

Electronic Supplementary Information (ESI)

Upgrading gasoline to high octane number using Zeolite-like Metal Organic Framework molecular sieve with ana-topology

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1. Materials and general procedures

All reagents were obtained from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a PANalytical X'Pert PRO diffractometer 45 kV, 40 mA for Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of $1.0^\circ \text{ min}^{-1}$ and a step size of 0.02° in 2θ .

Single-crystal X-ray diffraction data Single-crystal X-ray diffraction data were collected using a Bruker X8 PROSPECTOR APEX2 CCD diffractometer (Cu $K\alpha$, $\lambda = 1.54178 \text{ \AA}$). Indexing was performed using APEX2 (Difference Vectors method).^{S1} Data integration and reduction were performed using SaintPlus 6.01.^{S2} Absorption correction was performed by analytical method implemented in SADABS.^{S3} Space group was determined using XPREP implemented in APEX2.^{S1} Structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2014 (full-matrix least-squares on F^2) contained in WinGX.^{S4} Crystal data and refinement conditions are shown in Table S1.

Variable Temperature Powder X-ray Diffraction (VT-PXRD) measurements were collected on a PANalytical X'Pert MPD-PRO X-ray diffractometer equipped with an Anton-Parr CHC+ variable temperature stage. Measurements were collected at 45 kV, 40 mA for Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) with a scan speed of $1.0^\circ \text{ min}^{-1}$ and a step size of 0.02° in 2θ . Samples were placed under vacuum during analysis and the sample was held at the designated temperatures for at least 15 minutes between each scan.

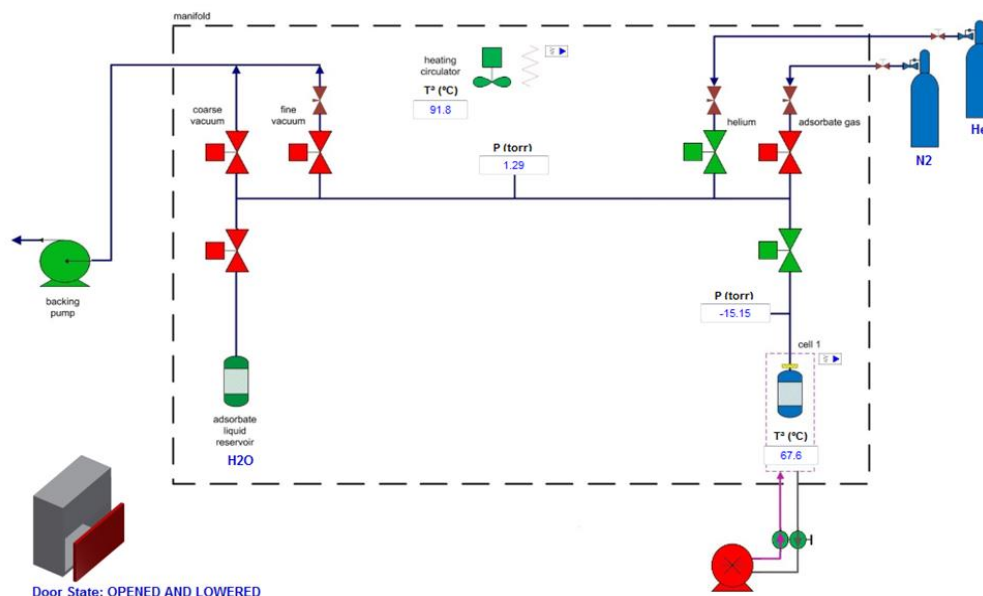
High resolution dynamic thermogravimetric analysis (TGA) were performed under a continuous N_2 and/or O_2 flow and recorded on a TA Instruments hi-res TGA Q500 thermogravimetric analyzer with a heating rate of 1°C per minute.

Vapour and Gas sorption:

Low pressure gas adsorption measurements were performed on 3-Flex Surface Characterization Analyser (Micromeritics) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using liquid argon baths at 87 K. The apparent surface areas were determined from the argon adsorption isotherms collected at 87 K by applying the Brunauer-Emmett-Teller (BET) model. Pore size analyses were performed using a DFT pore model system.

As-synthesized sample of **ana-ZMOF** was washed with $3 \times 20 \text{ mL}$ of anhydrous DMF and immersed in 10 mL of methanol for 7 days, during which time the methanol was replaced three times per day. The solid was then dried at 105°C under vacuum for 24 h to yield activated samples.

A volumetric apparatus Vstar1 vapour sorption analyser from Quantachrome instruments was used for collecting *n*-pentane, *iso*-pentane, *n*-butane and *iso*-butane adsorption isotherms at 293 K. Schematic diagram of the instrument is shown in the scheme 1, from the screenshot of the software window.



Scheme S1. Schematic diagram of Vstar1 vapour sorption analyser.

