Electronic Supplementary Material (ESI) for CrystEngComm.

Combination effect of ligands and ionic liquid components on the structure and properties in manganese metal–organic frameworks

Zhen Wei[a,b], Ling Xu[a*], Bing Liu[c*], Huan Jiao[a]

Table S1. Crystal and structure refinement data for compounds **1-5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{38}H_{38}Cl_2Mn_3N_4O_{12}$	$C_{40}H_{42}Cl_2Mn_3N_4O_{12}$	$C_{38}H_{38}Br_2Mn_3N_4O_{12}$	$C_{40}H_{42}Br_2Mn_3N_4O_{12}$	$C_{42}H_{46}Br_2Mn_3N_4O_{12}$
Formula weight	978.44	1006.50	1067.36	1095.42	1123.47
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	13.2885(3)	13.5591(3)	13.5252(8)	13.7103(3)	13.8296(4)
b/Å	9.6523(2)	10.4987(2)	9.6460(5)	10.5170(2)	10.4308(3)
c/Å	18.1669(5)	16.6622(5)	18.4119(12)	16.7248(4)	17.0480(8)
β/°	109.574(3)	110.430(3)	110.747(7)	110.262(3)	109.760(4)
V/Å^3	2195.51(9)	2222.72(9)	2246.3(2)	2262.34(9)	2314.43(14)
Z	2	2	2	2	2
ρ_{calc} g/cm^3	1.480	1.504	1.578	1.608	1.612
μ/mm^{-1}	1.033	1.023	2.670	2.653	2.596
F(000)	998.0	1030.0	1070.0	1102.0	1632.0
Crystal size/mm^3	0.3×0.2×0.05	0.2×0.15×0.08	0.4×0.4×0.2	0.12×0.08×0.04	0.2×0.1×0.1
2θ range/°	7.44 to 50.04	6.4 to 50	7.36 to 50.06	7.1 to 50.04	7.38 to 50.02
Reflections collected	20852	20837	11164	17334	9636
Independent reflections	3859 [R_{int} = 0.0310, R_{sigma} = 0.0229]	3882 [R_{int} = 0.0293, R_{sigma} = 0.0219]	3923 [R_{int} = 0.0304, R_{sigma} = 0.0349]	3970 [R_{int} = 0.0259, R_{sigma} = 0.0223]	4076 [R_{int} = 0.0271, R_{sigma} = 0.0367]
GOF	1.026	1.013	1.013	1.025	1.024
Final R indexes [I≥2σ (I)]	R_1 = 0.0370, wR_2 = 0.1070	R_1 = 0.0378, wR_2 = 0.1201	R_1 = 0.0440, wR_2 = 0.1118	R_1 = 0.0315, wR_2 = 0.0787	R_1 = 0.0371, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0452, wR_2 = 0.1129	R_1 = 0.0475, wR_2 = 0.1275	R_1 = 0.0609, wR_2 = 0.1242	R_1 = 0.0422, wR_2 = 0.0848	R_1 = 0.0569, wR_2 = 0.1001
Largest diff. peak/hole / e Å^{-3}	0.76/-0.39	0.95/-0.54	1.03/-0.54	0.59/-0.44	0.58/-0.36

$R_1 = (\Sigma||F_o| - |F_c||) / \Sigma |F_o|)$. $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w |F_o^2|^2)]^{1/2}$

Table S2. Crystal and structure refinement data for compounds **6-9** and **11**.

