

Encapsulation of [bmim⁺][Tf₂N⁻] in different ZIF-8 metal analogues and evaluation of their CO₂ selectivity over CH₄ and N₂ using molecular simulation

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Supplementary Information

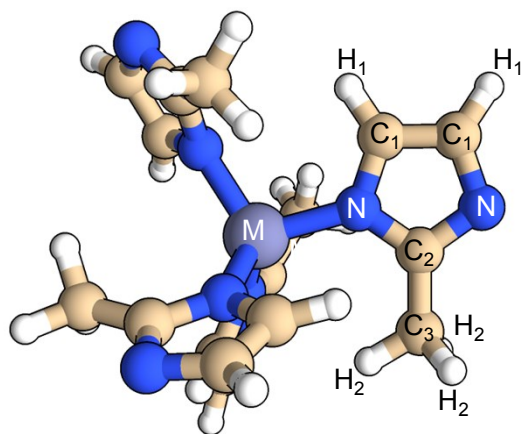


Table S-1. LJ parameters for the original ZIF-8 and its metal analogues (common values for all cases)

Site	σ (Å)	ϵ/k_B (K)
M	1.96	6.290
N	3.25	85.548
H1	2.51	7.548
H2	2.65	7.900
C1	3.40	43.772
C2	3.40	43.277
C3	3.40	55.053

Table S-2. Coulombic parameters for the original ZIF-8 and its metal analogues

Atom type	Partial charge (e)			
	CdIF-1	ZIF-8	ZIF-67	BeIF-1
M*	1.1901	1.3429	1.3497	1.6627
N	-0.6532	-0.6822	-0.6956	-0.6646
C1	-0.0583	-0.0622	-0.0581	-0.0896
C2	0.7379	0.7551	0.7846	0.6287
H1	0.095	0.0912	0.0910	0.0875
C3	-0.2771	-0.2697	-0.3094	-0.1824
H2	0.059	0.0499	0.0584	0.0186

*M: metal center which is Cd, Zn, Co and Be for CdIF-1, ZIF-8, ZIF-67 and BeIF-1, respectively.

Force field parameters for the Ionic liquid (IL)

1-Butyl-3 methylimidazolium bis(trifluoromethanesulfonyl) Imide ([bmim⁺][Tf₂N⁻])

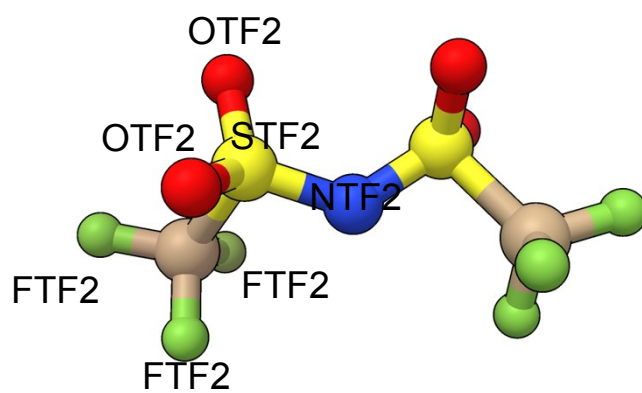
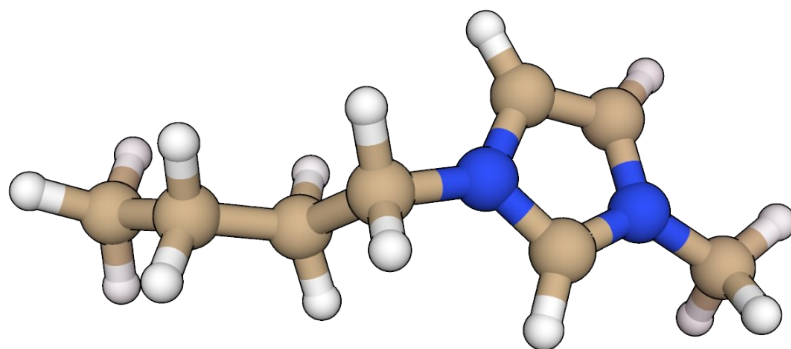
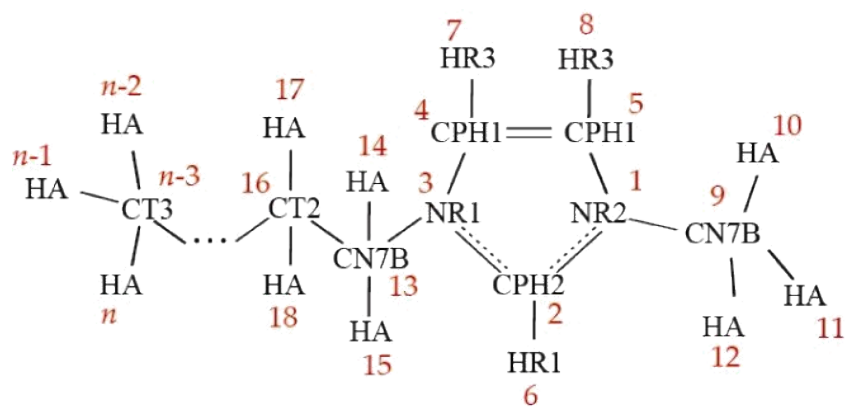