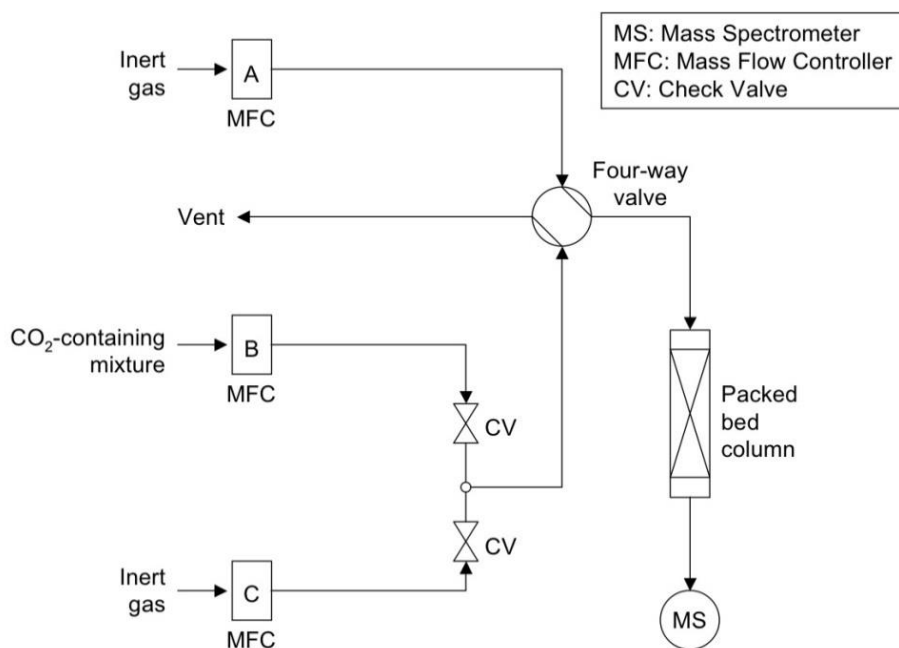
For the vapour sorption experiments, high purity liquid pentane and *iso*-pentane was taken in adsorbate liquid reservoir, while *n*-butane and *iso*-butane cylinders were connected to adsorbate gas port. In a typical experiment sample was activated in-situ at 105°C under dynamic vacuum for 12 hours. Temperature was increased to 105°C from room temperature at the rate of 1°C·min⁻¹. Activated sample was used for corresponding isotherm measurement. All the sorption of hydrocarbon was carried out at 20°C sample temperature. Manifold temperature was maintained at 40°C throughout the measurement. Sorption data was processed by using Helmholtz equation. This equation is recommended from NIST (National Institute of Standards and Technologies) of USA for pentane and *iso*-pentane. It is suitable for pentane at temperatures between 143.47-600 K and pressures to 1000 bar; for *iso*-pentane at temperatures between 112.65-600 K and pressures to 10000 bar; for *n*-butane at temperatures between 134.895-575 K and pressures to 690 bar and for *iso*-butane at temperatures between 113.73-575 K and pressures 350 bar.

Column Breakthrough Test Set-up, Procedure and Measurements:

The experimental set-up used for dynamic breakthrough measurements is shown in Scheme 2. The gas manifold consisted of three lines fitted with mass flow controllers Line “A” is used to feed an inert gas, most commonly helium, to activate the sample before each experiment. The other two lines, “B” and “C” feed a pure or pre-mixed gases. Whenever required, gases flowing through lines “B” and “C” may be mixed before entering a column packed with **ana**-ZMOF using a four-way valve. In a typical experiment, 2.4 g of adsorbent (in the column) was treated at 423 K overnight under vacuum in a separate oven.

After the sample is degassed, the column is backfilled with argon and mounted in the set-up. Before starting each experiment, helium reference gas is flushed through the column and then the gas flow is switched to the desired gas mixture at the same flow rate of 8 cm³·min⁻¹ (10 cm³·min⁻¹

¹ for CO₂/N₂). The gas mixture downstream the column was monitored using a Hiden mass-spectrometer.



Scheme 2. Representation of the column breakthrough experiment.

Experimental Methods

• Synthesis of ana-ZMOF

A solution containing Y(NO₃)₃ (0.1 mmol), Imidazole-4,5-dicarboxylate (ImDC, 0.2 mmol), KCl (0.1 mmol), 0.1 ml 3.5M HNO₃ in DMF, 2 ml DMF was prepared in a 20 ml vial and heated to 115°C for 48 h. Colourless crystals were harvested and air dried (Yield: 45%). Elemental Analysis for calculated formula $[\text{DMA}]_2[\text{K}_3\text{Y}_3(\text{ImDC})_6] \cdot 2\text{Cl} \cdot 0.31\text{H}_2\text{O}$: C = 26.61% (theo.: 27.65%), H = 1.89% (1.95%), N = 11.20% (13.28%).

2. Single Crystal X-ray Data

As-synthesized **ana**-ZMOF crystallizes in the cubic space group $Ia-3d$. C–N distances in dimethylammonium cation were restrained to 1.48(1) Å and U_{ij} components of anisotropic thermal parameters of its C and N atoms were restrained to be isotropic: ISOR 0.006, ISOR 0.01 and ISOR 0.009 were applied to N3A, C6A and C7A, respectively. The cation is disordered over two position with equal occupancies of 0.5. Hydrogen atoms are placed at calculated positions and refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$ ($1.5U_{eq}(C)$ in the case of methyl groups). Strongly delocalized electron density was found in 16 voids in the structure with total volume of 829 Å³ per unit cell. The SQUEEZE procedure revealed 49 electrons per unit cell which was assumed as 5 water molecules per unit cell. The final formula is $[\text{DMA}^+]_2[\text{K}_3\text{Y}_3(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)_6] \cdot 2\text{Cl} \cdot 0.31\text{H}_2\text{O}$.

Table S1. Crystal data and structure refinement conditions for as-synthesized **ana**-ZMOF.

Empirical formula	$C_{34}H_{28.62}Cl_2K_3N_{14}O_{24.31}Y_3$
Formula weight	1477.26
Crystal system, space group	Cubic, $Ia-3d$
Unit cell dimensions	$a = 28.006(4) \text{ \AA}$
Volume	$21966(9) \text{ \AA}^3$
Z, calculated density	16, 1.787 Mg m^{-3}
$F(000)$	11730
Temperature (K)	100.0(1)
Radiation type, λ	Cu $K\alpha$, $1.54178 \text{ \AA}$
Absorption coefficient	7.90 mm^{-1}
Absorption correction	Multi-scan
Max and min transmission	0.753 and 0.659
Crystal size	$0.03 \times 0.03 \times 0.03 \text{ mm}$
Shape, colour	Cubic, colourless
θ range for data collection	$3.9\text{--}67.2^\circ$
Limiting indices	$-33 \leq h \leq 33, -28 \leq k \leq 26, -32 \leq l \leq 33$
Reflection collected / unique / observed with $I > 2\sigma(I)$	73418 / 1647 ($R_{\text{int}} = 0.034$) / 1595
Completeness to $\theta_{\text{max}} = 67.2^\circ$	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1647 / 20 / 140
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.028, wR_2 = 0.091$
Final R indices (all data)	$R_1 = 0.029, wR_2 = 0.091$
Weighting scheme	$[\sigma^2(F_o^2) + (0.0612P)^2 + 70.2357P]^{-1*}$
Goodness-of-fit	1.09
Largest diff. peak and hole	0.92 and $-0.46 \text{ e \AA}^{-3}$