	6	**7**	**8**	**9**	**11**
Empirical formula	$C_{68}H_{54}Mn_3N_4O_{16}$	$C_{55}H_{45}Mn_2N_6O_{15}$	$C_{58}H_{24}Mn_2N_6O_{15}$	$C_{61}H_{26}Mn_2N_6O_{15}$	$C_{209}H_{170}Mn_9N_{12}O_{54}$
Formula weight	1347.97	1139.85	1154.71	1192.76	4208.03
Temperature/K	152.99	293(2)	293(2)	293(2)	153.01
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	C2/m	C2/m	C2/m	P-1
a/Å	18.2308(7)	18.1886(10)	18.1583(12)	18.2596(9)	13.5482(4)
b/Å	17.8579(6)	21.2528(9)	21.2584(12)	21.4975(8)	15.5614(5)
c/Å	18.6949(6)	16.2865(7)	16.2295(8)	16.3016(6)	27.8886(9)
α/°	90.00	90.00	90.00	90.00	102.9370(10)
β/°	95.9480(10)	118.757(5)	118.484(6)	118.718(4)	92.1900(10)
γ/°	90.00	90.00	90.00	90.00	112.3730(10)
V/Å^3	6053.6(4)	5519.2(5)	5506.5(6)	5611.9(4)	5249.2(3)
Z	4	4	4	4	1
ρ_{calc} g/cm^3	1.479	1.372	1.393	1.412	1.331
μ/mm^{-1}	0.692	0.529	0.532	0.525	0.604
F(000)	2772.0	2348.0	2336.0	2416.0	2165.0
Crystal size/mm^3	0.50×0.40×0.30	0.30×0.20×0.05	0.20×0.20×0.10	0.4×0.2×0.1	0.200×0.150×0.10
2θrange for data collection/°	8.56 to 50.06	8.18 to 50.04	6.94 to 50.04	7.56 to 50.06	6.8 to 50.06
Reflections collected	49458	26303	25999	26315	179532
Independent reflections	5304[R_{int}=0.0365,R_{sigma}=0.0163]	4974[R_{int}=0.0509, R_{sigma}=0.0398]	4979[R_{int}=0.0671,R_{sigma}=0.0540]	5019[R_{int}=0.0403,R_{sigma}=0.0314]	18384[R_{int}=0.0526,R_{sigma}=0.0256]
GOF	1.069	1.027	1.012	1.088	1.009
Final R indexes [I≥2σ (I)]	R_1=0.0787,wR_2=0.1995	R_1=0.0783,wR_2=0.2078	R_1=0.0614,wR_2=0.1589	R_1=0.0588,wR_2=0.1596	R_1=0.0721,wR_2=0.1981
Final R indexes [all data]	R_1=0.0877,wR_2=0.2074	R_1=0.0985,wR_2=0.2294	R_1=0.0920,wR_2=0.1872	R_1=0.0731,wR_2=0.1716	R_1=0.0811,wR_2=0.2103
Largest diff. peak/hole / e Å^{-3}	1.16/-0.75	2.04/-0.52	0.59/-0.48	1.23/-0.54	1.79/-0.97

$R_1 = (\Sigma||F_o| - |F_c||) / \Sigma |F_o|)$. $wR_2 = [\Sigma (w(F_o^2 - F_c^2)^2) / \Sigma (w |F_o^2|^2)]^{1/2}$

Table S3. Selected bond distances (Å) and bond angles (º) of compounds **1-5**.

