Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

The Effect of SO_2 on CO_2 Capture in Zeolitic Imidazolate Frameworks

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S1. Zeolitic imidazolate frameworks (ZIFs)

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S1. Zeolitic imidazolate frameworks (ZIFs)

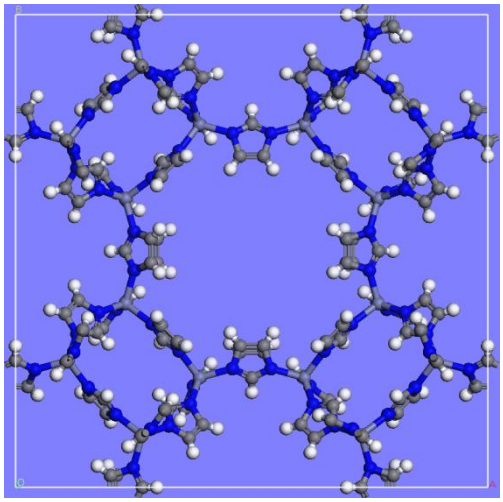

Fig. S1 ZIF-10 unit cell. ZIF-10 belongs to the MER topology. In the ZIF-10 framework, each Zn atom is bridged by four imidazolate (IM) linkers.The unit cell lengths of ZIF-10 are: a = 27.061Å b = 27.061 Å, c = 19.406 Å, and angles $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$.

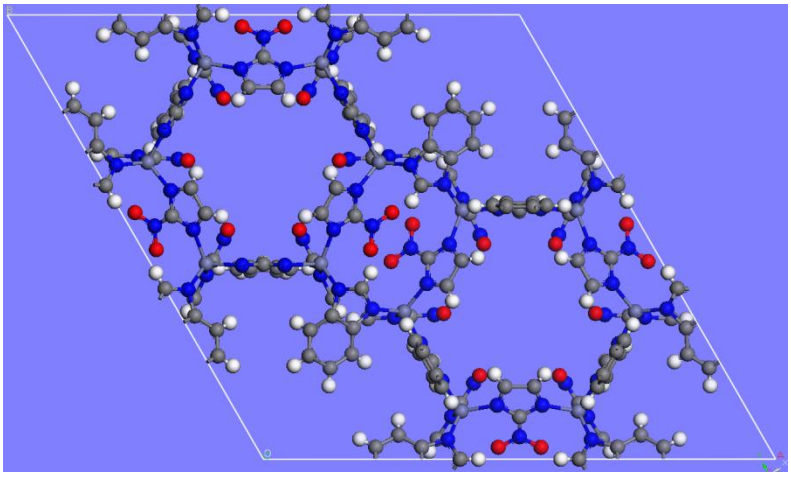

Fig. S2 ZIF-68 unit cell. ZIF-68 has the GME topology. In the ZIF-68 framework, each Zn atom is bridged by two different liners: benzimidazole (bIM) and 2-nitroimidazole (nIM). The framework has small side pockets as well as large pore channels. The unit cell lengths of ZIF-68 are: a = 26.64 Å b = 26.64 Å, c = 18.488 Å, and angles $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 120^o$.

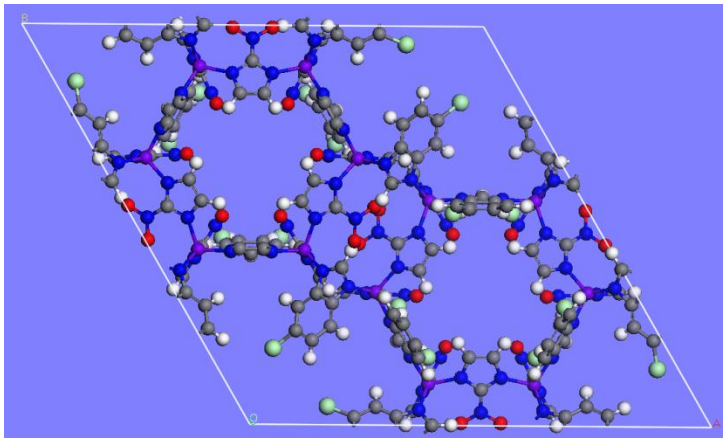

Fig. S3 ZIF-69 unit cell. ZIF-69 has the GME topology. In the ZIF-68 framework, each Zn atom is bridged by two different liners: 5-chlorobenzimidazole (cbIM) and 2-nitroimidazole (nIM). The framework has small side pockets as well as large pore channels. The unit cell lengths of ZIF-69 are: a = 26.084 Å b = 26.084 Å, c = 19.408 Å, and angles $\alpha = 90^{o}$, $\beta = 90^{o}$, $\gamma = 120^{o}$.

