Electronic Supplementary Information

Selection of suitable ZIF-8/ionic liquid (IL) based composite for the selective CO_2 capture: The role of anions at the interface‡

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Grand Canonical Monte Carlo (GCMC) Simulations:

The force field parameters used for different framework atoms and gas molecules are given in Table S1 and S2.

Table S1 Force field parameters used for IL@ZIF-8 complexes.

Atom	UFF		Dreiding FF		GenericMOFs FF	
	ε_i (K)	σ_i (Å)	ε_i (K)	σ_i (Å)	ε_i (K)	σ_i (Å)
C	52.83	3.85	47.86	3.47	47.86	3.47
H	22.14	2.89	7.65	2.85	7.65	2.85
N	34.72	3.66	38.95	3.26	38.95	3.26
Zn	62.40	2.76	27.68	4.54	62.40	2.46
O	30.19	3.50	48.16	3.03	48.16	3.03
S	137.88	4.04	173.11	3.59	173.11	3.59
P	153.48	4.15	161.03	3.70	161.03	3.70
Cl	114.23	3.95	142.56	3.52	142.56	3.52
F	25.16	3.36	36.48	3.09	36.48	3.09
B	90.58	4.08	47.81	3.58	47.81	3.58

Table S2 LJ parameters and charges used for gas molecules.

CO_2	ε (K)	σ (Å)	Charge
O	79.0	3.05	-0.35
C	27.0	2.80	0.70
O	79.0	3.05	-0.35

N_2	ε (K)	σ (Å)	Charge
N	36.0	3.31	-0.482
N_COM	--	--	0.964
N	36.0	3.31	-0.482

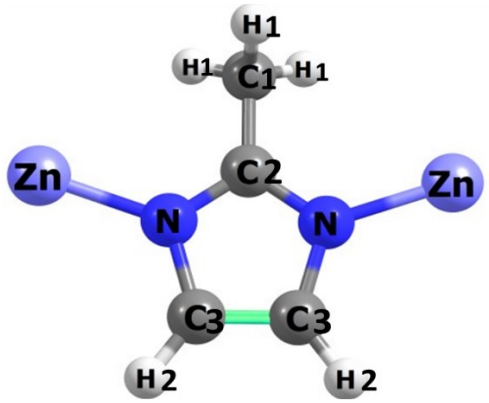
CH_4	Energy ε (K)	Distance σ (Å)	Charge
C	158.5	3.72	--

Table S3 He void for different composites calculated using Dreiding force field.

Composite	He void
ZIF-8	0.48
[BMIM][BF_4]@ZIF-8	0.38
[BMIM][PF_6]@ZIF-8	0.39
[BMIM][Cl]@ZIF-8	0.40
[BMIM][CF_3CO_2]@ZIF-8	0.38
[BMIM][OTF]@ZIF-8	0.38
[BMIM][NO_3]@ZIF-8	0.38
[BMIM][TF_2N]@ZIF-8	0.34
[BMIM][DCA]@ZIF-8	0.38
[BMIM][N_3]@ZIF-8	0.39
[BMIM][SCN]@ZIF-8	0.38
[BMIM][NO_2]@ZIF-8	0.40

Table S4 Calculated atomic charges (average) for ZIF-8 framework with the atom types using charge equilibration method.

Atom type in ZIF-8	**Charge (a.u.)**
Zn	0.330
N	-0.175
C1	-0.250
C2	0.158
C3	0.003
H1	0.076
H2	0.019



Atom types considered for ZIF-8 framework

Table S5 Average charges for each atom type of non-nitrogen based ILs, calculated using charge equilibration method.

[BMIM][BF_4]		**[BMIM][PF_6]**		**[BMIM][OTF]**		**[BMIM][CF_3CO_2]**		**[BMIM][Cl]**	
Atom type	Charge	Atom type	Charge	Atom type	Charge	Atom type	Charge	Atom type	Charge
N	-0.118	N	-0.111	N	-0.117	N	-0.116	N	-0.116
C1	-0.114	C1	-0.104	C1	-0.104	C1	-0.110	C1	-0.113
C2	0.116	C2	0.097	C2	0.097	C2	0.078	C2	0.072
C3	0.025	C3	0.009	C3	0.010	C3	0.006	C3	0.005
C4	-0.002	C4	-0.017	C4	-0.004	C4	-0.016	C4	-0.015
C5	-0.098	C5	-0.077	C5	-0.106	C5	-0.091	C5	-0.092
C6	-0.021	C6	-0.033	C6	-0.012	C6	-0.027	C6	-0.027
C7	-0.166	C7	-0.155	C7	-0.170	C7	-0.163	C7	-0.163
H1	0.078	H1	0.063	H1	0.060	H1	0.063	H1	0.065
H2	0.063	H2	0.112	H2	0.053	H2	0.055	H2	0.059
H3	0.024	H3	0.024	H3	0.024	H3	0.024	H3	0.024
H4	0.047	H4	0.069	H4	0.041	H4	0.039	H4	0.067
H5	0.083	H5	0.070	H5	0.083	H5	0.052	H5	0.048
H6	0.037	H6	0.058	H6	0.036	H6	0.030	H6	0.027
H7	0.062	H7	0.061	H7	0.069	H7	0.057	H7	0.056
B	2.682	P	1.006	S	0.316	C1(anion)	0.755	Cl	-0.354
F	-0.901	F	-0.393	C(anion)	0.738	C2(anion)	0.122		
				F	-0.479	O	-0.170		
				O	-0.201	F	-0.478		

Table S6 Average charges for each atom type of nitrogen based ILs, calculated using charge equilibration method.