1	2	3	4	5
Mn1-Cl1=2.3407(9)	Mn1-Cl1=2.3926(8)	Mn1-O11=2.103(3)	Mn1-Br1=2.5420(5)	Mn1-O11=2.202(3)
Mn1-O11=2.063(2)	Mn1-O11=2.030(2)	Mn1-O13^{2}=2.158(3)	Mn1-O11=2.160(2)	Mn1-O13^{2}=2.129(2)
Mn1-O13^{1}=2.066(2)	Mn1-O13^{1}=2.143(2)	Mn1-O22=2.217(2)	Mn1-O12=2.418(2)	Mn1-O21=2.151(3)
Mn1-O21=2.442(2)	Mn1-O14^{1}=2.480(2)	Mn2-Br1=2.4919(7)	Mn1-O13^{1}=2.037(2)	Mn2-Br1=2.5514(6)
Mn1-O22=2.173(2)	Mn1-O22^{2}=2.057(2)	Mn2-O12^{1}=2.065(3)	Mn1-O21=2.069(2)	Mn2-O11^{4}=2.487(3)
Mn2-O12=2.1078(19)	Mn2-O12=2.136(2)	Mn2-O14^{3}=2.071(3)	Mn2-O12=2.193(2)	Mn2-O12^{4}=2.141(3)
Mn2-O14^{1}=2.148(2)	Mn2-O14^{1}=2.198(2)	Mn2-O21=2.409(3)	Mn2-O14^{1}=2.132(2)	Mn2-O14=2.046(3)
Mn2-O22=2.2246(19)	Mn2-O21=2.148(2)	Mn2-O22=2.179(3)	Mn2-O22=2.154(2)	Mn2-O22^{4}=2.090(3)
Cl1-Mn1-O21=92.73(7)	Cl1-Mn1-O14^{1}=148.48(6)	O11-Mn1-O11^{1}=180.000(1)	Br1-Mn1-C17=124.11(7)	O11^{1}-Mn1-O11=180.0(2)
O11-Mn1-Cl1=102.87(7)	O11-Mn1-Cl1=108.29(6)	O11-Mn1-O13^{2}=93.62(13)	O11-Mn1-Br1=96.99(6)	O13^{3}-Mn1-O11=88.96(11)
O11-Mn1-O13^{1}=106.57(10)	O11-Mn1-O13^{1}=99.82(11)	O11-Mn1-O13^{3}=86.38(13)	O11-Mn1-O12=56.38(8)	O13^{2}-Mn1-O11=91.04(11)
O11-Mn1-O21=147.78(8)	O11-Mn1-O14^{1}=94.18(8)	O11^{1}-Mn1-O22=88.25(10)	O12-Mn1-Br1=149.58(5)	O13^{2}-Mn1-O13^{3}=180.00(11)
O11-Mn1-O22=91.76(8)	O11-Mn1-O22^{2}=126.08(11)	O11-Mn1-O22=91.75(10)	O13^{1}-Mn1-Br1=106.08(6)	O13^{2}-Mn1-O21=88.96(11)
O13^{1}-Mn1-Cl1=109.39(7)	O13^{1}-Mn1-Cl1=97.92(6)	O13^{2}-Mn1-O13^{3}=180.0	O13^{1}-Mn1-O11=100.01(11)	O13^{3}-Mn1-O21=91.04(11)
O13^{1}-Mn1-O21=94.18(9)	O13^{1}-Mn1-O14^{1}=55.59(7)	O13^{3}-Mn1-O22=86.69(11)	O13^{1}-Mn1-O12=93.99(9)	O21-Mn1-O11=84.06(12)
