Salt Metathesis in Three Dimensional Metal Organic Frameworks (MOFs) with Unprecedented Hydrolytic Regenerability

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Section S1. Detailed synthetic procedures of ligands and MOFs with IR spectrum and PXRD patterns:

Materials and general methods. All reagents were commercially available and used as received from Sigma Aldrich. Single crystal data were collected on Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_a radiation (λ =0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of all MOFs reported in the paper was mounted on nylon CryoLoop (Hampton Research) with Paraton-N (Hampton Research). Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu K_{α} radiation ($\lambda = 1.5406$ Å), with a scan speed of 2° min⁻¹ with a step size of 0.02° in 20. Fourier transform infrared (FT-IR) spectra were taken on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600-4000 cm⁻¹ region or using a Diamond ATR (Golden Gate). Thermogravimetric experiments (TGA) were carried out in the temperature range of 25-800 °C on a SDT Q600 TG-DTA analyzer under N₂ atmosphere at a heating rate of 8 °C min⁻¹. All low pressure water adsorption experiments (up to 1 bar) were performed on the *Quantachrome* Autosorb-iQ-MP automatic volumetric instrument. Leica M-80 optical microscope with hot stage and camera attachment was used for collecting photographs. SEM images were obtained with a FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nanosized film) prior to imaging by a SCD 040 Balzers Union as well as by sprinkling the powder on carbon tape. Solid state NMR (SSNMR) was taken in a Bruker 300 MHz NMR spectrometer and Ligand NMR data were taken in Bruker 200 MHz NMR spectrometer.

Synthesis

N-(4-Pyridylmethyl)-L-valine.HCO₂Na [*l*-L_{HCO2}]: To an aqueous solution (10 mL) of L-valine (2 g, 17 mmol) and Na₂CO₃ (0.91 g, 8.5 mmol), 4-pyridinecarboxaldehyde (1.82 g, 17 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and cooled in an ice bath. NaBH₄ (0.76 g, 20.4 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3N HCO₂H was used to adjust the pH to 7. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL x 3), and the filtrate was evaporated to get white powder (2.9 g, 70% yield). IR (KBr, cm⁻¹): v_{OH} , 3421; v_{as} (CO₂), 1562; v_{s} (CO₂), 1409. ¹H NMR (D₂O, ppm): -CH₃ (1.21, d, 3H), -CH₃ (1.35, d, 3H), -CH (3.20, m, 1H), -HN-CH (3.65, m, 1H), -CH₂ (3.82, dd, 2H), py-H (7.34, d, 2H), py-H (8.38, d, 2H).

N-(4-Pyridylmethyl)-L-valine.CH₃CO₂Na [*l*-L_{CH3CO2}]: The ligand N-(4-Pyridylmethyl)-L-valine. **CH₃CO₂Na** [*l*-L_{CH3CO2}] was prepared exactly as *l*-L_{CH3CO2} only CH₃CO₂H was used instead of HCO₂H for pH adjustment upto pH 7. Yield, 3.4 g, 70%. IR (KBr, cm⁻¹): v_{OH} , 3420; v_{as} (CO₂), 1560; v_{s} (CO₂), 1411. ¹H NMR (D₂O, ppm): -CH₃ (1.20, d, 3H), -CH₃ (1.33, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH₂ (3.79, dd, 2H), py-H (7.34, d, 2H), py-H (8.37, d, 2H).

N-(4-Pyridylmethyl)-L-alanine.NaCl [*l***-L1_{Cl}]:** To an aqueous solution (10 mL) of L-alanine (1.52 g, 17 mmol) and Na₂CO₃ (0.91 g, 8.5 mmol), 4-pyridinecarboxaldehyde (1.82 g, 17 mmol) in MeOH (10 mL) was added slowly. The solution was stirred for 1 h and cooled in an ice bath. NaBH₄ (0.76 g, 20.4 mmol) in 10 mL of water was added. The mixture was stirred for 1 h, and 3N HCl was used to adjust the pH to 7. The solution was stirred further for 2 h and then evaporated to dryness. The solid was extracted in hot and dry MeOH (150 mL x 3), and the filtrate was evaporated to get white powder (2.9 g, 70% yield). IR (KBr, cm⁻¹): v_{OH}, 3421; v_{as}(CO₂), 1562; v_s(CO₂), 1409. ¹H NMR (D₂O, ppm): -HN-CH (3.65, m, 1H), -CH₂ (3.82, dd, 2H), py-H (7.31, d, 2H), py-H (8.38, d, 2H).

N-(4-Pyridylmethyl)-L-alanine.NaBr [*l*-L1_{Br}]: The ligand N-(4-Pyridylmethyl)-L-alanine.NaBr (*l*-L1_{Br}) was prepared exactly as *l*-L1_{Cl}, only HBr was used instead of HCl for pH adjustment. Yield, 3 g, 72% IR (KBr, cm⁻¹): v_{OH} , 3419; $v_{as}(CO_2)$, 1570; $v_s(CO_2)$, 1421. ¹H NMR (D₂O, ppm): -CH₃ (1.20, d,

3H), -CH₃ (1.34, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH₂ (3.80, dd, 2H), py-H (7.30, d, 2H), py-H (8.37, d, 2H).

N-(4-Pyridylmethyl)-L-alanine.HCO₂Na [*l*-L1_{HCO2}]: The ligand N-(4-Pyridylmethyl)-L-alanine.HCO2Na (*l*-L1_{HCO2}) was prepared exactly as *l*-L1_{Cl}, only HCO₂H was used instead of HCl for pH adjustment. Yield, 3 g, 74% IR (KBr, cm⁻¹): v_{OH} , 3419; $v_{as}(CO_2)$, 1570; $v_s(CO_2)$, 1421. ¹H NMR (D₂O, ppm): -CH₃ (1.34, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH₂ (3.80, dd, 2H), py-H (7.35, d, 2H), py-H (8.37, d, 2H).