$$*P = (F_o^2 + 2F_c^2)/3$$

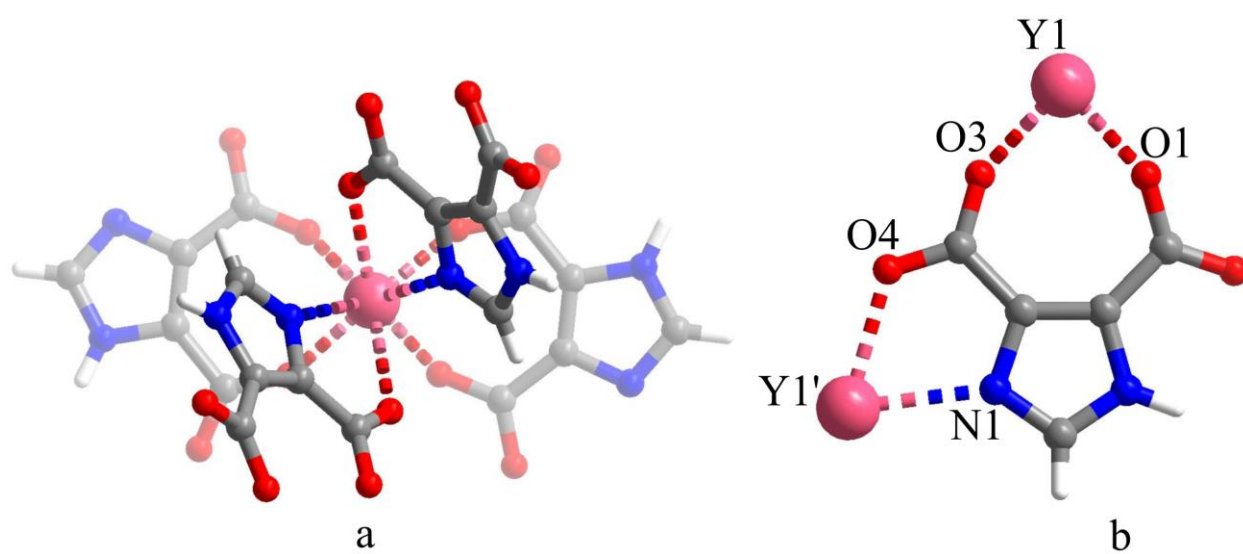


Figure S1. Y^{3+} coordination: (a) Y^{3+} environment and (b) $\mu_2-\kappa N,O:\kappa O',O''$ ImDC²⁻ binding mode.

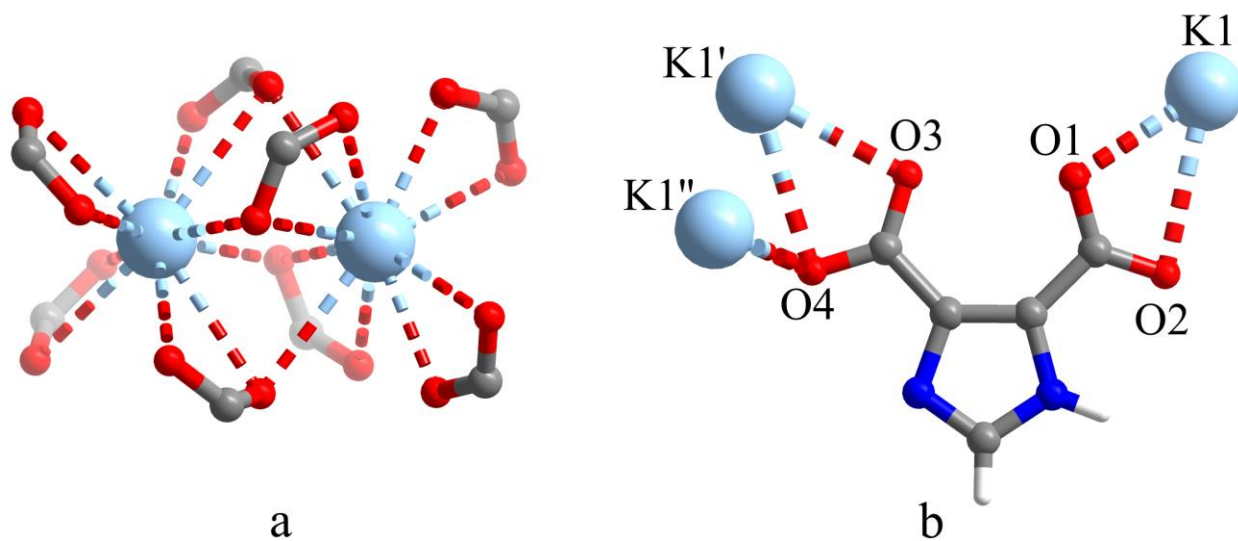


Figure S2. K^+ coordination: (a) Two K^+ coordinates 8 carboxylate groups and (b) $\mu_2\text{-}\eta^2$: η^1 - and η^2 -binding modes of carboxylic groups.

