SUPPLEMENTARY INFORMATION

Evaluation of the influence of various metals in iron-rich acid mine drainage on crystallinity, morphology and textural properties of iron-based MIL-101

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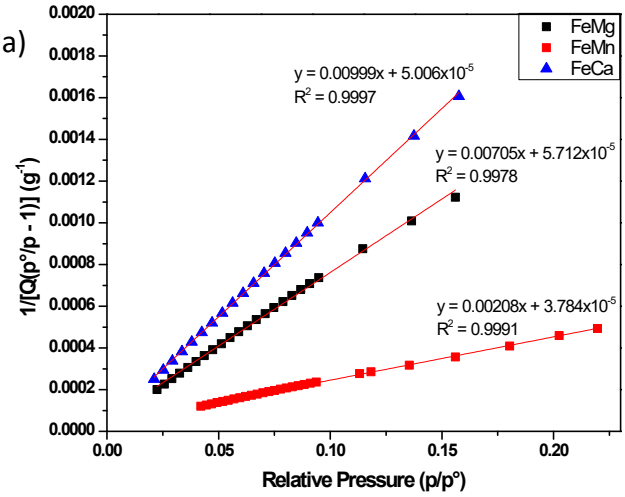
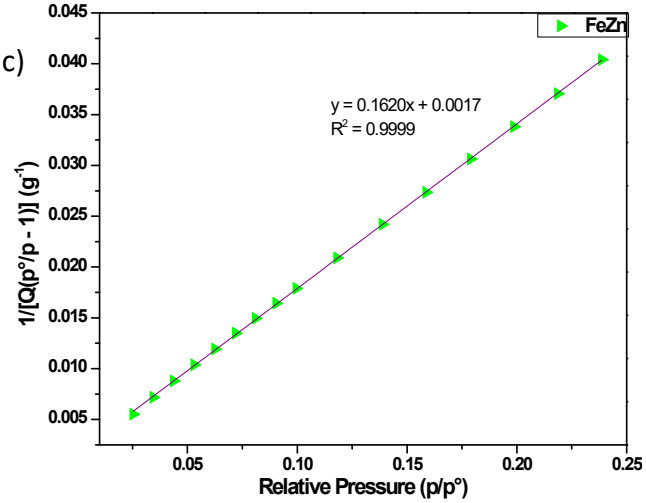
S1. Linear plots used to determine BET surface area of MIL-101 bimetallic and trimetallic MOFs

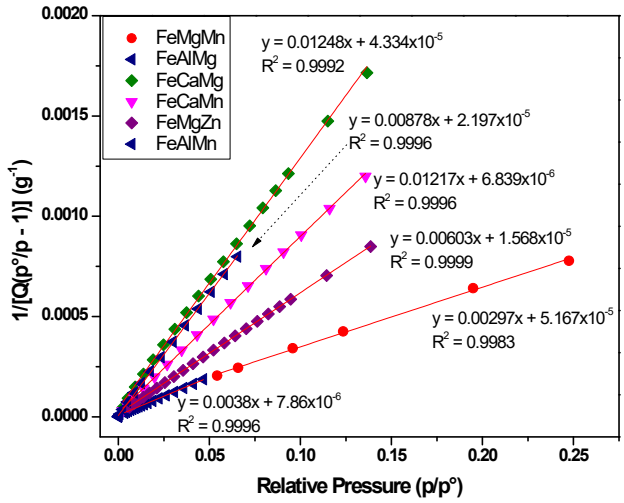
(a)



(b)

(c)





(d)

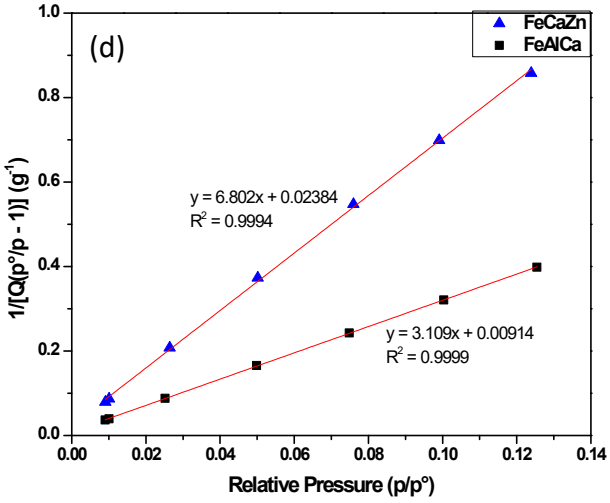


Figure S1: Linear BET plot in the selected pressure range (a and b) for bimetallic combinations and (c and d) trimetallic combinations

