

## Supporting Information

# **High Capacity Oil Denitrogenation Over Azine and Tetrazine Decorated Metal-Organic Frameworks: Critical Roles of Hydrogen-Bonding**

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## Section S1. Synthesis of MOF powders

**[Zn(OBA)(BPDB)<sub>0.5</sub>]<sub>n</sub>·2DMF (TMU-4).** The mixture of H<sub>2</sub>OBA (0.128 g, 0.5 mmol), BPDB (0.105 g, 0.5 mmol) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.07 g, 0.3 mmol) in 20 mL DMF were ultrasonicated in an ultrasonic bath at ambient temperature and atmospheric pressure for 60 min. The resulting yellow powder was isolated by centrifugation, washed with DMF three times and dried at 80°C. Yield: 83%. IR data (KBr pellet,  $\nu/\text{cm}^{-1}$ ): selected bands: 445(w), 523(w), 659(m), 692(m), 776(m), 875(m), 1021(w), 1089(m), 1159 (s), 1241(vs), 1389(vs), 1412(vs), 1500(s), 1568(s), 1608(vs), 1679(vs), 2926(w) and 3414(w-br). Elemental analysis (%) calculated for

$[\text{Zn}_2(\text{C}_{14}\text{O}_5\text{H}_8)_2(\text{C}_{12}\text{H}_{10}\text{N}_4)] \cdot (\text{C}_3\text{NOH}_7)_2$ : C: 55.3, H: 4.0, N: 8.4; Found: C: 55.8, H: 4.2, N: 8.5.

**[Zn(OBA)(BPDH)<sub>0.5</sub>]<sub>n</sub>·1.5DMF (TMU-5).** A powdered sample of TMU-5 was synthesized by mixing Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1 mmol), H<sub>2</sub>OBA (0.26 g, 1 mmol) and BPDH (0.17 g, 0.7 mmol) in 30 mL of DMF and sonicating for 60 min at room temperature and pressure. The mixture was then centrifuged and the resulting powder washed with DMF and dried at 80 °C for 48 hour. Yield: 0.35g (80% based on OBA). IR data (KBr pellet,  $\nu/\text{cm}^{-1}$ )-selected bands: 652(s), 779(m), 873(m), 1021(m), 1092(m), 1162(s), 1233(vs), 1397(vs), 1499(m), 1631(vs), 1671(vs) and 3414(w-br). Elemental analysis (%) found for  $[\text{Zn}(\text{C}_{14}\text{O}_5\text{H}_8)(\text{C}_{14}\text{N}_4\text{H}_{14})_{0.5}] \cdot (\text{C}_3\text{ONH}_7)_{1.5}$ : C, 54.8; H, 4.2; N, 8.8.

**[Zn(OBA)(H<sub>2</sub>DPT)<sub>0.5</sub>]<sub>n</sub>·DMF (TMU-34).** TMU-34 powder was synthesized from a mixture of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1 mmol), H<sub>2</sub>OBA (0.26 g, 1 mmol), and H<sub>2</sub>DPT (0.24 g, 1 mmol) in DMF (30 mL). The mixture was sonicated for 160 min at ambient temperature and atmospheric pressure. It was then centrifuged and the resulting powder was washed with DMF and dried at room temperature. Yield: 0.34 g (78% based on OBA). IR (KBr pellet,  $\text{cm}^{-1}$ ): selected bands: 661 (m), 778 (m), 872 (m), 1162 (s), 1241 (vs), 1407 (vs), 1607 (vs), 1674 (s), 2928 (m), 3273; Elemental analysis (%) calculated for  $[\text{Zn}(\text{C}_{14}\text{O}_5\text{H}_8)(\text{C}_{12}\text{N}_6\text{H}_{10})_{0.5}] \cdot (\text{C}_3\text{ONH}_7)$ : C 53.8, N 10.9, H 3.9; found: C 54.1, N 11.4, H 4.1.

**[Zn(OBA)(DPT)<sub>0.5</sub>]<sub>n</sub>·DMF (TMU-34(-2H)).** A powdered sample of TMU-34(-2H) was synthesized by mixing Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (0.22 g, 1 mmol), H<sub>2</sub>OBA (0.26 g, 1 mmol) and DPT (0.24 g, 1 mmol) in 30 mL of DMF/acetonitrile (1:1) and sonicating for 60 min at ambient temperature and atmospheric pressure. The mixture was then centrifuged and the resulting powder washed with DMF and dried at 80 °C for 48 hour. Yield: 0.37g (85% based on OBA). IR

data (KBr pellet,  $\text{v}/\text{cm}^{-1}$ )-selected bands: 656(w), 780(w), 874(w), 1091(w), 1160(m), 1231(m), 1399(vs), 1500(s), 1629(s), 1672(s), 3429(m). Elemental analysis (%) found for  $[\text{Zn}(\text{C}_{14}\text{O}_5\text{H}_8)(\text{C}_{12}\text{N}_6\text{H}_8)_{0.5}]\cdot(\text{C}_3\text{ONH}_7)$ : C: 54.0, N: 10.9, H: 3.9.