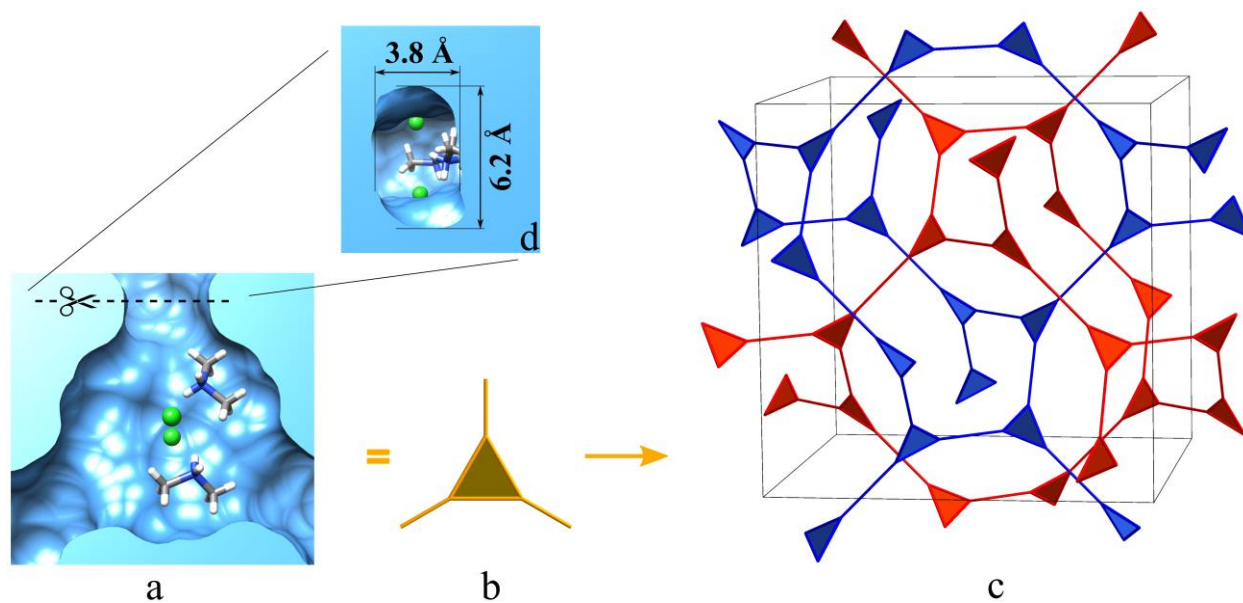


Figure S3. Triangular cages (a) can be viewed as 3-connected triangles (b) and then the channels in the *ana*-ZMOF can be represented as two interpenetrated *srs*-nets. Different colour scheme was used to emphasise spatial separation of the channels. There are only two of six possible DMA positions in the cage are shown in (a). The channel aperture is shown in the cross-section (d).

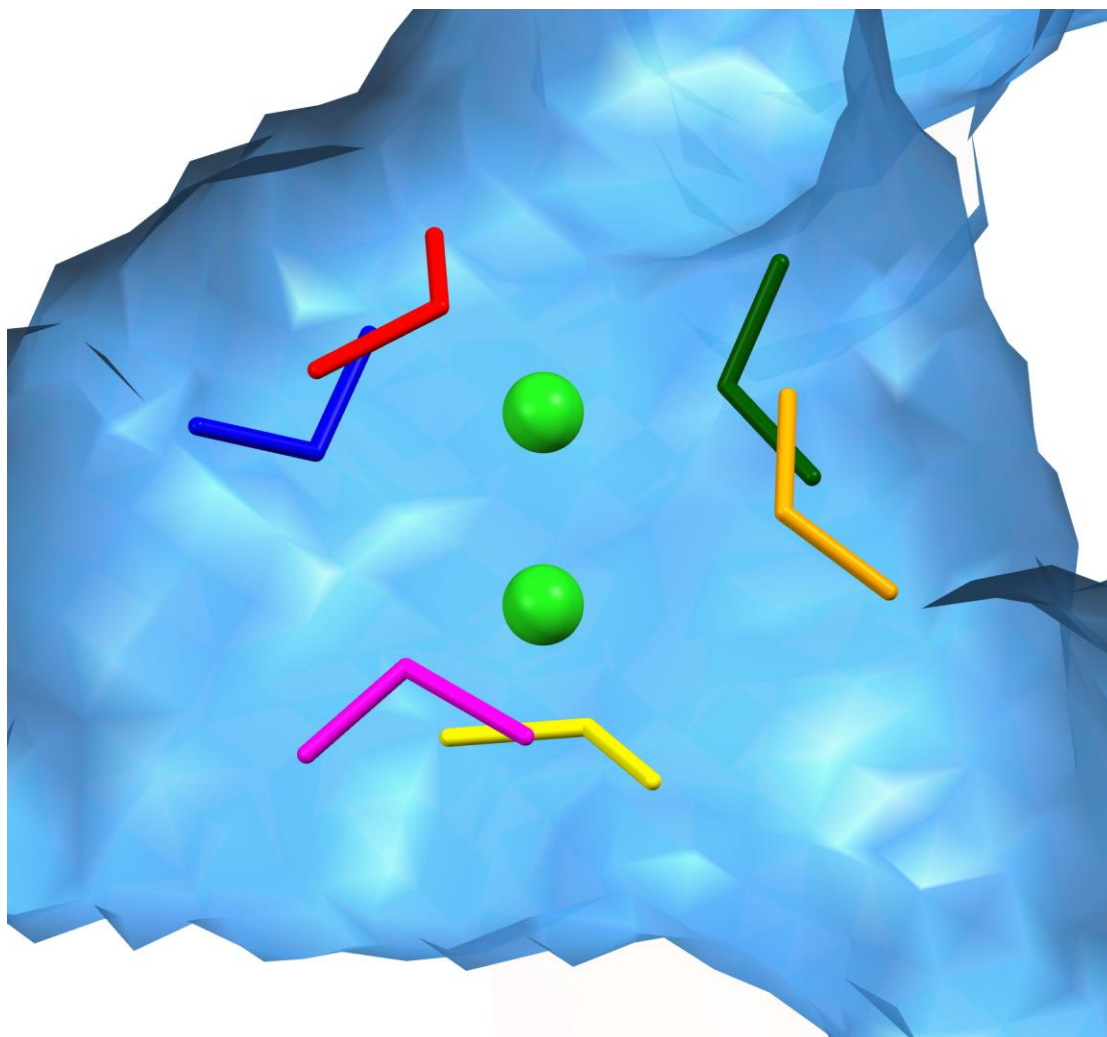


Figure S4. Each cage contains two (DMA)Cl pairs. Dimethylammonium cations are disordered over 6 positions marked with different colours.

3. Powder X-ray Diffraction

Experimental and calculated powder X-ray diffraction (PXRD) patterns for **ana**-ZMOF, indicate the phase purity of the as-synthesised sample. The as-synthesised MOF was treated at different pH levels and observed that the compound is stable from pH 3 to pH 10. This compound also has a very good stability towards water as well in many other organic solvents.