S2. Synthesis and characterization of MIL-88B metallic combinations (bimetallic and trimetallic)

All the MIL-88B MOFs were synthesized using AMD-Fe and PET-BDC as precursors. In a typical procedure, 1 g of AMD-Fe was dissolved in 5 mL HCl, followed by the addition of a specific amount of various metal salts to make bimetallic and trimetallic combinations as outlined in Table 1. In a separate beaker, 1 g of PET-BDC was dissolved in 50 mL DMF and 5 mL CH_3COOH. The two solutions were transferred into a Teflon-lined autoclave, placed in a conventional oven and heated at 110 °C for 20 h. The red precipitate formed was then separated from the solvent via centrifugation, followed by washing with DMF and hot ethanol twice, respectively. The product was then dried at 60 °C under vacuum overnight.

S2.1. Powder X-ray diffraction (PXRD)

The PXRD patterns show the majority of samples displaying sharp peaks at 2θ of 8.5° and 10, which are characteristic of MIL-88B.

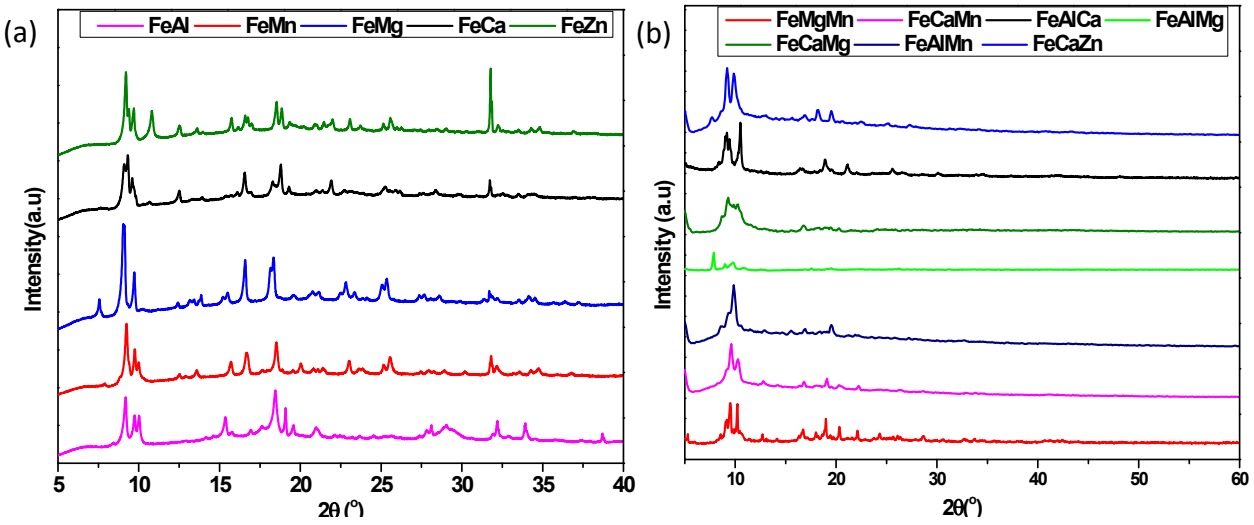


Figure S2: Powder X-ray diffraction patterns for MIL-88B synthesized from (a) bimetallic and (b) trimetallic combinations

Both bimetallic and trimetallic combinations displayed major bands at 1390 and 1597 cm^{-1} are attributed to v_{as}(COO) and v_s(COO) vibration bands, which are characteristic absorption bands of carboxylate. The vibrational band at 1659 cm^{-1} is assigned to C=O stretching. The weak bands at 1050 and 750 cm^{-1} are assigned to C-H bending vibrations of the benzene ring. The coordination of the carboxylate to the metal cluster (Fe-O) is confirmed by the absorption band at 550 cm^{-1}.