## Section S2. Calculations for measuring the removal efficiency

Removal efficiency (%) of NCCs at time t(min) was calculated by the equation (1):

$$\text{Removal Efficiency (RE\%)} = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

where  $C_0$  (mgN.L<sup>-1</sup>) is the initial concentration of NCCs and  $C_t$  (mgN.L<sup>-1</sup>) is the concentration of NCCs at any specified time in the solution.

The adsorption amount  $q_t$  (mgN.g<sup>-1</sup>) at time t (min) was calculated as follows:

$$q_t = (C_0 - C_t)V/m \quad (2)$$

where  $C_0$  and  $C_t$  (mgN.L<sup>-1</sup>) are the NCC concentrations at the initial, any time t, and equilibrium in the solution, respectively. V(L) is the volume of the NCC solution and m (g) is the mass of MOF adsorbents.

Since the calculation are based on GC analysis and n-dodecane as internal standard, we can use equation (3) for calculation of RE(%):

$$(A_{\text{NCC}}/C_{\text{NCC}}) = F \times (A_{\text{IS}}/C_{\text{IS}}) \quad (3)$$

Where  $A_{\text{NCC}}$  and  $A_{\text{IS}}$  are the area of GC peak of NCC analyt and internal standard, and  $C_{\text{NCC}}$  and  $C_{\text{IS}}$  are the concentration of analyte and internal standard. Replacement of equation (3) in equation (1) leads to equation (4) in a way that RE(%) can be calculated directly from equation (4) as follows:

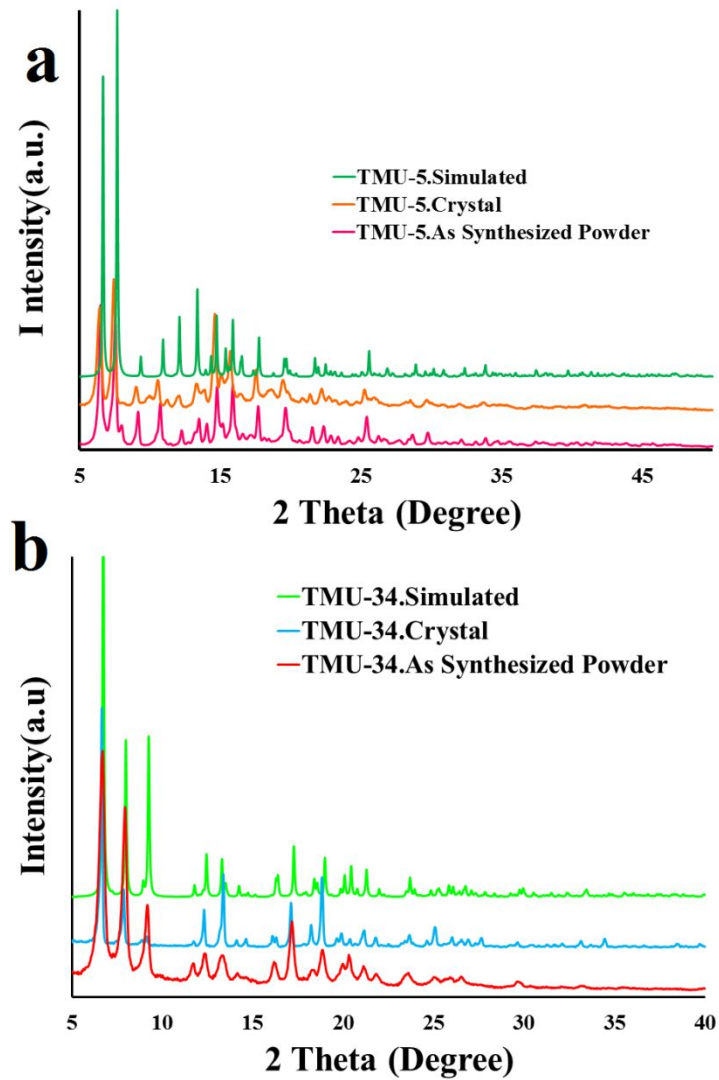
$$\text{RE(\%)} = (R^0 - R^t) / R^0 \times 100 \quad (4)$$

Where  $R_0$  and  $R_t$  are proportion of percentage of peak area of analyte rather internal standard at beginning ( $R^0 = A_{\text{NCC}}^0 / A_{\text{IS}}^0$ ) and time t ( $R^t = A_{\text{NCC}}^t / A_{\text{IS}}^t$ ).