O13^{1}-Mn1-O22=117.42(8)	O22^{2}-Mn1-Cl1=95.59(7)	O13^{2}-Mn1-O22=93.31(11)	O13^{1}-Mn1-O21=127.82(11)	O21^{1}-Mn1-O11=95.94(12)
O22-Mn1-Cl1=124.11(6)	O22^{2}-Mn1-O13^{1}=124.36(11)	O22^{1}-Mn1-O22=180.000(1)	O21-Mn1-Br1=95.67(7)	O21^{1}-Mn1-O11^{1}=84.06(12)
O22-Mn1-O21=56.44(8)	O22^{2}-Mn1-O14^{1}=88.21(9)	O12^{1}-Mn2-Br1=102.22(9)	O21-Mn1-O11=124.04(11)	O21-Mn1-O11^{1}=95.94(12)
O12^{2}-Mn2-O12=180.00(17)	O12-Mn2-O12^{2}=180.0	O12^{1}-Mn2-O14^{3}=105.78(12)	O21-Mn1-O12=89.44(9)	O21-Mn1-O21^{1}=180.00(18)
O12-Mn2-O14^{1}=93.58(10)	O12^{2}-Mn2-O14^{3}=91.34(10)	O12^{1}-Mn2-O21=148.02(11)	O12-Mn2-O12^{2}=180.00(12)	O11^{4}-Mn2-Br1=151.88(7)
O12-Mn2-O14^{3}=86.42(10)	O12-Mn2-O14^{3}=88.66(9)	O12^{1}-Mn2-O22=91.66(11)	O14^{3}-Mn2-O12=88.17(9)	O12^{4}-Mn2-Br1=98.59(7)
O12^{2}-Mn2-O22=91.32(8)	O12-Mn2-O14^{1}=91.34(9)	O14^{3}-Mn2-Br1=109.28(9)	O14^{1}-Mn2-O12=91.83(9)	O12^{4}-Mn2-O11^{4}=55.46(9)
O12-Mn2-O22=88.68(8)	O12-Mn2-O21=90.78(9)	O14^{3}-Mn2-O21=95.53(12)	O14^{3}-Mn2-O14^{1}=180.00(10)	O14-Mn2-Br1=104.11(8)
O14^{3}-Mn2-O14^{1}=180.00(14)	O14^{3}-Mn2-O14^{1}=180.00(11)	O14^{3}-Mn2-O22=118.39(11)	O14^{3}-Mn2-O22=90.62(9)	O14-Mn2-O11^{4}=92.11(11)
O14^{1}-Mn2-O22=86.47(9)	O21-Mn2-O14^{1}=95.35(9)	O21-Mn2-Br1=92.59(9)	O14^{1}-Mn2-O22=89.38(9)	O14-Mn2-O12^{4}=99.79(12)
O14^{3}-Mn2-O22=93.53(9)	O21-Mn2-O14^{3}=84.65(9)	O22-Mn2-Br1=124.13(7)	O22-Mn2-O12=84.36(9)	O14-Mn2-O22^{4}=133.06(13)
O22-Mn2-O22^{2}=180.00(13)	O21^{2}-Mn2-O21=180.00(12)	O22-Mn2-O21=56.88(10)	O22^{2}-Mn2-O22=180.0	O22^{4}-Mn2-Br1=94.43(9)