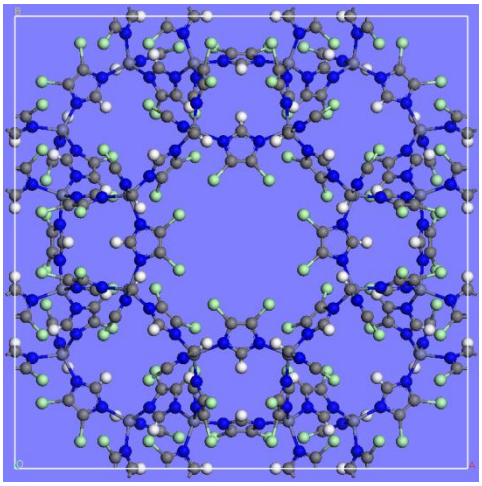

Fig. S4 ZIF-71 unit cell. ZIF-71 has the RHO topology. In the ZIF-71 framework, each Zn atom is bridged by 4,5-dicholoroimidazolate (dcIM). The framework contains large cages of connected by small windows. The unit cell lengths of ZIF-71 are: a = 28.554 Å b = 28.554 Å, c = 28.554 Å, and angles $\alpha = 90^{o}$, $\beta = 90^{o}$, $\gamma = 90^{o}$.

S2. Partial atomic charges derived from DFT calculations

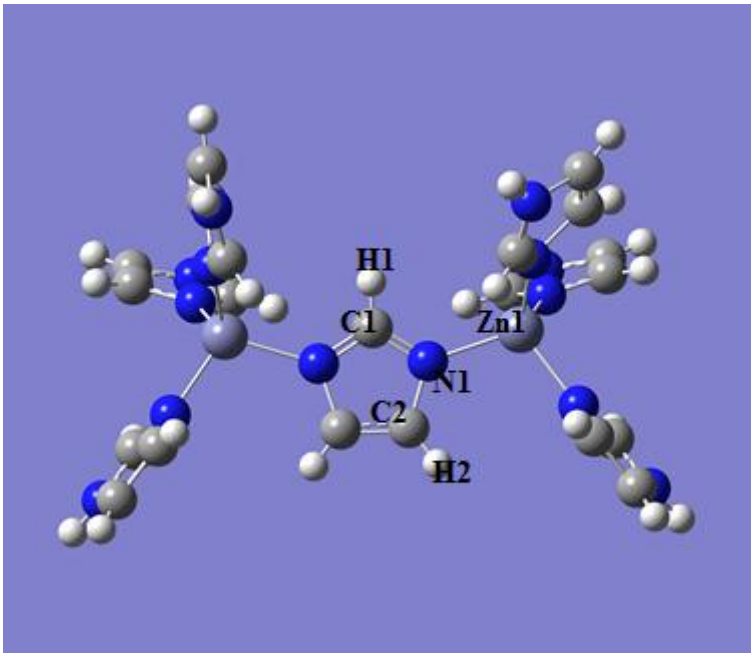

Fig. S5 Cluster $(Zn_2C_{21}N_{14}H_{27})^{+3}$ used for deriving partial charges on ZIF-10

Table S1 Partial atomic charges for ZIF-10 atoms.

Atom type	Zn1	N1	C1	H1	C2	H2
Charge (e)	0.176	-0.1265	0.062	0.089	-0.211	0.218

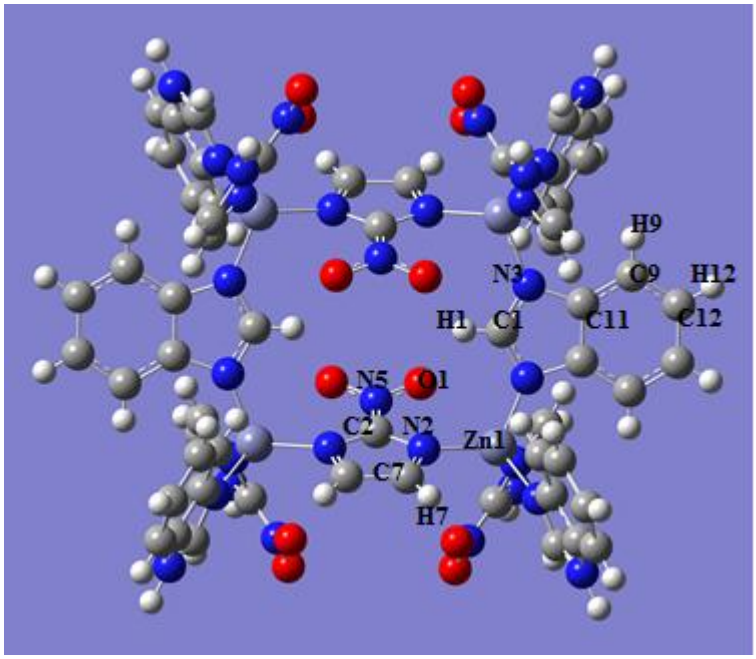

Fig. S6 Cluster $(Zn_4C_{60}N_{30}H_{50}O_{12})^{+4}$ used for deriving partial charges on ZIF-68

Table S2 Partial atomic charges for ZIF-68 atoms.