**Selectivity tests.** Selectivity measurements calculated based on equation (7) as follows:

$$S_{\text{NCC/T}} = (Q_{\text{NCC}}/Q_t) / (C_{\text{NCC}}/C_T) \quad (7)$$

where  $Q_{NCC}$  and  $Q_t$  are maximum adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ) of NCC analytes and thiophene as reference.  $C_{NCC}$  and  $C_T$  are concentration of NCC analytes and thiophene in liquid phase after selective adsorption process.



**Figure S1.** Combination of PXRD patterns of sonochemically synthesized TMU-frameworks with their simulated and crystalline patterns. **(a)** TMU-5. **(b)** TMU-34.

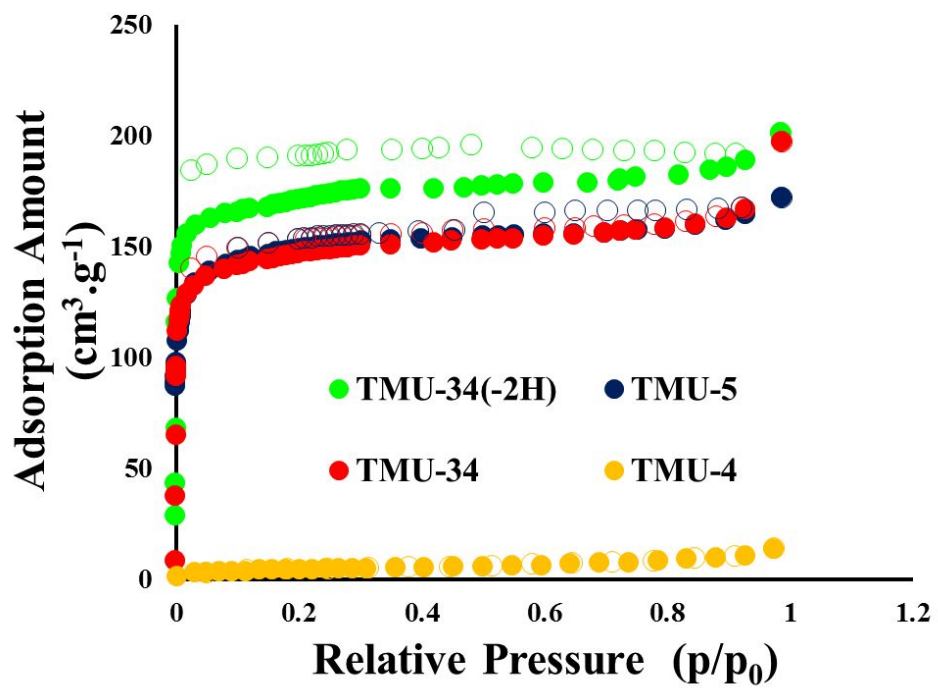
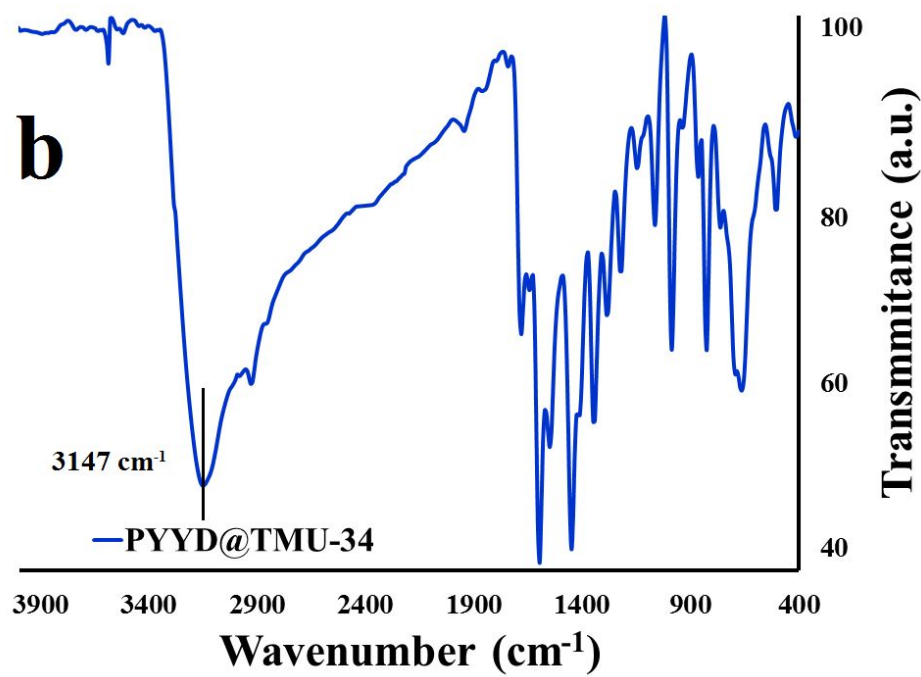
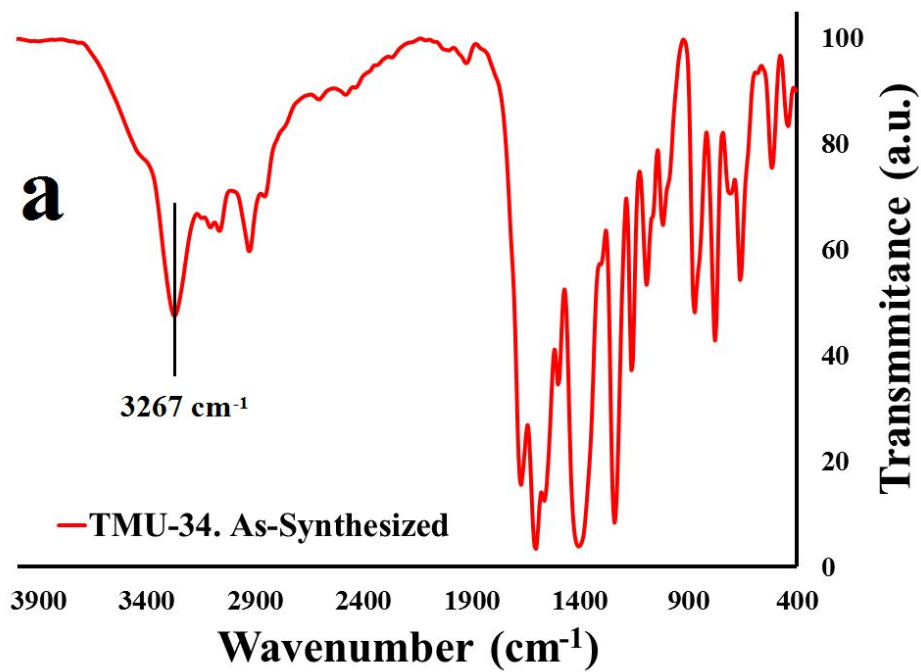
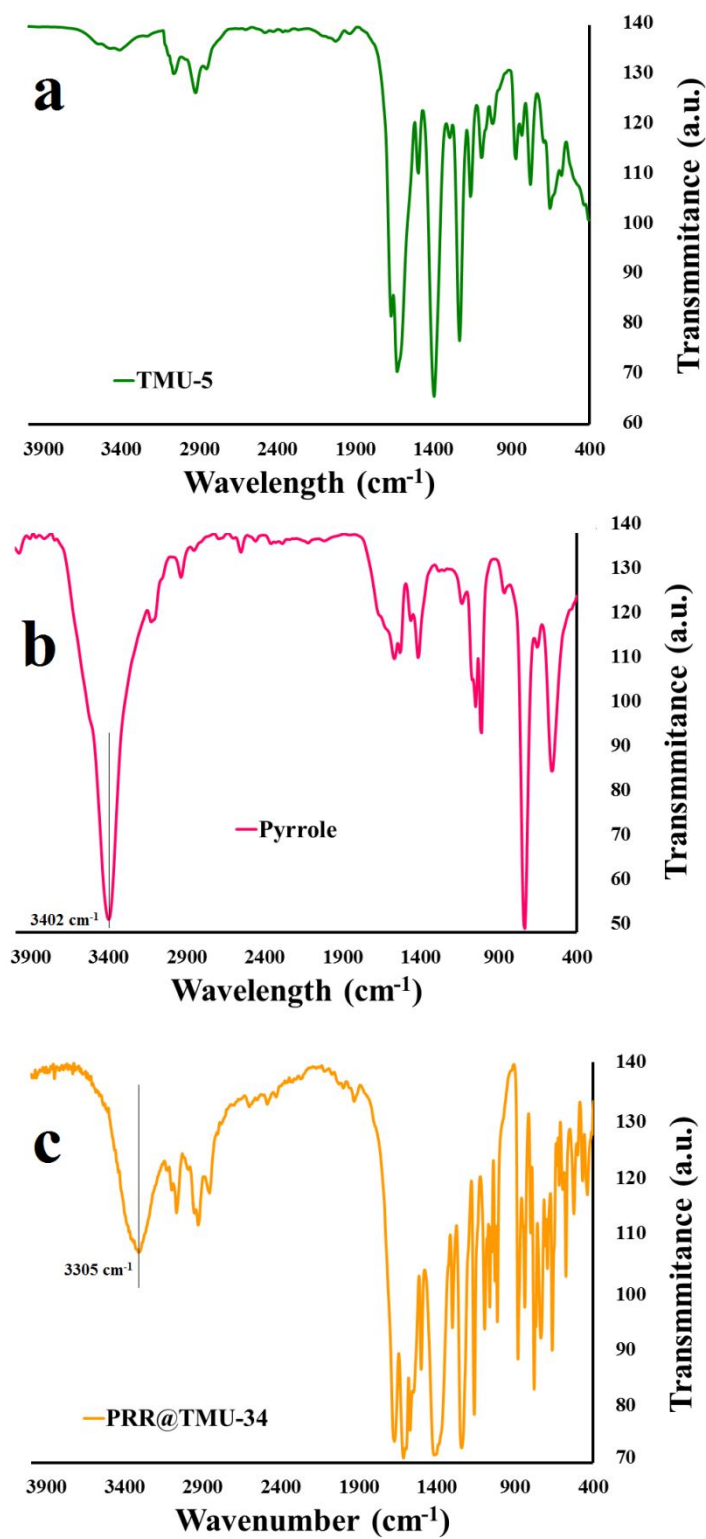