[BMIM][DCA]		**[BMIM][N_3]**		**[BMIM][NO_2]**		**[BMIM][NO_3]**		**[BMIM][Tf_2N]**		**[BMIM][SCN]**	
Atom type	Charge	Atom type	Charge	Atom type	Charge	Atom type	Charge	Atom type	Charge	Atom type	Charge
N	-0.120	N	-0.119	N	-0.118	N	-0.118	N	-0.116	N	-0.120
C1	-0.106	C1	-0.101	C1	-0.110	C1	-0.101	C1	-0.101	C1	-0.102
C2	0.080	C2	0.074	C2	0.076	C2	0.074	C2	0.089	C2	0.077
C3	0.005	C3	0.005	C3	0.005	C3	0.006	C3	0.008	C3	0.005
C4	-0.016	C4	-0.014	C4	-0.015	C4	-0.016	C4	-0.013	C4	-0.017
C5	-0.091	C5	-0.092	C5	-0.092	C5	-0.088	C5	-0.092	C5	-0.090
C6	-0.027	C6	-0.025	C6	-0.027	C6	-0.028	C6	-0.018	C6	-0.028
C7	-0.163	C7	-0.165	C7	-0.163	C7	-0.161	C7	-0.168	C7	-0.162
H1	0.055	H1	0.049	H1	0.061	H1	0.050	H1	0.063	H1	0.049
H2	0.019	H2	0.037	H2	0.038	H2	0.047	H2	0.048	H2	0.021
H3	0.024	H3	0.023	H3	0.024	H3	0.024	H3	0.024	H3	0.023
H4	0.035	H4	0.035	H4	0.032	H4	0.040	H4	0.050	H4	0.036
H5	0.051	H5	0.054	H5	0.049	H5	0.055	H5	0.072	H5	0.049
H6	0.029	H6	0.031	H6	0.028	H6	0.036	H6	0.050	H6	0.029
H7	0.057	H7	0.058	H7	0.085	H7	0.058	H7	0.079	H7	0.055
N1	-0.172	N1	-0.044	N(anion)	-0.011	N(anion)	0.043	N(anion)	-0.107	S	-0.062
N2	-0.151	N2	-0.086	O	-0.132	O	-0.136	S	0.261	C	0.067
C	0.142							O	-0.169	N(anion)	-0.134
								C	0.770		
								F	-0.474		