Table S-3. Partial charges and LJ parameters for [bmim⁺]

Atom	Partial Charge q (e)	σ (\AA)	ϵ/k_B (K)
NR1	0.146046	3.296	100.644
CPH1	-0.006432	3.207	25.161
NR2	0.092254	3.296	100.644
CPH2	-0.193107	3.207	25.161
CPH2	-0.152475	3.207	25.161
HR1	0.208287	1.604	23.148
HR2	0.205544	2.616	3.925
HR3	0.184183	2.616	3.925
CN7B	-0.171877	4.054	10.064
HA	0.119267	2.352	11.071
HA	0.148216	2.352	11.071
HA	0.087322	2.352	11.071
CN7B	0.005903	4.054	10.064
HA	0.054165	2.352	11.071
HA	0.045561	2.352	11.071
CT2	0.076942	3.875	27.677
HA	-0.029155	2.352	11.071
HA	0.000652	2.352	11.071
CT2	0.227458	3.875	27.677
HA	-0.024423	2.352	11.071
HA	-0.051806	2.352	11.071
CT3	-0.261600	3.671	40.258
HA	0.061505	2.352	11.071
HA	0.051733	2.352	11.071
HA	0.136136	2.352	11.071

Table S-4. Partial charges and LJ parameters for [Tf₂N⁻]

Atom	Partial Charge q (e)	σ (Å)	ϵ/k_B (K)
CTF2	0.348789	3.499	33.212
FTF2	-0.131010	2.951	26.671
STF2	0.858581	3.549	125.805
OTF2	-0.534882	2.960	105.676
NTF2	-0.449451	3.250	85.547

Table S-5. Bond stretching potential parameters for [bmim⁺]

$$u(l) = \frac{k_l}{2}(l - l_o)^2$$

Atom 1	Atom 2	k_l (kcal mol ⁻¹ Å ⁻²)	l_o (Å)
CN7B	NR1	220.00	1.4762
CN7B	NR2	220.00	1.4762
CPH1	NR1	400.00	1.3819
CPH1	NR2	400.00	1.3819
CPH2	NR1	400.00	1.3366
CPH2	NR2	400.00	1.3366
CPH1	CPH1	410.00	1.3610
CPH2	HR1	340.00	1.0779
CPH1	HR3	365.00	1.0775
CN7B	HA	309.00	1.0889
CT2	HA	309.00	1.0954
CT3	HA	322.00	1.0935
CN7B	CT2	200.00	1.5308
CT2	CT2	222.50	1.5373
CT2	CT3	222.50	1.5314