Figure S2. Nitrogen adsorption analysis of as-synthesized TMU-frameworks.

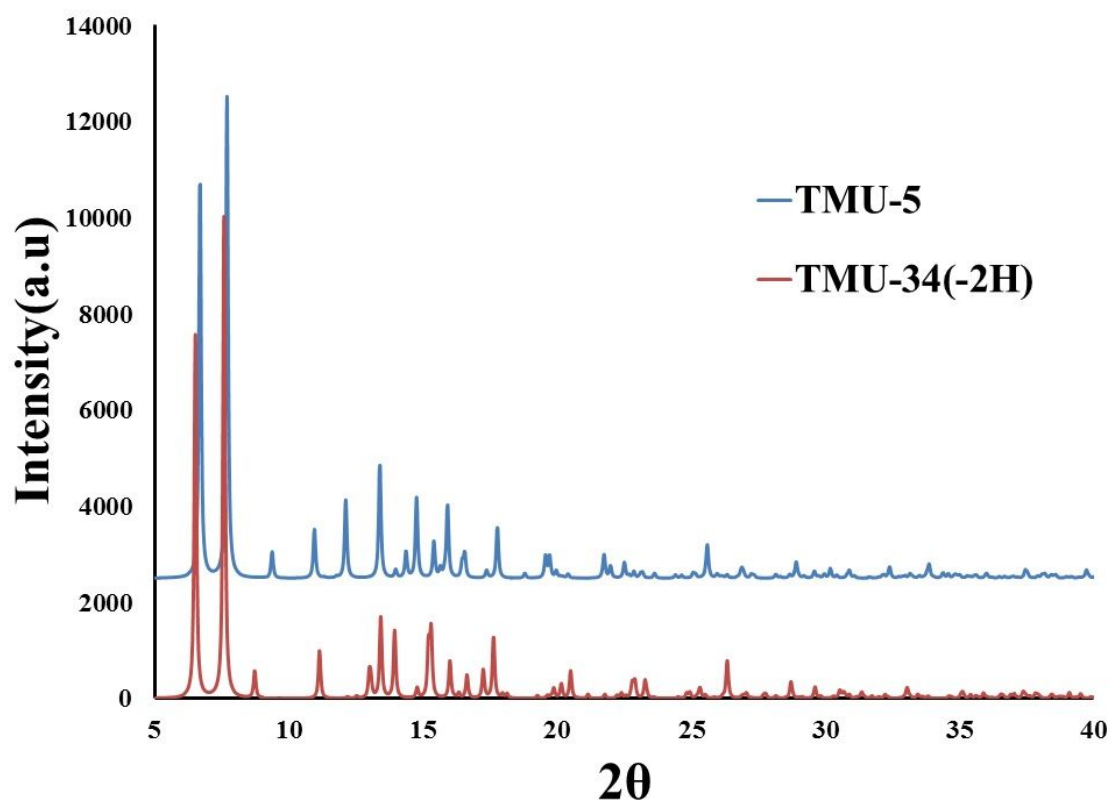


**Figure S3.** FT-IR spectra of TMU-34 before (a) and after (b) removal of basic NCCs.





**Figure S4.** FT-IR spectra of TMU-5 before ADN process (a), pyrrole (b) and pyrrole@TMU-5 after ADN process (c).



**Figure S5.** Comparison of PXRD patterns of TMU-5 and TMU-34(-2H) frameworks.

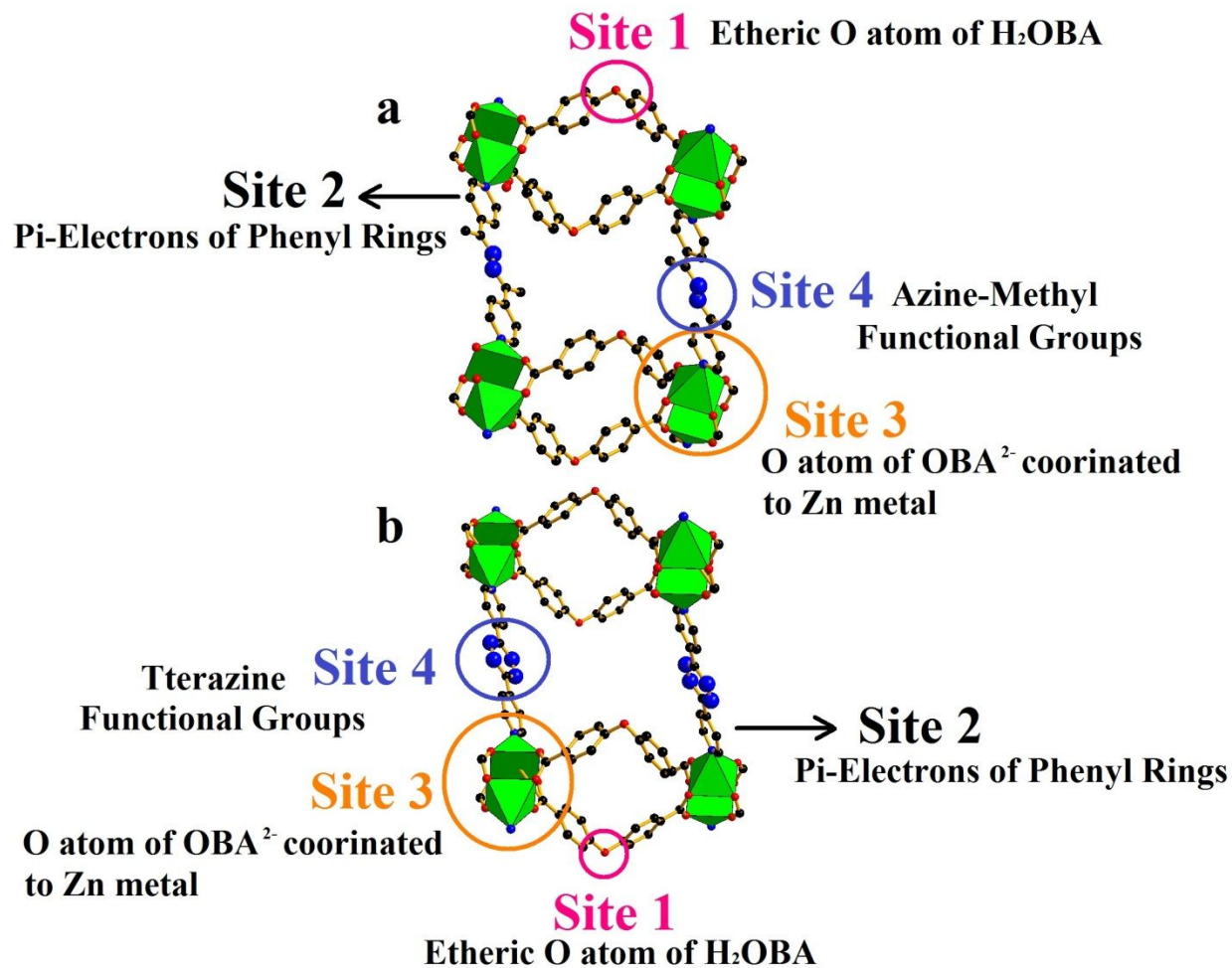
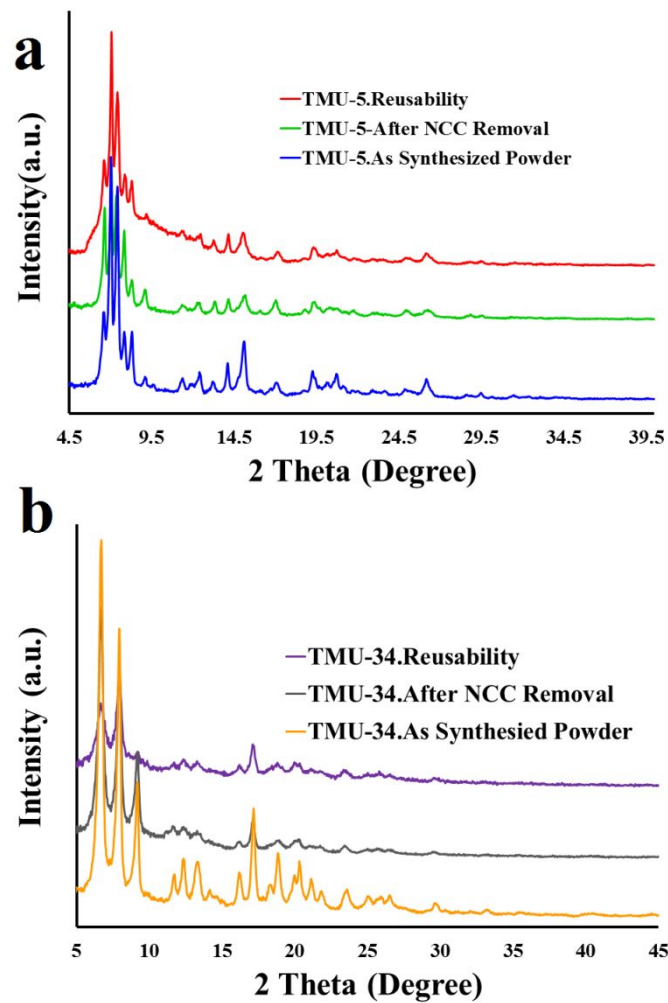
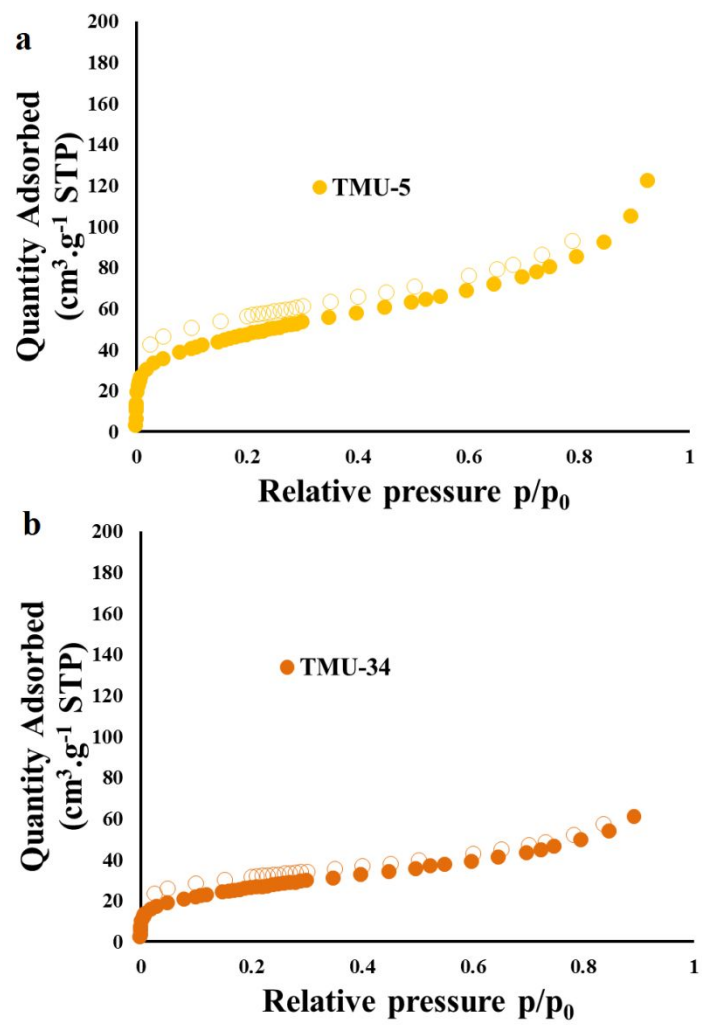