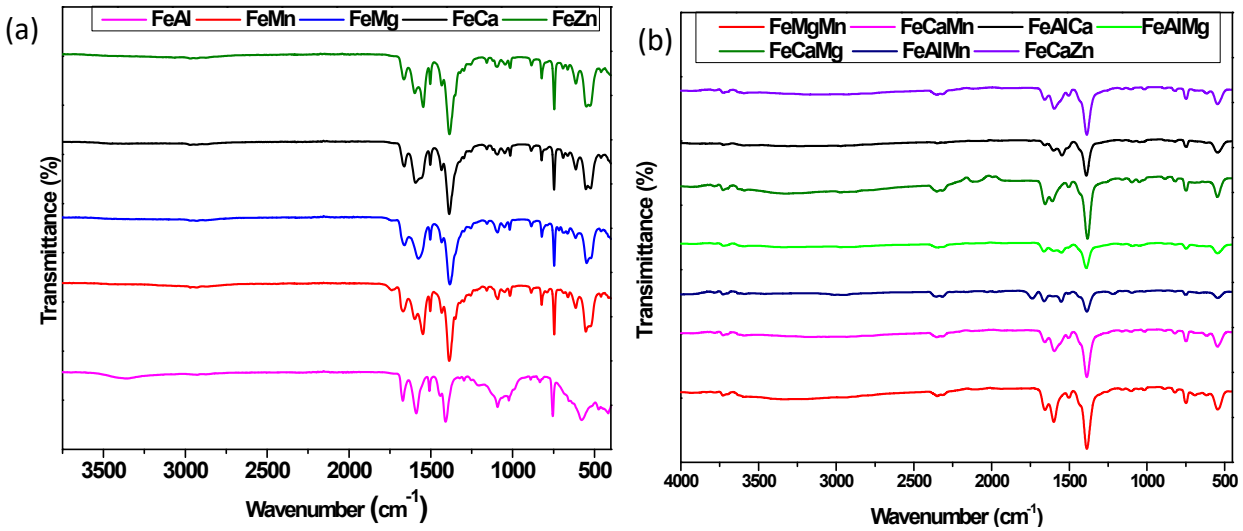


Figure S3: Fourier transform infrared spectroscopy patterns for MIL-88B synthesized from (a) bimetallic and (b) trimetallic combinations

S2.2. Scanning electron microscopy (SEM)

SEM revealed the trigonal bipyramidal morphology associated with MIL-88B. The particle size of the materials varied, with some bulge crystals with mixed octahedral phases associated with MIL-101 and elongated spindle-like crystals.

