Utilization of Counter Anions for Charge Transportation in Electrical Device Fabrication of Zn(II) Metal-Organic Frameworks.

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Supporting Information

Synthesis and Characterization of H_2MBP :

3.2 g of pyrazole and 1.6 ml of dibromomethane were mixed together in a 100 ml teflon container of an autoclave and it was kept under 200℃ in air oven for 2 hrs. Then it was allowed to cool down slowly to room temperature without changing its position. The product was then dissolved in hot water and transferred to a 100 ml beaker. The resulting solution thus obtained was neutralised with dropwise addition of dilute aqueous NaOH solution and the entire addition process was done with continuous stirring. A white precipitate was formed and the pH of the medium was kept to be slightly acidic. The precipitate was filtered and washed with distilled water for several times to get rid of HBr (formed during high temp. substitution reaction). The product thus obtained was dried at room temperature and recystallized from absolute ethanol (yield: 72% with respect to pyrazole).

Anal. Calcd. (found) for C_7 H_8 N_4 (H_2MBP) (%): C, 56.74 (56.81); H, 5.44 (5.48); N, 37.81 (36.76).

IR (400-4000 cm-1): 3139b, 2945b, 1623vw, 1506w, 1444w, 1392m, 1350m, 1267vw, 1134m, 1049w, 1000s, 956s, 921w, 871s, 813vs, 742m, 707w, 651w, 611m.

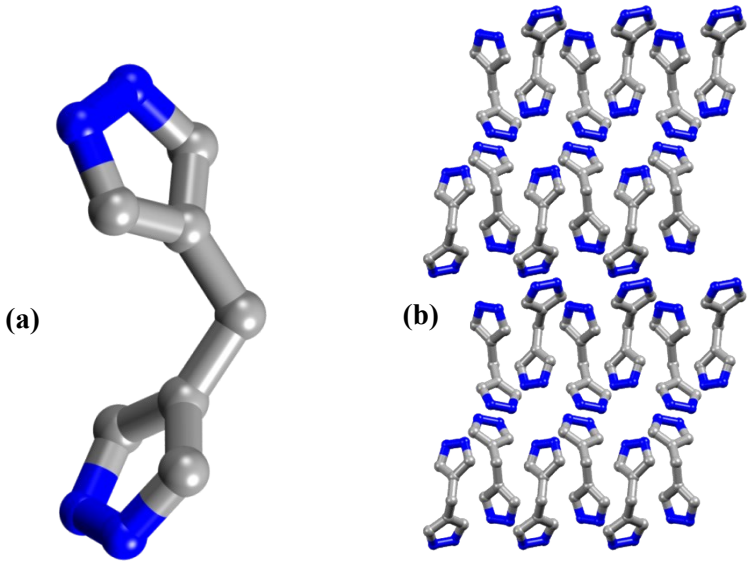


Fig. SI 1: Crystal structure o H_2MBP showing (a) asymmetric unit o the same and (b) packing diagram along the crystallographic axis ‘c’

Table SI-1: Crystallographic Data and Refinement Parameters of H_2MBP, compound **1** & compound **2**.

Identification code	**H_2MBP**	**Compound 1**	**Compound 2**
Empirical formula	$C_7H_8N_4$	$C_{21}H_{24}B_2F_8N_{12}Zn$	$C_{56}H_{104}N_{32}O_{44}S_6Zn_6$
Formula weight	148.17	683.51	2514.29
Temperature/K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/n	C 2/c	P 21/c
a/Å	5.3811(2)	16.1359(6)	20.8720(5)
b/Å	16.1944(6)	9.8928(3)	14.6735(3)
c/Å	8.2691(4)	17.8077(6)	17.4832(4)
α/°	90	90	90
β/°	98.500(2)	111.927(1)	114.2720(10)
γ/°	90	90	90
Volume/Å^3	712.68(5)	2636.99(16)	4881.18(19)
Z	4	4	2
no. of rflns collected	9029	16822	72029
no. of unique rflns	1868	3799	17164
no. of obsd rflns (I > 2σ(I))	1700	2719	11892
R1 (I > 2σ(I))	0.0463	0.0467	0.0520
wR2 (> 2σ(I))	0.1237	0.0959	0.1278
CCDC no.	2018310	2018311	2018312

Selected Bond Lengths and Angles of Compound 1 and Compound 2:

Table SI-2:

Compound 1		
Bond lengths	Bond angles	
Zn1 N1A 2.1340(18)	N1A Zn1 N1A 180.0	N1A Zn1 N3 87.79(7)
Zn1 N1A 2.1340(18)	N1A Zn1 N1 91.00(7)	N1 Zn1 N3 92.47(6)
Zn1 N1 2.1882(18)	N1A Zn1 N1 89.00(7)	N1 Zn1 N3 87.53(6)
Zn1 N1 2.1883(18)	N1A Zn1 N1 89.00(7)	N3 Zn1 N3 180.0
Zn1 N3 2.2246(17)	N1A Zn1 N1 91.00(7)	C1 N1 Zn1 131.77(15)
Zn1 N3 2.2246(17)	N1 Zn1 N1 180.00(9)	N2 N1 Zn1 118.75(13)
	N1A Zn1 N3 87.79(7)	C4 N3 Zn1 126.97(15)
	N1A Zn1 N3 92.21(7)	N4 N3 Zn1 122.14(13)
	N1 Zn1 N3 87.53(6)	C1A N1A Zn1 133.21(14)
	N1 Zn1 N3 92.47(6)	N2A N1A Zn1 120.37(13)
	N1A Zn1 N3 92.21(7)	

