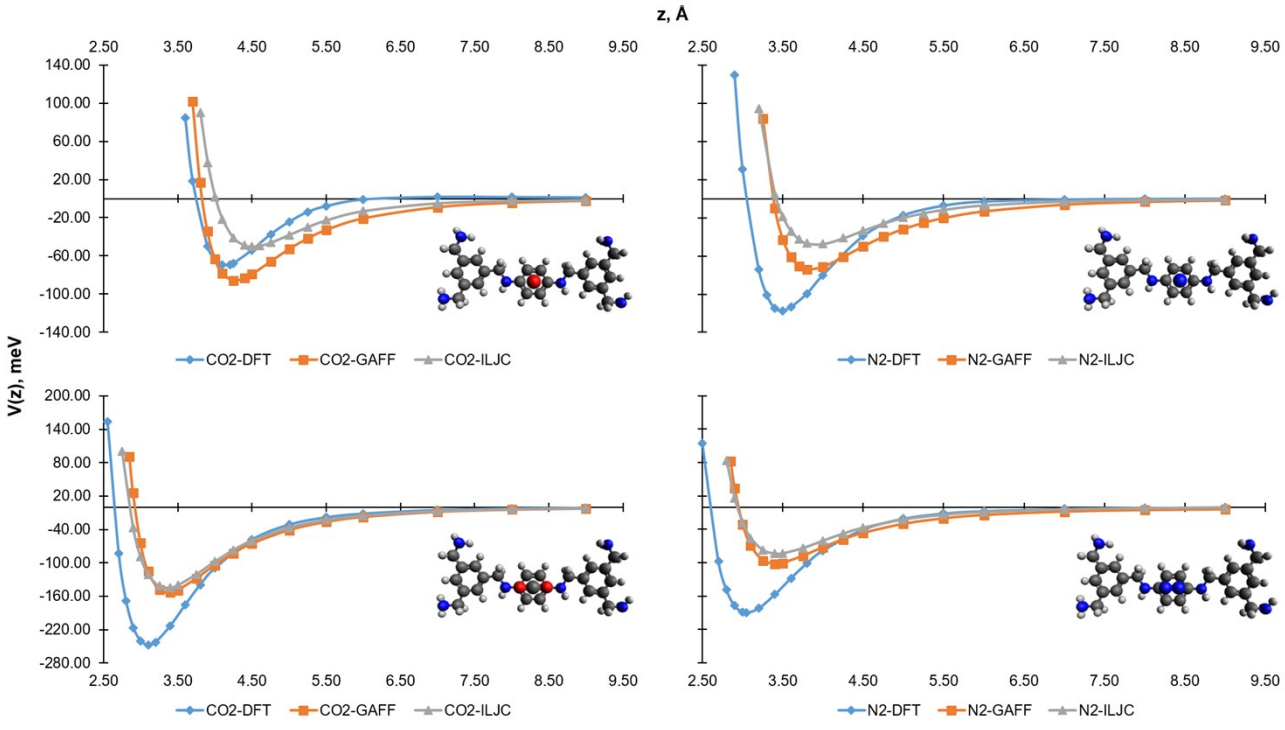

Fig. S5. Adsorption energy profiles of IPB-2H as a function of z (i.e., distance from the linker)

Note: the adsorption energy of CO_2 and N_2 at the center of IPB-2H pore were too small and negligible, thus the in-pore adsorption energy profiles were not calculated further.

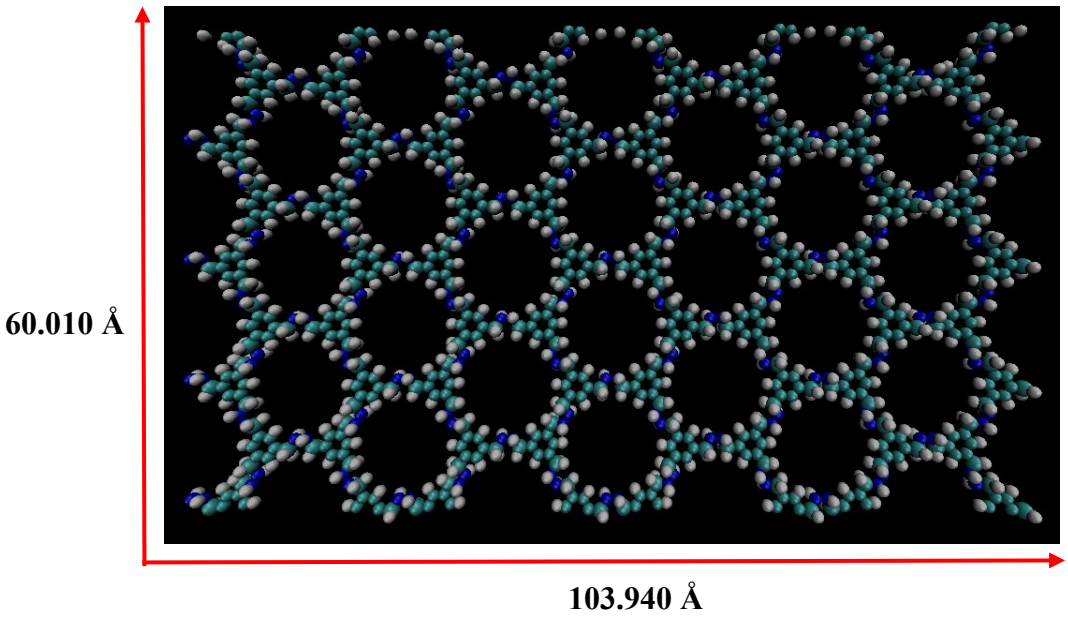

Fig. S6. Dimension of IPB-1H used for MD simulations. A periodic boundary condition was applied in all directions of the simulation box to simulate an infinite planar sheet