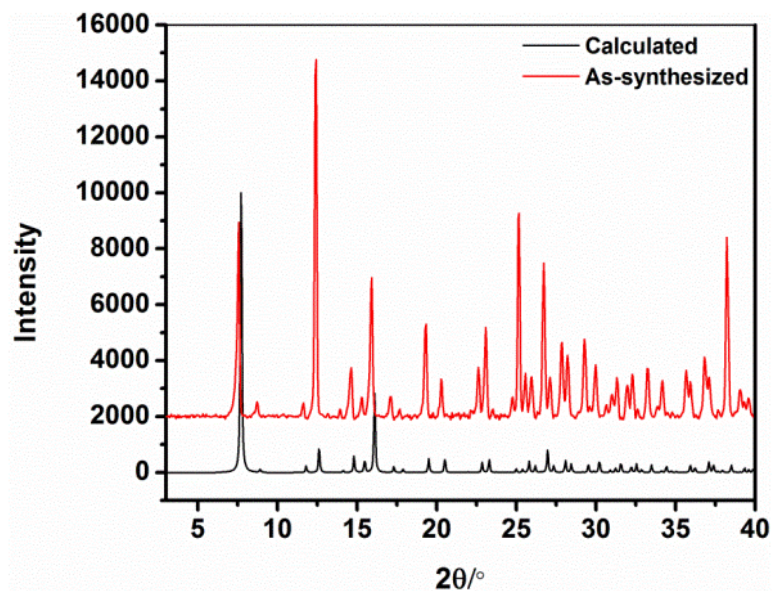


Figure S5. Experimental and calculated powder X-ray diffraction patterns indicating the phase purity of **ana**-ZMOF.

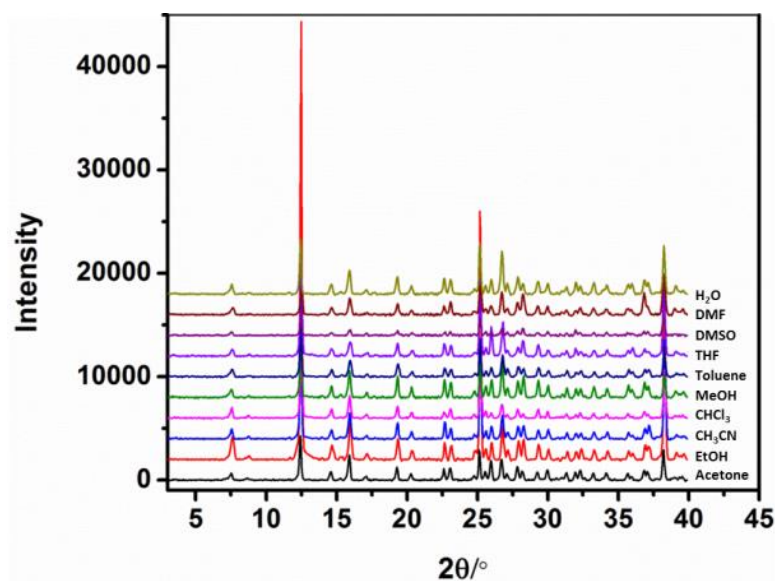


Figure S6. PXRD patterns of **ana**-ZMOF after soaking in different solvents for 24 h.

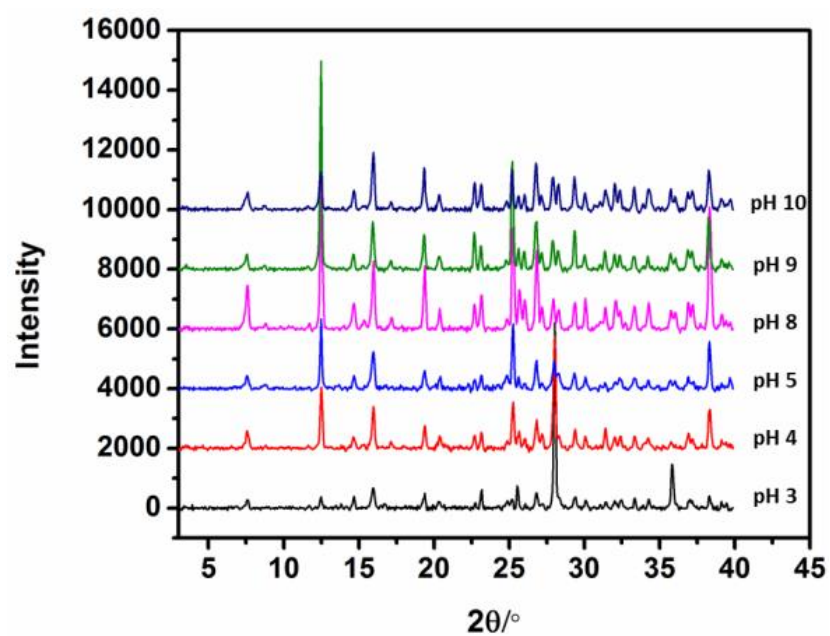


Figure S7. Chemical stability of *ana*-ZMOF at different pH conditions.

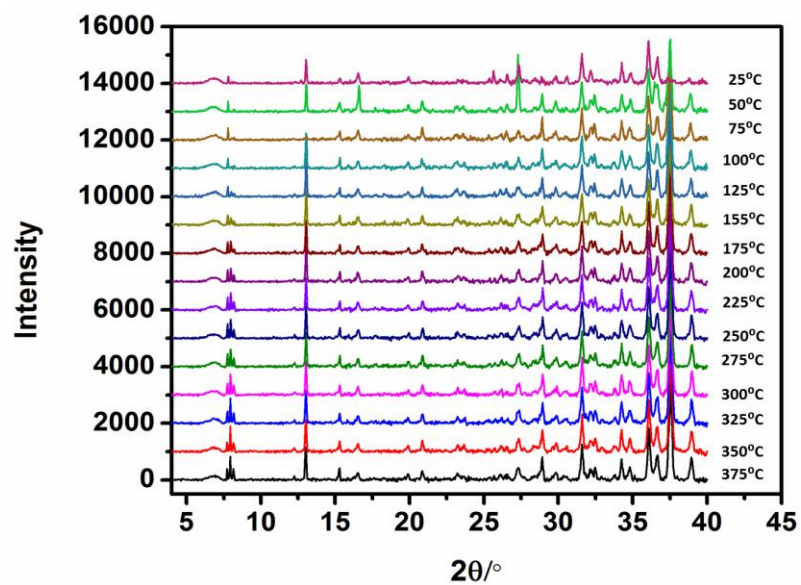


Figure S8. Variable Temperature PXRD patterns of *ana*-ZMOF.