Symmetry code: **1**):^{1} 1/2+X, -1/2-Y, 1/2+Z; ^{2} 1-X, -Y, -Z; ^{3} 1/2-X, 1/2+Y, -1/2-Z; **2**): ^{1} X, 5/2-Y, 1/2+Z; ^{2} -X, 2-Y, -Z;^{3} -X, -1/2+Y, -1/2-Z; **3**): ^{1} -X, 1-Y, 1-Z; ^{2} 1/2+X, 1/2-Y, 1/2+Z; ^{3} -1/2-X, 1/2+Y, 1/2-Z; **4**): ^{1} X, 5/2-Y, -1/2+Z; ^{2} -X, 2-Y, -Z;^{3} -X, -1/2+Y, 1/2-Z; **5**): ^{1} -X, -Y, -Z; ^{2} X, 1/2-Y, -1/2+Z; ^{3} -X, -1/2+Y, 1/2-Z; ^{4} X, 1/2-Y, 1/2+Z.

Table S4. Selected bond distances (Å) and bond angles (º) of compounds **6-9**.

6	7	8	9
Mn1-O11=2.2588(11)	Mn1-O11^{1}=2.1356(13)	Mn1-O11=2.1168(11)	Mn1-O11=2.136(2)
Mn1-O12=2.2583(14)	Mn1-O12=2.1488(11)	Mn1-O21^{1}=2.1504(10)	Mn1-O12^{1}=2.149(2)
Mn1-O21^{1}=2.1021(12)	Mn1-O21^{2}=2.1230(13)	Mn1-O22^{2}=2.1275(11)	Mn1-O21^{2}=2.123(3)
Mn1-O31=2.3534(16)	Mn1-O31=2.2258(13)	Mn1-O31=2.2210(11)	Mn1-O31=2.228(2)
Mn1-O32=2.1692(13)	Mn1-O1W=2.1770(12)	Mn1-O1W=2.2880(8)	Mn1-O1W=2.185(2)
Mn1-O41^{2}=2.0655(15)	Mn1-O2W=2.2876(10)	Mn1-O2W=2.1770(11)	Mn1-O2W=2.2943(18)
Mn2-O11=2.1534(10)	O11^{1}-Mn1-O12=94.64(5)	O11-Mn1-O21^{1}=172.17(4)	O11-Mn1-O12^{1}=93.89(10)
Mn2-O22^{1}=2.1204(13)	O11^{1}-Mn1-O21^{2}=91.13(5)	O11-Mn1-O22^{2}=91.57(4)	O11-Mn1-O31=177.99(9)
Mn2-O51=2.2678(12)	O11^{1}-Mn1-O31=178.60(4)	O11-Mn1-O31=90.24(4)	O11-Mn1-O1W=90.26(9)

O11-Mn1-O31=93.46(5)	O11^{1}-Mn1-O1W=90.41(5)	O11-Mn1-O1W=88.00(4)	O11-Mn1-O2W=88.61(8)
O12-Mn1-O11=57.44(4)	O11^{1}-Mn1-O2W=89.22(4)	O11-Mn1-O2W=95.15(4)	O12^{1}-Mn1-O31=84.32(9)
O12-Mn1-O31=87.91(6)	O12-Mn1-O31=84.14(5)	O21^{1}-Mn1-O31=83.90(4)	O12^{1}-Mn1-O1W=90.60(9)
O21^{1}-Mn1-O11=98.34(4)	O12-Mn1-O1W=90.95(5)	O21^{1}-Mn1-O1W=86.84(4)	O12^{1}-Mn1-O2W=86.62(8)
O21^{1}-Mn1-O12=155.77(5)	O12-Mn1-O2W=86.53(4)	O21^{1}-Mn1-O2W=90.13(4)	O21^{2}-Mn1-O11=91.43(10)
O21^{1}-Mn1-O31=94.51(6)	O21^{2}-Mn1-O12=172.29(5)	O22^{2}-Mn1-O21^{1}=94.20(4)	O21^{2}-Mn1-O12^{1}=171.91(10)
O21^{1}-Mn1-O32=95.55(5)	O21^{2}-Mn1-O31=90.03(5)	O22^{2}-Mn1-O31=177.90(3)	O21^{2}-Mn1-O31=90.25(10)
O32-Mn1-O11=148.23(5)	O21^{2}-Mn1-O1W=94.13(5)	O22^{2}-Mn1-O1W=88.69(4)	O21^{2}-Mn1-O1W=95.47(10)
O32-Mn1-O12=105.83(5)	O21^{2}-Mn1-O2W=88.43(5)	O22^{2}-Mn1-O2W=90.13(4)	O21^{2}-Mn1-O2W=87.42(10)
O32-Mn1-O31=56.94(6)	O31-Mn1-O2W=90.03(4)	O31-Mn1-O1W=90.31(3)	O31-Mn1-O2W=90.36(7)
O41^{2}-Mn1-O11=114.97(5)	O1W-Mn1-O31=90.28(5)	O2W-Mn1-O31=90.77(4)	O1W-Mn1-O31=90.68(8)
O41^{2}-Mn1-O12=94.44(6)	O1W-Mn1-O2W=177.42(4)	O2W-Mn1-O1W=176.66(4)	O1W-Mn1-O2W=176.92(9)
O41^{2}-Mn1-O21^{1}=96.25(6)			
O41^{2}-Mn1-O31=147.60(6)			
O41^{2}-Mn1-O32=91.59(6)			
O11-Mn2-O11^{3}=100.56(5)			
O11-Mn2-O51=158.84(4)			
O11-Mn2-O51^{3}=100.57(4)			
O22^{4}-Mn2-O11=93.90(4)			
O22^{1}-Mn2-O11=84.71(4)			
O22^{4}-Mn2-O22^{1}=177.83(6)			
O22^{4}-Mn2-O51=86.80(5)			
O22^{1}-Mn2-O51=95.10(5)			
O51-Mn2-O51^{3}=58.36(7)			