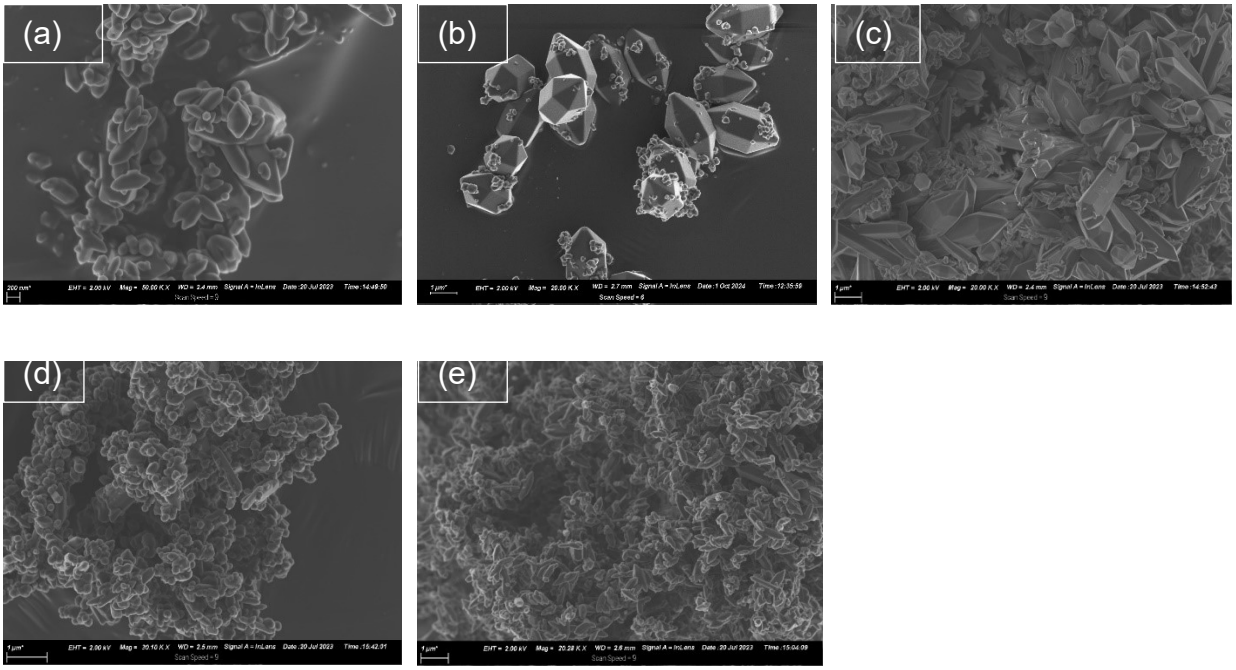


Figure S4: SEM images of MIL-88B synthesized from bimetallic combinations: (a) FeAl (b) FeMn (c) FeMg (d) FeCa and (e) FeZn

The trigonal bipyramidal morphology is visible for all samples. There is presence of octahedral morphology and rod-like materials intertwined with MIL-88B crystals.

