Electronic Supplementary Material (ESI) for Dalton Transactions.

Combination Effect of Ionic Liquid Components on Structure and Property in 1,4-benzenedicarboxylate based Zinc Metal-Organic Frameworks

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Table S1. Crystal and structure refinement data for compounds **1**-**6**.

Compounds	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{34}Cl_2N_4O_{12}Zn_3$	$C_{38}H_{38}Cl_2N_4O_{12}Zn_3$	C8H6O5Zn	$C_{36}H_{34}Br_2N_4O_{12}Zn_3$	$C_{38}H_{38}Br_2N_4O_{12}Zn_3$	$C_{40}H_{42}Br_2N_4O_{12}Zn_3$
Color and Habit	colorless prism	colorless prism	colorless prism	colorless Block	colorless Block	colorless Block
Crystal Size (mm^3)	0.20×0.02×0.01	0.40×0.15×0.08	0.10×0.10×0.05	0.40×0.30×0.10	0.40×0.40×0.10	0.40×0.20×0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	12.7216(7)	12.7659(6)	17.9537(10)	12.9467(5)	13.0114(5)	13.1135(14)
b (Å)	9.4960(7)	9.5790(4)	6.3506(3)	9.4171(3)	9.4909(4)	9.7503(6)
c (Å)	18.0900(11)	18.0520(8)	7.2542(4)	18.3370(7)	18.3354(6)	18.2437(18)
β (°)	108.228(7)	108.206(5)	91.419(5)	108.906(4)	109.114(4)	110.202(12)
V ($Å^3$)	2075.7(2)	2096.97(16)	826.85(8)	2115.04(13)	2139.41(14)	2189.1(3)
Z	2	2	4	2	2	2
Fw	981.68	1009.73	247.50	1070.60	1098.65	1126.71
D_{calcd} (Mgm^{-3})	1.571	1.599	1.988	1.681	1.705	1.709
μ (mm^{-1})	1.912	1.895	2.960	3.639	3.600	3.521
F (000)	996	1028	496	1068	110	1132
ϑ (°)	3.43-25.03	3.43-25.03	3.40-25.01	3.82-25.02	3.80-25.02	3.75-25.02
Reflections measured	7356	20009	1391	8442	8248	9730
Independent reflections	3626	3683	728	3715	3764	3837
	(R_{int} = 0.0408)	(R_{int} = 0.0515)	(R_{int} = 0.0223)	(R_{int} = 0.0407)	(R_{int} = 0.0242)	(R_{int} = 0.0519)
Observed Reflection [$I>2\sigma(I)$]	2561	3208	672	2951	3145	2858
Final R_1, wR_2 indices (obs.)	0.0605, 0.1267	0.0444, 0.1282	0.0290, 0.0720	0.0456, 0.1135	0.0389, 0.1004	0.0551, 0.1315
R_1, wR_2 indices (all)	0.0735, 0.1314	0.0522, 0.1373	0.0320, 0.0740	0.0627, 0.1259	0.0512, 0.1075	0.0806, 0.1494
S	1.001	1.085	1.061	1.083	1.047	1.039
$(\Delta/\sigma)_{max/min}$	0.000, 0.000	0.001, 0.000	0.000, 0.000	0.000, 0.000	0.000, 0.000	0.000, 0.000
$(\Delta\rho)_{max/min}$ ($eÅ^{-3}$)	2.698, -0.803	1.482, -0.548	0.310, -0.481	1.122, -0.473	1.236, -0.483	1.112, -0.857

Table S2. Crystal and structure refinement data for compounds **7**-**11**.