CT1	CN7B	200.00	1.5240
CT1	HA	322.00	1.0893

Table S-6. Angle bending potential parameters for [bmim⁺]

$$u(\theta) = \frac{k_{\theta}}{2}(\theta - \theta_0)^2$$

Atom 1	Atom 2	Atom 3	k_{θ} (kcal mol ⁻¹ rad ⁻²)	θ_0 (degrees)
CT2	CN7B	NR1	140.00	112.34
CPH1	NR1	CPH2	130.00	108.25
CPH1	NR2	CPH2	130.00	108.25
HA	CN7B	NR1	30.00	109.41
HA	CN7B	NR2	30.00	109.41
HR1	CPH2	NR1	25.00	125.44
HR1	CPH2	NR2	25.00	125.44
NR1	CPH1	CPH1	130.00	107.28
NR2	CPH1	CPH1	130.00	107.28
NR1	CPH2	NR2	130.00	109.11
HR3	CPH1	CPH1	25.00	130.74
NR2	CPH1	HR3	25.00	122.04
NR1	CPH1	HR3	25.00	122.04
HA	CN7B	HA	35.50	108.44
HA	CN7B	CT2	33.40	111.68
HA	CT2	CN7B	33.40	109.13
CN7B	CT2	CT2	58.35	111.50
CT2	CT2	CT3	58.00	112.34
CT2	CT2	CT2	58.00	112.34
HA	CT2	HA	35.50	106.13

HA	CT3	HA	35.50	107.24
CT2	CT2	HA	26.50	108.43
CT2	CT3	HA	34.60	111.62
CT3	CT2	HA	34.60	109.47
CN7B	NR2	CPH2	130.00	125.75
CN7B	NR1	CPH2	130.00	125.75
CN7B	NR2	CPH1	130.00	125.67
CN7B	NR1	CPH1	130.00	125.67
HA	CT1	HA	35.50	108.27
HA	CT1	CN7B	33.40	110.64
HA	CN7B	CT1	33.40	111.58
NR1	CN7B	CT1	140.00	112.31

Table S-7. Torsional potential parameters for [bmim⁺]

$$u(\chi) = k_{\chi}[1 + \cos(m\chi - \delta)]$$

Atom 1	Atom 2	Atom 3	Atom 4	k_{χ} (kcal mol ⁻¹)	m	δ (deg)
CPH2	NR1	CPH1	CPH1	14.000	2	180
CPH2	NR2	CPH1	CPH1	14.000	2	180
NR1	CPH1	CPH1	NR2	14.000	2	180
NR1	CPH2	NR2	CPH1	14.000	2	180
NR2	CPH2	NR1	CPH1	14.000	2	180
HR1	CPH2	NR1	CPH1	3.000	2	180
HR1	CPH2	NR2	CPH1	3.000	2	180
HR3	CPH1	CPH1	HR3	2.000	2	180
CPH1	CPH1	NR1	CN7B	0.000	1	0
CPH1	CPH1	NR2	CN7B	0.000	1	0

HR3	CPH1	NR2	CPH2	3.000	2	180
HR3	CPH1	NR1	CPH2	3.000	2	180
NR1	CPH1	CPH1	HR3	3.000	2	180
NR2	CPH1	CPH1	HR3	3.000	2	180
NR1	CPH2	NR2	CN7B	0.000	2	180
NR2	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR1	CN7B	0.000	2	180
HR1	CPH2	NR2	CN7B	0.000	2	180
HR3	CPH1	NR1	CN7B	0.000	2	180
HR3	CPH1	NR2	CN7B	0.000	2	180
CPH2	NR1	CN7B	HA	0.195	2	180
CPH2	NR2	CN7B	HA	0.195	2	180
CPH1	NR2	CN7B	HA	0.000	3	0
CPH1	NR1	CN7B	HA	0.000	3	0
CPH2	NR1	CN7B	CT2	0.100	3	180
CPH1	NR1	CN7B	CT2	0.200	4	0
NR1	CN7B	CT2	CT2	0.000	3	0
HA	CT2	CT3	HA	0.160	3	0
CT2	CT2	CT3	HA	0.160	3	0
NR1	CN7B	CT2	HA	0.000	3	0
CN7B	CT2	CT2	CT3	0.150	1	0
HA	CN7B	CT2	HA	0.195	3	0
CT2	CT2	CN7B	HA	0.195	3	0
HA	CT2	CT2	CN7B	0.195	3	0
HA	CT2	CT2	HA	0.195	3	0
HA	CT2	CT2	CT3	0.195	3	0
HA	CT1	CN7B	HA	0.195	3	0