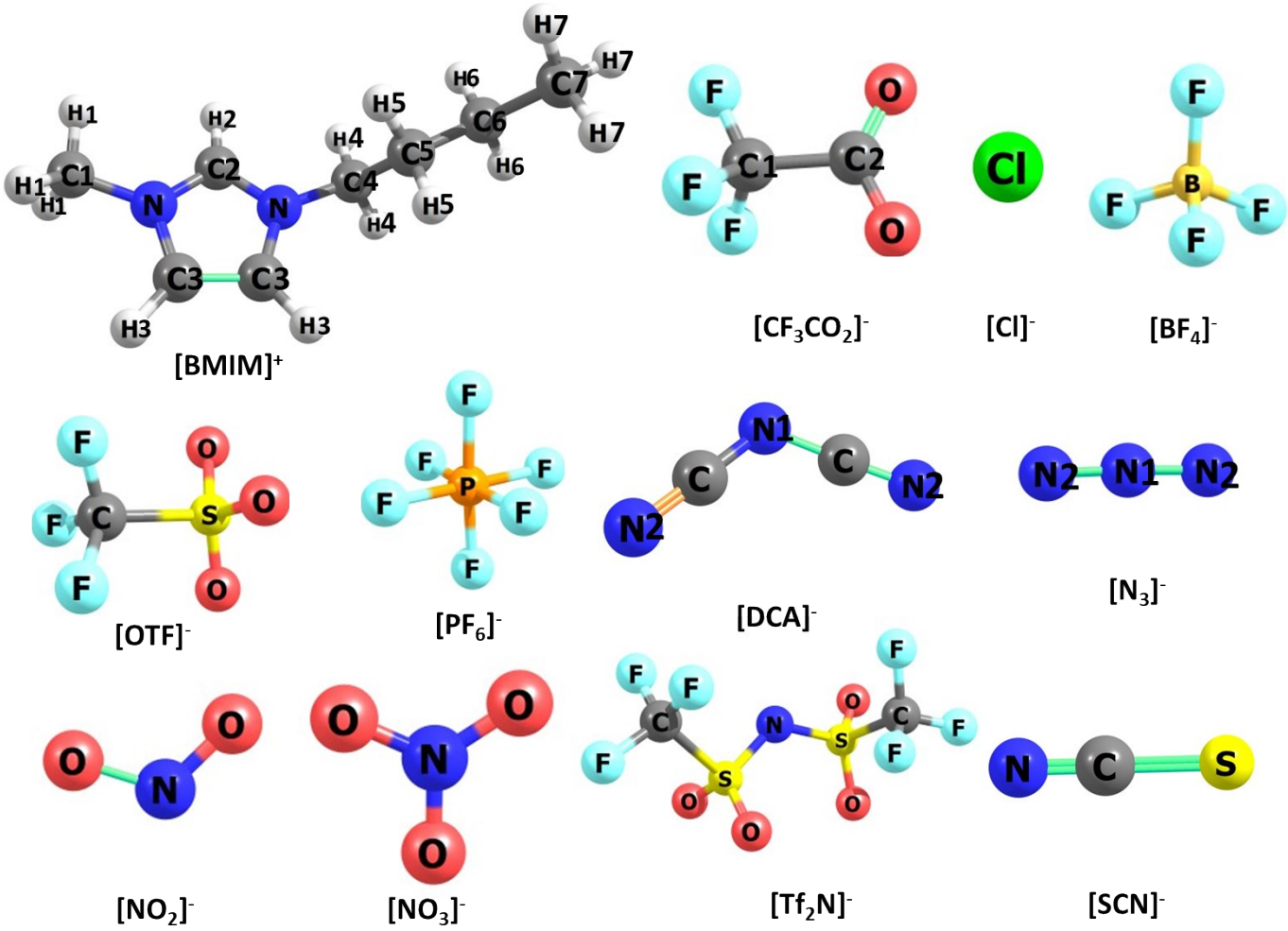


Fig. S1 Structure of cation ($[BMIM]^+$) and various anions used in this study, along with their atom types. The selected anions are trifluoroacetate $[CF_3CO_2]^-$, tetrafluoroborate $[BF_4]^-$, hexafluorophosphate $[PF_6]^-$, chloride $[Cl]^-$, and trifluoromethanesulfonate $[OTF]^-$ which are non-N based and nitrogen based anions are thiocyanate $[SCN]^-$, nitrite $[NO_2]^-$, nitrate $[NO_3]^-$, dicyanamide $[DCA]^-$, azide $[N_3]^-$, and bis(trifluoromethylsulfonyl)imide $[Tf_2N]^-$.

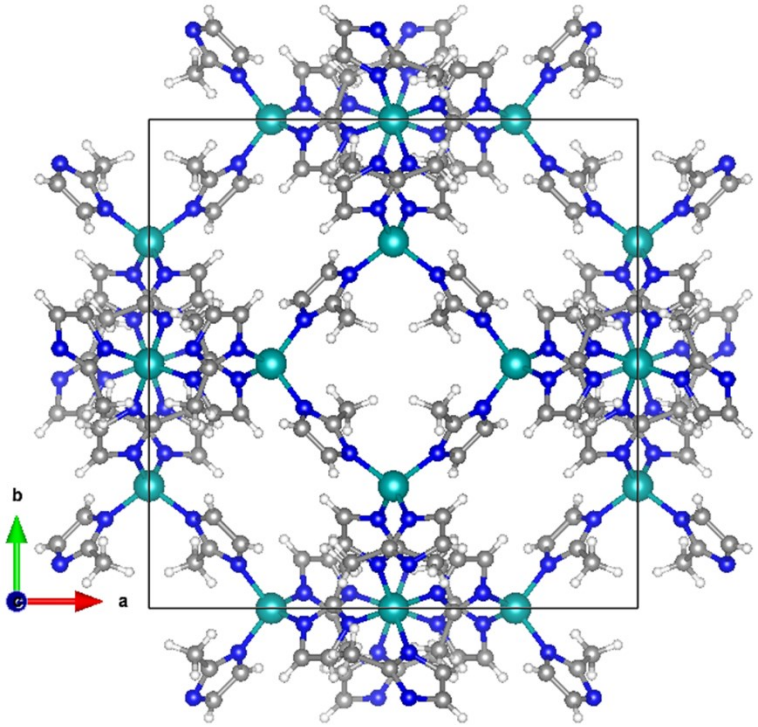


Fig. S2 Non-optimized ZIF-8 crystal structure obtained from experimental data[1]