Thermogravimetric analysis

The compound is stable up to *c.a.* 300°C and the structure start decomposing at higher temperature.

The initial weight loss is attributed to solvent molecules.

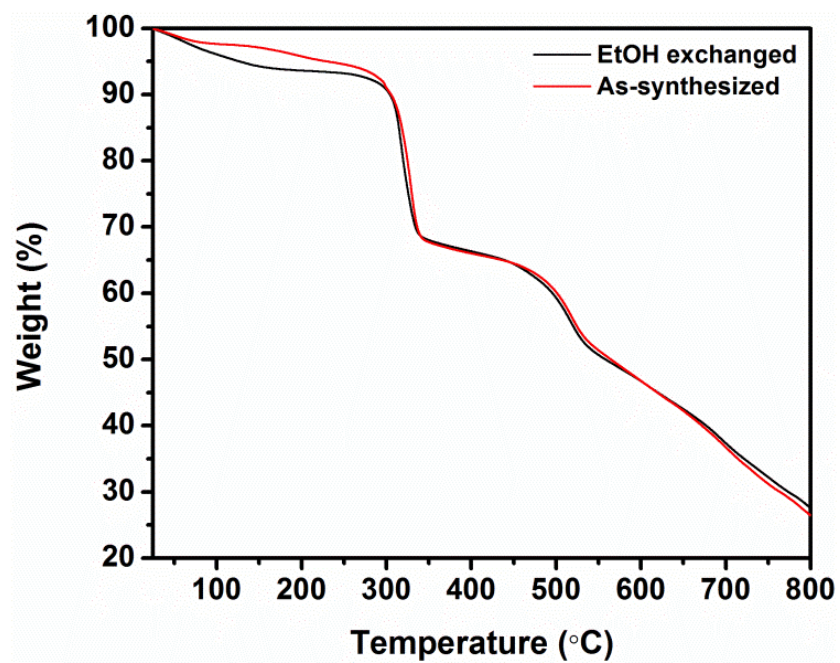


Figure S9. TGA plot of *ana*-ZMOF confirming thermal stability of the sample till 300°C.

4. Low-Pressure Vapour and Gas Adsorption Measurements

Sorption Experiments

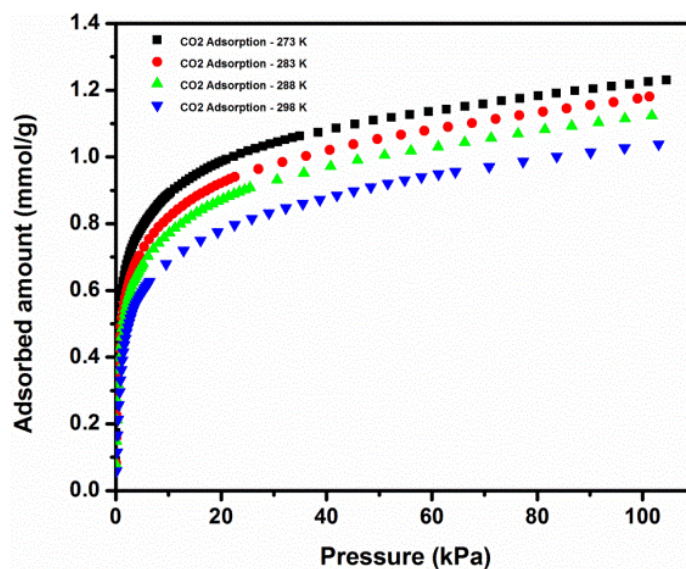


Figure S10. CO₂ adsorption isotherms on *ana*-ZMOF at different temperatures.

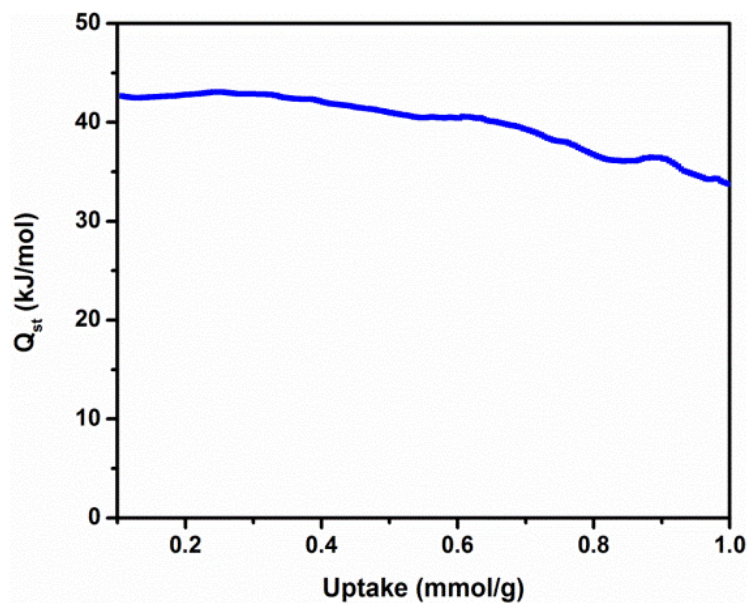


Figure S11. Q_{st} of CO₂ adsorption on *ana*-ZMOF.