Table SI-3:

Compound 2		
Bond lengths	Bond angles	
Zn1 N1 2.066(2)	N1 Zn1 N1 180.0	S2 O24 Zn2 156.07(14)
Zn1 O1WS 2.106(2)	N1 Zn1 O1WS 89.92(10)	S3 O31 Zn3 161.96(17)
Zn1 O2WS 2.149(3)	N1 Zn1 O1WS 90.08(10)	C1 N1 Zn1 131.7(2)
Zn2 N1A 1.989(3)	N1 Zn1 O1WS 89.92(10)	N2 N1 Zn1 122.7(2)
Zn2 N3 1.990(2)	O1WS Zn1 O1WS 180.0	C4 N3 Zn2 127.5(2)
Zn2 N1B 1.999(3)	N1 Zn1 O2WS 91.69(10)	N4 N3 Zn2 126.69(18)
Zn2 O11 2.080(2)	N1 Zn1 O2WS 88.31(10)	C1A N1A Zn2 129.5(2)
Zn2 O24 2.384(2)	O1WS Zn1 O2WS 88.19(12)	N2A N1A Zn2 124.85(19)
Zn3 N3B 1.983(2)	O1WS Zn1 O2WS 91.81(12)	C4A N3A Zn3 129.3(2)
Zn3 N1C 1.999(2)	N1 Zn1 O2WS 88.31(10)	N4A N3A Zn3 125.3(2)
Zn3 N3A 2.009(2)	N1 Zn1 O2WS 91.69(10)	C1B N1B Zn2 127.3(2)
Zn3 O31 2.051(2)	O1WS Zn1 O2WS 91.81(12)	N2B N1B Zn2 126.65(19)
Zn3 O22 2.405(2)	O1WS Zn1 O2WS 88.19(12)	C4B N3B Zn3 129.7(2)
Zn4 O4WS 2.023(6)	O2WS Zn1 O2WS 180.0	N4B N3B Zn3 123.20(19)

Zn4 O4WS 2.023(6)	N1A Zn2 N3 126.26(10)	C1C N1C Zn3 127.5(2)
Zn4 N3C 2.070(3)	N1A Zn2 N1B 114.26(11)	N2C N1C Zn3 126.33(19)
Zn4 O3WS 2.249(5)	N3 Zn2 N1B 118.87(10)	N4C N3C Zn4A 119.1(3)
N3C Zn4A 1.991(8)	N1A Zn2 O11 95.86(10)	C4C N3C Zn4A 135.6(3)
N3C Zn4A 2.233(7)	N3 Zn2 O11 92.40(10)	N4C N3C Zn4 122.4(2)
Zn4A Zn4A 0.870(11)	N1B Zn2 O11 89.26(10)	C4C N3C Zn4 133.4(3)
Zn4A O3WT 1.996(12)	N1A Zn2 O24 88.78(9)	N4C N3C Zn4A 124.1(3)
Zn4A O4WT 2.030(11)	N3 Zn2 O24 88.66(9)	C4C N3C Zn4A 129.6(4)
Zn4A O3WT 2.184(10)	N1B Zn2 O24 84.49(9)	Zn4A N3C Zn4A 22.8(3)
	O11 Zn2 O24 173.36(9)	Zn1 O1WS H1WA 109.8
	N3B Zn3 N1C 125.74(10)	Zn1 O1WS H1WB 109.8
	N3B Zn3 N3A 110.72(10)	Zn1 O2WS H2WA 122.3
	N1C Zn3 N3A 122.68(10)	Zn1 O2WS H2WB 136.8
	N3B Zn3 O31 95.40(10)	Zn4 O3WS H3WA 109.5
	N1C Zn3 O31 91.24(10)	Zn4 O3WS H3WB 109.8
	N3A Zn3 O31 92.74(10)	Zn4 O4WS H4WA 116.9
	N3B Zn3 O22 90.88(9)	Zn4 O4WS H4WB 138.6
	N1C Zn3 O22 88.30(9)	Zn4A Zn4A O3WT 90.5(10)
	N3A Zn3 O22 81.30(9)	N3C Zn4A O3WT 101.8(4)
	O31 Zn3 O22 172.57(9)	Zn4A Zn4A O4WT 148.5(11)
	O4WS Zn4 O4WS 180.00(8)	N3C Zn4A O4WT 101.5(4)
	O4WS Zn4 N3C 90.02(18)	O3WT Zn4A O4WT 112.2(6)
	O4WS Zn4 N3C 89.99(18)	Zn4A Zn4A O3WT 66.0(9)
	O4WS Zn4 N3C 89.98(18)	N3C Zn4A O3WT 81.0(4)
	O4WS Zn4 N3C 90.01(18)	O3WT Zn4A O3WT 156.5(3)
	N3C Zn4 N3C 180.0(2)	O4WT Zn4A O3WT 89.7(5)
	O4WS Zn4 O3WS 82.4(2)	Zn4A Zn4A N3C 62.7(8)
	O4WS Zn4 O3WS 97.6(2)	N3C Zn4A N3C 157.2(3)
	N3C Zn4 O3WS 88.37(17)	O3WT Zn4A N3C 79.7(4)
	N3C Zn4 O3WS 91.63(17)	O4WT Zn4A N3C 98.9(4)
	O4WS Zn4 O3WS 97.6(2)	O3WT Zn4A N3C 88.9(4)
	O4WS Zn4 O3WS 82.4(2)	Zn4A O3WT Zn4A 23.5(3)
	N3C Zn4 O3WS 91.63(17)	Zn4A O3WT H3WC 120.2
	N3C Zn4 O3WS 88.37(17)	Zn4A O3WT H3WD 120.2
	O3WS Zn4 O3WS 180.0(3)	Zn4A O4WT H4WC 115.0
	S1 O11 Zn2 151.58(18)	Zn4A O4WT H4WD 110.8