Figure S6. Structural Representation of TMU-5 and TMU-34(-2H).



**Figure S7.** PXRD patterns of TMU-5 (a) and TMU-34 (b) before and after adsorptive denitrogenation process.



**Figure S8.**  $\text{N}_2$  adsorption of TMU-5 (a) and TMU-34 (b) after recyclability tests.

**Table S1.** Comparison of crystallographic data of TMU-5 and TMU-34(-2H).

Compound	TMU-5	TMU-34(-2H)
Crystal system	Monoclinic	Monoclinic
Space group	$C_{2/c}$	$C_{2/c}$
Unit Cell Dimensions	$a = 26.8080(14) \text{ \AA}$ $b = 8.1923(5) \text{ \AA}$ $c = 23.3025(16) \text{ \AA}$ $\alpha = 90.00^\circ$ $\beta = 98.956(7)^\circ$ $\gamma = 90.00^\circ$	$a = 27.932(6) \text{ \AA}$ $b = 7.5323(15) \text{ \AA}$ $c = 23.999(5) \text{ \AA}$ $\alpha = 90.00^\circ$ $\beta = 103.99(3)^\circ$ $\gamma = 90.00^\circ$
Cell volume, $\text{\AA}^3$	5055.3(5)	4899.4(3)

**Table S2.** Adsorption capacity for applied MOFs in adsorptive-denitrogenation process.

Adsorbent MOF	Condition Time/Concentration/weight/ solution volume	Total Pore Volume (cm <sup>3</sup> .g <sup>-1</sup> )	QUI (mg.g <sup>-1</sup> )	QUI (cc.g <sup>-1</sup> )	IND (mg.g <sup>-1</sup> )	IND (cc.g <sup>-1</sup> )	Ref.
<b>TMU-5</b>	<b>4 h/500 mg.L<sup>-1</sup>/50 mg/ 25 cc</b>	<b>0.30</b>	---	---	<b>578 (37.2)</b>	<b>0.494</b>	<b>This Work</b>
<b>TMU-34</b>	<b>4 h/500 mg.L<sup>-1</sup>/50 mg/ 25 cc</b>	<b>0.28</b>	<b>602 (40.6)</b>	<b>0.590</b>	---		<b>This Work</b>
MIL-101	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	1.55	420	0.412	194	0.166	1
MIL-101-ED	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	1.47	301	0.305	336	0.287	1
Uio-66	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.498	---	---	213	0.182	2
Uio-66-NH <sub>2</sub>	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.307	---	---	312	0.266	2
MIL-125	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.534	75	0.074	150	0.128	3
MIL-125-NH <sub>2</sub>	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.604	260	0.255	450	0.385	3
MIL-125-NH <sub>3</sub> <sup>+</sup>	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.571	546	0.536	583	0.498	3
MIL-100-Cr	2 h/1200 mg.L <sup>-1</sup> /5 mg/5 cc	0.985	420	0.412	149	0.127	4
MIL-100-Cr- CuCl	2 h/1200 mg.L <sup>-1</sup> /5 mg/5 cc	0.635	457	0.448	171	0.146	4
MIL-100-Fe	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.834	357	0.350	~86	0.074	5
MIL-100-Fe- AlCl <sub>3</sub>	4 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.424	417	0.409	~64	0.055	5
Cu <sub>3</sub> (BTC) <sub>2</sub>	Breakthrough conditions	---	---	---	(22)*	---	6
CPO-27-Ni	Breakthrough conditions	---	---	---	(11)*	---	6
CPO-27-Co	Breakthrough conditions	---	---	---	(10)*	---	6
MIL-100-Fe	Breakthrough conditions	---	---	---	(36)*	---	6
ML-100-Cr	Breakthrough conditions	---	---	---	(37)*	---	6
MIL-100-Al	Breakthrough conditions	---	---	---	(34)*	---	6
MIL-101-Cr	Breakthrough conditions	---	---	---	(40)*	---	6
MIL-101-Cr	2 h/- mg.L <sup>-1</sup> /50 mg/5 cc	1.32	(31)*	---	(22)*	---	7
MIL-100-Fe	2 h/- mg.L <sup>-1</sup> /50 mg/5 cc	0.84	(20)*	---	(10)*	---	7
Cu-BTC	2 h/- mg.L <sup>-1</sup> /50 mg/5 cc	0.51	(19)*	---	(34)*	---	7
MIL-101	12 h/- mg.L <sup>-1</sup> /- mg/- cc	1.96	417	0.409	395	0.338	8
P-pANI-MIL- 101	12 h/- mg.L <sup>-1</sup> /- mg/- cc	1.57	556	0.545	602	0.515	8
Uio-66	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.44	142	0.140	127	0.109	9
Uio-66-NH <sub>2</sub>	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.40	122	0.120	182	0.156	9
Uio-66-NH <sub>3</sub> <sup>+</sup>	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.30	218	0.214	230	0.197	9
Uio-66-COOH (30%)	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.36	138	0.135	183	0.156	9
Uio-66-COONa (30%)	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.20	99	0.097	136	0.116	9
Uio-66-OH	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.29	156	0.153	174	0.149	9
Uio-66-(OH) <sub>2</sub>	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.26	198	0.194	224	0.191	9

Uio-66-SO <sub>3</sub> H	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	0.31	128	0.125	170	0.145	9
Ade-MIL-101	12 h/2000 mg.L <sup>-1</sup> /5 mg/5 cc	1.64	466	0.457	491	0.420	10
pAde-MIL-101	12 h/2000 mg.L <sup>-1</sup> /5 mg/5 cc	1.53	532	0.522	511	0.438	10
MIL-125	6 h/2000 mg.L <sup>-1</sup> /3 mg/5 cc	0.57	103	0.101	264	0.226	11
MIL-125-NH <sub>2</sub>	6 h/2000 mg.L <sup>-1</sup> /3 mg/5 cc	0.60	460	0.451	502	0.429	11
MIL-125-VFG	6 h/2000 mg.L <sup>-1</sup> /3 mg/5 cc	0.59	546	0.535	637	0.544	11
MIL-101	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	1.89	481	0.441	244	0.209	12
GO/MIL-101	12 h/1000 mg.L <sup>-1</sup> /5 mg/5 cc	2.09	549	0.504	319	0.273	12
*: The numbers in parentheses are based on (wt%).							



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