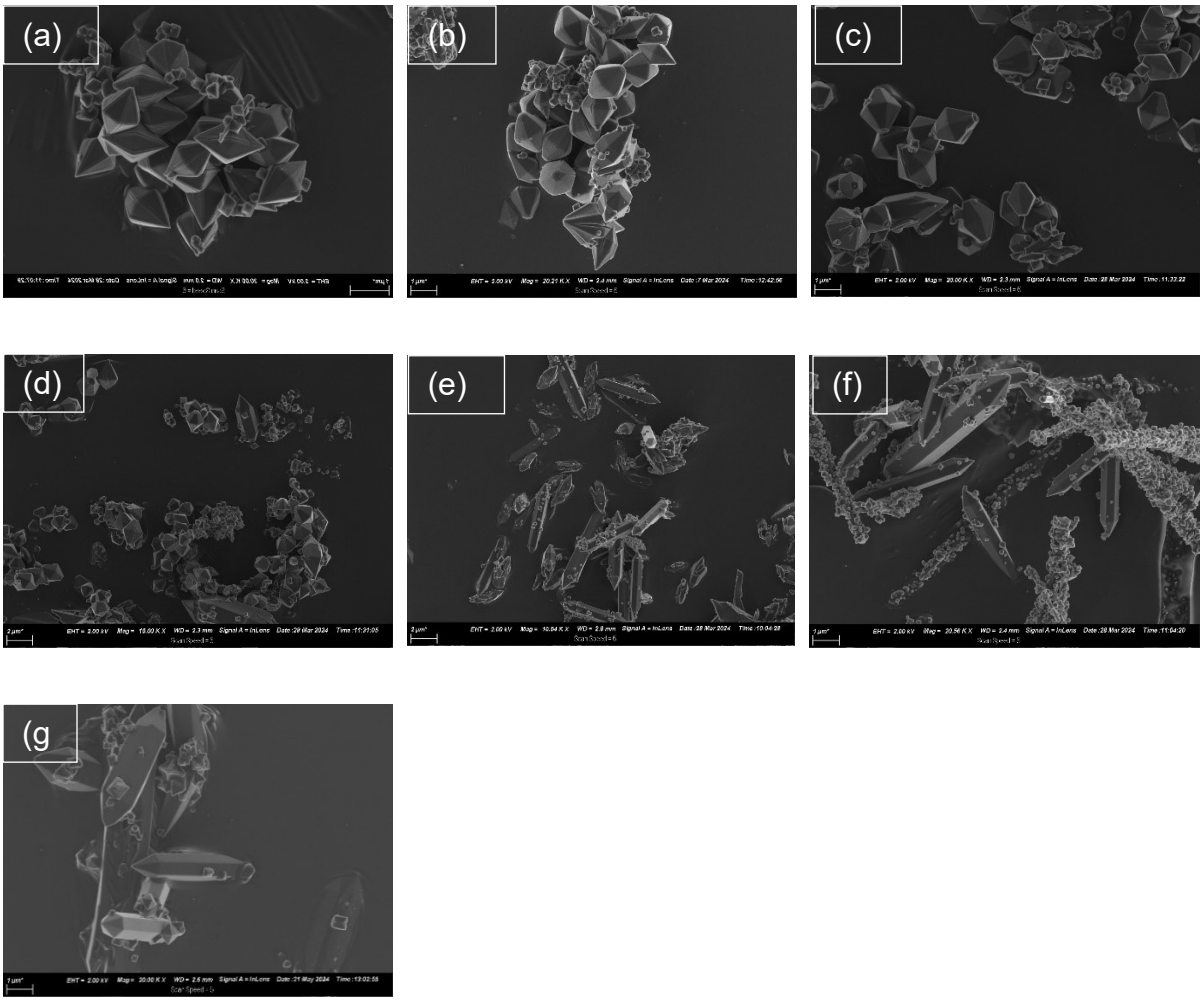


Figure S5: SEM images of MIL-88B synthesized from trimetallic combinations: (a) FeMgMn, (b) FeAlMg, (c) FeAlCa, (d) FeMgZn, (e) FeCaMn, (f) FeAlMn, (g) FeCaZn and (h) FeCaMg

S2.3. Thermogravimetric analysis (TGA)

Fig. S6a and **b** show the TGA profiles of FeM-MIL-88B and FeM_1M_2-MIL-88B samples, respectively. The plots display a two-step mass loss which is commonly associated with iron-

based MOF structures. The initial mass loss (5 - 30 %) at temperatures below 150 °C is attributed to loss of moisture and/or solvents molecules trapped within the cavities and/or interacting with open metal sites. The carboxylate ligand is thermally stable up to 400 °C for all samples. The remaining mass for all samples was almost identical, ranging between 25 % - 30%, which is usually observed for Fe-MOFs.

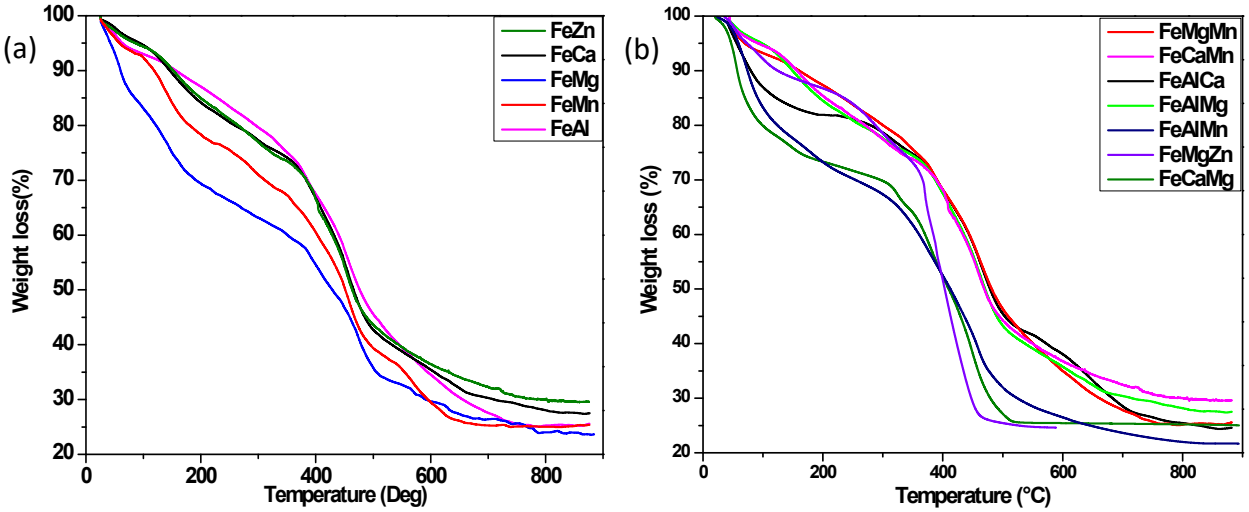


Figure S6: TGA profiles of MIL-88B synthesized from (a) bimetallic and (b) trimetallic combinations

S2.4. N_2 isotherms and pore size distribution

Figure S7a and b shows isotherms of bimetallic and trimetallic MOF samples obtained using N_2 at 77 K. The samples exhibited a combination of Type I(b) and Type IV (a) which is typical for micro and narrow mesoporous materials. The pore size distribution (**S7c and d)** confirms that materials are made of micropores (<2 nm) and narrow mesopores (<3.5 nm). FeZn-MIL-101 samples had large mesopores (>20 nm).