	S2 O22 Zn3 151.32(13)	

IR Data:

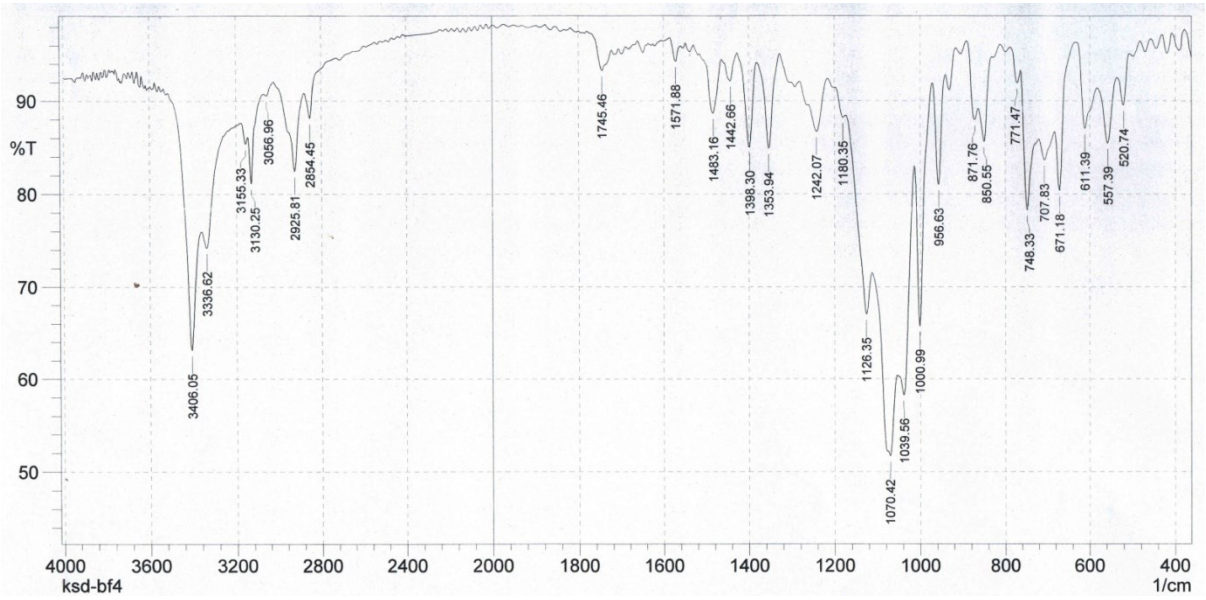


Fig. SI-2: IR data of Compound **1.**

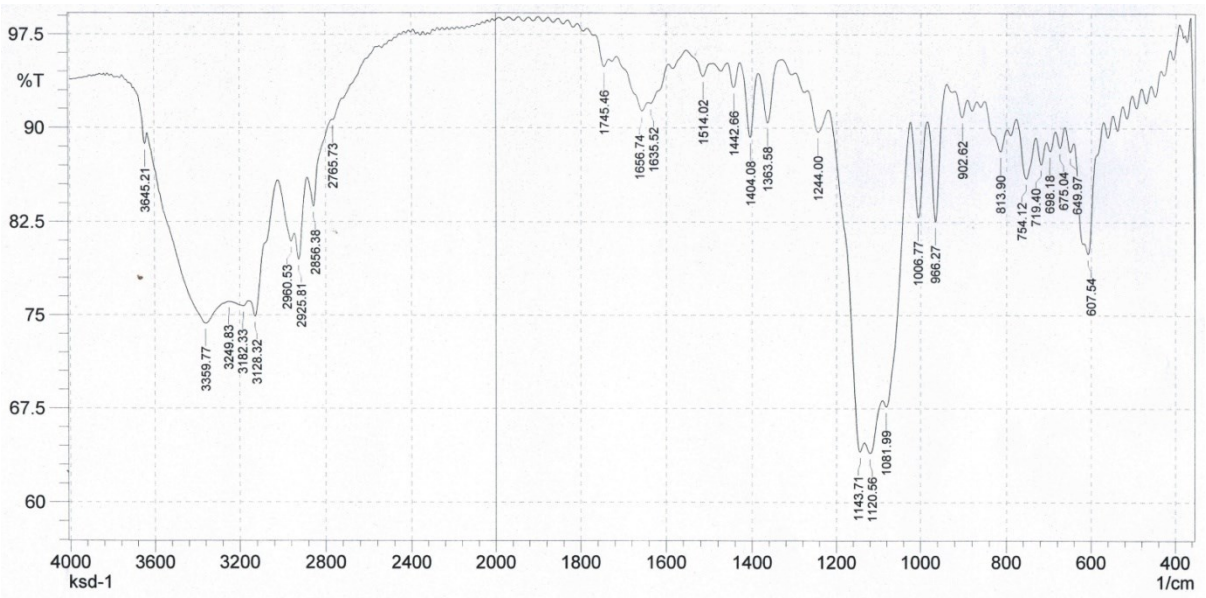


Fig. SI-3: IR data of Compound **2.**

PXRD Data:

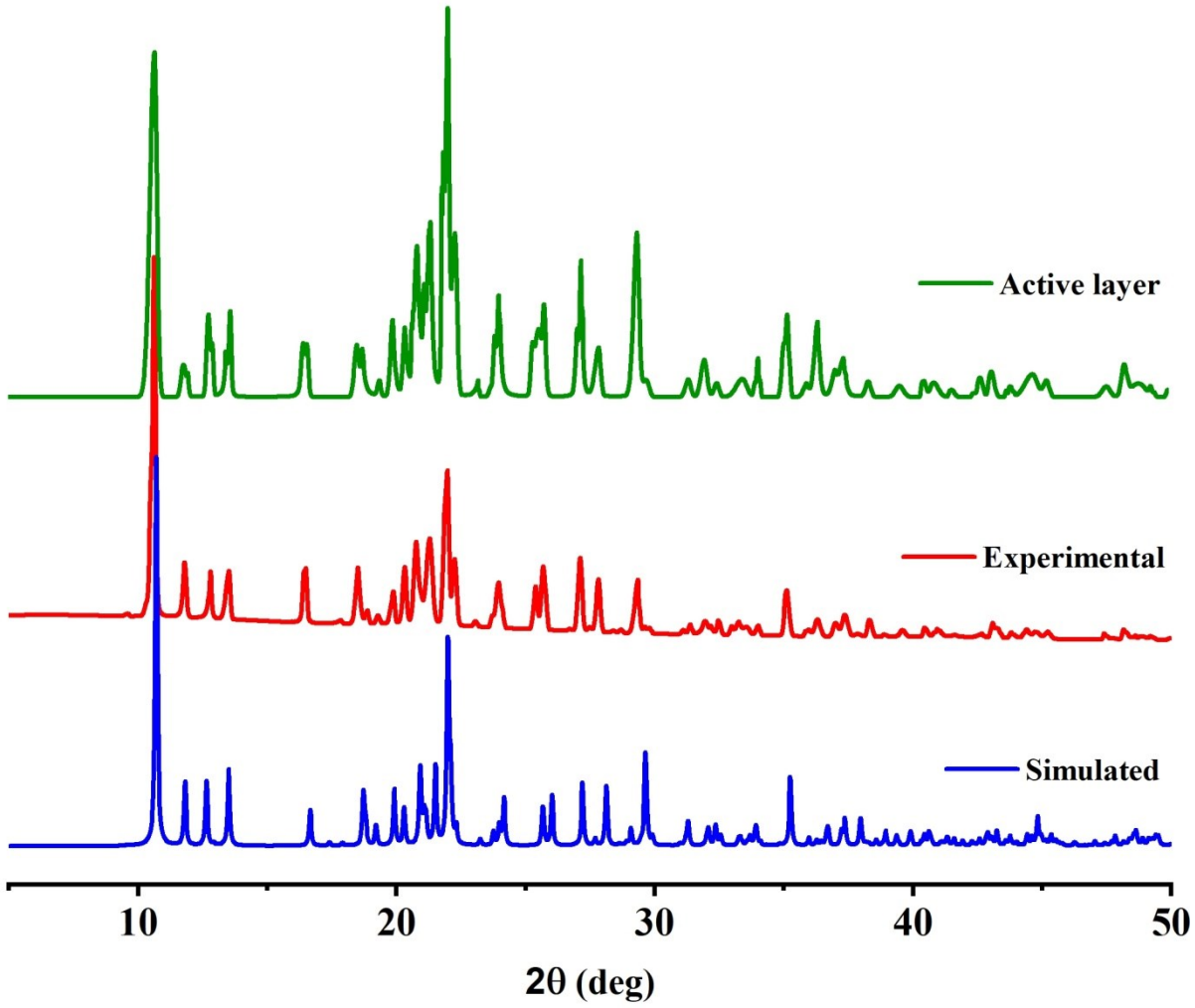


Fig. SI-4: PXRD data of Compound **1.**

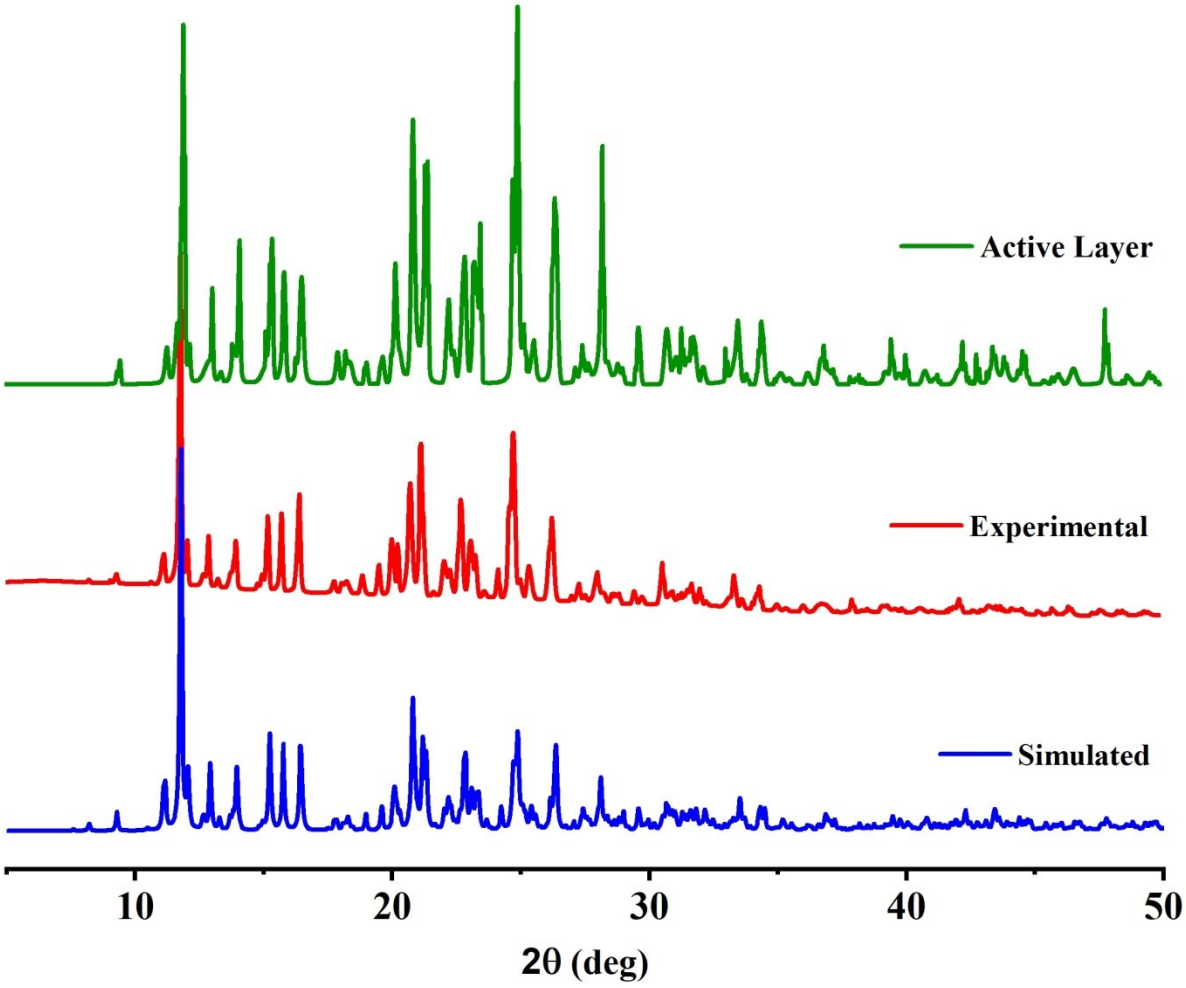


Fig. SI-5: PXRD data of Compound **2.**

HRSEM Images:

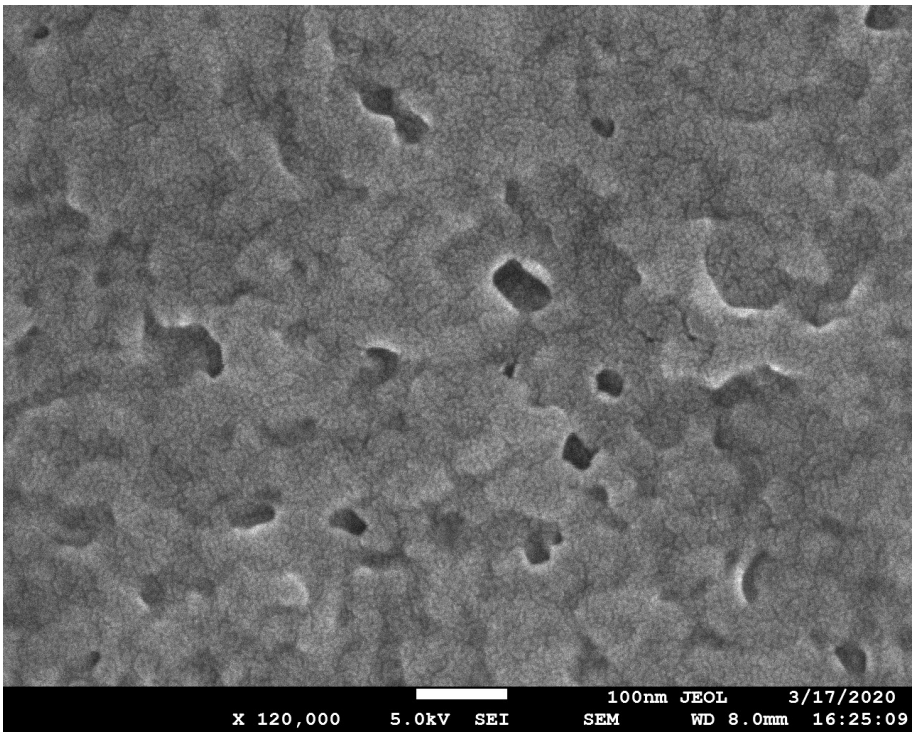


Fig. SI-6: HRSEM image of Compound **1.**