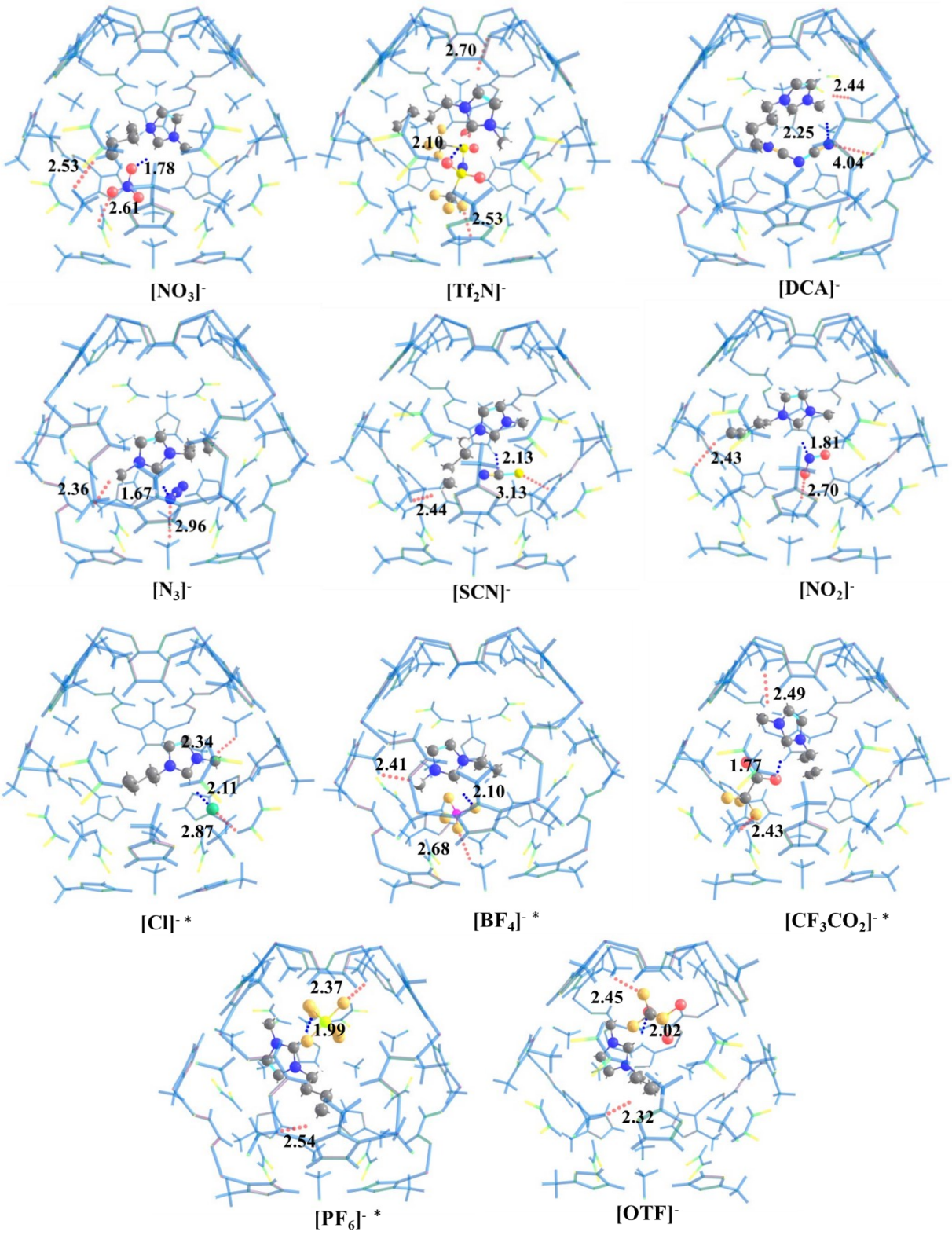


Fig. S3 Optimized geometries of different [BMIM][X]$^-$@ZIF-8 complexes with shortest interaction distances. Blue and red dotted lines indicates IL-Il and IL-ZIF-8 distances, respectively. (*Ref. no: 36)

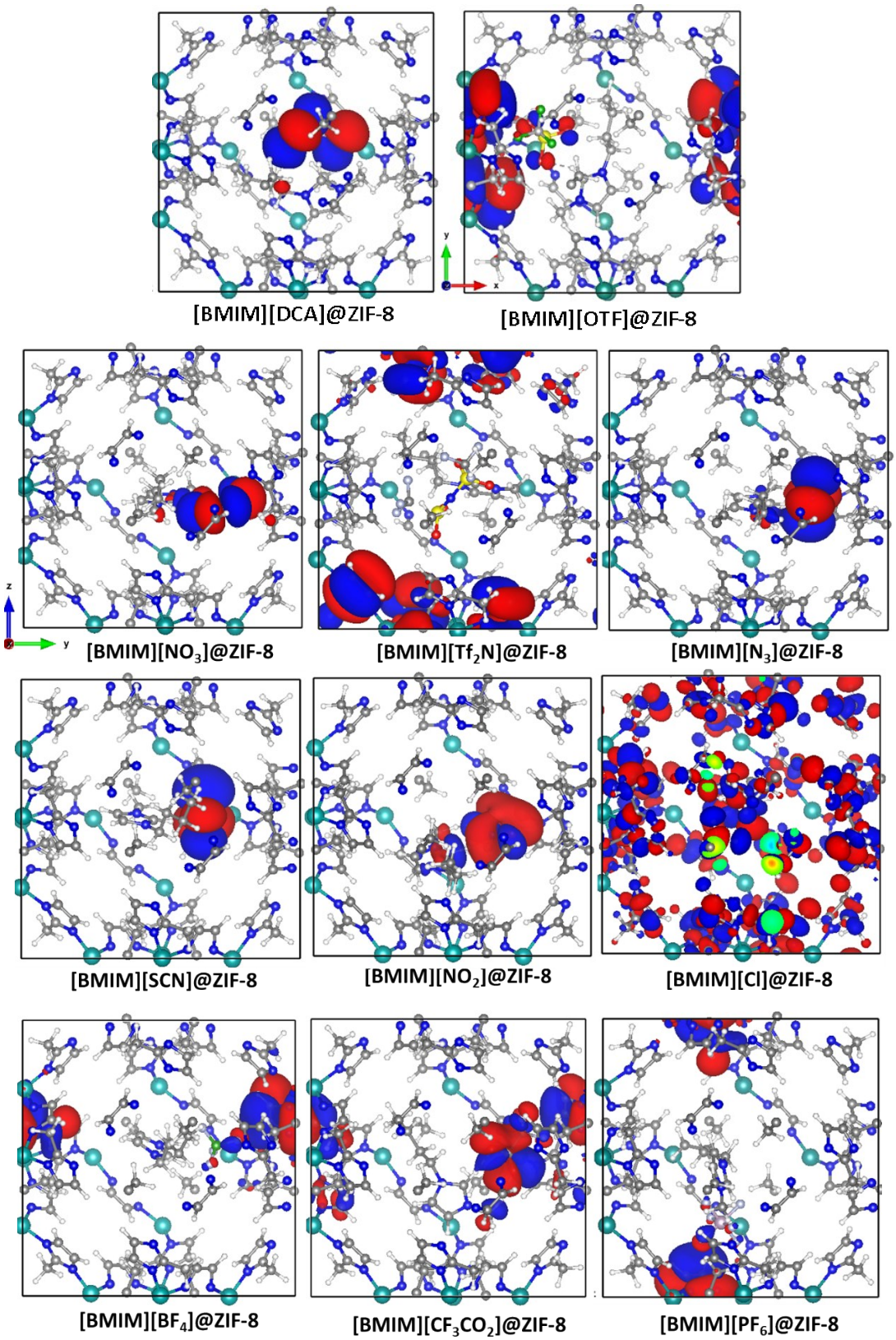


Fig. S4 Electron density maps of various nitrogen and non-nitrogen based ILs@ZIF-8 nanopore structure used in this study (isosurface value=0.01 a.u.).