Atom type	**Zn1**	**N2**	**C7**	**H7**	**C2**	**C1**
Charge (e)	0.3	-0.35	0.01	0.15	0.56	0.16
Atom type	**N5**	**O1**	**H1**	**N3**	**C11**	**C9**
Charge (e)	0.44	-0.43	0.016	-0.148	0.045	-0.192
Atom type	**H9**	**C12**	**H12**			
Charge (e)	0.151	-0.152	0.178			

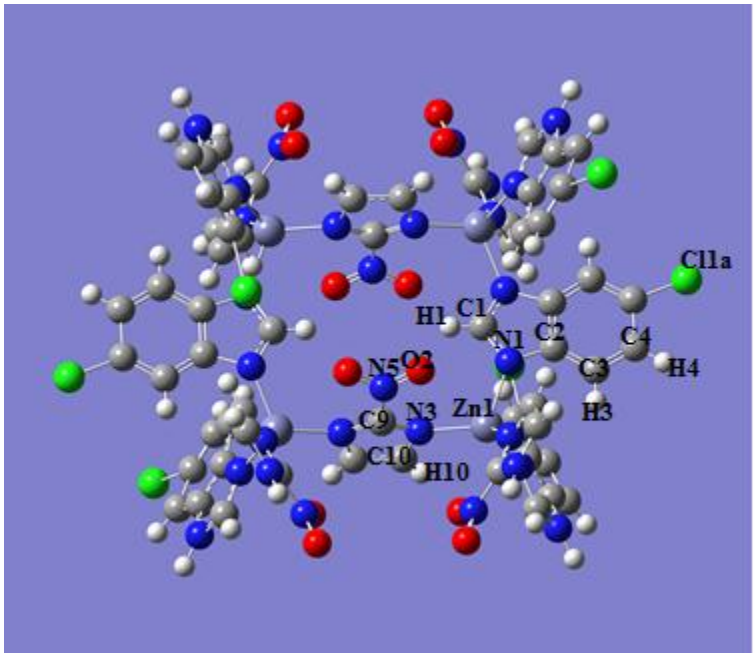

Fig. S7 Cluster $(Zn_4C_{60}N_{30}H_{44}O_{12}Cl_6)^{+4}$ used for deriving partial charges on ZIF-69

Table S3 Partial atomic charges for ZIF-69 atoms.

Atom type	**Zn1**	**O2**	**N1**	**N5**	**C9**	**N3**
Charge (e)	0.083	-0.452	0.00	0.796	0.204	-0.136
Atom type	**C10**	**H10**	**H1**	**C1**	**C2**	**C3**
Charge (e)	-0.18	0.233	0.151	-0.12	0.032	-0.066
Atom type	**H3**	**C4**	**H4**	**Cl1a**		
Charge (e)	0.074	-0.133	0.09	0.052		

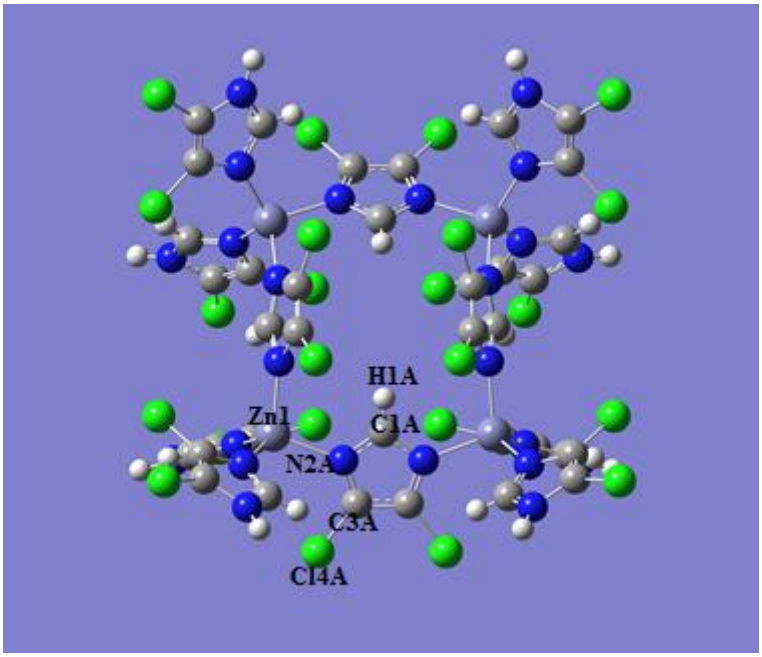

Fig. S8 Cluster $(Zn_4C_{36}N_{24}H_{20}Cl_{24})^{+4}$ used for deriving partial charges on ZIF-71

Table S4 Partial atomic charges for ZIF-71 atoms.

Atom type	Zn1	H1A	C1A	N2A	C3A	Cl4A
Charge (e)	-1.56	0.346	-0.92	0.898	-0.314	0.093

S3. Force field parameters

Table S5 LJ potential parameters for ZIF framework atoms, taken from Ref [1].