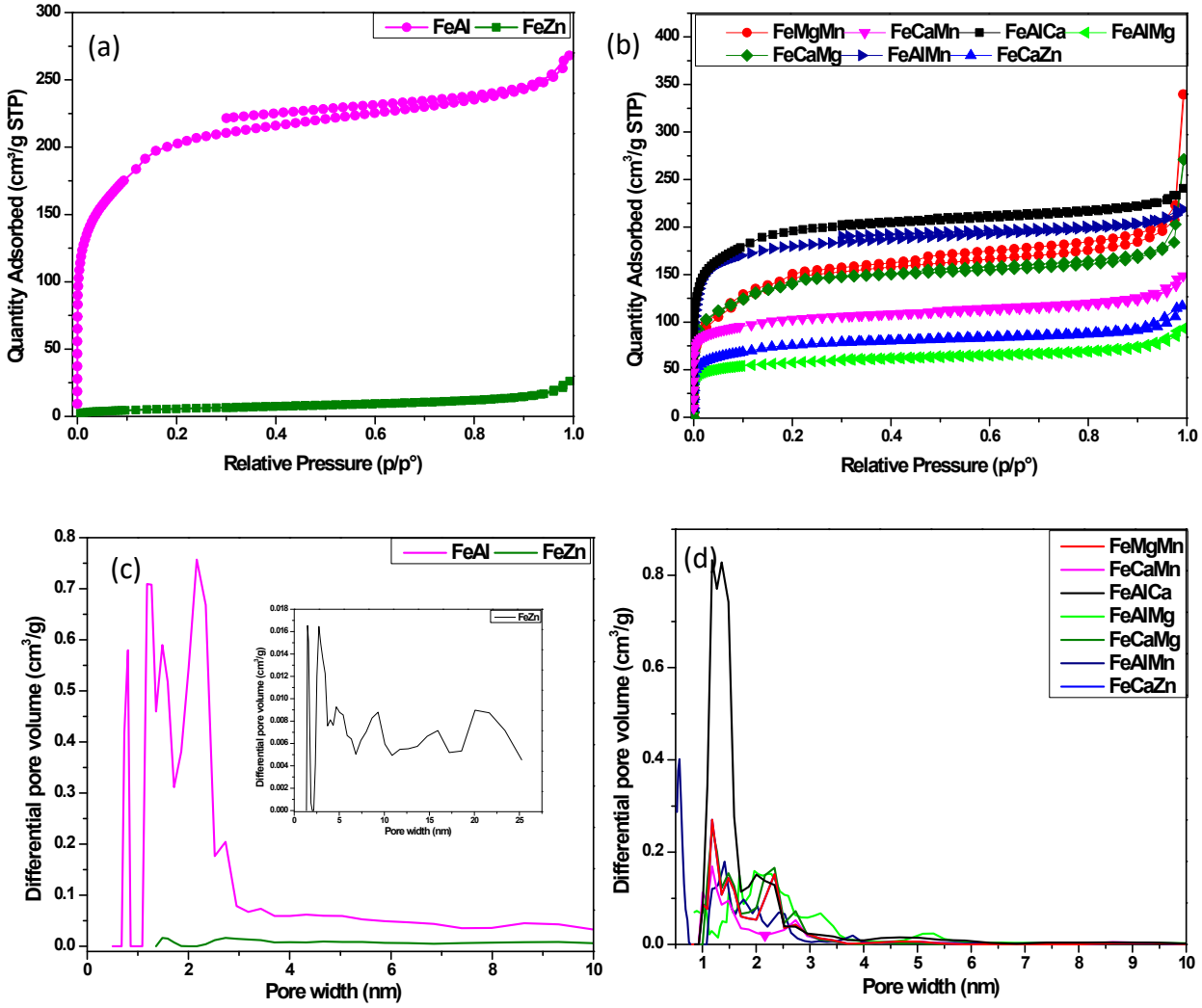


Figure S7: N_2 sorption isotherms for MIL-88B synthesized from (a) bimetallic and (b) trimetallic combinations; and pore size distribution for MIL-88B synthesized from (c) bimetallic and (d) trimetallic combinations