HA	CT1	CN7B	NR1	0.000	3	0
CT1	CN7B	NR1	CPH2	0.100	3	180
CT1	CN7B	NR1	CPH1	0.200	4	0

Table S-8. Improper torsional potential parameters for [bmim⁺]

$$u(\psi) = k_{\psi}(\psi - \psi_0)^2$$

Atom 1	Atom 2	Atom 3	Atom 4	k_{ψ} (kcal mol ⁻¹ rad ⁻²)	ψ (degrees)
CPH2	NR1	NR2	HR1	0.5	0
NR1	CPH1	CPH2	CN7B	0.6	0
NR2	CPH1	CPH2	CN7B	0.6	0
CPH1	CPH1	NR2	HR3	0.5	0
CPH1	CPH1	NR1	HR3	0.5	0

Table S-9. Bond stretching potential parameters for [Tf₂N⁻]

$$u(l) = \frac{k_l}{2}(l - l_0)^2$$

Atom 1	Atom 2	k_l (kcal mol ⁻¹ Å ⁻²)	l_0 (Å)
CTF2	FTF2	441.80	1.3230
CTF2	STF2	235.42	1.8180
STF2	OTF2	637.07	1.4420
NTF2	STF2	372.01	1.5700

Table S-10. Angle bending potential parameters for [Tf₂N⁻]

$$u(\theta) = \frac{k_{\theta}}{2}(\theta - \theta_0)^2$$

Atom 1	Atom 2	Atom 3	k_{θ} (kcal mol ⁻¹ rad ⁻²)	θ_0 (degrees)
FTF2	CTF2	FTF2	93.33	107.10
STF2	CTF2	FTF2	82.93	111.80
CTF2	STF2	OTF2	103.97	102.80
OTF2	STF2	OTF2	115.80	118.50
OTF2	STF2	NTF2	94.51	113.60
CTF2	STF2	NTF2	97.51	100.20
STF2	NTF2	STF2	80.19	125.60

Table S-11. Torsional potential parameters for [Tf₂N⁻]

$$u(\chi) = k_{\chi}[1 + \cos(m\chi - \delta)]$$

Atom 1	Atom 2	Atom 3	Atom 4	k_{χ} (kcal mol ⁻¹)	m	δ (degrees)
TF2	CTF2	STF2	OTF2	0.1734	3	0
STF2	NTF2	STF2	OTF2	-0.0018	3	0
FTF2	CTF2	STF2	NTF2	0.1580	3	0
STF2	NTF2	STF2	CTF2	7.8329	1	0
				-2.4904	2	180
				-0.7636	3	0

Force field parameters for gas molecules

Table S-12. LJ and Coulombic parameters for the gas molecules in the TraPPE Potential

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Molecule	UA	Partial Charge q (e)	σ (Å)	ϵ/k_B (K)
CO ₂ (TraPPE)	C	+0.700	2.80	27.00
	O	-0.350	3.05	79.00
N ₂ (TraPPE)	N	-0.482	3.31	36.00
	M	+0.964	0.00	0.00
CH ₄ (OPLS-AA)	C	-0.240	3.50	32.21
	H	0.060	2.50	15.10

Table S-13. Bonds length and angle parameters in the TraPPE-UA potential

$$u(l) = \frac{k_l}{2}(l - l_0)^2$$

$$u(\theta) = \frac{k_\theta}{2}(\theta - \theta_0)^2$$

Adsorbate	Bond	k_l (K)	l_0 (Å)	Angle	k_θ (K)	θ_0 (degrees)
CO ₂	C-O	rigid	1.16	O-C-O	rigid	180.0
N ₂	N-M	rigid	0.55	N-M-N	rigid	180.0
CH ₄	C-H	331	1.09	H-C-H	35	109.5