Atoms	ε/*k* (K)	σ (Å)
Zn	53.40	2.46155
O	21.75	3.118
C	40.27	3.43
N	22.72	3.26
H	14.14	2.57
Cl	99.23	3.516

Table S6 LJ potential parameters and charges for Guest gas molecules. "com" in the table refers to the center position pseudo atom.

Molecules/atoms		ε/*k* (K)	σ (Å)	q (e)	Refs
CO_2	C_CO_2	27.0	2.80	0.70	2
	O_CO_2	79.0	3.05	0.35	
H_2O	Ow	89.633	3.097	0.0	3
	Hw	-	-	+0.241	
	Lw	-	-	-0.241	
N_2	N_N_2	36.0	3.31	-0.4048	2
	com_N_2	0	0	0.8096	
	com_O_2	0	0	0.224	
SO_2	S_SO_2	73.8	3.39	0.59	4
	O_SO_2	79.0	3.05	-0.295	

S4. Simulated pure CO_2 and N_2 isotherms and N_2 uptake from flue gas mixture

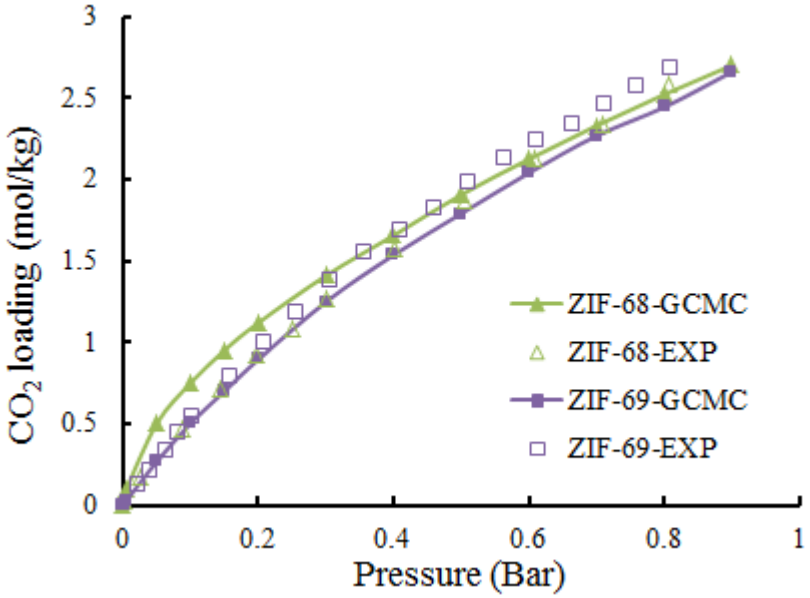

Fig. S9 Comparison of simulated pure CO_2 isotherms and experimental data[5] in ZIF-68 and ZIF-69 up to 1 bar pressure at 273K. (GCMC = simulated data, EXP = experimental data)

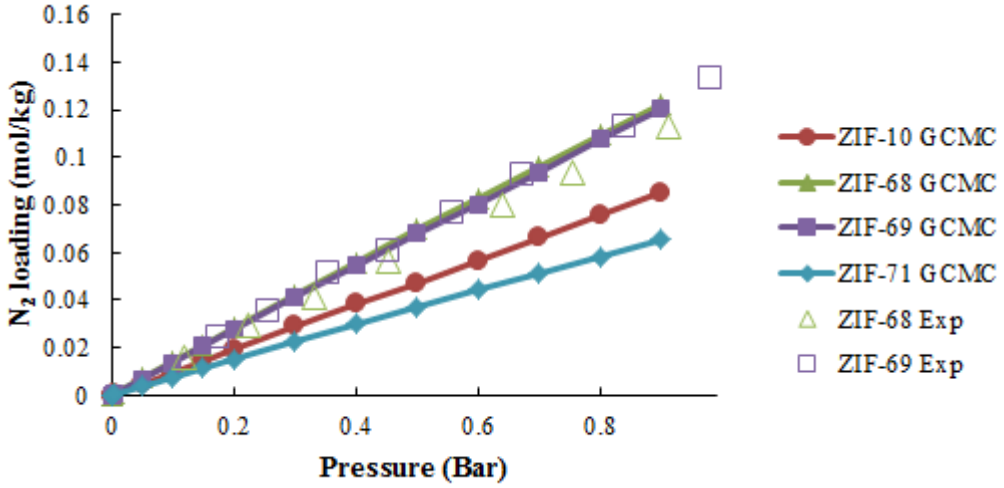

Fig. S10 Simulated pure N_2 isotherms in ZIF-10, ZIF-68, ZIF-69 and ZIF-71 up to 1 bar pressure at 298K.