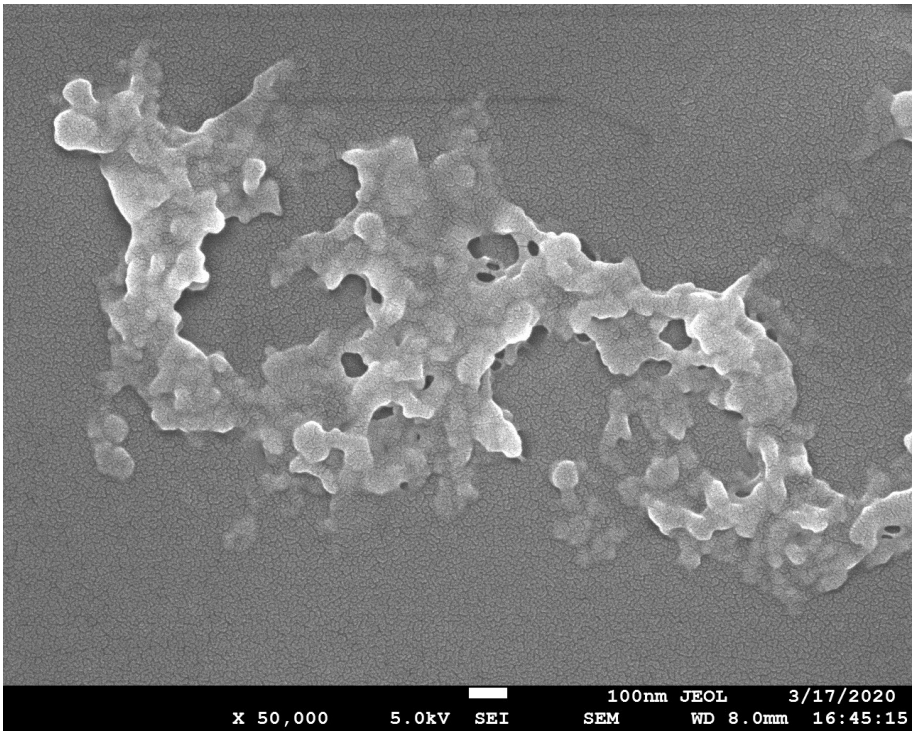
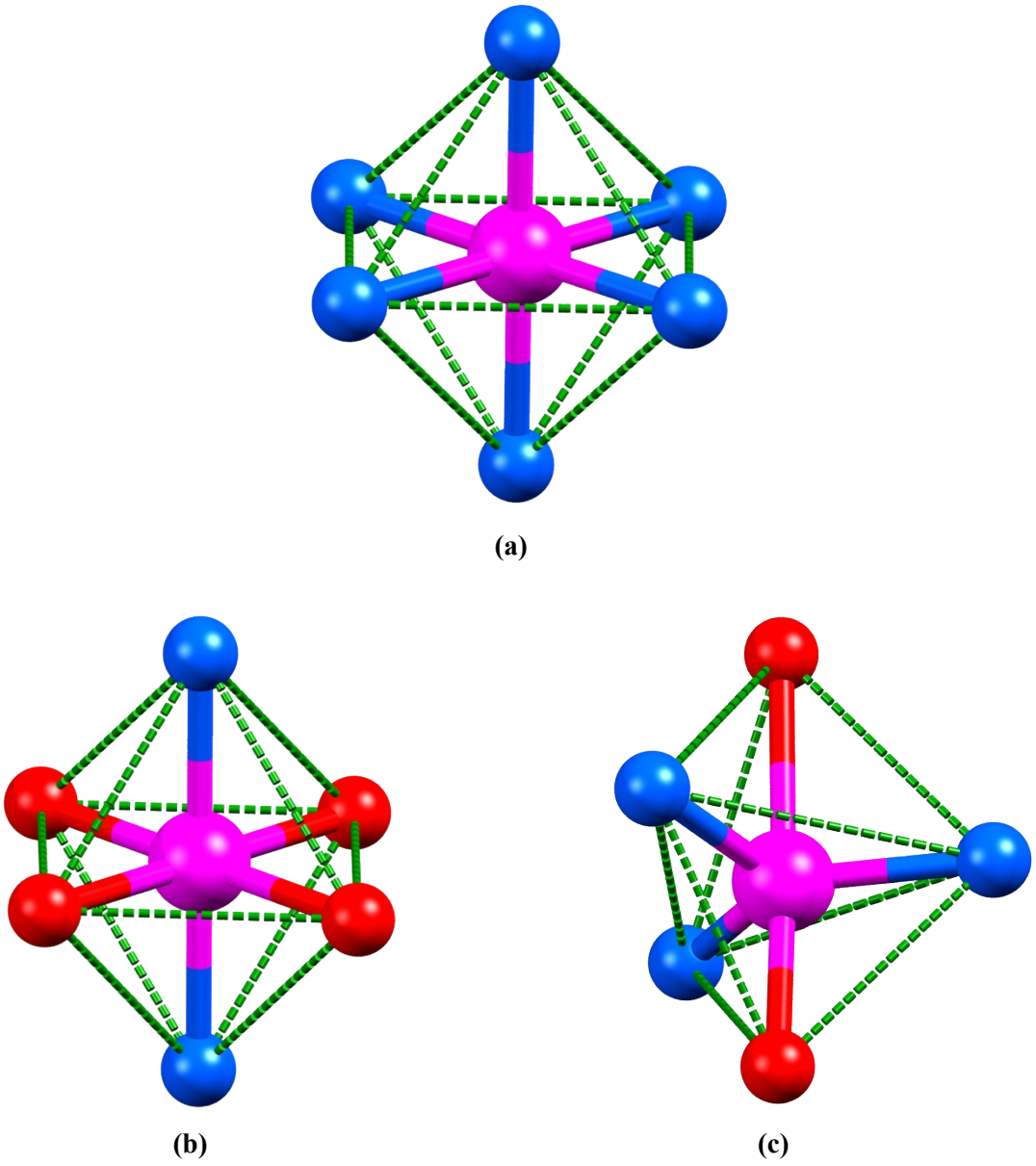