A weighed amount (50mg) of l-L_{HCO2}/l-L1_{HCO2} was taken in a 2ml vial along with 1ml H₂O to dissolve fully and then left for crystallization. At first, HCO₂Na crystallized out from solution and then the ligand got crystallized (CCDC No. 918497-918498).

N-(4-Pyridylmethyl)-L-alanine.CH₃CO₂Na [*l*-L1_{CH3CO2}]: The ligand N-(4-Pyridylmethyl)-Lalanine.CH₃CO2Na (*l*-L1_{CH3CO2}) was prepared exactly as *l*-L1_{Cl}, only CH₃CO₂H was used instead of HCl for pH adjustment. Yield, 3 g, 70%. IR (KBr, cm⁻¹): v_{OH} , 3419; v_{as} (CO₂), 1570; v_{s} (CO₂), 1421. ¹H NMR (D₂O, ppm): -CH₃ (1.34, d, 3H), -CH (3.24, m, 1H), -HN-CH (3.63, m, 1H), -CH₂ (3.70, dd, 2H), py-H (7.35, d, 2H), py-H (8.37, d, 2H).

 $[Zn(l-L_{HCO2})(HCO_2)](H_2O)_2$ (ValZnFor): To an aqueous solution (0.5ml) of $l-L_{HCO2}$ (0.055 g, 0.2 mmol), $Zn(CH_3CO_2)_2.2H_2O$ (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a 15ml vial for 12h at room temperature to produce rod shaped transparent crystals (0.023 g, 71% yield). IR (KBr, cm⁻¹): v_{OH}, 3420; v_{N-H}, 2975; v_{as}(CO₂), 1589; v_s(CO₂), 1397. v_{C-N},1627. Elemental Analysis: Calculated- C (40.51%), H (5.25%), N (8.59%); Found C (40.54%), H (5.28%), N (8.57%). CCDC No. 918487.

 $[Zn(l-L_{CH3CO2})(CH_3CO_2)](H_2O)_2$ (ValZnOAc): To an aqueous solution (0.25ml) of $l-L_{CH3CO2}$ (0.058 g, 0.2 mmol), Zn(CH₃CO₂)₂.2H₂O (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a 15ml vial for 24h at room temperature to produce rod shaped transparent crystals (0.026 g, 72% yield). IR (KBr, cm⁻¹): v_{OH}, 3425; v_{N-H}, 2970; v_{as}(CO₂), 1592; v_s(CO₂), 1395. v_{C-N},1622.

Elemental Analysis: Calculated- C (35.65%), H (4.62%), N (7.60%); Found C (35.60%), H (4.64%), N (7.62%). CCDC No. 918488.

 $[Zn(l-L1_{Cl})(Cl)](H_2O)_2$ (AlaZnCl): To an aqueous solution (0.5ml) of $l-L1_{Cl}$ (0.048 g, 0.2 mmol), Zn(CH₃CO₂)₂.2H₂O (0.022 g, 0.1 mmol) in 5ml MeOH was added and sonicated for 10 min. The clear solution was kept in a 15ml vial for 24 h at room temperature to produce rod shaped transparent crystals (0.025 g, 75% yield). IR (KBr, cm⁻¹): v_{OH}, 3421; v_{N-H}, 2977; v_{as}(CO₂), 1589; v_s(CO₂), 1395. v_{C-N},1626. Elemental Analysis: Calculated- C (40.51%), H (5.25%), N (8.59%); Found C (40.57%), H (5.21%), N (8.62%). CCDC No. 918489.

 $[Zn(l-L1_{Br})(Br)](H_2O)_2$ (AlaZnBr): To an aqueous solution (0.75ml) of $l-L1_{Br}$ (0.057 g, 0.2 mmol), Zn(CH₃CO₂)₂.2H₂O (0.022 g, 0.1 mmol) in 5ml MeOH was added and sonicated for 10 min. The clear solution was kept in a 15ml vial for 24 h at room temperature to produce rod shaped transparent crystals (0.026 g, 70% yield). IR (KBr, cm⁻¹): v_{OH}, 3427; v_{N-H}, 2974; v_{as}(CO₂), 1590; v_s(CO₂), 1394. v_{C-N},1623. Elemental Analysis: Calculated- C (34.45%), H (4.62%), N (7.60%); Found C (35.68%), H (4.60%), N (7.63%). CCDC No. 918490.

 $[Zn(l-L1_{HCO2})(HCO_2)](H_2O)_2$ (AlaZnFor): To an aqueous solution (0.5ml) of $l-L1_{HCO2}$ (0.05 g, 0.2 mmol), $Zn(CH_3CO2)_2.2H_2O$ (0.022 g, 0.1 mmol) was added and sonicated for 10 min. The clear solution was kept in a tightly capped 5ml vial for 24 h at 90 °C to produce rod shaped transparent crystals (0.023 g, 71% yield). IR (KBr, cm⁻¹): v_{OH}, 3424; v_{N-H}, 2975; v_{as}(CO₂), 1589; v_s(CO₂), 1397. v_{C-N},1627. Elemental Analysis: Calculated- C (40.51%), H (5.25%), N (8.59%); Found C (40.54%), H (5.28%), N (8.57%). CCDC No. 918491.