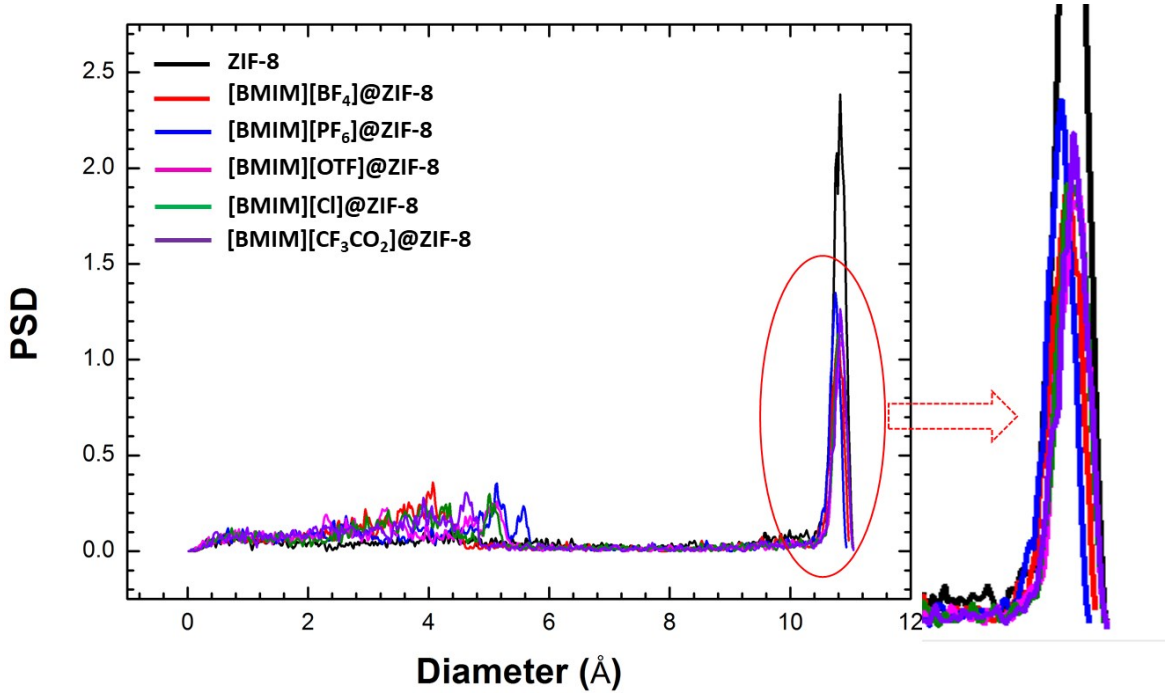


Fig. S5 Pore-size distribution of pristine ZIF-8 and different non N-based composite materials.

