

## Supporting Information:

# Elucidating Molecular Oxygen Adsorption in ZIF-8 through Integrated Experimental and Computational Studies

Chitrangda Singh<sup>1,2</sup>, Priyam Mangal<sup>1</sup>, Priyanka Surya<sup>3</sup>, Sweta Singh<sup>3</sup>, Sreedevi  
Upadhyayula<sup>2\*</sup>, Rashi Mathur<sup>1\*</sup>

<sup>1</sup>Applied Chemistry and Nanomaterial Science Department, Institute of Nuclear  
Medicine and Allied Sciences, Defence Research and Development Organization,  
Timarpur, New Delhi-110054, India.

<sup>2</sup>Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz  
Khas, New Delhi-110016, India.

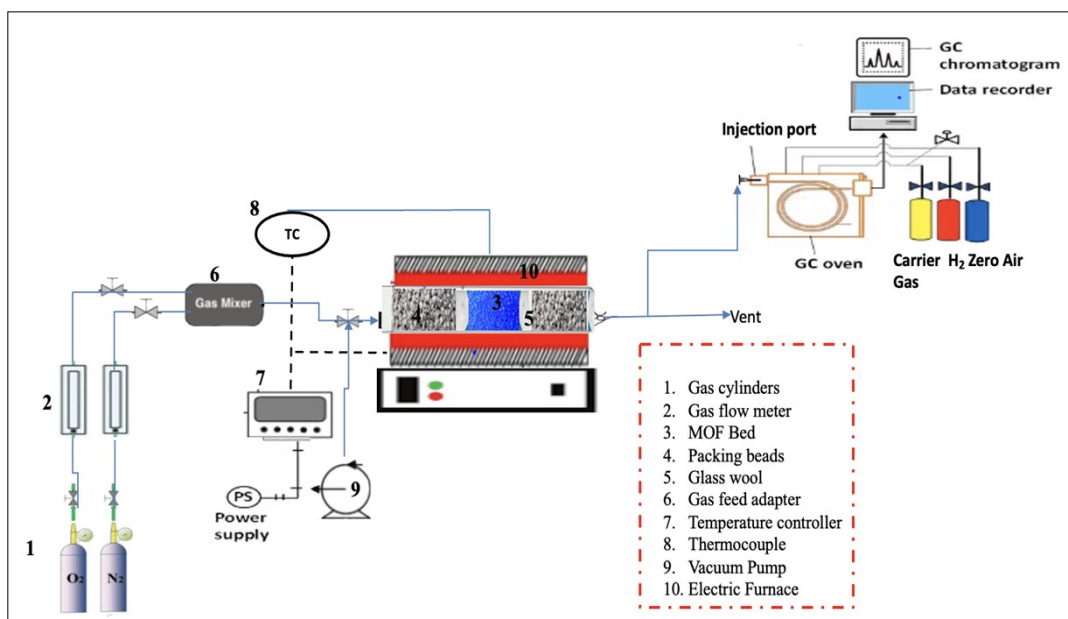
<sup>3</sup>Clinical Research and Medical Management Department, Institute of Nuclear  
Medicine and Allied Sciences, Defence Research Development Organization,  
Timarpur, New Delhi-110054, India.

\*Corresponding Authors E-mails: [rashimathur07@gmail.com](mailto:rashimathur07@gmail.com),  
[sreedevi@chemical.iitd.ac.in](mailto:sreedevi@chemical.iitd.ac.in)

### *Table of Contents*

1. **Fig. S1.** Schematic representation of process for molecular oxygen adsorption  
with fixed bed reactor packed with ZIF-8 powder sample.....Page no.S2
2. **Table S1.** Fitted Parameters of Column Adsorption Model.....Page  
no.S3