 $[Zn(l-L1_{CH3CO2})(CH_3CO_2)](H_2O)_2$ (AlaZnOAc): To an aqueous solution (0.25ml) of $l-L1_{CH3CO2}$ (0.044 g, 0.2 mmol), Zn(CH₃CO₂)₂.2H₂O (0.022 g, 0.1 mmol) in 6ml MeOH was added and sonicated for 10 min. The clear solution was kept in a 15ml vial for 36 h at room temperature to produce rod shaped transparent crystals (0.026 g, 72% yield). IR (KBr, cm⁻¹): v_{OH}, 3423; v_{N-H}, 2970; v_{as}(CO₂), 1592; v_s(CO₂), 1395. v_{C-N},1622. Elemental Analysis: Calculated- C (35.65%), H (4.62%), N (7.60%); Found C (35.60%), H (4.64%),N(7.62%). CCDC No. 918492.



Figure S1: Schematic representation of the synthesis scheme of all eight MOFs with ball and stick model of SBU.

IR Absorption spectrums:



Figure S2. IR Absorption spectrum of a) l-L_{Cl}(green) b) ValZnFor (violet) c) AlaZnCl (black) and d) AlaZnNO₃ (blue).





Figure S3. Experimental PXRD patterns of a) ValZnFor b) ValZnOAc c) AlaZnCl d) AlaZnBr e) AlaZnFor and f) AlaZnOAc compared with the simulated one, exhibiting their phase purity.



Figure S4. Experimental PXRD patterns of ValZnNO₃ and AlaZnNO₃ compared with the simulated one, exhibiting their phase purity.

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures:

General Data Collection and Refinement Procedures:

Single crystal data were collected on Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_{α} radiation (λ =0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of all MOFs reported in the paper was mounted on nylon CryoLoop (Hampton Research) with Paraton-N (Hampton Research).

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In every case frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker SMART*⁴ software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using *CELL_NOW*². In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data were integrated using Bruker *SAINT*³ software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program *SADABS*⁴. The space group determinations and tests for merohedral twinning were carried out using *XPREP*³. In these cases, the highest possible space group was chosen.

Structures were solved by direct methods and refined using the *SHELXTL* 97^5 software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. In some cases, modeling of solvent water molecules in these MOFs became difficult due to dynamic nature of oxygen and hydrogen molecules within the large pores in the frameworks. Increasing the exposure time of the crystal to X-rays did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal contributes to the background and the 'washing out' of the weaker data. Unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens have not yet been fruitful. Single Crystal X-ray Diffraction data for all the MOFs was collected at 100(2) K if otherwise stated. Structures were examined using the *ADDSYM* subroutine of *PLATON*⁷ to assure that no additional symmetry could be applied to the models. All ellipsoids in *ORTEP* diagrams are displayed at the 50% probability level. For some MOFs elevated R-values are commonly encountered for the reasons expressed above by some research groups.⁸⁻¹⁷

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Experimental and Refinement Details for MOFs:

Colorless rod shaped crystal ($0.50 \times 0.20 \times 0.10 \text{ mm}^3$) was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)¹⁹ and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_a radiation (λ =0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Analysis of the data showed negligible decay during collection. The structure was solved in the hexagonal *P*61 space group, with *Z* = 6, using direct methods. All non-hydrogen atoms were refined anisotropically. Very high displacement parameters, high esd's and partial occupancy due to the disorder make it impossible to determine accurate positions for the hydrogen atoms in water molecules. Crystallographic data (excluding structure factors) for the structures are reported in this paper have been deposited with the CCDC as deposition No.CCDC 918487–918500, 926615–926616.

Table S1. Crystal Data and Structure Refinement for the MOFs (100K).

	ValZnFor	ValZnOAc	AlaZnCl	AlaZnBr	AlaZnFor	AlaZnOAc
Formula	C12 H19 N2 O6 Zn	C13 H22 N2 O6 Zn	C9 H15 Cl N2 O4 Zn	C9 H15 Br N2 O4 Zn	C10 H15 N2 O6 Zn	C11 H17 N2 O6 Zn
Mr	352.69	367.72	316.07	360.53	324.64	338.66
Temperature	100(2)K	100(2)K	100(2)K	100(2)K	100(2)K	100(2)K
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61
a (Å)	17.7336(11)	17.4542(6)	17.4587(2)	17.7440(3)	17.5911(7)	17.5806(7)
<i>b</i> (Å)	17.7336(11)	17.4542(6)	17.4587(2)	17.7440(3)	17.5911(7)	17.5806(7)
c (Å)	10.3433(8)	10.3953(3)	10.24475(14)	10.17155(19)	10.1716(3)	10.1486(2)
V[Å ³]	2817.0(5) Å ³	2742.63(16) Å ³	2704.31(6) Å ³	2773.45(12) Å ³	2725.87(17) Å ³	2716.5(3) Å ³
Z	6	6	6	6	6	6
$\rho_{calcd}[g \ cm^{-1}]$	1.233	1.321	1.150	1.281	1.172	1.227
Absorption coefficient	1.329	1.368	1.513	3.492	1.368	1.376
<i>F</i> (000)	1074	1128	948	1056	978	2264
θ range[°]	3.03-29.24	3.33 - 29.10	3.07-29.14	3.05 - 29.22	3.06 - 29.11	3.07 - 28.05
Reflections collected	7392	6242	19898	6778	8057	6610
Independent reflections	3718	2991	4382	4042	3676	3289
GOF	1.108	1.102	1.142	1.093	1.090	1.073
Flack Parameter ¹⁸⁻²⁰	-0.05	0.01	0.003	-0.012	-0.03	-0.04
Final $R1$, $wR2[I > 2\sigma(I)]$	$R_1 = 0.0711,$ $wR_2 = 0.1895$	$R_1 = 0.0546,$ $wR_2 = 0.1480$	$R_1 = 0.0420,$ w $R_2 = 0.1237$	$R_1 = 0.0482,$ $wR_2 = 0.1309$	$R_1 = 0.0645,$ $wR_2 = 0.1891$	$R_1 = 0.0732,$ $wR_2 = 0.1952$
R indices (all data)	$R_1 = 0.0793,$ w $R_2 = 0.2060$	$R_1 = 0.0586,$ $wR_2 = 0.1505$	$R_1 = 0.0436,$ $wR_2 = 0.1253$	$R_1 = 0.0507,$ $wR_2 = 0.1351$	$R_1 = 0.0783,$ $wR_2 = 0.2059$	$R_1 = 0.0903,$ $wR_2 = 0.2109$

Table S2. Crystal data and structure refinement for ValZnNO₃.