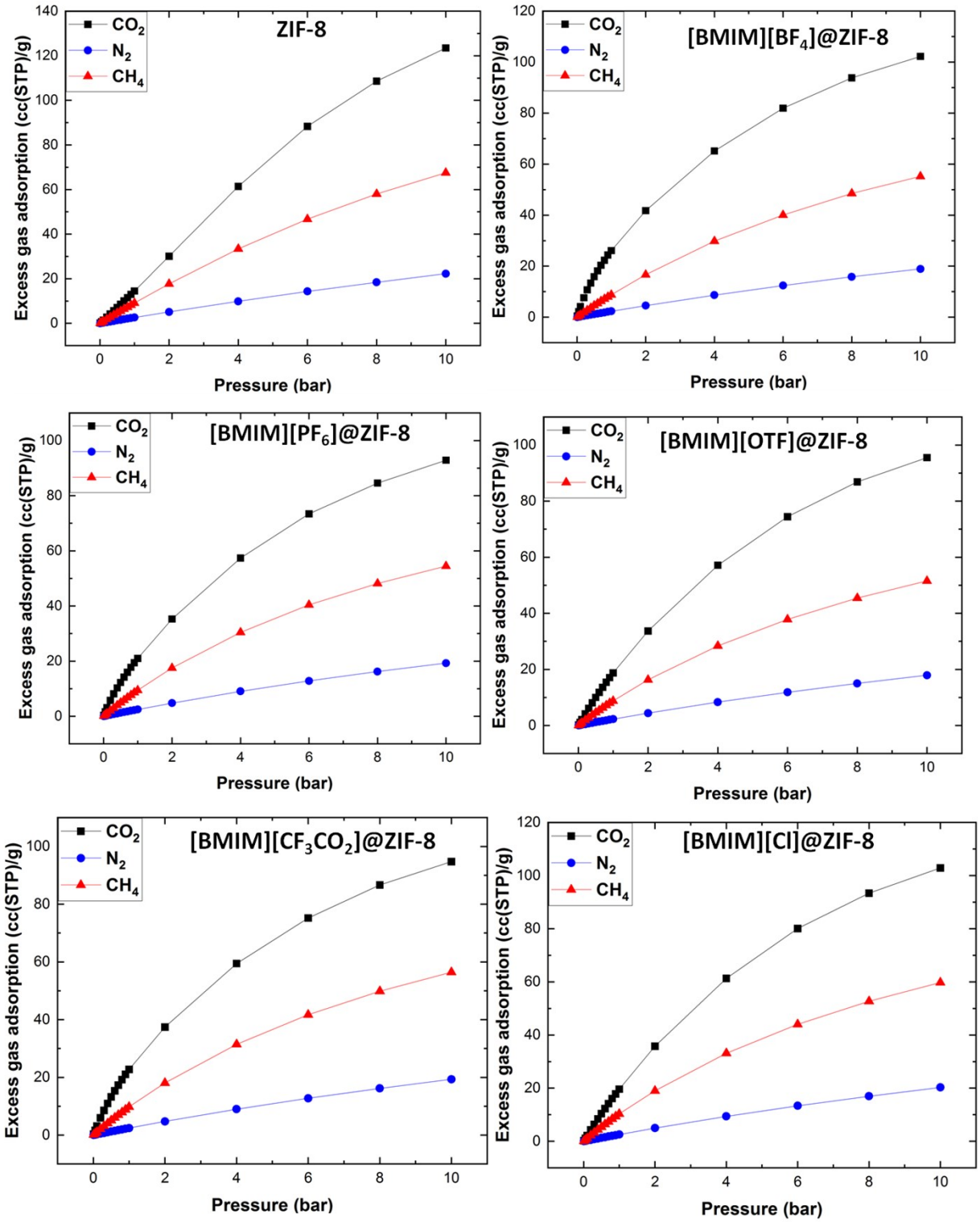


Fig. S6 Single component adsorption isotherms for CO_2, N_2 and CH_4 gases in ZIF-8 and various non-N anionic complexes, calculated using Dreiding force field.

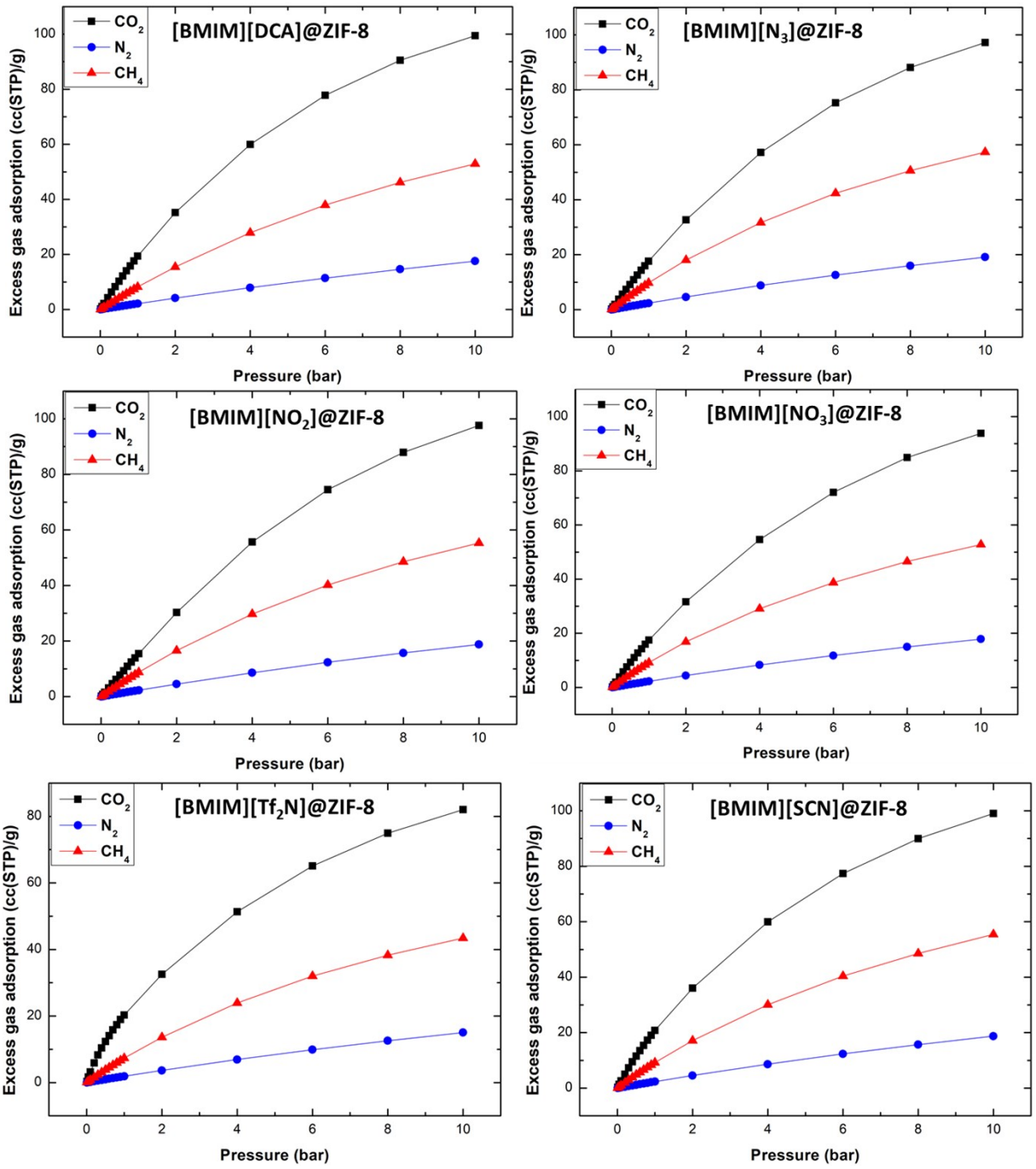


Fig. S7 Single component adsorption isotherms for CO_2, N_2 and CH_4 in different N-based complexes