Compounds	**7**	**8**	**9**	**10**	**11**
Empirical formula	$C_2H_4O_6Zn$	$C_{36}H_{34}I_2N_4O_{12}Zn_3$	$C_{38}H_{38}I_2N_4O_{12}Zn_3$	$C_{40}H_{42}I_2N_4O_{12}Zn_3$	$C_{42}H_{46}I_2N_4O_{12}Zn_3$
Color and Habit	colorless prism	colorless Block	colorless Prism	colorless Block	colorless Prism
Crystal Size (mm^3)	0.40×0.20×0.08	0.20×0.10×0.05	0.20×0.20×0.02	0.22×0.14×0.08	0.12×0.03×0.02
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/c	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	11.786(3)	13.2282(8)	13.3440(9)	13.2721(12)	13.3605(10)
b (Å)	5.3955(5)	9.3686(3)	9.4033(6)	9.6225(7)	9.8772(4)
c (Å)	9.712(3)	18.6590(7)	18.5203(12)	18.4952(12)	18.3026(9)
β (°)	126.22(3)	110.270(5)	110.126(7)	107.452(8)	108.303(7)
V ($Å^3$)	498.3(2)	2169.20(17)	2182.0(2)	2253.3(3)	2293.1(2)
Z	4	2	2	2	2
Fw	189.42	1164.58	1192.63	1220.69	1248.74
D_{calcd} (Mgm^{-3})	2.525	1.783	1.815	1.799	1.809
μ (mm^{-1})	4.881	3.130	3.114	3.017	2.967
F (000)	376	1140	1172	1204	1236
ϑ (°)	4.29-25.00	3.77-25.02	3.74-25.03	3.73-25.02	3.69-25.03
Reflections measured	832	9024	8579	9682	9289
Independent reflections	439 (R_{int} = 0.0318)	3806 (R_{int} = 0.0432)	3821 ($_{Rint}$ = 0.0732)	3945 (R_{int} = 0.0463)	4028 (R_{int} = 0.0786)
Observed Reflection [$I>2\sigma(I)$]	413	2841	1901	3008	2361
Final R_1, wR_2 indices (obs.)	0.0399 0.1071	0.0451, 0.1061	0.0753, 0.1491	0.0715, 0.1770	0.0628, 0.1129
R_1, wR_2 indices (all)	0.0418, 0.1086	0.0702, 0.1210	0.1437, 0.1775	0.0932, 0.1920	0.1243, 0.1383
S	1.086	1.018	1.020	1.070	0.997
$(\Delta/\sigma)_{max/min}$	0.000, 0.000	0.000, 0.000	0.008, 0.001	0.009, 0.001	0.000, 0.000
$(\Delta\rho)_{max/min}$ ($eÅ^{-3}$)	1.190, -0.958	0.752, -1.287	1.713, -1.204	1.867, -1.267	1.110, -0.642

Table S3. Selected bond distances (Å) and bond angles (º) of compounds **1**-**4**.

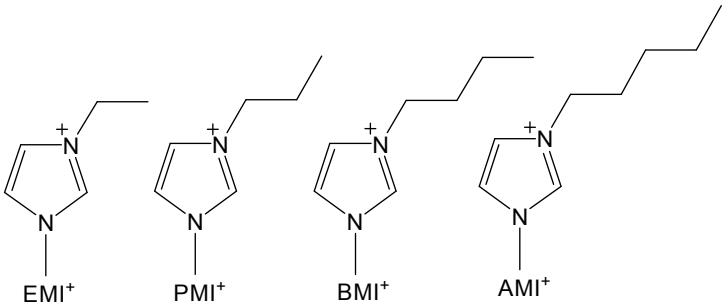
1	**2**	**3**	**4**
Zn1-O14#1 = 1.952(4)	Zn1-O13#1 = 1.963(2)	Zn1-O12#1 = 1.946(2)	Zn1-O11 = 1.950(3)
Zn1-O12#2 = 1.955(4)	Zn1-O11 = 1.965(2)	Zn1-O1W = 1.976(3)	Zn1-O13#1 = 1.964(3)
Zn1-O21 = 1.976(4)	Zn1-O21 = 1.976(2)	Zn1-O11 = 2.182(2)	Zn1-O21#2 = 1.977(3)
Zn1-Cl1 = 2.2096(18)	Zn1-Cl1 = 2.2086(11)	O12#1-Zn(1-O12#2 = 138.85(13)	Zn1-Br1 = 2.3493(7)
Zn2-O11 = 2.021(4)	Zn2-O14#1 = 2.029(2)	O12#1-Zn1-O1W = 110.57(7)	Zn2-O14#1 = 2.021(3)
Zn2-O13#1 = 2.046(4)	Zn2-O12 = 2.050(2)	O12#1-Zn1-O11 = 93.74(8)	Zn2-O12 = 2.066(3)
Zn2-O21 = 2.200(4)	Zn2-O21 = 2.205(2)	O12#2-Zn1-O11 = 88.27(8)	Zn2-O21 = 2.194(3)
O14#1-Zn1-O12#2 = 110.1(2)	O13#1-Zn1-O11 = 110.83(13)	O1W-Zn1-O11 = 87.14(5)	O11-Zn1-O13#1 = 109.58(15)
O14#1-Zn1-O21 = 109.80(16)	O13#1-Zn1-O21 = 100.54(10)	O11#3-Zn1-O11 = 174.28(10)	O11-Zn1-O21#2 = 110.93(13)
O12#2-Zn1-O21 = 101.53(16)	O11-Zn1-O21 = 110.47(10)	C14-O11-Zn1 = 123.86(17)	O13#1-Zn1-O21#2 = 101.80(13)
O14#1-Zn1-Cl1 = 112.72(13)	O13#1-Zn1-Cl1 = 104.59(9)	C14-O12-Zn1#1 = 122.09(19)	O11-Zn1-Br1 = 113.08(11)
O12#2-Zn1-Cl1 = 105.76(13)	O11-Zn1-Cl1 = 111.42(8)		O13#1-Zn1-Br1 = 105.02(10)
O21-Zn1-Cl1 = 116.18(14)	O21-Zn1-Cl1 = 118.16(8)		O21#2-Zn1-Br1 = 115.50(9)
O11-Zn2-O13#3 = 95.37(18)	O14#2-Zn2-O12 = 84.78(12)		O14#1-Zn2-O12 = 95.68(14)
O11-Zn2-O13#1 = 84.63(18)	O14#1-Zn2-O12 = 95.22(12)		O14#3-Zn2-O12 = 84.32(14)
O11-Zn2-O21#2 = 91.41(15)	O14#2-Zn2-O21 = 88.16(10)		O14#1-Zn2-O21 = 88.63(12)
O11-Zn2-O21 = 88.59(15)	O14#1-Zn2-O21 = 91.84(10)		O14#3-Zn2-O21 = 91.37(12)
O13#3-Zn2-O21 = 91.84(16)	O12-Zn2-O21 = 88.34(10)		O12#2-Zn2-O21 = 87.86(12)
O13#1-Zn2-O21 = 88.16(16)	O12-Zn2-O21#3 = 91.66(10)		O12-Zn2-O21 = 92.14(12)
Synmmerty codes: #1 = -x+5/2, y+1/2, -z+1/2; #2 = -x+2, -y+2, -z; #3 = x-1/2, -y+3/2, z-1/2.	Synmmerty codes: #1 = x+1/2, -y+1/2, z+1/2; #2 = -x-1/2, y+1/2, -z+1/2; #3 = -x, -y+1, -z+10.	Synmmerty codes: #1 = -x, -y+1, -z+1; #2 = x, -y+1, z+1/2; #3 = -x, y, -z+3/2.	Synmmerty codes: #1 = x-1/2, -y+5/2, z-1/2; #2 = -x+2, -y+2, -z; #3 = -x+5/2, y-1/2, -z+1/2.