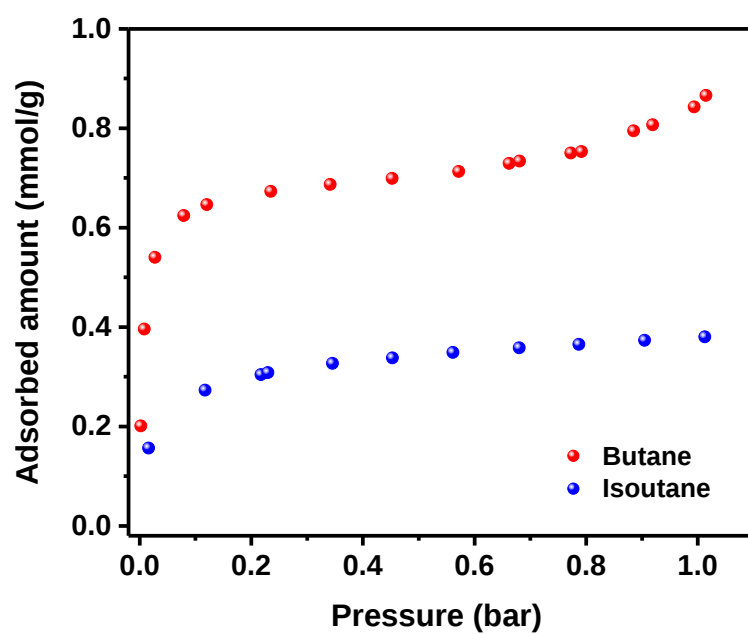


Figure S12: Adsorption isotherms of *n*-butane and iso-butane for *ana*-ZMOF at 293 K.

5. Column Breakthrough Experiments

Column breakthrough experiments were carried out as described in materials and general procedures section.

For these experiments, the need of continuous analysis in column breakthrough adsorption test limits our choice of gas analysers to mass-spectrometry. *n*-butane and *iso*-butane being very similar molecule with same molecular weight, it is difficult to distinguish them by mass spectrometer simultaneously. Butane and *iso*-butane have almost identical fragmentation pattern except intensities of few fragments, irrespective of the mass fragment selected. There will be always overlap of mass fragments of one component over the other in this case. After several blank experiments (without sample) with pure gases and mixture, we selected mass 29 and mass 39 for *n*-butane and *iso*-butane respectively. Although mass 29 for *n*-butane overlaps with *iso*-butane and mass 39 for *iso*-butane overlaps with *n*-butane, they were the mass fragment pair with minimum overlap. Blank experiments with pure gases and mixture suggest that despite the overlap it is possible to distinguish between pure *n*-butane and *iso*-butane with their mixture qualitatively by mass spectrometer as shown in figures S13-S15

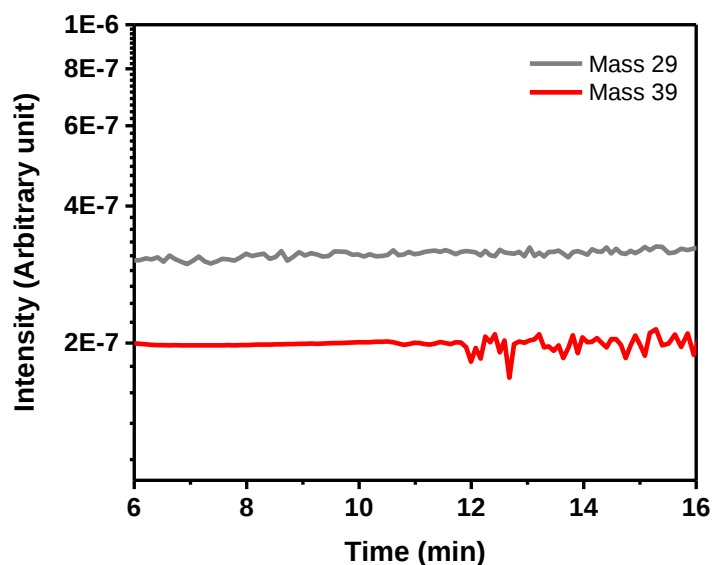


Figure S13. Mass fragmentation for pure *n*-butane during blank experiment without column. It can be seen that butane produces both mass 29 and mass 39 fragments with similar intensity. Mass 29 fragment intensity is approximately 1.5 times higher than that of mass 39 fragment in case of *n*-butane.

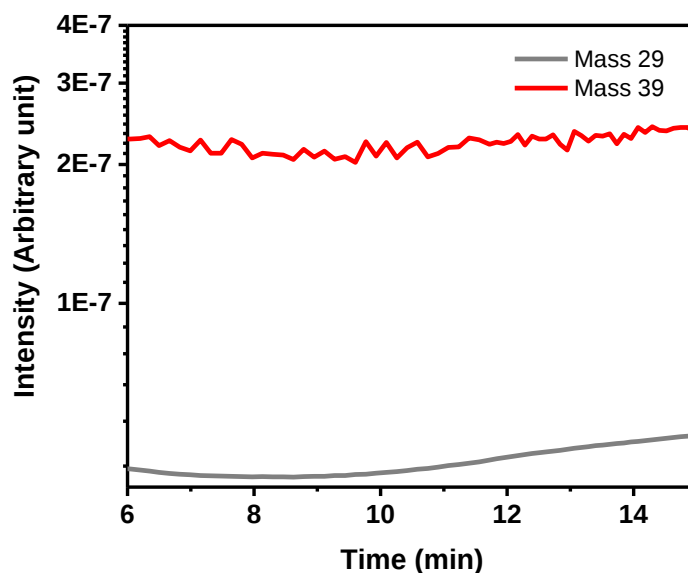


Figure S14. Mass fragmentation for pure *iso*-butane during blank experiment without column. It can be seen that *iso*-butane produces both mass 39 and mass 29 fragments. Mass 39 fragment intensity is approximately 4-5 times higher than that of mass 29 fragment in case of *iso*-butane.

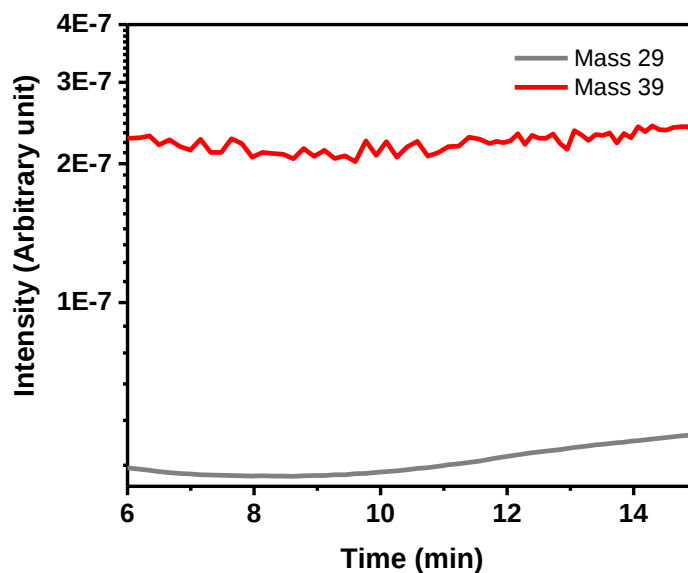


Figure S15. Mass fragmentation for 1:1 mixture of *n*-butane and *iso*-butane during blank experiment without column. It can be seen that 1:1 mixture of *n*-butane and *iso*-butane produces both mass 39 and mass 29 fragments with similar intensity. Mass 39 fragment intensity is approximately 1.5 times higher than that of mass 29 fragment in case of 1:1 mixture of *n*-butane and *iso*-butane.