Table S1: Textural properties of the prepared MIL-88B samples from bimetallic and trimetallic combinations

Sample label	BET (m^2/g)	Pore volume (cm^3/g)	Average pore Size (nm)	H_2 uptake at 77 K, 1 bar (wt%)
FeAl	744	0.32	1.36	1.34
FeZn	134	0.22	15	0.40
FeMgM	525	0.31	1.62	0.47
FeMgZn	215	0.13	2.20	0.61
FeCaZn	510	0.30	1.46	0.67
FeAlMg	501	0.27	1.62	0.50
FeCaMn	381	0.2	2.1	0.71
FeAlCa	716	0.35	1.9	0.99
FeAlMn	684	0.32	1.88	1.05

S2.5. Hydrogen adsorption

Fig. S8a and b shows H_2 adsorption isotherms obtained at 77 K and 1 bar. Only two of the bimetallic combination MOFs were tested for H_2 adsorption, where FeAl-MIL-88B displayed 1.3 wt% H_2 which is reasonable for the available surface area. Due to low surface area and pore volume, FeZn-MIL-88B performed poorly at 0.4 wt% H_2. For trimetallic combinations, the best performing samples are FeAlCa-MIL-88B and FeAlMn-MIL-88B with H_2 adsorption of 1.05 and 0.99 wt%, respectively. **Table S1** shows H_2 adsorption of the other trimetallic combinations.

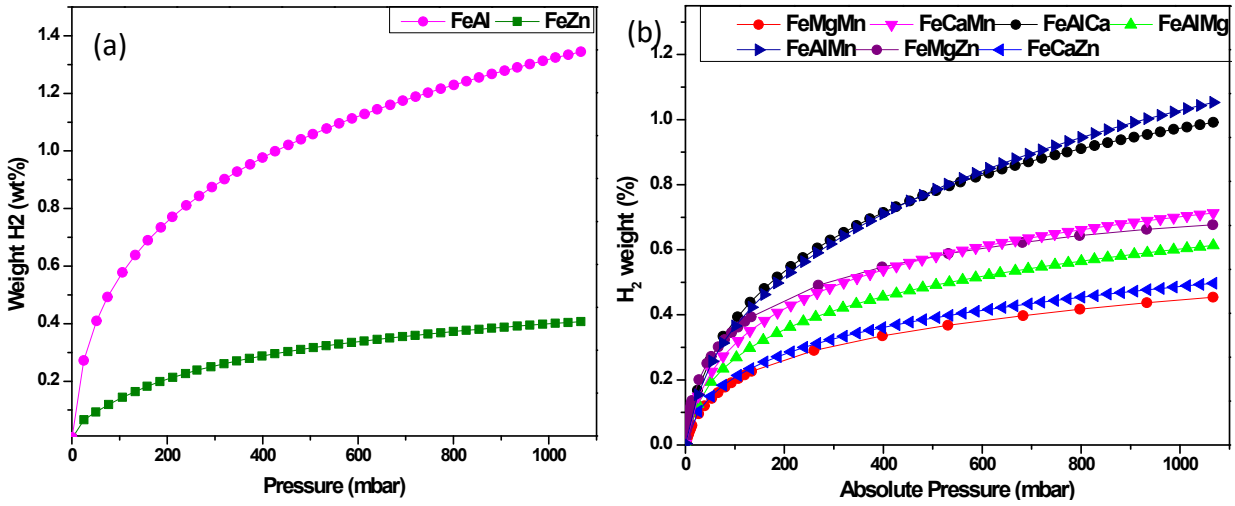


Figure S8: (a) and (b) Hydrogen uptake for MIL-88B synthesized from bimetallic and trimetallic combinations 77 K at 1 bar