Identification code	ValZnNO3	
Empirical formula	C44 H70 N12 O23 Zn2	
Formula weight	1265.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>C</i> 2	
Unit cell dimensions	$a = 25.117(2)$ Å $\alpha = 90^{\circ}$.	
b = 5.7802(4) Å	$\beta = 120.744(14)^{\circ}.$	
c = 21.993(2) Å	$\gamma = 90^{\circ}$.	
Volume	2744.2(4) Å ³	
Ζ	2	
Density (calculated)	1.532 Mg/m ³	
Absorption coefficient	0.966 mm ⁻¹	
F(000)	1324	
Crystal size	0.6 x 0.3 x 0.2 mm ³	
Theta range for data collection	3.35 to 28.12°.	
Index ranges	-32<=h<=16, -7<=k<=4, -28<=l<=28	
Reflections collected	4507	
Independent reflections	3756 [R(int) = 0.0261]	
Completeness to theta = 25.00°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.824 and 0.713	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3756 / 5 / 328	
Goodness-of-fit on F ²	1.110	
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.1815	
R indices (all data)	R1 = 0.0947, wR2 = 0.1821	
Absolute structure parameter	0.00(3)	
Largest diff. peak and hole	2.250 and -1.623 e.Å ⁻³	

Table S3. Crystal data and structure refinement for AlaZnNO₃.

Identification code	AlaZnNO3		
Empirical formula	$C_{18}H_{24}N_6O_{10}Zn$		
Formula weight	549.82		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	P21212		
Unit cell dimensions	a = 12.8683(3) Å	α= 90°.	
	b = 16.2028(4) Å	β= 90°.	
	c = 5.47060(10) Å	$\gamma = 90^{\circ}$.	
Volume	1140.63(4) Å ³		
Ζ	2		
Density (calculated)	1.601 Mg/m ³		
Absorption coefficient	1.144 mm ⁻¹		
F(000)	568		
Crystal size	0.6 x 0.4 x 0.3 mm ³		
Theta range for data collection	2.97 to 29.17°.		
Index ranges	-16<=h<=10, -20<=k<=17, -6<=l<=6		
Reflections collected	3822		
Independent reflections	2349 [R(int) = 0.0209]		
Completeness to theta = 25.00°	99.6 %		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	2349 / 0 / 160		
Goodness-of-fit on F ²	1.077		
Final R indices [I>2sigma(I)]	R1 = 0.0272, $wR2 = 0.0629$		
R indices (all data)	R1 = 0.0309, wR2 = 0.0648		
Absolute structure parameter	-0.019(12)		

Table S4. Crystal data and structure refinement for Val.

Identification code	Val		
Empirical formula	$C_{11}H_{16}N_2O_2$		
Formula weight	208.26		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	monoclinic		
Space group	P21		
Unit cell dimensions	a = 7.7973(4) Å	= 90°.	
	b = 5.9954(2) Å	= 104.675(5)°.	
	c = 12.1886(6) Å	= 90°.	
Volume	551.20(4) Å3		
Z	2		
Density (calculated)	1.255 Mg/m3		
Absorption coefficient	0.087 mm-1		
F(000)	224		
Crystal size	0.5 x 0.3 x 0.2 mm3		
Theta range for data collection	3.46 to 28.85°.		
Index ranges	-9<=h<=10, -7<=k<=4, -12<=l<=16		
Reflections collected	2472		
Independent reflections	1843 [R(int) = 0.0172]		
Completeness to theta = 28.85°	88.3 %		
Refinement method	Full-matrix least-squares on F2		
Data / restraints / parameters	1843 / 1 / 138		
Goodness-of-fit on F2	1.069		
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1562		
R indices (all data)	R1 = 0.0610, wR2 = 0.1624		
Absolute structure parameter	-5(3)		
Largest diff. peak and hole	0.223 and -0.200 e.Å $-^{3}$		

Table S5. Crystal data and structure refinement for Ala.

Identification code	Ala	
Empirical formula	$C_9 H_{12} N_2 O_2$	
Formula weight	180.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 5.3147(2) Å	α= 90°.
	b = 8.7308(3) Å	$\beta = 91.651(4)^{\circ}$
	c = 9.8683(4) Å	$\gamma = 90^{\circ}$.
Volume	457.71(3) Å ³	
Ζ	2	
Density (calculated)	1.308 Mg/m ³	
Absorption coefficient	0.094 mm ⁻¹	
F(000)	192	
Crystal size	0.5 x 0.3 x 0.2 mm ³	
Theta range for data collection	3.12 to 28.96°.	
Index ranges	-5<=h<=7, -6<=k<=11,	-12<=l<=12
Reflections collected	2061	
Independent reflections	1512 [R(int) = 0.0604]	
Completeness to theta = 25.00°	99.9 %	
Refinement method	Full-matrix least-square	s on F ²
Data / restraints / parameters	1512 / 1 / 119	
Goodness-of-fit on F ²	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0663, wR2 = 0.1	677
R indices (all data)	R1 = 0.0800, wR2 = 0.1	771
Absolute structure parameter	0(3)	
Largest diff. peak and hole	0.291 and -0.233 e.Å ⁻³	

Table S6. Crystal data and structure refinement for AlaZnCl 293K.