Column breakthrough experiments were also carried out using pure *n*-butane and *iso*-butane.

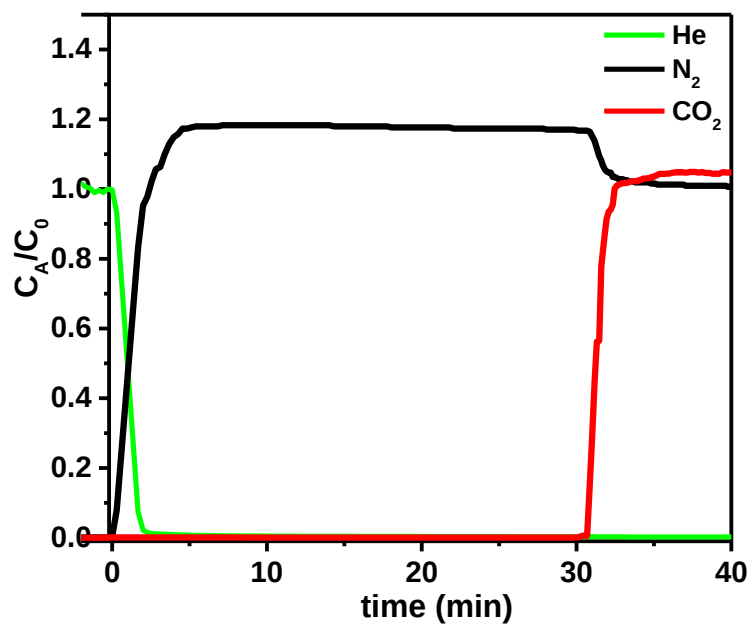


Figure S16. Column breakthrough test for **ana**-ZMOF with 10% CO₂ 90% N₂ mixture with flow rate of 10 cm³·min⁻¹.

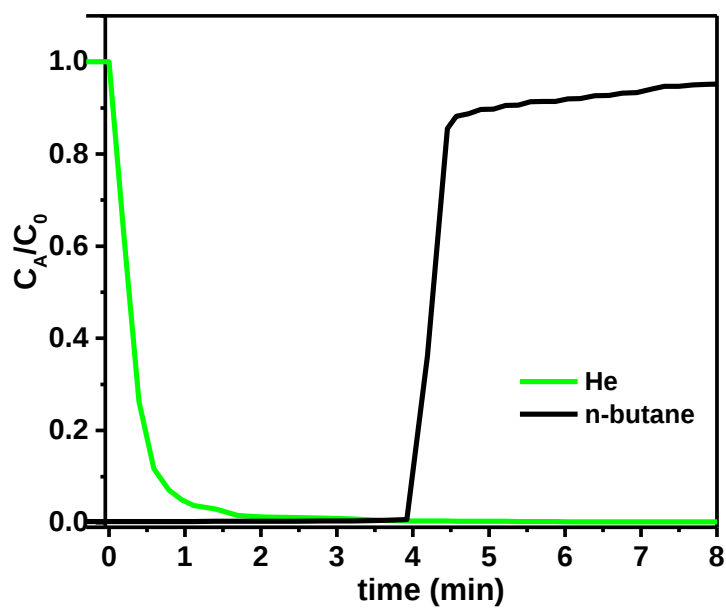


Figure S17. Column breakthrough test for **ana**-ZMOF using single gas *n*-butane with flow rate of 8 cm³·min⁻¹.

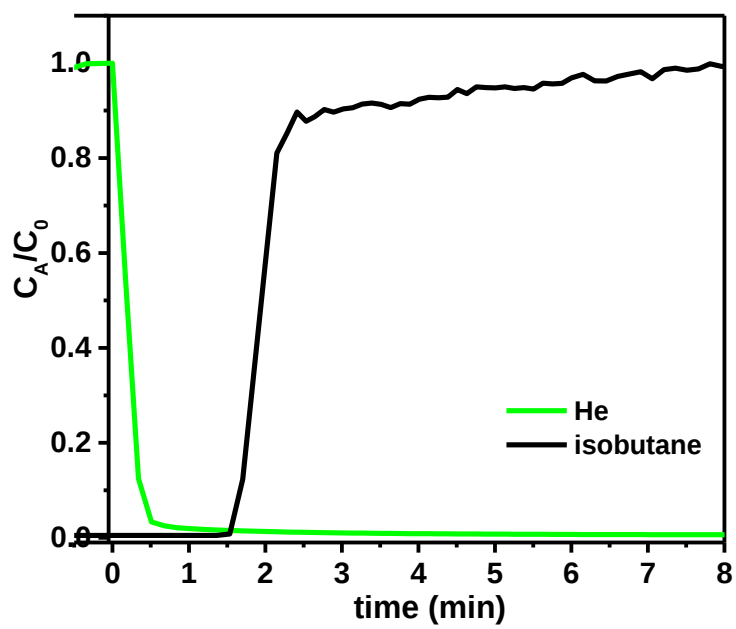


Figure S18. Column breakthrough test for **ana**-ZMOF using single gas *iso*-butane with flow rate of 8 $\text{cm}^3 \cdot \text{min}^{-1}$.

6. References

- S1. APEX2. Bruker AXS Inc, Madison, Wisconsin, USA, 2014.
- S2. SAINT. Bruker AXS. Inc, Madison, Wisconsin, USA, 2014.
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- S4. SHELXS-97, SHELXL-2014. G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8; WinGX. L. J. Farrugia, *J. Appl. Cryst.* 2012, **45**, 849-854.