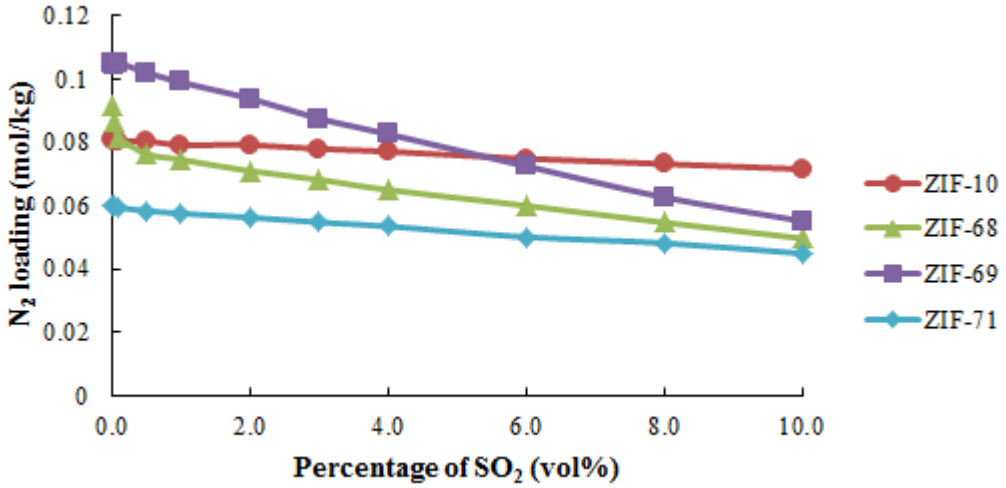

Fig. S11 The N_2 uptake as a function of SO_2 feed concentration from flue gas mixture in ZIF-10, ZIF-68, ZIF-69 and ZIF-71 up to 1 bar pressure.

S5. Snapshots and adsorption density profiles a from GCMC simulations

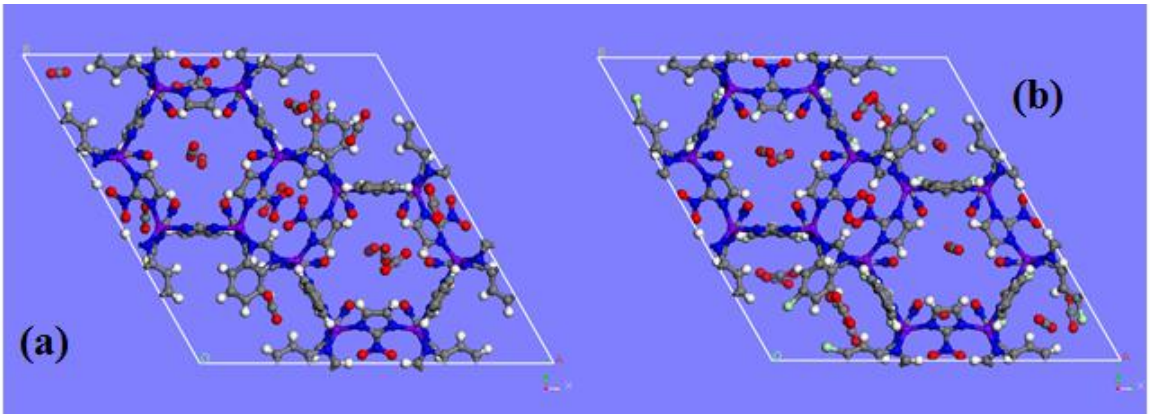

Fig. S12 Simulated pure CO_2 adsorption snapshot in ZIF-68 (298K, 0.3bar). (Grey = Carbon, red = Oxygen, white = Hydrogen, blue = Nitrogen, purple = Zinc)

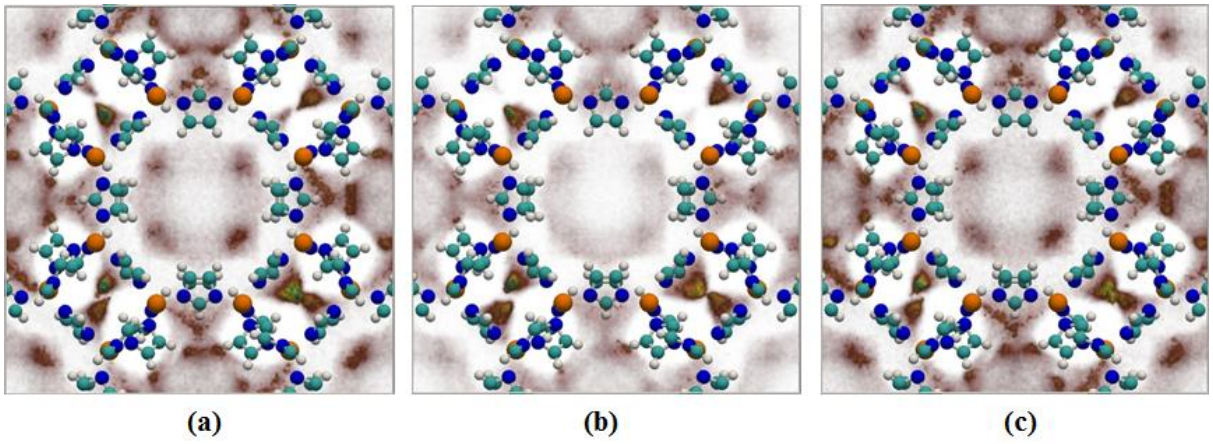

Fig. S13 Simulated adsorption density profiles in ZIF-10 **(a)** CO_2 adsorbed from a CO_2/N_2 (15%/85%) mixture, **(b)** SO_2 and **(c)** CO_2 adsorbed from a $CO_2/N_2/SO_2$ (15%/81%/4%) mixture, (cyan = carbon,, white = hydrogen, red = oxygen, orange = zinc).