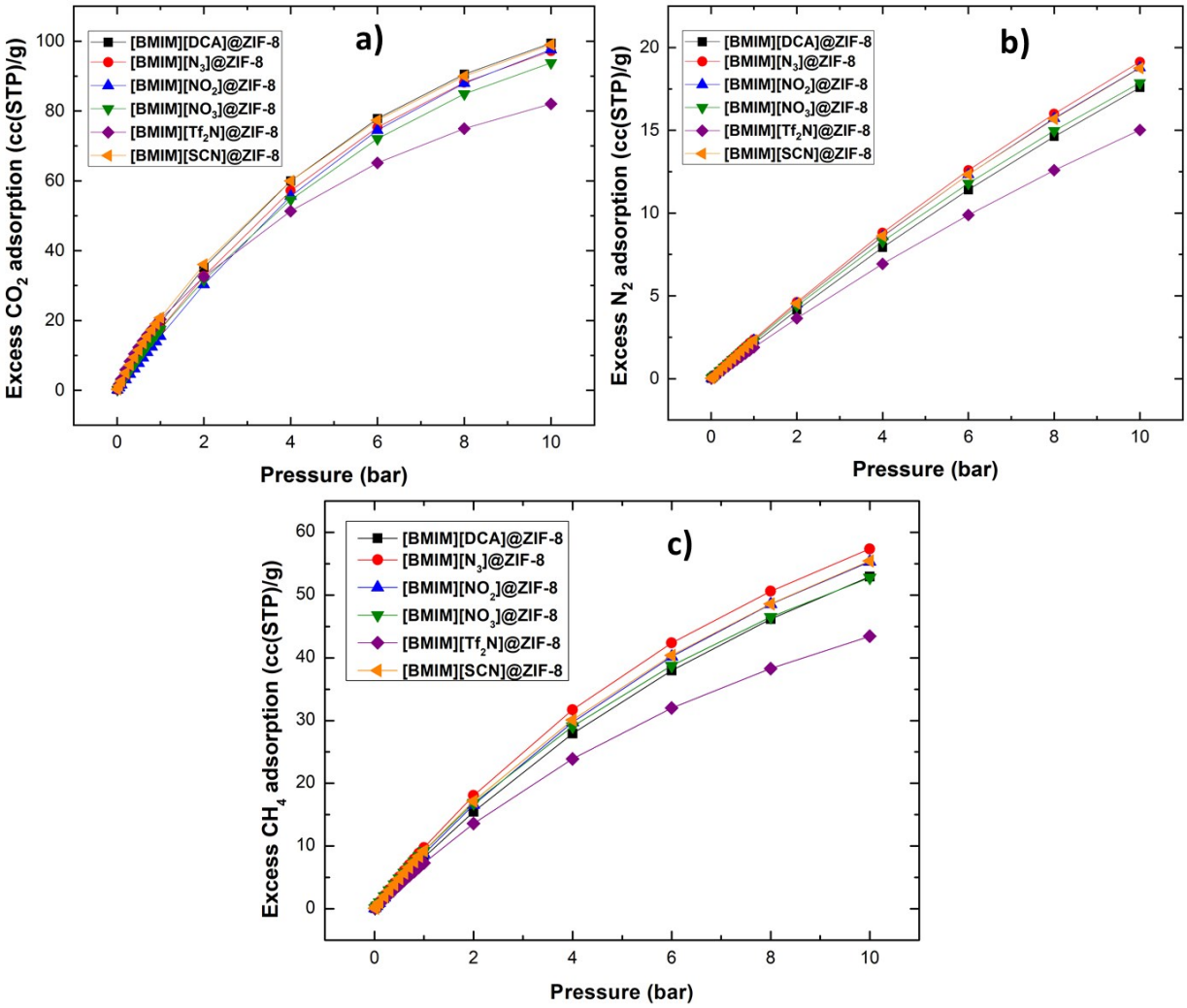


Fig. S8 Comparison of gas adsorption isotherm of N based anionic ILs@ZIF-8 composites were calculated using Dreiding force field for (a) CO_2, (b) N_2 and (c) CH_4.