Table S-14. Data values for Figure 3

ZIF	P (bar)	CO ₂ loading (mmol g ⁻¹)	Statistical uncertainty (mmol g ⁻¹)
ZIF-67	0.06	0.070	0.001
	0.23	0.249	0.005
	0.51	0.57	0.01
	1.14	1.35	0.01
	2.57	3.170	0.002
	5.87	6.03	0.02
	13.59	8.03	0.05
	33.82	8.86	0.01
BeIF-1	0.06	0.33	0.04
	0.23	1.11	0.01
	0.51	2.58	0.01
	1.14	4.92	0.02
	2.57	6.97	0.02
	5.87	8.37	0.03
	13.59	9.22	0.06
	33.82	9.50	0.03
CdIF-1	0.06	0.036	0.001
	0.23	0.116	0.002
	0.51	0.28	0.01
	1.14	0.629	0.002
	2.57	1.52	0.01
	5.87	3.85	0.03
	13.59	7.35	0.01
	33.82	8.92	0.07

Table S-15. Data values for Figure 4

ZIF	IL composition (wt%)	CO ₂ loading (mmol g ⁻¹)	Statistical uncertainty (mmol g ⁻¹)
ZIF-8	0.00	0.06	
	0.02	0.06	0.01
	0.12	0.11	0.01
	0.21	0.13	0.01
	0.31	0.13	0.02
	0.32	0.12	0.01
	0.35	0.08	0.03
	0.38	0.03	0.01
CdIF-1	0.00	0.037	0.001
	0.11	0.064	0.001
	0.20	0.078	0.002
	0.29	0.11	0.01
	0.34	0.10	0.01
	0.38	0.07	0.01
	0.42	0.03	0.01
	0.43	0.01	0.01
BeIF-1	0.00	0.33	0.04
	0.17	0.57	0.09
	0.29	0.49	0.05
	0.34	0.33	0.05
	0.38	0.11	0.03
ZIF-67	0.00	0.073	0.001
	0.14	0.13	0.02
	0.24	0.21	0.01
	0.32	0.15	0.04
	0.40	0.02	0.01

Table S-16. Data values for Figures 5 and 6

ZIF	IL composition (wt%)	APV	CO ₂ /N ₂ Selectivity	Statistical uncertainty	CO ₂ /CH ₄ Selectivity	Statistical uncertainty
				CO ₂ /N ₂		CO ₂ /CH ₄
CdIF-1	0.00	1.00	8.86	3.13	5.66	0.58
	0.11	0.83	14.93	0.99	12.83	0.30
	0.20	0.64	23.21	3.05	17.75	0.96
	0.29	0.38	41.25	3.50	28.70	2.17
	0.34	0.28	59.66	0.57	43.10	3.45
	0.38	0.18	78.16	13.45	46.13	8.01
	0.42	0.087	95.16	21.17	54.10	11.63
	0.43	0.059	80.52	30.03	43.83	16.53
BeIF-1	0.00	1	17.98	3.33	11.72	1.55
	0.17	0.64	41.75	7.71	24.34	3.91
	0.29	0.26	73.79	15.49	38.48	10.18
	0.34	0.17	98.07	14.57	54.69	11.59
	0.38	0.073	118.68	25.24	51.89	11.78
ZIF-67	0.00	1	10.55	1.30	7.99	0.53
	0.14	0.76	20.17	3.47	15.55	2.65
	0.24	0.49	40.91	0.92	28.37	1.80
	0.32	0.25	60.88	5.88	38.14	5.15
	0.40	0.079	111.81	14.89	45.94	11.03
ZIF-8	0.00	1	9.30		7.40	
	0.02	0.95	10.17	1.02	8.11	0.57
	0.21	0.46	26.46	2.65	16.88	1.18
	0.31	0.22	64.39	8.88	39.81	3.75
	0.32	0.18	76.27	10.23	46.18	6.43
	0.38	0.033	55.05	9.14	29.29	11.73

Monte Carlo simulations details

In all simulations, a super-cell of eight ($2 \times 2 \times 2$) unit cells was used. The pristine metal ZIF analogues were based on structural information that can be found in our previous work.³

Insertion of ILs (for the preparation of the various metal IL@ZIFs analogues)

The IL@ZIF metal analogues were designed and built based on the individual pristine metal ZIF analogues, by inserting ILs, based on the methodology described in the main text and on the following Monte Carlo (MC) simulation details.