3. **Table S2.** Lennard–Jones intermolecular potential parameters based on the universal force field (UFF), Lennard–Jones potential equation, and Lorentz–Berthelot mixing rule.....*Page no.S4*
4. **Fig. S2.** Mean square displacement graph (a) Oxygen MSD curve ZIF-8P with solvent( $0.093 \text{ \AA}^2/\text{ps}$ ) (b) Oxygen MSD curve ( $14.37 \text{ \AA}^2/\text{ps}$ ) in presence of solvent in ZIF-8S.....*Page no. S5*
5. **Fig. S3.** Adsorption Configuration : Vertical views about the structures of oxygen diffusion in the aperture. Bond distances are in  $\text{\AA}$ . .....*Page no.S5-S6*
6. **Table S3.** Consolidated list of labelled  $\text{Zn}_{\text{MOF}} \cdots \text{O}_{\text{Oxygen molecule}}$ ;  $\text{N}_{\text{ligand}} - \text{O}_{\text{O}_2}$ ;  $\text{C}_{\text{ring}} - \text{O}_{\text{O}_2}$  distance that appears in the Figure S3.....*Page no.S7*
7. **Fig. S4:** Henry’s constant trend with respect to temperature observed for ZIF-8P and ZIF-8S model.....*Page no.S8*



**Fig. S1.** Schematic representation of process for molecular oxygen adsorption with fixed bed reactor packed with ZIF-8 powder.

**Table S1.** Fitted Parameters of Column Adsorption Model

<b><u>S.No.</u></b>	<b><u>Models</u></b>	<b><u>Parameters</u></b>	<b><u>Oxygen as Adsorbate</u></b>
<b><u>1.</u></b>	<b><u>Thomas model - ZIF-8</u></b>	$K_{Th}$ (mL/mg.min)	<u>0.002</u>
		$Q_o$ (mg/g)	25.7
		$R^2$	<u>0.97019</u>
<b><u>2.</u></b>	<b><u>Adam-Bohart Model</u></b>	$K_{AB}$ (mL/mg.min)	<u>0.0023</u>
		$N_o$ (mg/L)	<u>2.954</u>
		$R^2$	<u>0.97</u>
<b><u>3.</u></b>	<b><u>Yoon-Nelson Model</u></b>	$K_{YN}$ (min <sup>-1</sup> )	<u>0.09</u>
		$\tau$ (min)	8
		$R^2$	<u>0.9731</u>

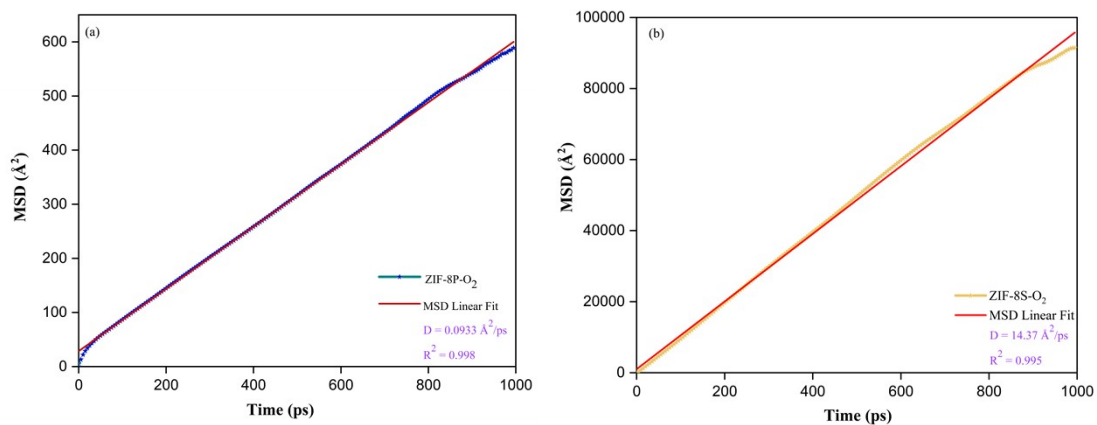
**Table S2.** Lennard–Jones intermolecular potential parameters based on the Dreiding force field, Lennard–Jones potential equation, and Lorentz–Berthelot mixing rule