Identification code	AlaZnCl 293K		
Empirical formula	$C_{9}H_{13}ClN_{2}O_{3}Zn$		
Formula weight	298.06		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Hexagonal		
Space group	<i>P</i> 61		
Unit cell dimensions	a = 17.5285(3) Å	α= 90°.	
	b = 17.5285(3) Å	β= 90°.	
	c = 10.26523(16) Å	$\gamma = 120^{\circ}$.	
Volume	2731.43(9) Å ³		
Ζ	6		
Density (calculated)	1.080 Mg/m ³		
Absorption coefficient	1.490 mm ⁻¹		
F(000)	900		
Crystal size	0.5 x 0.2x 0.1 mm ³		
Theta range for data collection	3.06 to 29.03°.		
Index ranges	-20<=h<=15, -17<=k<=22, -8<=l<=13		
Reflections collected	7363		
Independent reflections	3615 [R(int) = 0.0253]		
Completeness to theta = 29.03°	88.1 %		
Refinement method	Full-matrix least-squares on F ²	2	
Data / restraints / parameters	3615 / 1 / 146		
Goodness-of-fit on F ²	1.115		
Final R indices [I>2sigma(I)]	R1 = 0.0510, $wR2 = 0.1547$		
R indices (all data)	R1 = 0.0541, $wR2 = 0.1588$		
Absolute structure parameter	0.01(2)		
Largest diff. peak and hole	1.026 and -0.478 e.Å ⁻³		

Table S7. Crystal data and structure refinement for AlaZnCl 323K.

Identification code	AlaZnCl 323K		
Empirical formula	$C_9 H_{11} Cl N_2 O_2 Zn$		
Formula weight	280.04		
Temperature	323(2) K		
Wavelength	0.71073 Å		
Crystal system	Hexagonal		
Space group	<i>P</i> 61		
Unit cell dimensions	a = 17.6015(3) Å	α= 90°.	
	b = 17.6015(3) Å	β= 90°.	
	c = 10.26898(17) Å	$\gamma = 120^{\circ}$.	
Volume	2755.22(9) Å3		
Ζ	6		
Density (calculated)	1.013 Mg/m3		
Absorption coefficient	1.470 mm-1		
F(000)	852		
Crystal size	0.5x 0.2x 0.1 mm3		
Theta range for data collection	3.05 to 29.21°.		
Index ranges	-16<=h<=20, -5<=k<=23, -12<=l<=9		
Reflections collected	7970		
Independent reflections	3979 [R(int) = 0.0224]		
Completeness to theta = 29.21°	89.5 %		
Refinement method	Full-matrix least-squares on F2	2	
Data / restraints / parameters	3979 / 1 / 137		
Goodness-of-fit on F2	1.157		
Final R indices [I>2sigma(I)]	R1 = 0.0557, wR2 = 0.1821		
R indices (all data)	R1 = 0.0584, WR2 = 0.1874		
Absolute structure parameter	0.00(3)		
Largest diff. peak and hole	1.785 and -0.533 e.Å-3		

Table S8. Crystal data and structure refinement for AlaZnFor 200K.

Identification code	AlaZnFor 200K		
Empirical formula	$C_{10}H_{14}N_2O_5Zn$		
Formula weight	307.63		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	Hexagonal		
Space group	<i>P</i> 61		
Unit cell dimensions	a = 17.5911(7) Å	α= 90°.	
	b = 17.5911(7) Å	β= 90°.	
	c = 10.1716(3) Å	$\gamma = 120^{\circ}$.	
Volume	2725.88(18) Å ³		
Ζ	6		
Density (calculated)	1.117 Mg/m ³		
Absorption coefficient	1.361 mm ⁻¹		
F(000)	936		
Crystal size	0.6 x 0.2 x 0.2 mm ³		
Theta range for data collection	3.06 to 29.11°.		
Index ranges	-19<=h<=20, -22<=k<=12, -7<=l<=12		
Reflections collected	8057		
Independent reflections	3676 [R(int) = 0.0293]		
Completeness to theta = 29.11°	87.5 %		
Refinement method	Full-matrix least-squares on F ²	2	
Data / restraints / parameters	3676 / 1 / 164		
Goodness-of-fit on F ²	1.069		
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1949		
R indices (all data)	R1 = 0.0805, $wR2 = 0.2128$		
Absolute structure parameter	0.00(3)		
Largest diff. peak and hole	1.376 and -0.444 e.Å ⁻³		

Table S9. Crystal data and structure refinement for AlaZnFor 293K.

Identification code	AlaZnFor 293K		
Empirical formula	$C_{10}H_{12}N_2O_4Zn$		
Formula weight	289.61		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Hexagonal		
Space group	<i>P</i> 61		
Unit cell dimensions	a = 17.686(2) Å	α= 90°.	
	b = 17.686(2) Å	β= 90°.	
	c = 10.1964(13) Å	$\gamma = 120^{\circ}$.	
Volume	2762.2(6) Å ³		
Ζ	6		
Density (calculated)	1.045 Mg/m ³		
Absorption coefficient	1.336 mm ⁻¹		
F(000)	888		
Crystal size	0.6 x 0.2 x 0.2 mm ³		
Theta range for data collection	3.05 to 29.51°.		
Index ranges	-22<=h<=9, -19<=k<=21, -7<=l<=13		
Reflections collected	7796		
Independent reflections	3521 [R(int) = 0.0922]		
Completeness to theta = 29.51°	86.1 %		
Refinement method	Full-matrix least-squares on F ²	1	
Data / restraints / parameters	3521 / 1 / 155		
Goodness-of-fit on F ²	1.044		
Final R indices [I>2sigma(I)]	R1 = 0.0564, WR2 = 0.1656		
R indices (all data)	R1 = 0.1188, wR2 = 0.2546		
Absolute structure parameter	-0.04(5)		
Largest diff. peak and hole	1.139 and -0.471 e.Å ⁻³		

Table S10. Crystal data and structure refinement for ValZnBF4.