Fig. SI-7: HRSEM image of Compound **2.**

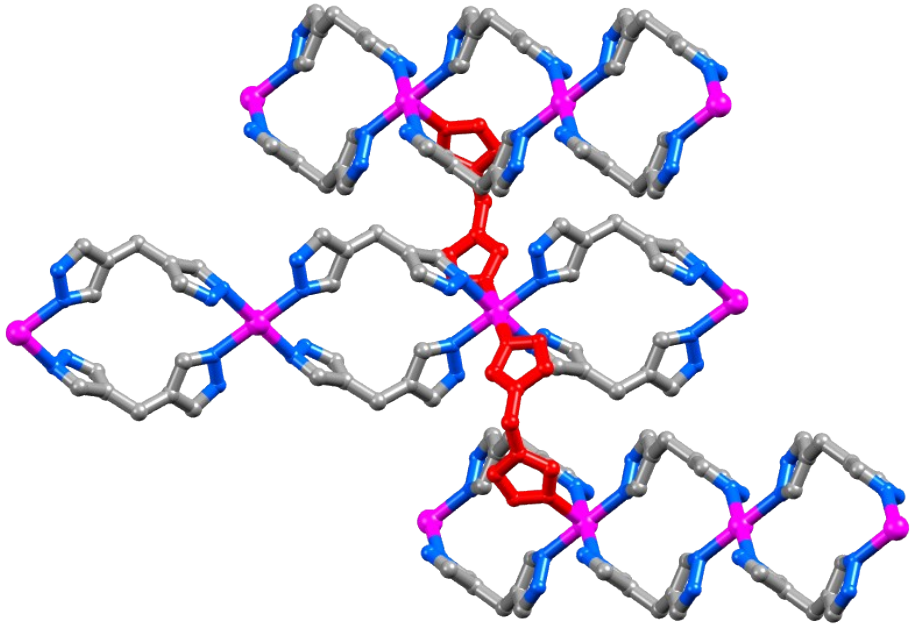
Geometry of metal centre in MOFs:



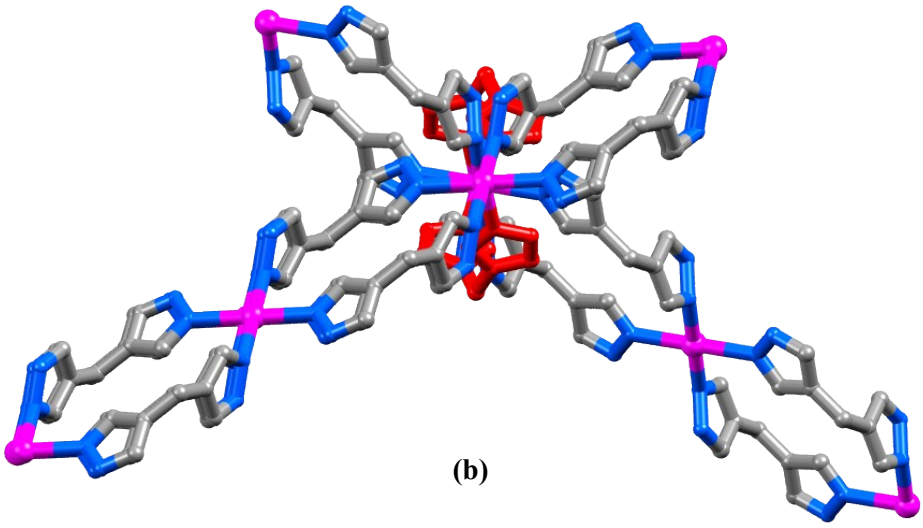
(a) **(b)** **(c)**

Fig. SI-8: Geometry of Zn centre (Pink: Zinc, Blue: Nitrogen and Red: Oxygen) showing (a) only octahedral (Oh) in Compound **1**, (b) octahedral (Oh) in MOF-2 and (c) trigonal bipyramidal (tbp) in Compound **2**.

Various structural aspects of MOFs:

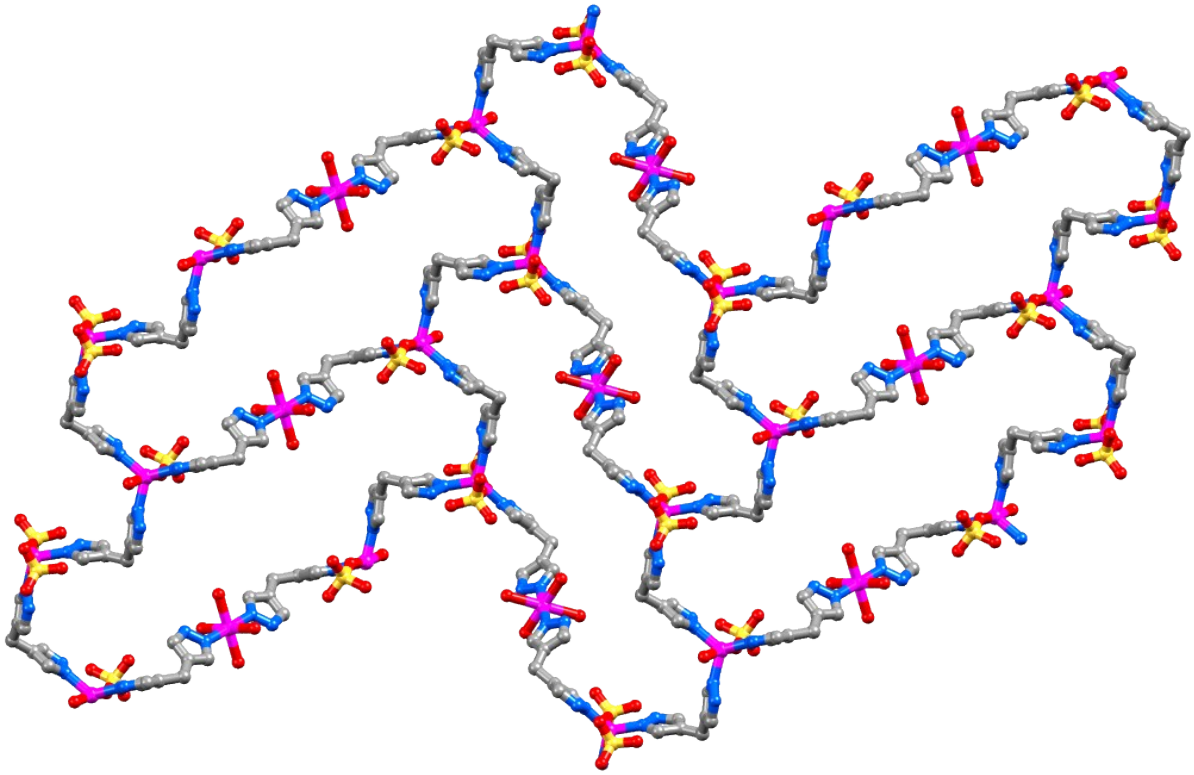


(a)

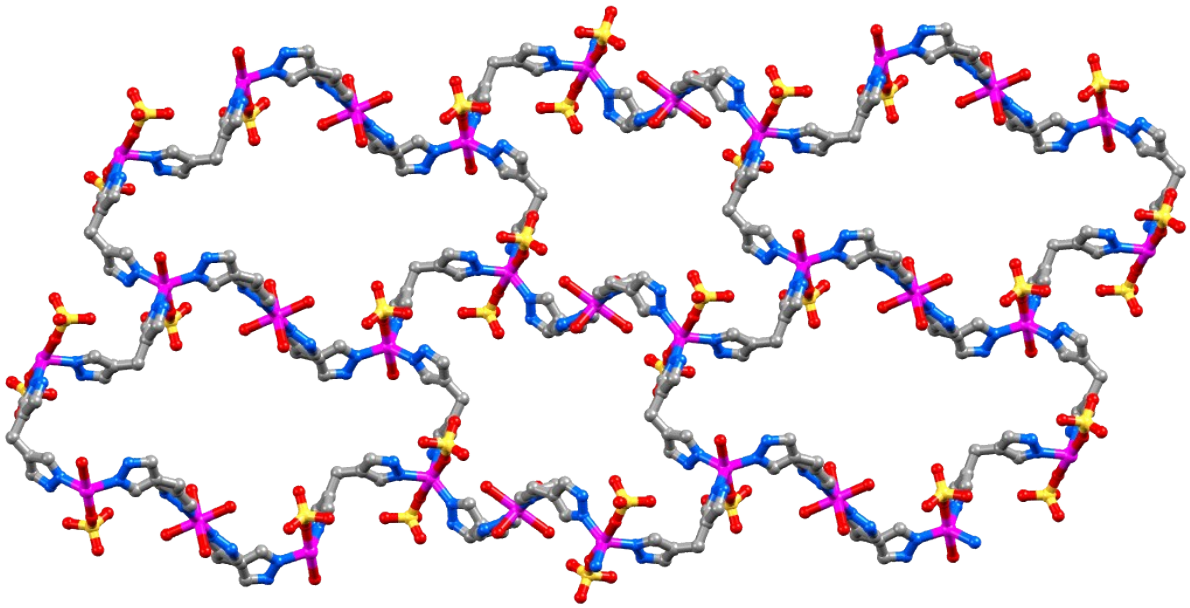


(b)

Fig. SI-9: Compound **1** showing (a) bridging propagation of H_2MBP unit (in red) between two adjacent mutually orthogonal polymeric chains and (b) top view of the same.



(a)



(b)

Fig. SI-10: (a) and (b) both shows packing diagram of Compound **2.**

Thermionic Emission Theory:

According to Thermionic Emission theory, the forward bias current density can be expressed as

$$J = J_0\left[exp\left(\frac{q\,V}{\eta\,K\,T}\right) - 1\right] \quad \text{(SI-1)}$$

When V=0, J=J_0=Saturation Current Density= $A^*T^2exp\left(-\frac{q\Phi_B}{KT}\right)$ (SI-2)

Where, q=Electronic Charge, V=Applied Voltage, η= Ideality Factor, K=Boltzman's Constant, T=Temperature in Kelvin scale, Φ_B= Barrier potential Height, A^*= Rechardson's constant and was considered as 1.2×10^6 A m^{-2} K^{-2}.

Cheung's method:

According to Cheung's model, when a series resistance is designed as a series combination of resistor and diode, then the voltage across the diode can be substituted as the voltage drop across the series combination of diode and resistor. Then equation (1) can be drafted as,

$$J = J_0\left[exp\left(\frac{q\,(V - I\,R_S)}{\eta\,K\,T}\right)\right] \quad \text{(SI-3)}$$

Where, IR_S term indicates the voltage drop across the series resistance of the semiconductor diode. Inserting the value of saturation current density into equation (3), and differentiate with respect to lnJ, we get,

$$\frac{dV}{d\ln J} = A\,J\,R_S + \frac{\eta\,K\,T}{q} \quad \text{(SI-4)}$$

Where, Rs=series resistance, q=Electronic Charge, η= Ideality Factor, K=Boltzman's Constant, T=Temperature in Kelvin scale

As stated in the Cheung model, the current density-reliant function H(J) can be written as,

$$H(J) = V - \frac{\eta K T}{q} \ln\left(\frac{J}{A^* T^2}\right) = A J R_S + \eta \Phi_B \quad \text{(SI-5)}$$

Where, $\Phi_B =$ Barrier height, A^*= Rechardson's constant and was considered as 1.2×10^6 A m^{-2} K^{-2}