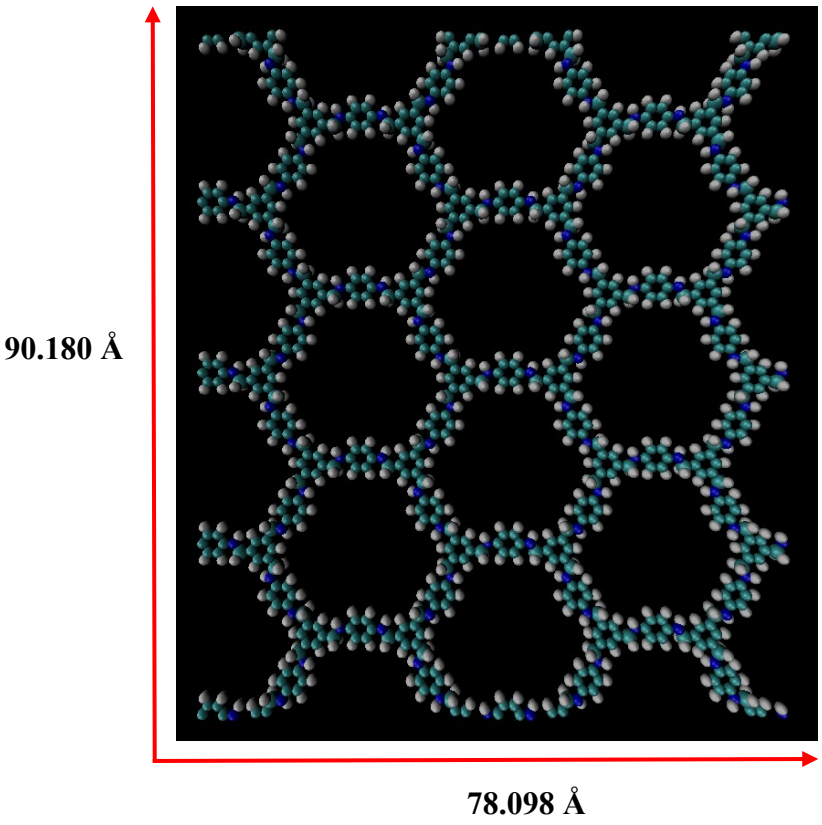

Fig. S7. Dimension of IPB-2H used for MD simulations. A periodic boundary condition was applied in all directions of the simulation box to simulate an infinite planar sheet