Site	Type	$\epsilon/k_B$ (K)	$\sigma$ (Å)
<b>Oxygen</b>			
<b>O<sub>2</sub></b>	O-O	48.156	3.033
<b>ZIF-8</b>			
<b>H</b>	H	7.649	2.846
<b>C</b>	C	47.854	3.473
<b>N</b>	N	38.948	3.263
<b>Zn</b>	Zn	27.676	4.045

Lennard–Jones potential ( $U_{LJ}$ ):  $U_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$ , ( $\epsilon$ : the lowest value of the potential energy,  $\sigma$ : the distance where the pair potential is zero, and  $r$ : the distance between two particles)[1]

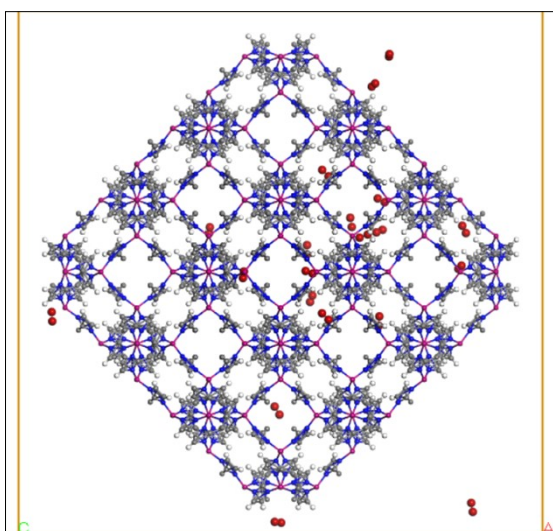
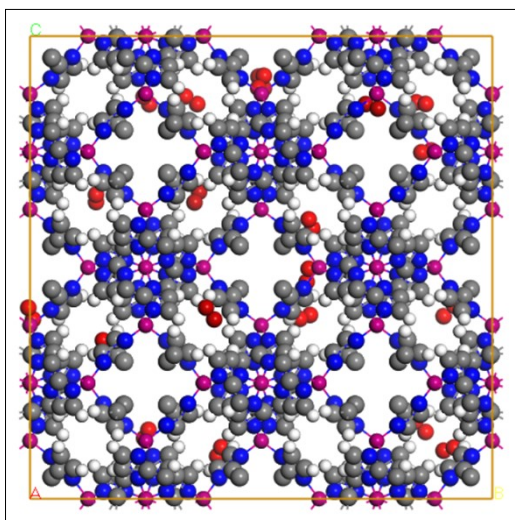
Lorentz–Berthelot mixing rule ( $\sigma_{ij}$ ) for calculating unlike pairs:

$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ ,  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ . **Bond length:** constrain O–O to **1.210 Å** (“Constraint: Distance geometry)