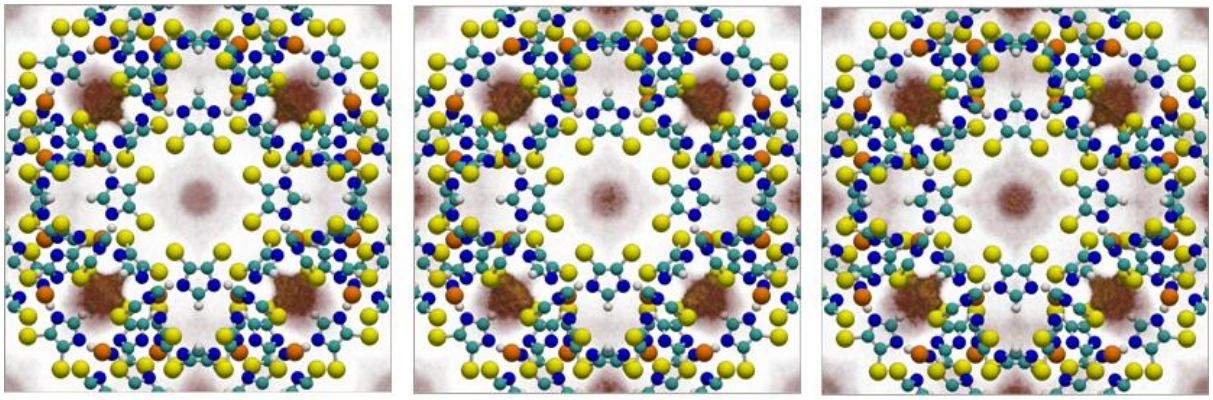

Fig. S14 Simulated adsorption density profiles in ZIF-71 **(a)** CO_2 adsorbed from a CO_2/N_2 (15%/85%) mixture, **(b)** SO_2 and **(c)** CO_2 adsorbed from a $CO_2/N_2/SO_2$ (15%/81%/4%) mixture, (cyan = carbon,, white = hydrogen, red = oxygen, orange = zinc, yellow = chlorine).

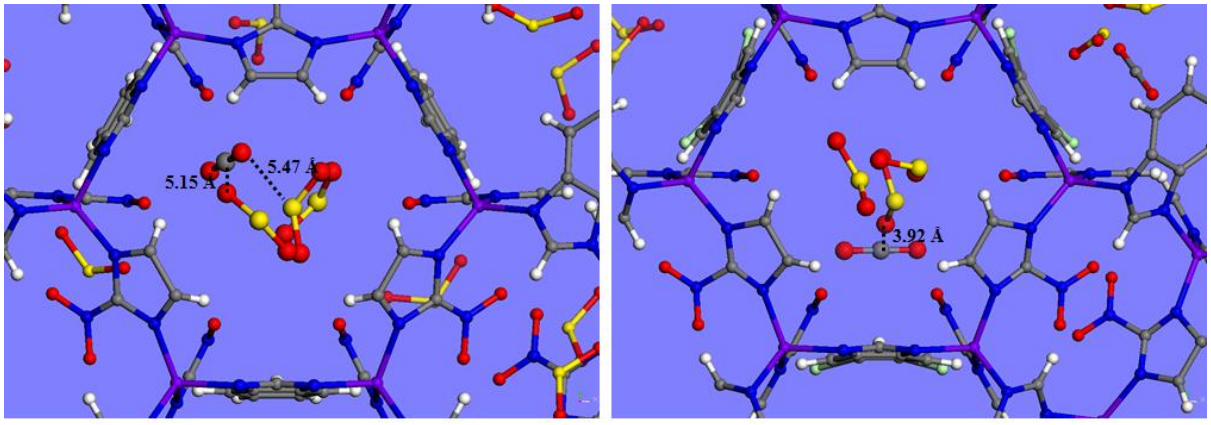

Fig. S15 Simulated adsorption snapshots **(a)** in ZIF-68, **(b)** in ZIF-69 from $CO_2/N_2/SO_2$ (15%/81%/4%) mixture 298K 1 bar. (Grey = Carbon, red = Oxygen, white = Hydrogen, blue = Nitrogen, purple = Zinc, Teal= Chlorine)