Table S4. Selected bond distances (Å) and bond angles (º) of compounds **5**-**8**.

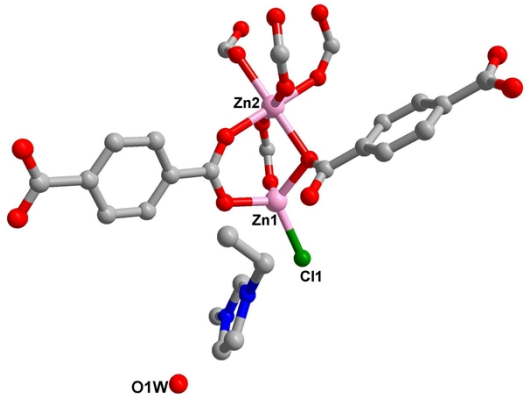
5	**6**	**7**	**8**
Zn1-O14#1 = 1.956(3)	Zn1-O12 = 1.964(4)	Zn1-O1 = 2.072(4)	Zn1-O11= 1.947(4)
Zn1-O12#2 = 1.962(3)	Zn1-O14#1 = 1.972(4)	Zn1-O2#2 = 2.086(4)	Zn1-O13#1= 1.968(4)
Zn1-O21 = 1.976(3)	Zn1-O21 = 1.994(4)	Zn1-O1W = 2.115(4)	Zn1-O21= 1.970(4)
Zn1-Br1 = 2.3537(6)	Zn1-Br1 = 2.3547(10)	O1-Zn1-O1#1 = 80.76(19)	Zn1-I1= 2.5472(8)
Zn2-O11 = 2.032(3)	Zn2-O13#1 = 2.018(4)	O1-Zn1-O2#2 = 179.83(17)	Zn2-O14#1= 2.022(4)
Zn2-O13#1 = 2.060(3)	Zn2-O11 = 2.071(4)	O1-Zn1-O2#3 = 99.39(14)	Zn2-O12= 2.065(4)
Zn2-O21 = 2.196(3)	Zn2-O21 = 2.217(4)	O2#2-Zn1-O2#3 = 80.5(2)	Zn2-O21= 2.187(4)
O14#1-Zn1-O12#2 = 110.09(14)	O12-Zn1-O14#1 = 109.07(17)	O1-Zn1-O1W#1 = 88.84(15)	O11-Zn1-O13#1= 108.79(19)
O14#1-Zn1-O21 = 110.99(12)	O12-Zn1-O21 = 112.70(16)	O1-Zn1-O1W = 89.15(15)	O11-Zn1-O21= 110.91(17)
O12#2-Zn1-O21 = 100.90(12)	O14#1-Zn1-O21 = 100.89(16)	O1#1-Zn1-O1W = 88.84(15)	O13#1-Zn1-O21= 102.29(17)
O14#1-Zn1-Br1 = 112.27(9)	O12-Zn1-Br1 = 109.99(13)	O2#2-Zn1-O1W = 90.93(16)	O11-Zn1-I1= 114.42(13)
O12#2-Zn1-Br1 = 103.97(9)	O14#1-Zn1-Br1 = 103.23(13)	O2#3-Zn1-O1W = 91.09(15)	O13#1-Zn1-I1= 104.54(13)
O21-Zn1-Br1 = 117.56(8)	O21-Zn1-Br1 = 119.64(11)	O1W#1-Zn1-O1W = 177.4(2)	O21-Zn1-I1= 114.78(11)
O11-Zn2-O13#3 = 95.56(13)	O13#2-Zn2-O11 = 85.03(18)		O14#2-Zn2-O12= 84.52(19)
O11-Zn2-O13#1 = 84.44(13)	O13#1-Zn2-O11 = 94.97(18)		O14#1-Zn2-O12= 95.48(19)
O11-Zn2-O21#2 = 91.23(11)	O13#2-Zn2-O21 = 88.38(15)		O12-Zn2-O21#3= 92.00(15)
O11-Zn2-O21 = 88.77(11)	O13#1-Zn2-O21 = 91.62(15)		O14#2-Zn2-O21= 88.92(15)
O13#3-Zn2-O21 = 92.10(11)	O11-Zn2-O21 = 89.29(15)		O14#1-Zn2-O21= 91.08(16
O13#1-Zn2-O21 = 87.90(11)	O11#3-Zn2-O21 = 90.71(15)		O12-Zn2-O21= 88.00(15)