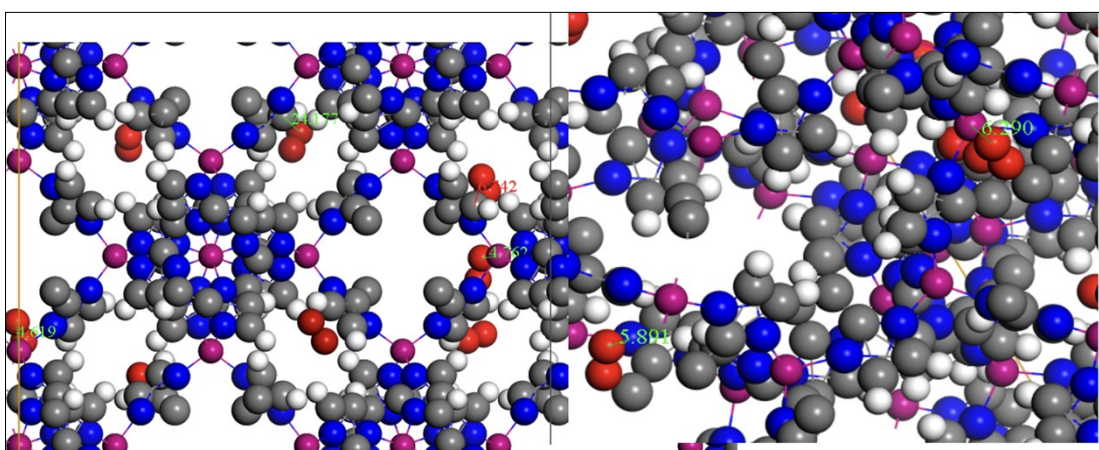


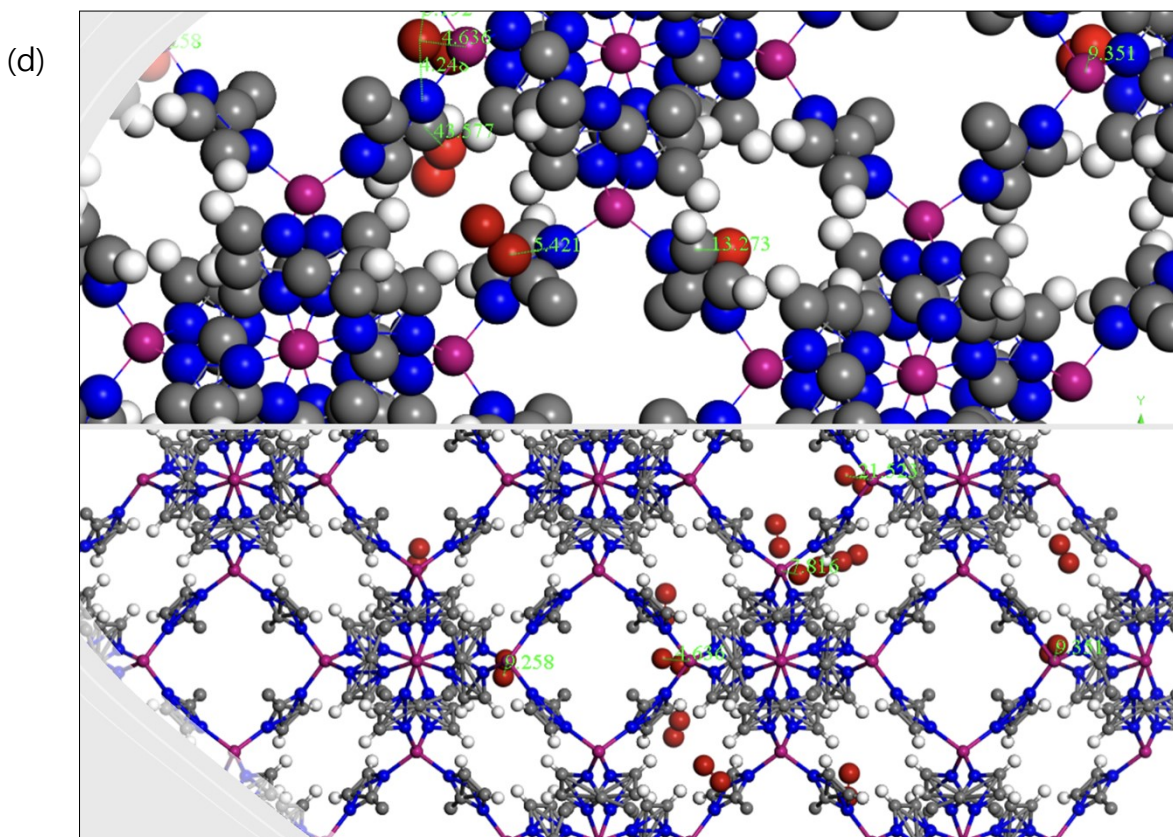
**Fig. S2.** Mean square displacement graph (a) Oxygen MSD curve ZIF-8P with solvent( $0.093 \text{ Å}^2/\text{ps}$ ) (b) Oxygen MSD curve ( $14.37 \text{ Å}^2/\text{ps}$ ) in presence of solvent in ZIF-8S.