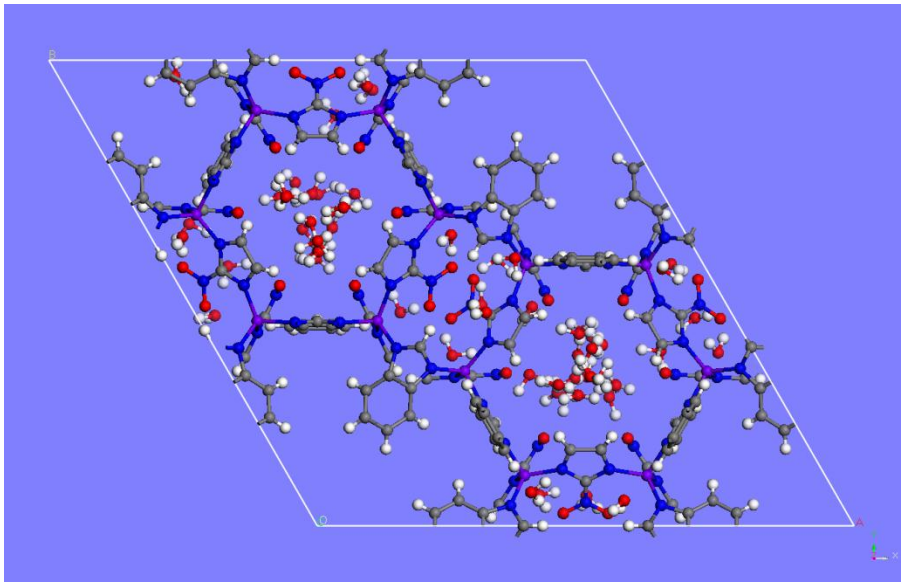

Fig. S16 Simulated pure water adsorption snapshot in ZIF-68 (298K, 0.2 bar). (Grey = Carbon, red = Oxygen, white = Hydrogen, blue = Nitrogen, purple = Zinc)

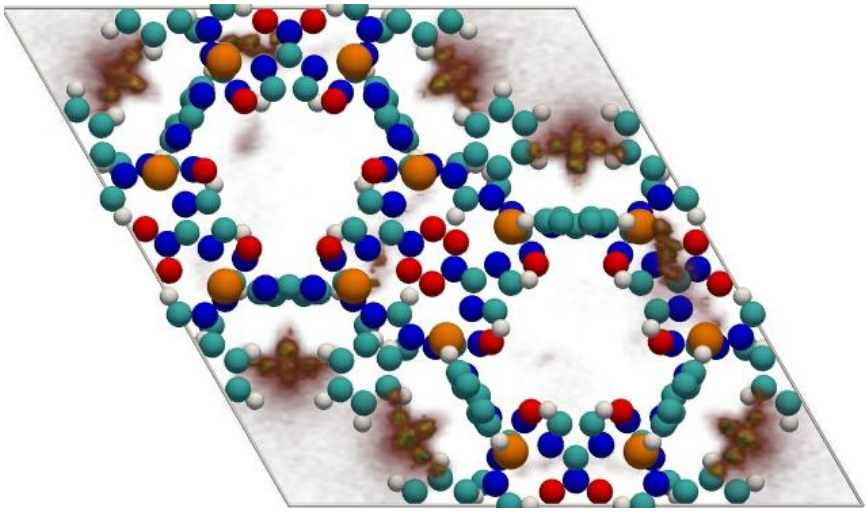

Fig. S17 Simulated CO_2 adsorption density profile from a $CO_2/N_2/SO_2/H_2O$ (15%/80.9%/0.1%/4%) mixture in ZIF-68. (cyan = carbon, white = hydrogen, red = oxygen, yellow = chlorine, orange = zinc).

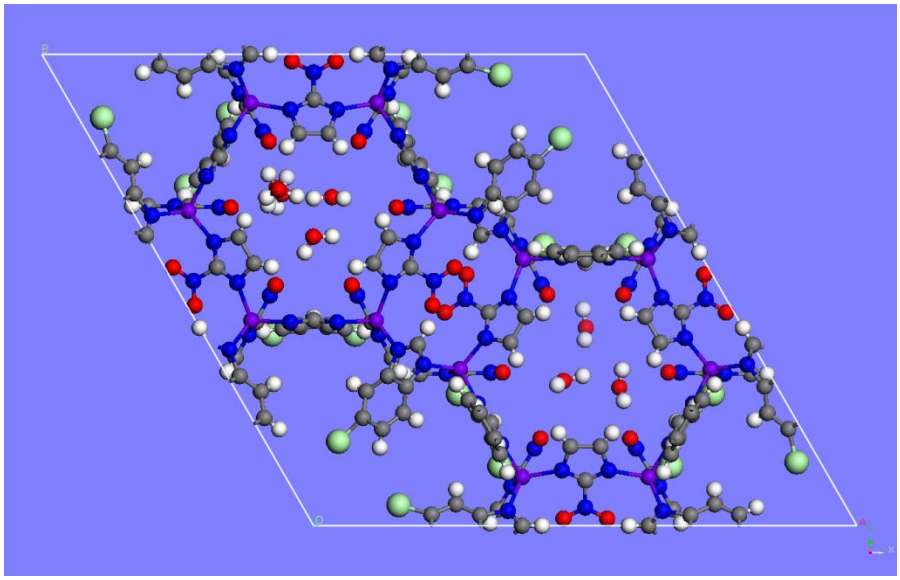

Fig. S18 Simulated pure water adsorption snapshot in ZIF-69 (298K, 0.2 bar). (Grey = Carbon, red = Oxygen, white = Hydrogen, blue = Nitrogen, purple = Zinc, teal = Chlorine)