Synmmerty codes: #1 = -x+5/2, y-1/2, -z+1/2; #2 = -x+2, -y, -z; #3 = x-1/2, -y+1/2, z-1/2.	Synmmerty codes: #1 = x-1/2, -y+3/2, z-1/2; #2 -x+3/2, y-1/2, -z+1/2; #3 = -x+1, -y+1, -z.	Synmmerty codes: #1 = -x, y, -z+1/2; 2 = -x, y+1, -z+1/2; #3 = x, y+1, z.	Synmmerty codes:#1 = x-1/2, -y+5/2, z-1/2; #2 = -x+5/2, y-1/2, -z+1/2; #3 = -x+2, -y+2, -z.

Table S5. Selected bond distances (Å) and bond angles (º) of compounds **9**-**11**.

9	**10**	**11**
Zn1-O21 = 1.947(9)	Zn1-O12= 1.949(4)	Zn1-O13#1= 1.976(4)
Zn1-O14#1 = 1.962(7)	Zn1-O24#1= 1.970(4)	Zn1-O11= 1.980(3)
Zn1-O12#2 = 1.961(8)	Zn1-O22= 1.983(3)	Zn1-O21= 1.995(4)
Zn1-I1 = 2.537(2)	Zn1-I1= 2.5656(7)	Zn1-I1= 2.5669(9)
Zn2-O13 = 2.015(10)	Zn2-O13#1= 2.020(4)	Zn2-O14#1= 2.022(4)
Zn2-O11#2 = 2.010(9)	Zn2-O11= 2.065(3)	Zn2-O12= 2.058(3)
Zn2-O21 = 2.204(9)	Zn2-O22= 2.197(3)	Zn2-O21= 2.230(4)
O21-Zn1-O14#1 = 105.8(3)	O12-Zn1-O24#1= 108.20(17)	O13#1-Zn1-O11= 106.32(16)
O21-Zn1-O12#2 = 105.4(4)	O12-Zn1-O22= 113.08(16)	O13#1-Zn1-O21= 103.56(15)
O14#1-Zn1-O12#2 = 109.2(4)	O24#1-Zn1-O22= 100.17(14)	O11-Zn1-O21= 114.56(16)
O21-Zn1-I1 = 119.6(3)	O12-Zn1-I1= 110.85(11)	O13#1-Zn1-I1= 101.85(13)
O14#1-Zn1-I1 = 108.6(3)	O24#1-Zn1-I1= 103.25(12)	O11-Zn1-I1= 111.02(12)
O12#2-Zn1-I1 = 107.9(3)	O22-Zn1-I1= 119.59(10)	O21-Zn1-I1= 117.69(11)
O13-Zn2-O11#2 = 84.7(4)	O13#2-Zn2-O11= 85.45(16)	O14#1-Zn2-O12= 94.27(16)
O13-Zn2-O11#3 = 95.3(4)	O13#1-Zn2-O11= 94.55(16)	O14#2-Zn2-O12= 85.73(16)
O13-Zn2-O21 = 91.6(4)	O13#2-Zn2-O22= 89.16(14)	O12-Zn2-O21#3= 91.79(14)
O13#1-Zn2-O21 = 88.4(4)	O13#1-Zn2-O22= 90.84(14)	O14#1-Zn2-O21= 92.49(15)
O11#2-Zn2-O21 = 89.2(4)	O11#3-Zn2-O22= 92.20(14)	O14#2-Zn2-O21= 87.51(15)
O11#3-Zn2-O21 = 90.8(4)	O11-Zn2-O22= 87.80(14)	O12-Zn2-O21= 88.21(14)
Synmmerty codes: #1 = -x, -y, -z; #2 = -x+1/2, y-1/2, z+1/2; #3 = x-1/2, -y+1/2, z-1/2.	Synmmerty codes: #1 = x, -y+5/2, z+1/2; #2 = -x+2, y-1/2, -z-1/2; #3 = -x+2, -y+2, -z.	Synmmerty codes: #1 = x, -y+5/2, z-1/2; #2 = -x, y-1/2, -z+1/2; #3 = -x, -y+2, -z.