Identification code	ValZnBF4		
Empirical formula	$C_{22}H_{33}BF_4N_4O_5Zn$		
Formula weight	585.73		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	<i>P</i> 21		
Unit cell dimensions	a = 8.2288(7) Å	α= 90°.	
	b = 17.0237(14) Å	β=106.686(9)°.	
	c = 9.8162(8) Å	$\gamma = 90^{\circ}$.	
Volume	1317.20(19) Å ³		
Ζ	2		
Density (calculated)	1.472 Mg/m ³		
Absorption coefficient	1.000 mm ⁻¹		
F(000)	604		
Crystal size	0.5x 0.3 x 0.2 mm ³		
Theta range for data collection	2.86 to 29.08°.		
Index ranges	-10<=h<=11, -20<=k<=22, -7<=l<=12		
Reflections collected	6515		
	0010		
Independent reflections	4545 [R(int) = 0.0204]		
Independent reflections Completeness to theta = 29.08°	4545 [R(int) = 0.0204] 85.0 %		
Independent reflections Completeness to theta = 29.08° Refinement method	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ²	2	
Independent reflections Completeness to theta = 29.08° Refinement method Data / restraints / parameters	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ² 4545 / 1 / 313	2	
Independent reflections Completeness to theta = 29.08° Refinement method Data / restraints / parameters Goodness-of-fit on F ²	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ² 4545 / 1 / 313 1.078	2	
Independent reflections Completeness to theta = 29.08° Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)]	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ² 4545 / 1 / 313 1.078 R1 = 0.0539, wR2 = 0.1659	2	
Independent reflections Completeness to theta = 29.08° Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data)	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ² 4545 / 1 / 313 1.078 R1 = 0.0539, wR2 = 0.1659 R1 = 0.0561, wR2 = 0.1705	2	
Independent reflections Completeness to theta = 29.08° Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data) Absolute structure parameter	4545 [R(int) = 0.0204] 85.0 % Full-matrix least-squares on F ² 4545 / 1 / 313 1.078 R1 = 0.0539, wR2 = 0.1659 R1 = 0.0561, wR2 = 0.1705 0.023(17)	2	

Table S11. Crystal data and structure refinement for ValZnClO4.

Identification code	ValZnClO4	
Empirical formula	C ₂₂ H ₃₃ Cl N ₄ O ₉ Zn	
Formula weight	598.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P21	
Unit cell dimensions	a = 10.7650(5) Å	α= 90°.
	b = 16.6683(7) Å	β=100.662(4)°
	c = 14.6753(7) Å	$\gamma = 90^{\circ}$.
Volume	2587.8(2) Å ³	
Ζ	4	
Density (calculated)	1.531 Mg/m ³	
Absorption coefficient	1.110 mm ⁻¹	
F(000)	1240	
Crystal size	0.5 x 0.3 x 0.2 mm ³	
Theta range for data collection	3.08 to 29.13°.	
Index ranges	-9<=h<=14, -21<=k<=21, -19<	<=l<=18
Reflections collected	13789	
Independent reflections	8553 [R(int) = 0.0251]	
Completeness to theta = 29.13°	86.0 %	
Refinement method	Full-matrix least-squares on F ²	2
Data / restraints / parameters	8553 / 1 / 675	
Goodness-of-fit on F ²	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1085	
R indices (all data)	R1 = 0.0495, wR2 = 0.1121	
Absolute structure parameter	-0.023(11)	
Largest diff. peak and hole	2.733 and -1.015 e.Å ⁻³	



Figure S5. ORTEP diagram of the asymmetric unit of a) ValZnFor b) ValZnOAc c) AlaZnBr d) AlaZnCl e) AlaZnFor f) AlaZnOAc. All ellipsoids in *ORTEP* diagrams are displayed at the 50% probability level.



Figure S6: ORTEP diagram of the asymmetric unit of a) Val (*l*-L_{Cl}) b) Ala (*l*-L_{1Cl}) c) ValZnNO₃ d) AlaZnNO₃ e)

ValZnClO₄ f) ValZnBF₄. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level.



Figure S7. AlaZnCl packing view from different angle a) c axis, b) b axis, c) a axis. d) Representative topological diagram of *unh* topology .

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Figure S8. Crystal packing view of a) Val(l-L_{Cl}) ligand through crystalligraphic *b* axis, b) ValZnNO₃ from *b* axis, c) Ala(l-L_{1_{Cl}}) ligand from *a* axis and d) AlaZnNO₃ through *c* axis e) ValZnBF₄ and f) ValZnClO₄ through *a* axis.

Section S3. Regenerability studies of the MOFs:



Figure S9: Regenerability experiment in the light of Powder XRD experiments for ValZnFor MOF. Upon deconstruction at 50 °C under sonication, highly crystalline MOFs converted into turbid amorphous solution, which upon further heating turned out to be clear solution. Gradual saturation upon evaporation of water leads to regeneration of crystallinity of the MOFs along with certain degree of amorphousness. However, complete evaporation regenerate the MOF particles with phase purity.

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Figure S10: Regenerability experiment in the light of SEM imaging. Upon deconstruction random morphology was observed whereas saturation results in parent rod shaped MOF architecture.