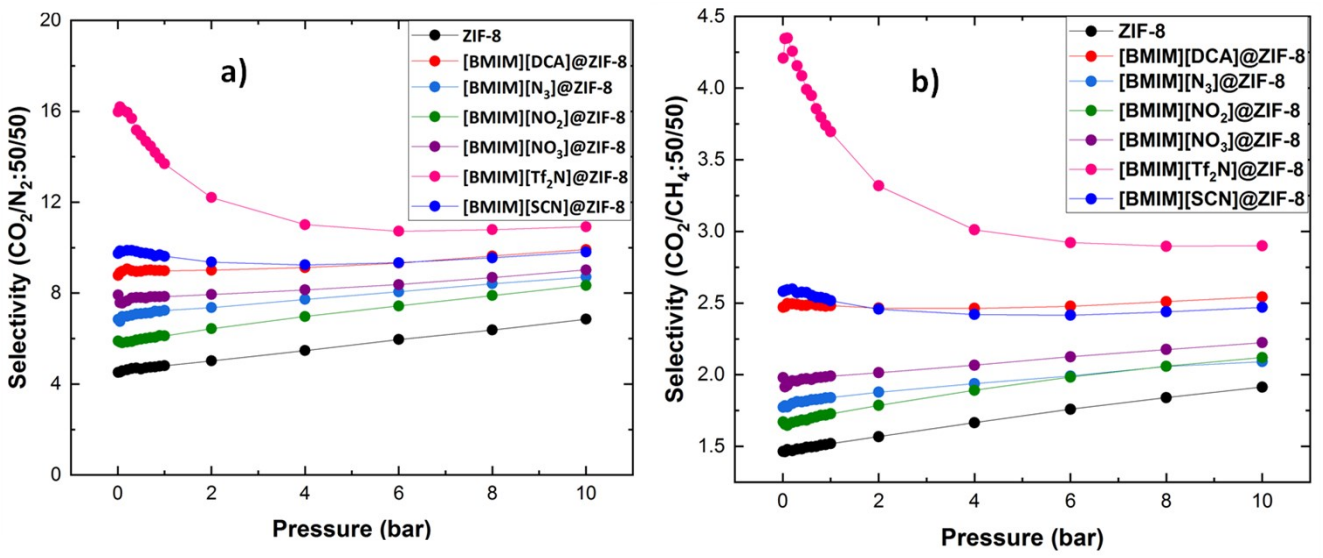


Fig. S9 Binary mixture selectivity of different N-based ILs incorporated with ZIF-8 materials for (a) CO_2/N_2 and (b) CO_2/CH_4.

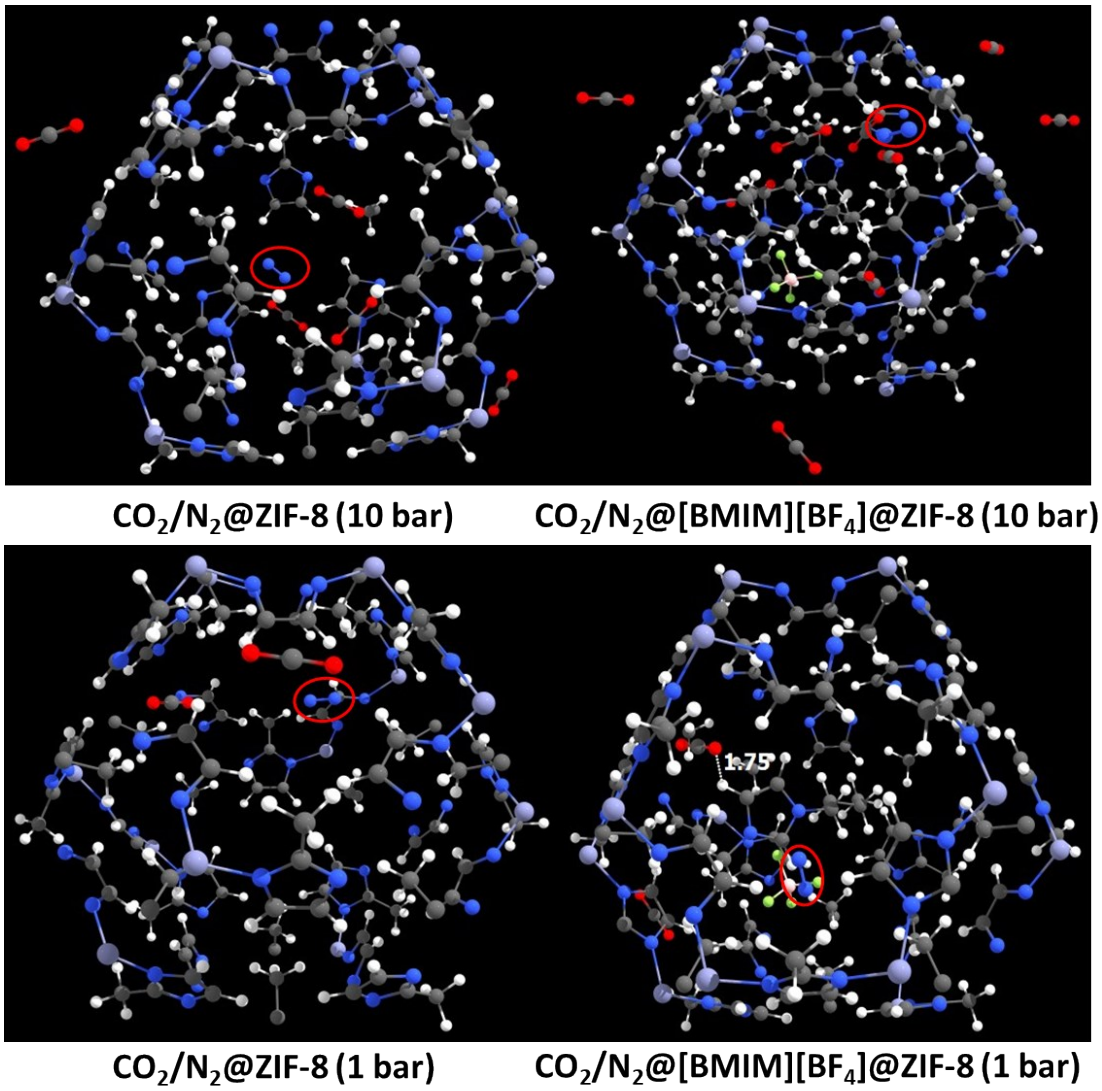


Fig. S10 Snapshots from the binary mixture (CO_2/N_2) adsorption of ZIF-8 and [BMIM][BF_4]@ZIF-8 at 10 (top) and 1 bar (bottom). The N_2 molecules are shown in red circles.

References:

1 K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci.*, 2006, **103**, 10186–10191.