Scheme S1. The structure motifs of RMI^+ cations



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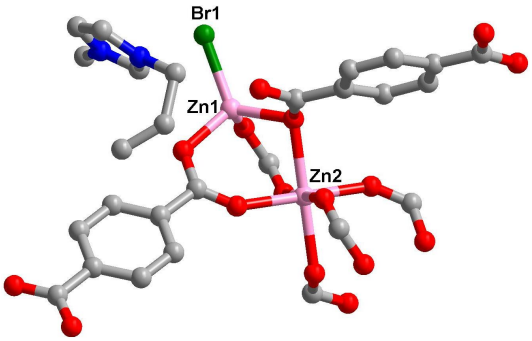

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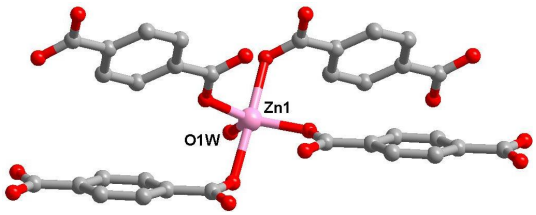

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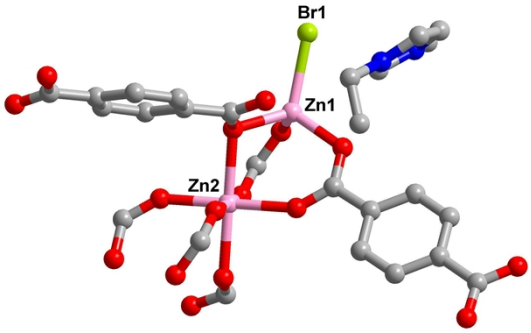

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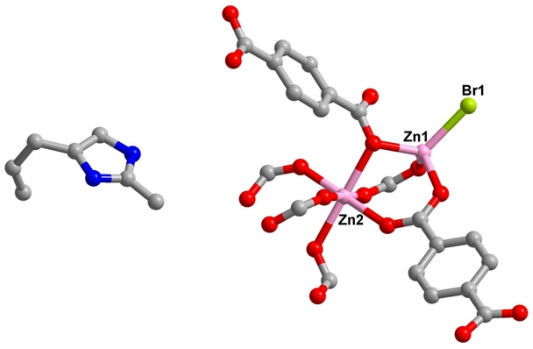

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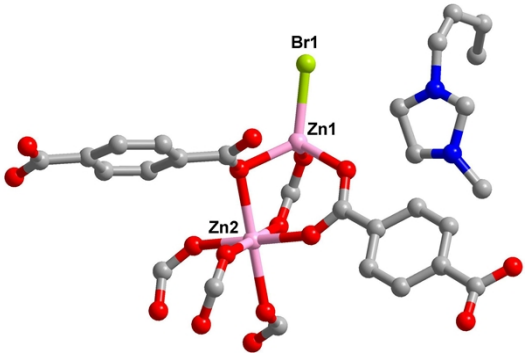

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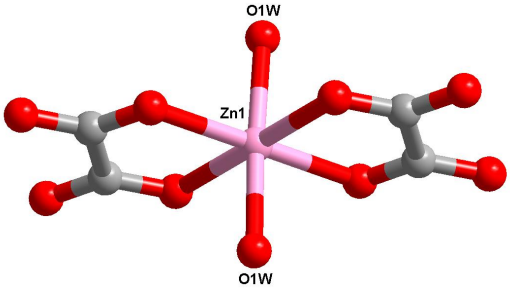