Figure S11: SEM image of the regenerated materials revealed retention of parent rod shaped morphology a) ValZnCl regenerated, b) ValZnBr regenerated, c) ValZnFor regenerated, d) ValZnOAc regenerated, e) AlaZnCl regenerated, f) AlaZnBr regenerated, g) AlaZnFor regenerated and h) AlaZnOAc regenerated.



Figure S12: EDX elemental analysis of all the regenerated MOFs, showing significant agreement with the parent MOFs. a) ValZnCl regenerated, b) ValZnBr regenerated, c) ValZnFor regenerated, d) ValZnOAc regenerated, e) AlaZnFor regenerated, f) AlaZnBr regenerated, g) AlaZnCl regenerated and h) AlaZnOAc regenerated.

a)	El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]	b)	El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
	O N C Zn Cl	8 7 6 30 17	K-series K-series K-series K-series K-series	34.36 23.13 21.87 10.90 9.74	34.36 23.13 21.87 10.90 9.74	35.43 27.24 30.04 2.75 4.53	13.2 10.0 9.0 0.5 0.4		O N C Zn Br	8 7 6 30 35	K-series K-series K-series K-series K-series	30.36 22.13 20.87 12.56 14.66	30.26 22.17 20.43 12.56 14.36	29.40 19.77 28.82 2.89 5.11	16.1 11.0 9.7 0.4 0.9
c)	El	AN	Total: Series	100.00 unn. C [wt.%]	100.0 norm. C [wt.%]	0 100. Atom. C [at.%]	.00 Error [%]	d)	El	AN	Total: Series	100.00 unn. C [wt.%]	norm. C [wt.%]	0 100. Atom. C [at.%]	00 Error [%]
	Zn O C N	30 8 6 7	K-series K-series K-series K-series	39.77 27.91 19.03 12.82	39.95 28.04 19.12 12.88	12.53 35.95 32.65 18.87	1.5 6.4 3.7 5.1		O C N Zn	8 6 7 30	K-series K-series K-series K-series	46.77 20.89 19.80 12.54	46.78 20.89 19.80 12.54	46.64 27.74 22.55 3.06	17.3 7.9 9.0 0.8
			Total:	99.53	100.00	100.00	_	f)			Total:	100.00	100.00	100.00	_
e) El	. AN	Series	unn. C [wt.%]	norm. ([wt.%]	2 Atom. ([at.%]	C Erro:] [%	r •)] -	ET	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
e	E1 0 N C C1 Zn	8 7 6 17 30	Series K-series K-series K-series K-series K-series	unn. C [wt.%] 38.17 22.28 17.59 14.94 5 7.02	38.17 22.28 17.59 14.94 7.02	Atom. [at.%] [at.%] 39.9 26.6 24.5 24.5 1.8	C Erro: [% 7 15. 4 10. 3 8. 6 0. 0 0.	r •)] - 6 9 6 5	Zn O Br N C	30 8 35 7 6	K-series K-series K-series K-series K-series K-series	unn. C [wt.%] 24.86 22.66 18.51 15.14 14.27	26.05 23.74 19.39 15.87 14.95	Atom. C [at.%] 8.85 32.96 5.39 25.16 27.65	[%] 1.1 6.2 1.8 6.2 3.3
e g) E1 0 N C Cl Zn) E1	8 7 6 17 30	K-series K-series K-series K-series K-series Total : Series	unn. C [wt.%] 38.17 22.28 17.59 14.94 7.02 100.00 unn. C [wt.%]	norm. C [wt.%] 38.17 22.28 17.59 14.94 7.02 100.00 norm. C [wt.%]	Atom. ([at.%] 7 39.9 3 26.6 9 24.5 4 7.0 2 1.8 1 100.0 2 1.8 1 100.0 2 Atom. ([at.%]	C Erro: [{% 7 15. 4 10. 3 8. 6 0. 0 0. 0 C Erro: [{%]	r 1) - 69 66 55 - h	E1 Zn O Br N C 	AN 30 8 35 7 6 	K-series K-series K-series K-series K-series Total: Series	unn. C [wt.%] 24.86 22.66 18.51 15.14 14.27 95.44 unn. C [wt.%]	norm. C [wt.%] 26.05 23.74 19.39 15.87 14.95 100.00 norm. C [wt.%]	Atom. C [at.%] 8.85 32.96 5.39 25.16 27.65 100.00 Atom. C [at.%]	[%] 1.1 6.2 1.8 6.2 3.3 Error [%]
e g) E1 0 N C C 2 n 0 C N 2 n 0 C N 0 N 0 N 0 N 	AN 8 7 6 17 30 17 30 AN 8 6 7 30	K-series K-series K-series K-series Total: Series K-series K-series K-series K-series	unn. C [wt.%] 38.17 22.28 17.59 14.94 7.02 100.00 unn. C [wt.%] 46.50 22.34 18.04 13.12	norm. C [wt.%] 38.17 22.28 17.59 14.94 7.02 100.00 norm. C [wt.%] 46.50 22.34 18.04 13.12	Atom. ([at.%] 39.9 26.6 24.5 7.0 21.8 1.0 100.0 (at.%] 46.46 29.74 20.52 3.21	C Erro 7 15. 4 10. 3 8. 6 0. 0 0. C Erro 0 C Erro 1 [%] 5 17.2 4 8.3 9 8.4 1 0.7	r 1) - - - - - - - - - - - - -	E1 Zn O Br N C E1 C Zn C Zn C N C N C	AN 30 8 35 7 6 AN 8 30 6 7	K-series K-series K-series K-series Total: Series K-series K-series K-series K-series	unn. C [wt.%] 24.86 22.66 18.51 15.14 14.27 95.44 unn. C [wt.%] 30.80 28.46 19.24 12.74	norm. C [wt.%] 26.05 23.74 19.39 15.87 14.95 100.00 norm. C [wt.%] 33.76 31.19 21.09 13.96	Atom. C [at.%] 8.85 32.96 5.39 25.16 27.65 100.00 Atom. C [at.%] 39.52 8.93 32.88 18.67	Error [%] 1.1 6.2 1.8 6.2 3.3 [%] 7.0 1.1 3.7 5.2

Figure S13: EDX elemental analysis data of all the regenerated MOFs. a) ValZnCl regenerated, b) ValZnBr regenerated, c) ValZnFor regenerated, d) ValZnOAc regenerated, e) AlaZnCl regenerated, f) AlaZnBr regenerated, g) AlaZnFor regenerated and h) AlaZnOAc regenerated.