IL cations and ions are subject to:

- Translation, where they are selected at random with a uniform probability of $1/N$, where N is the total number of molecules, and they translate following uniform distribution on the interval of maximum displacement (\pm maximum displacement in Å). Depending on the selected IL composition and the ZIF metal analogue, the number of IL pairs can reach up to 48, that correspond to 96 ions in total.
- Rotation, where they are selected at random with a uniform probability of $1/N$ and they rotate following uniform distribution on the interval of maximum rotation (\pm maximum rotation for species in degrees),
- Insertion, where they are selected at random with a uniform probability of $1/N$,
- Deletion, where they are selected at random with a uniform probability of $1/N$,
- Regrowth with configurational biased Monte Carlo (CBMC), where they are selected at random with a uniform probability of $1/N$. Then a bond is selected with uniform probability of $1/N_{\text{bonds}}$. Then the fragments on the one or the other side of the bond are deleted with equal probability. The deleted fragments are reinserted. For more details, one should refer to the Cassandra code's original publication¹ and manual.²

Sorption of CO₂, CH₄ and N₂

During the sorption simulations the following moves apply:

- Translation, where IL or adsorbate species is selected at random based on the mole fraction of species. Then, a molecule from the selected species is selected with a uniform probability of $1/N$, where N is the total number of molecules of the selected species, and they translate following uniform distribution on the interval of maximum displacement (\pm maximum displacement in Å). Depending on the selected IL composition and the ZIF metal analogue, the number of IL pairs can reach up to 48, that correspond to 96 ions in total. Regarding the number of adsorbates, depending on the ZIF and IL@ZIF metal variant, N ranges between 1 – 6 for the lowest pressure (0.065 bar) and 172 – 265 for the highest pressure (33.8 bar),

- Rotation, where an IL or adsorbate species is selected at random based on the mole fraction of species. Then, a molecule from the selected species is selected with a uniform probability of $1/N$ and they rotate following uniform distribution on the interval of maximum rotation (\pm maximum rotation for species in degrees),
- Insertion, which applies only to the adsorbates. An adsorbate molecule is selected with a uniform probability of $1/N$,
- Deletion, which applies only to the adsorbates. An adsorbate molecule is selected with a uniform probability of $1/N$,
- Regrowth, which applies only to the ILs. An IL anion or cation is selected with a uniform probability of $1/N$. Then a bond is selected with uniform probability of $1/N_{\text{bonds}}$. Then the fragments on the one or the other side of the bond are deleted with equal probability. The deleted fragments are reinserted. For more details, one should refer to the Cassandra code's original publication¹ and manual.²

Table S-17 summarizes the parameter and probability values for the two types of simulation (insertion of ILs and gas sorption).

Table S-17. MC simulation details for the insertion of ILs and sorption of various gases

Move		Type of simulation		
		Insertion of ILs cation or anion	Sorption	
			ILs (cation or anion)	Adsorbate (CO ₂ , N ₂ , CH ₄)
Translation	Percentage	20	20	20
	Max. displacement (Å)	1.0	1.0	2.0
Rotation	Percentage	20	20	20
	Max. rotations (deg.)	10.0	10.0	180.0
Regrowth	Percentage	10	20	-
Insertion	Percentage	25	-	20
Deletion	Percentage	25	-	20

For the insertion and adsorption runs with the configurational bias method of Cassandra code we used the following parameters (according to Cassandra code's nomenclature):

- Rcut_cbmc 6.5 Å (cutoff for partially regrown molecule),
- Kapp_ins 12 (equals the number of generated trial positions),
- Kappa_dih 10 (equals the number of generated trial dihedral angles),
- Ewald summation method (10^{-5} accuracy) (12 Å),
- Lennard-Jones 12-6 potential (14 Å).