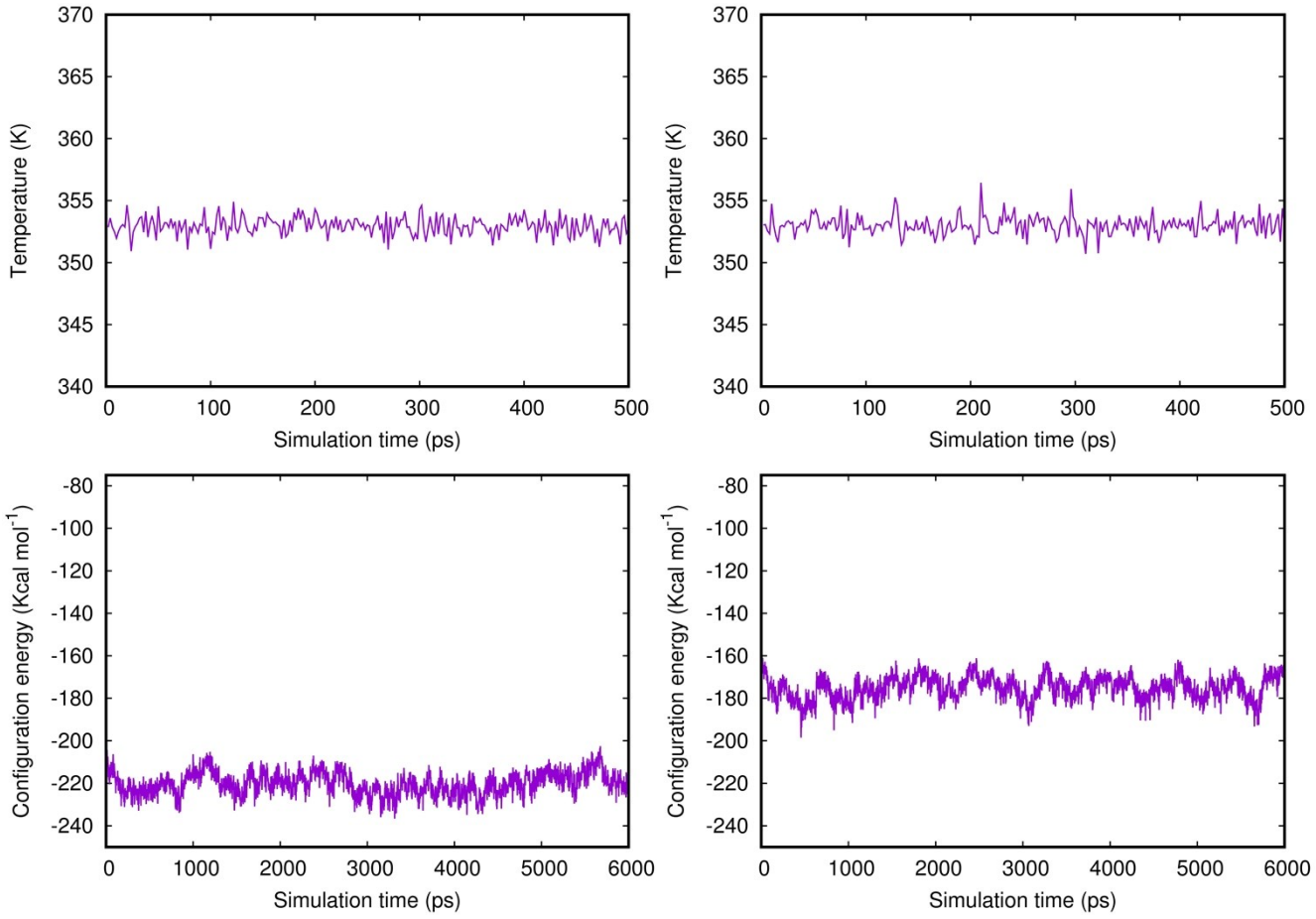

Fig. S8. The time evolution of temperature and energy of IPB-1H (left panel) and IPB-2H (right panel) systems for gaseous mixture at 5.47 atm and 353 K. Upper panel: temperature convergence evaluation during the equilibration period. Lower panel: energy convergence evaluation during the simulation (equilibration and production)

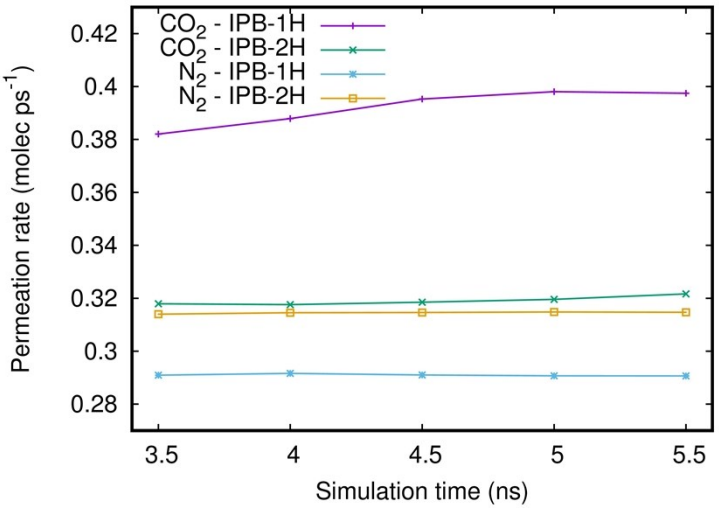

Fig. S9. The convergence of gas permeation rate evaluated at different production times for IPB-1H and IPB-2H in CO_2/N_2 gaseous mixture systems at 5.47 atm and 353 K

Table S6. The resume of temperature and energy fluctuations during the MD simulations

System	P (atm)	Temperature (K)			Configuration Energy (Kcal/mol)		
		Average	r.m.s. Fluctuation	Relative Fluctuation (%)	Average	r.m.s. Fluctuation	Relative Fluctuation (%)
IPB-1H	1.00	353	41.69	11.81	−203.68	4.24	2.08
	1.80	353	29.46	8.34	−206.08	3.49	1.69
	2.54	353	26.52	7.51	−209.13	4.88	2.33
	3.18	353	22.82	6.47	−212.84	5.26	2.47
	4.00	353	20.97	5.94	−214.33	5.06	2.36
	4.62	353	20.09	5.69	−217.19	5.43	2.50
	5.47	353	19.03	5.39	−220.95	5.49	2.48
IPB-2H	1.00	353	41.11	11.64	−159.27	4.44	2.79
	1.80	353	32.32	9.16	−161.56	4.60	2.84
	2.54	353	26.62	7.54	−164.26	4.23	2.57
	3.18	353	25.97	7.36	−164.68	3.82	2.32
	4.00	353	21.58	6.11	−167.91	4.61	2.75
	4.62	353	20.45	5.79	−170.86	4.42	2.59
	5.47	353	18.15	5.14	−175.05	5.44	3.11