Figure S14: UV-VIS spectroscopy of the solution revealed the deconstruction state has similarity with the ligand solution rather than the solid MOF.



Figure S15: Comparison of IR spectra of the parent MOF and regenerated material, showing peak to peak matching of these two compounds which eludes to their identical architecture.



Figure S16: The IR spectra of the deconstructed state clearly matches with the corresponding ligand solution spectra, which is shifted in case of as-synthesized MOFs. This experiment confirms the separation of the framework building blocks.



Figure S17: The solution state ¹³C NMR of deconstructed solution of AlaZnFor and ValZnCl matches well with the ligand solution. However, the solid MOF possess distinctly different peak positions.

Section S4. Variable Temperature Single Crystal X-Ray Diffraction (VT-SCXRD) and Variable Temperature Powder X-Ray Diffraction studies (VT-PXRD) of MOFs:

Colorless rod shaped crystal ($0.50 \times 0.20 \times 0.10 \text{ mm}^3$) was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)¹⁹ and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_a radiation (λ =0.71073 Å). The crystal was ramped *in situ* using hot N₂ flow for approximately 1h at different temperature prior to data collection. The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Analysis of the data showed negligible decay during collection. The structure was solved in the hexagonal *P*61 space group, with *Z* = 6, using direct methods. All non-hydrogen atoms were refined anisotropically. Very high displacement parameters, high esd's and partial occupancy due to the disorder make it impossible to determine accurate positions of the hydrogen atoms in water molecules.



Figure S18: Single crystal to single crystal transformation in AlaZnCl. ORTEP diagram (50% probability level) of the asymmetric unit of AlaZnCl and AlaZnFor at 293K and 323K and 200K and 293K, respectively.

Table S2. Crystal Data and Structure Refinement for the MOFs at variable temperatures (200K-323K).

	AlaZnCl @293K	AlaZnCl @323K	AlaZnFor @200K	AlaZnFor @293K
Formula	C9 H11 Cl N2 O3 Zn	C9 H11 Cl N2 O2 Zn	C10 H12 N2 O5 Zn	C10 H12 N2 O4 Zn
Mr	296.04	280.04	305.61	289.61
Temperature	293(2)K	323(2)K	200(2)K	293(2)K
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61	<i>P</i> 61
a (Å)	17.5285(3)	17.6015(3)	17.5911(7)	17.686(2)
<i>b</i> (Å)	17.5285(3)	17.6015(3)	17.5911(7)	17.686(2)
c (Å)	10.26523(16)	10.26898(17)	10.1716(3)	10.1964(13)
V[Å ³]	2731.43(9) Å ³	2755.22(9) Å ³	2725.88(18) Å ³	2762.2(6) Å ³
Z	6	6	6	6
$\rho_{calcd}[g \ cm^{-1}]$	1.080	1.013	1.117	1.045
Absorption coefficient	1.490	1.470	1.361	1.336
<i>F</i> (000)	900	852	936	888
θ range[°]	3.06 - 29.03	3.05 - 29.21	3.03-29.22	3.05 - 29.51
Reflections collected	7363	7970	8057	7796
Independent reflections	3615	3979	3676	3521
GOF	1.115	1.156	1.069	1.045
Flack Parameter	0.00(3)	0.01(2)	0.00(3)	-0.04(5)
Final $R1$, $wR2[I > 2\sigma(I)]$	$R_1 = 0.0510,$ $wR_2 = 0.1547$	$R_1 = 0.0557,$ $wR_2 = 0.1821$	$R_1 = 0.0666,$ $wR_2 = 0.1949$	$R_1 = 0.0564,$ $wR_2 = 0.1656$
R indices (all data)	$R_1 = 0.0541,$ $wR_2 = 0.1588$	$R_1 = 0.0584,$ $wR_2 = 0.1874$	$R_1 = 0.0805,$ $wR_2 = 0.2128$	$R_1 = 0.1188,$ $wR_2 = 0.2546$



Figure S19: VTPXRD pattern of ValZnFor and AlaZnCl operating from RT to 200 °C and compared with the simulated one showing retention of crystallinity even at high temperature range (~200 °C).





Figure S20. Thermogravimetric analysis data of all the MOFs. Note the high thermal stability of the halogen substituted MOFs than formate and acetate substituted MOFs.



Figure S21. Thermogravimetric analysis data of AlaZnNO3 and ValZnNO3 showing stability upto 210 °C.



Section S6. Water Sorption Properties of the MOFs.

Figure S22. a)Water vapor sorption profile comparison of AlaZnCl and ValZnCl at STP. b)Water vapor sorption profile comparison of AlaZnCl and AlaZnBr at STP. c) However, pore condensation behavior observed in ValZnOAc. ValZnFor, AlaZnFor and AlaZnOAc also exhibit similar behavior. d) Moisture stability of the MOFs under 98% relative humidity for 6 months showing their architectural rigidity.