Different configurations and convergence

Multiple configurations at each IL composition must be considered to ensure statistical accuracy. These configurations reflect the different initial conformations and distribution of the ILs in the ZIF cages, at a given IL composition. The desired number of IL molecules are inserted in the ZIF analogue under investigation, following the methodology described in the manuscript and in the section above with CBMC.

A simple factor is adopted to assess the deviation of the IL distribution in the cages from the uniform distribution:

$$\text{Deviation of ILs distribution from uniform distribution} = \sqrt{\frac{\sum_i^N (n_u - n_i)^2}{N}}$$

where n_u is the number of anion molecules in a given unit cell corresponding to a uniform distribution, n_i is the number of anion molecules in a given unit cell of the actual initial configuration and N is total the number of unit cells used in the simulation.

Then we estimate the average deviation from the uniform distribution for each composition, by averaging over all the different IL initial configurations. For a better understanding we plot average deviation values for selected IL composition points for every metal analogue.

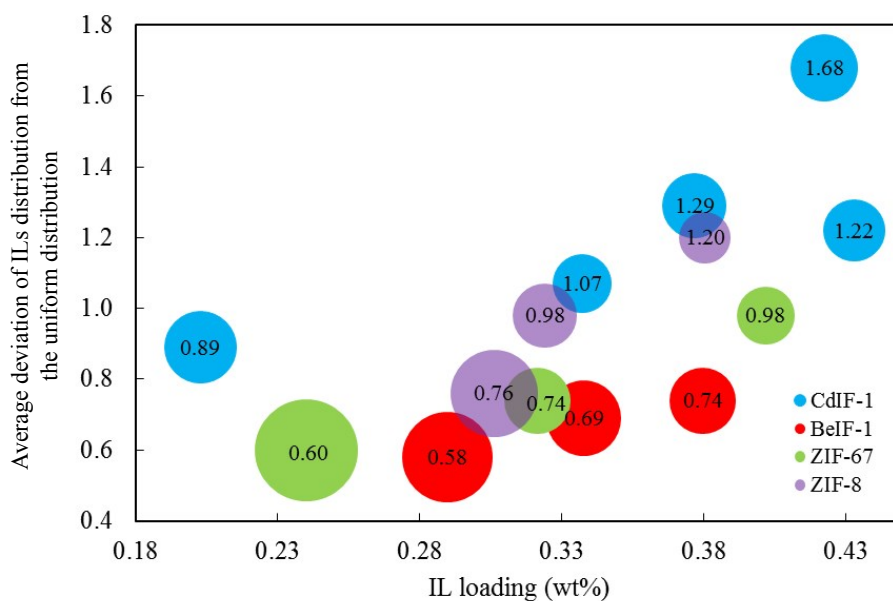


Figure S-1. Average deviation from uniform distribution for the distribution of ILs for various compositions points at each metal analogue.

The size of the circle corresponds to the coefficient of variance (CV), defined as:

$$CV = \frac{\sigma}{\text{average deviation from uniform distribution}}$$

Sampling more configurations in our calculations drives the CV to convergence as the following plot shows.