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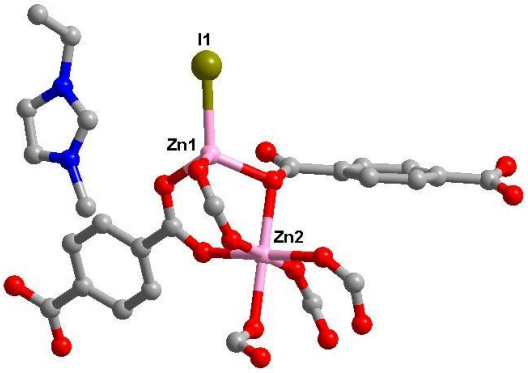

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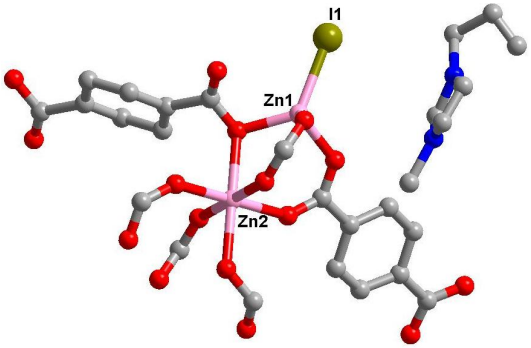
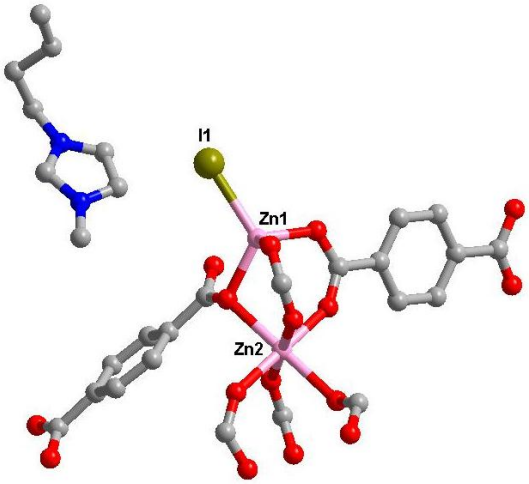
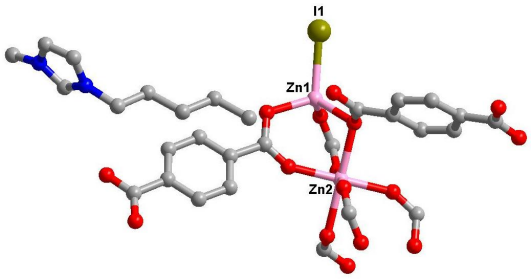


(9)



(10)



(11)

