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Supporting Information

# **A Comprehensive Methodology to Screen Metal-Organic Frameworks towards Sustainable Photofixation of Nitrogen**

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**Details regarding the Monte Carlo (MC) and Molecular Dynamics (MD) simulation in the paper.**

The structures were assumed rigid and potential parameters were assigned using Universal Force Field (UFF) (Rappe, Casewit, Colwell, Goddard, & Skiff, 1992). Lennard-Jones (LJ) potential was used to define adsorbate-adsorbate and adsorbate-MOF van der Waals interactions. The parameters is listed in Table S1. LJ and Columbic parameters for the adsorbates (N<sub>2</sub> and NH<sub>3</sub>) was carried out using TraPPE force field (Martin & Siepmann, 1998; Zhang & Siepmann, 2010). (Table S2). Pair interactions was defined by employing Lorentz-Berthelot mixing rules (Equations S1-S2). The van der Waals interactions were computed with a 12.8 Å cutoff radius with tail correction. A 2x2x2 unit cell is used in the simulations periodic boundary conditions were applied in all dimensions. Point charges were assigned using equilibration method, and Ewald summation method (Ewald, 1921) was used to estimate electrostatic interactions with a real space cutoff of 12 Å and accuracy of  $1 \times 10^{-6}$ .

$\sigma$  between species i and j is given by:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (\text{Equation S1})$$

while  $\epsilon$  between species i and j is given by:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (\text{Equation S2})$$

Table S1: Leannard Jones LJ potential parameters UFF)

Atom	$\sigma$ (Å)	$\epsilon/k_B$ (K)
Zn	1.96	6.29
Ti	3.25	85.55
H	2.51	7.55
C	2.65	7.90
N	3.40	43.77
O	3.40	43.28
Br	3.40	55.05

Table S2: LJ and Columbic Parameters (Adsorbates) in the TraPPE Potential

Adsorbate	UA	Partial Charge q (e)	$\sigma$ (Å)	$\epsilon/k_B$ (K)
N <sub>2</sub>	N	-0.482	3.31	36.00
	M	0	0	0
NH <sub>3</sub>	N	0	3.42	185.00
	H	+0.410	0	0
	m	-1.230	0	0

For the GCMC simulations. A total of  $2 \times 10^5$  total MC cycles were used with the first  $1 \times 10^4$  being equilibration cycles. The computations were carried out at 298.15 K and pressure range [1-10 bar]. The fugacity coefficients are calculated using Peng-Robinson (PR) equation of state [ref]. NVT ensemble MD was employed to estimate single gas diffusion coefficients by plotting mean square displacement. A total of  $5 \times 10^6$  cycles was used a time a step of 0.0005 ps. The vdW interactions were not turned off. Using the slope of the MSD, diffusion coefficients were estimated. For the computational work of heat of adsorption at infinite dilution, 50000 cycles was used with 5000 equilibration cycles.

## Supporting Figures (Figure S1-S2)

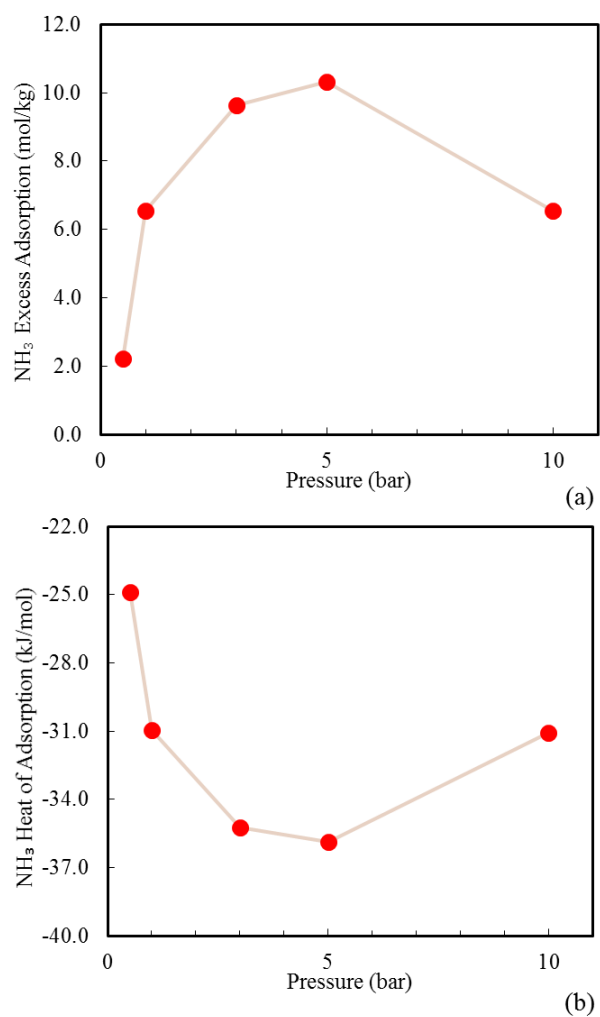


Figure S1 (a) Excess adsorption isotherm of  $\text{NH}_3$  at 298.15 K (b) Isosteric heat of adsorption of  $\text{NH}_3$  at 298.15 K as a function of pressure. Error bars are smaller than symbols' size.

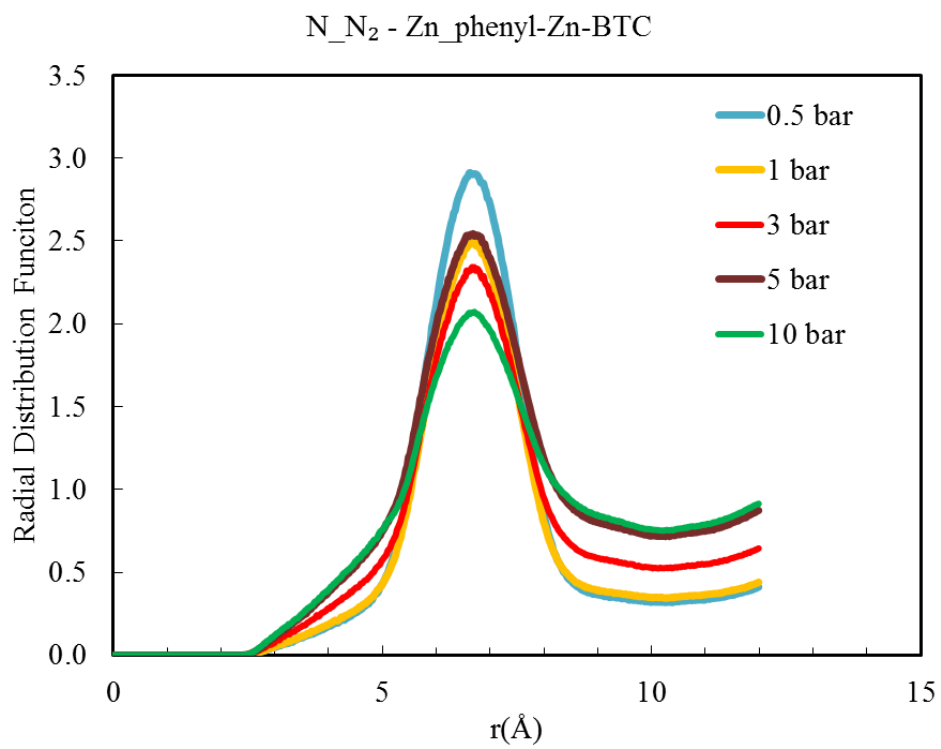


Figure S2. Radial distribution function between N atom in N<sub>2</sub> molecule and Zn in phenyl-Zn-BTC as a function pressure

## References

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