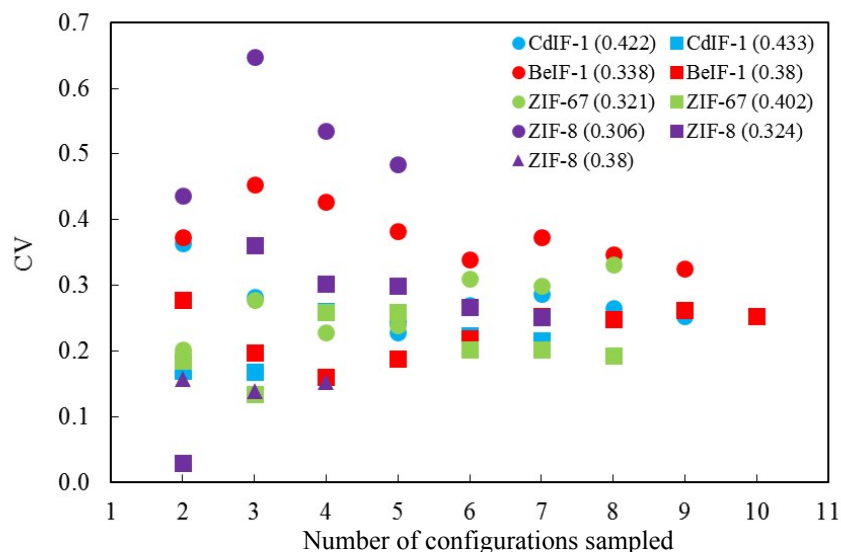


Figure S-2. CV as a function of number of IL configurations sampled in the calculations for two different compositions for every metal analogue.

For a better understanding of the effect that the number of configurations has on the estimated selectivity we have gathered results for two different IL compositions for each metal analogue. The selectivity of CO₂/CH₄ and CO₂/N₂ as a function of the number of configurations is shown in Figure S-3. It is clear that at least three configurations must be considered to reach good statistics, therefore we employed an additional number of configurations. This strategy was applied to all IL compositions.

Table S-18 summarizes the number of configurations employed in our calculations.

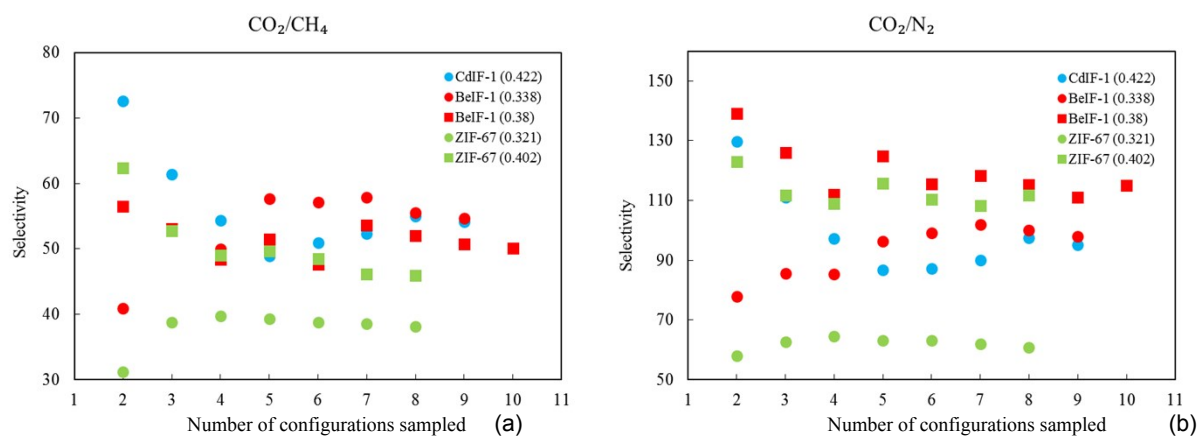


Figure S-3. Selectivity of (a) CO₂/CH₂ and (b) CO₂/N₂ as a function of the number of configurations considered in the simulations. In parenthesis for each metal analogue the IL composition is shown.

Table S-18. Number of configurations used to reach convergence in the sorption calculations for every metal IL@ZIF analogue and at a given IL composition

Structure	IL loading wt%	Number of structures
ZIF-67	0.14	3
	0.24	3
	0.32	8
	0.40	8
BeIF-1	0.17	3
	0.29	3
	0.34	9
	0.38	10
	0.11	3
	0.20	3
	0.29	3
CdIF-1	0.34	3
	0.38	3
	0.42	9
	0.43	5
ZIF-8	0.02	3
	0.21	3
	0.31	4
	0.32	7
	0.38	5

References

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