(a)



(c)





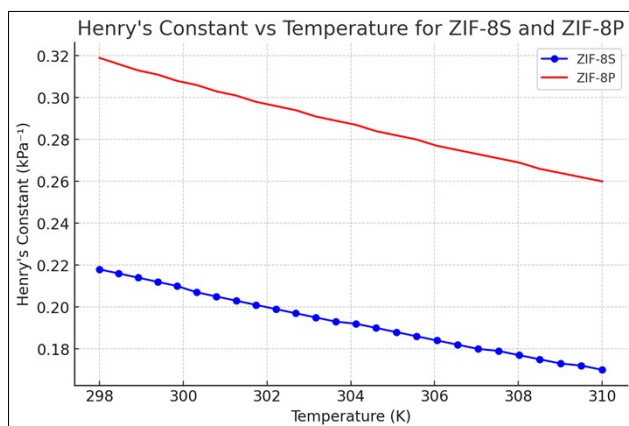
**Fig. S3:** Adsorption stable (lowest energy) configuration (a) oxygen saturated ZIF-8P Model (b) oxygen saturated ZIF-8S Model (c) onto and side-to-side view for oxygen interaction with ZIF-8P model labelled bond distances in green (d) onto and side-to-side view for oxygen interaction with ZIF-8S model. Color code: Zn = pink; N = blue; C = grey; H = white; O<sub>2</sub> = red; labelled distances in green.[3]

**Table S3.** Consolidated list of labelled  $Zn_{MOF} \cdots O_{Oxygen\ molecule}$ ;  $N_{ligand} - O_{O_2}$ ;  $C_{ring} - O_{O_2}$  distance that appears in the snapshots

Interaction type	Typical distance (Å)	Physical origin	Most abundant in	Colour code
<b>Type I (Open-metal physisorption) <math>Zn \cdots O_{O_2}</math></b>	4.6 – 6.2 (ZIF-8P) 4.6 – 9.3 (ZIF-	Lewis-acid polarisation of O <sub>2</sub> at the unsaturated Zn <sup>2+</sup> node; no electron	ZIF-8P (interior windows)	pink → red

	8S)	transfer (pure physisorption)		
<b>Type II (Secondary ligand contact)</b> $N_{\text{imidazole}} \cdots O_{O_2}$	4.2 – 5.8	Weak quadrupole–dipole or dispersion between $O_2$ and imidazolate N; contributes to cage “anchoring” once Type I is filled	Both models	blue → red
<b>Type III (Framework <math>\pi</math>-pore wall contact)</b> $C_{\text{ring}} \cdots O_{O_2}$	4.4 – 6.7	Pure van-der-Waals ( $O_2$ quadrupole with aromatic ring); dominates in the centre of sod cages	ZIF-8P only	grey → red

\*Longer 10–24 Å values in the snapshots (Figure S3) correspond to  $O_2$  in adjacent cages or in the external void and are omitted from the interaction analysis. (Distances  $> \approx 8$  Å are clearly non-bonding second-shell or cage-to-cage separations, but shown them for completeness exactly as displayed)



**Fig. S4.** Henry's constant trend with respect to temperature observed for ZIF-8P and ZIF-8S model.[2]

## References

[1] Hu, Z.; Zhang, L.; Jiang, J. Development of a force field for zeolitic imidazolate framework-8 with structural flexibility, *J. Chem. Phys.*, 2012, 136, 244703.

[2] Cezar, H. M.; Canuto, S.; Coutinho, K. DICE: A Monte Carlo Code for Molecular Simulation Including the Configurational Bias Monte Carlo Method, *J. Chem. Inf. Model.*, 2020, 60, 3472- 3488.

[3] Frenkel, D.; Smit, B., *Understanding Molecular Simulation: From Algorithms to Applications.* Elsevier Science: 2001.