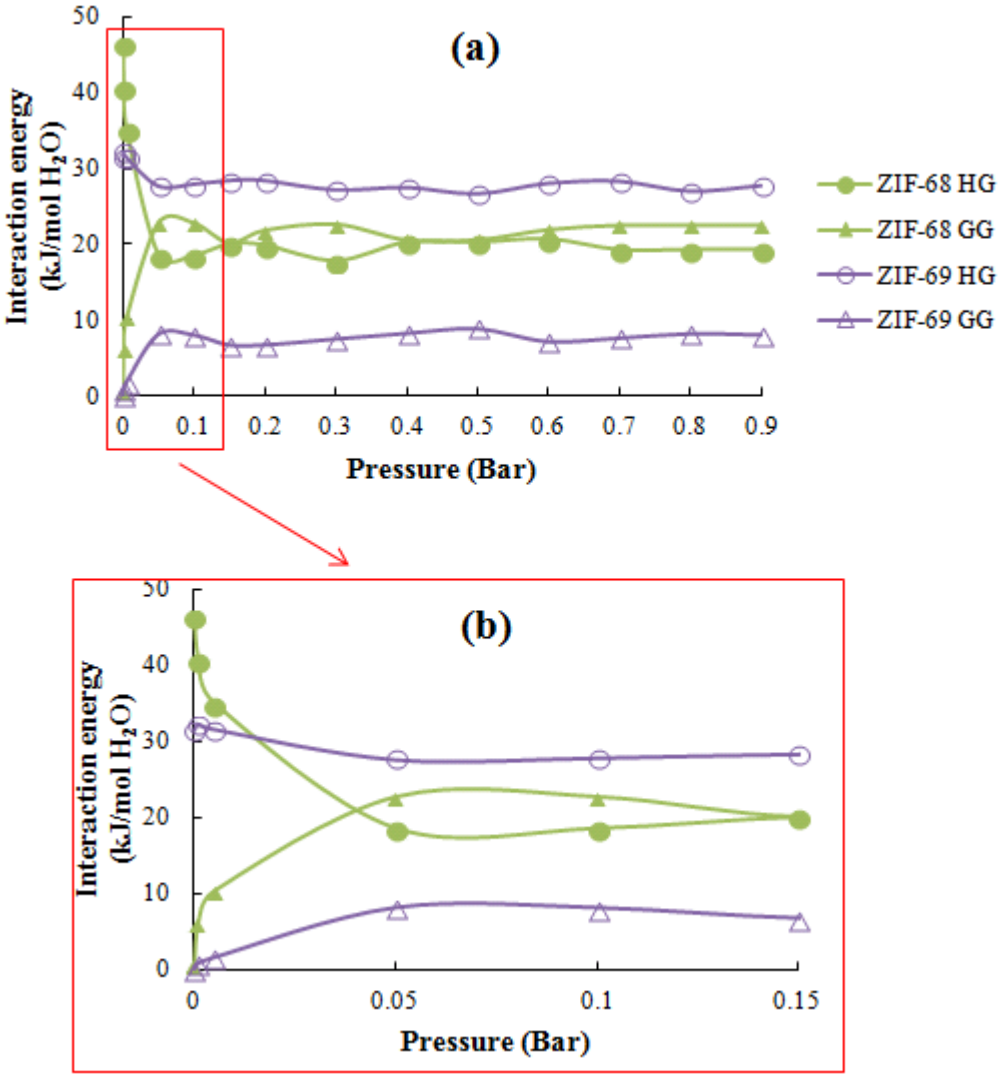

Fig. S19 Host-guest (HG) and guest-guest (GG) interaction energies for water adsorption in ZIF-68 and ZIF-69 at 298K as a function of H_2O pressure.

References

(1) Liu, B.; Smit, B. *J. Phys. Chem. C* **2010**, *114*, 8515-8522.
(2) Potoff, J. J.; Siepmann, J. I. *AlChE J.* **2001**, *47*, 1676-1682.
(3) Rick, S. W. *J. Chem. Phys* **2004**, *120*, 6085-6093.
(4) Ketko, M. H.; Kamath, G.; Potoff, J. J. *J. Phys. Chem. B* **2011**, *115*, 4949-4954.
(5) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939-943.