Fig. S1 Coordination spheres of Zn(II) centers in compounds **1-11.**

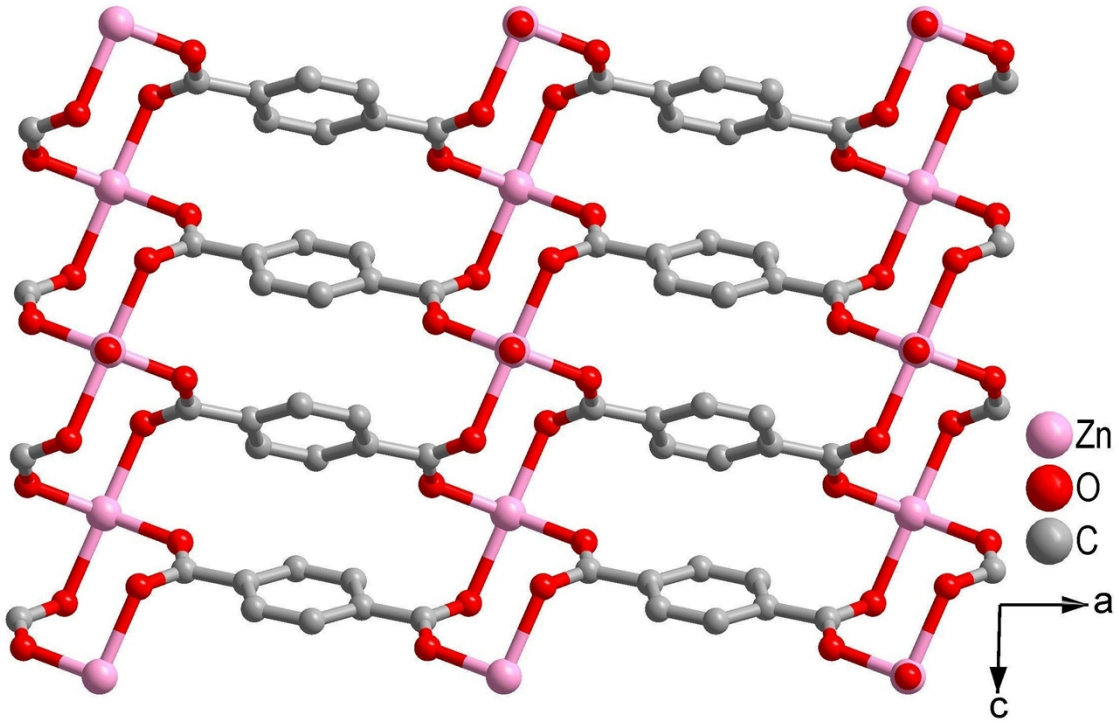
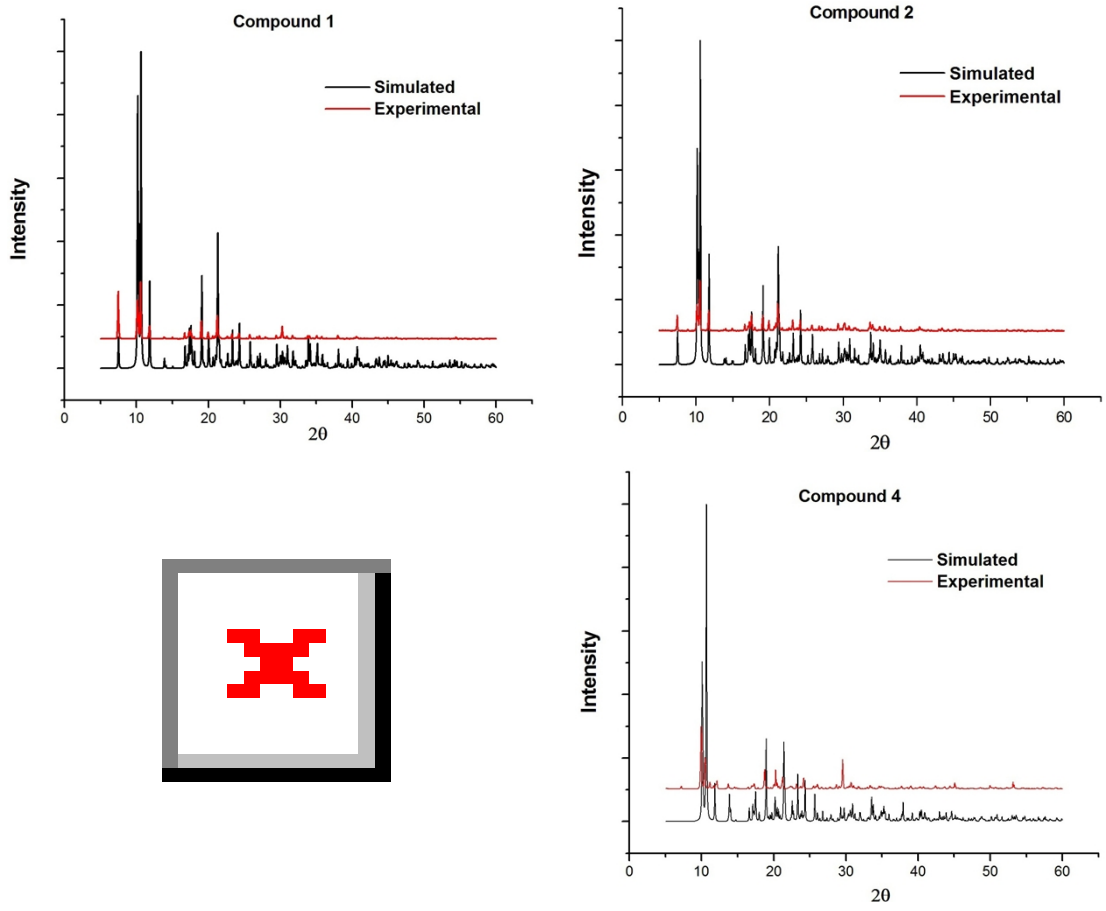
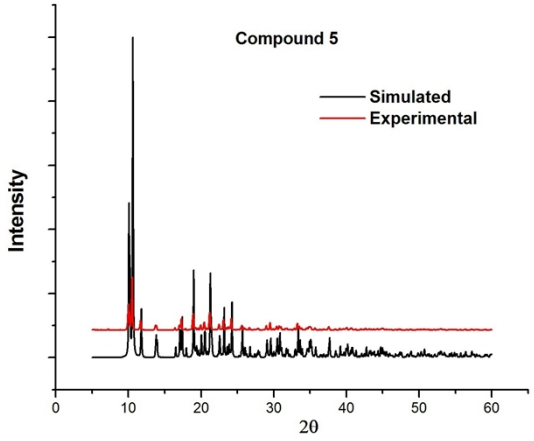
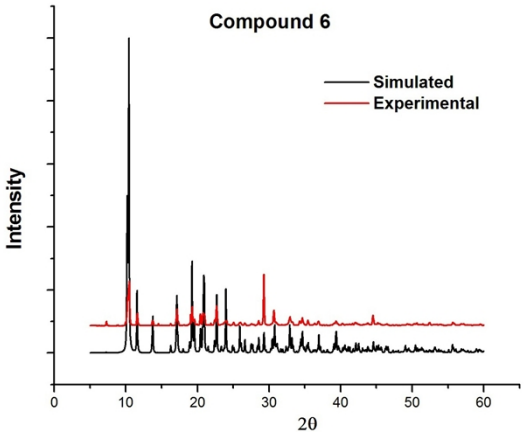
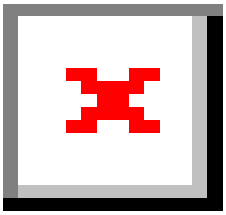


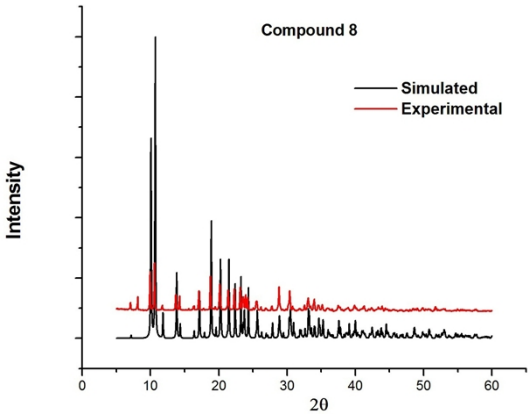
Fig. S2. The 2D layer along the ac-plane in compound **3**.

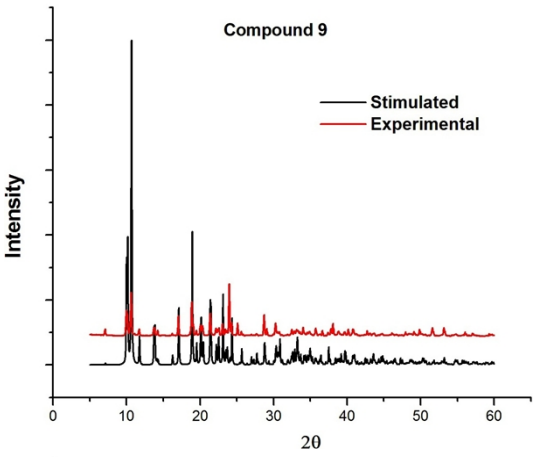


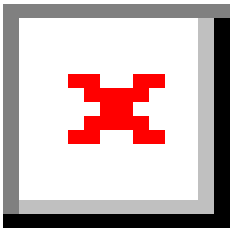

Compound 5
Simulated
Experimental
Intensity
0
10
20
30
40
50
60
2θ


Compound 6
Simulated
Experimental
Intensity
0
10
20
30
40
50
60
2θ




Compound 8
Simulated
Experimental
Intensity
0
10
20
30
40
50
60
2θ


Compound 9
Stimulated
Experimental
Intensity
0
10
20
30
40
50
60
2θ



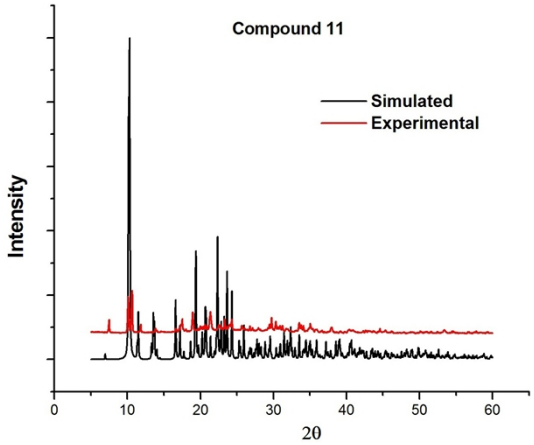

Compound 11
Simulated
Experimental
Intensity
0
10
20
30
40
50
60
2θ

Fig. S3 Comparison of X-ray powder diffraction patterns of compounds **1**-**11** to those simulated from single crystal structure data.