Symmetry code: **6**): ^{1} 1/2+X, 5/2-Y, -1/2+Z; ^{2} X, 1+Y, Z; ^{3} 1-X, Y, -1/2-Z; ^{4} 1/2-X, 5/2-Y, -Z; **7**): ^{1} -X, Y, -Z; ^{2} 1/2+X, 1/2-Y, 1+Z; **8**): ^{1} 1/2+X, 1/2-Y, 1+Z; ^{2} 1/2-X, 1/2-Y, -Z; **9**): ^{1} -X, Y, -Z; ^{2} 1/2-X, 1/2-Y, 1-Z; ^{3} -X, Y, -1-Z; ^{4} X, 1-Y, Z.

Table S5. Selected bond distances (Å) and bond angles (º) of compound **11**.

Mn1-O31=2.209(3)	O92-Mn1-O31^{1}=92.63(11)	O72-Mn3-O132=102.0(2)
Mn1-O31^{1}=2.209(3)	O92-Mn1-O31=87.37(11)	O132-Mn3-O61^{3}=154.0(3)
Mn1-O92^{1}=2.200(3)	O111-Mn1-O31=93.39(15)	O132-Mn3-O131=49.0(3)
Mn1-O92=2.200(3)	O111-Mn1-O31^{1}=86.61(15)	O32-Mn4-O31=57.73(13)
Mn1-O111=2.120(3)	O111-Mn1-O92^{1}=92.52(14)	O32-Mn4-O81^{4}=117.9(2)
Mn2-O12=2.140(3)	O111-Mn1-O92=87.48(14)	O81^{4}-Mn4-O31=170.32(15)
Mn2-O22^{2}=2.170(3)	O12-Mn2-O22^{2}=174.03(13)	O82^{4}-Mn4-O31=112.90(15)
Mn2-O52=2.235(3)	O12-Mn2-O52=88.98(13)	O82^{4}-Mn4-O32=89.23(16)
Mn2-O61^{3}=2.247(3)	O12-Mn2-O61^{3}=97.47(13)	O82^{4}-Mn4-O81^{4}=57.51(17)
Mn2-O71=2.140(3)	O12-Mn2-O71=89.68(13)	O91^{1}-Mn4-O31=87.15(14)
Mn2-O121=2.099(3)	O22^{2}-Mn2-O52=88.97(11)	O91^{1}-Mn4-O32=143.64(17)
Mn3-O11=2.077(3)	O22^{2}-Mn2-O61^{3}=84.85(11)	O91^{1}-Mn4-O81^{4}=95.1(2)
Mn3-O61^{3}=2.321(3)	O52-Mn2-O61^{3}=173.08(11)	O91^{1}-Mn4-O82^{4}=97.12(15)
Mn3-O62^{3}=2.195(4)	O71-Mn2-O22^{2}=84.78(12)	O91^{1}-Mn4-O112=101.23(18)
Mn3-O72=2.066(4)	O71-Mn2-O52=91.96(11)	O112-Mn4-O31=103.03(13)
Mn3-O131=2.428(4)	O71-Mn2-O61^{3}=90.58(11)	O112-Mn4-O32=96.16(19)
Mn3-O132=2.207(6)	O121-Mn2-O12=88.16(15)	O112-Mn4-O81^{4}=85.78(17)

Mn4-O31=2.312(4)	O121-Mn2-O22[2]=97.49(14)	O112-Mn4-O82[4]=140.23(17)
Mn4-O32=2.227(4)	O121-Mn2-O52=91.16(12)	O21[2]-Mn5-O51=94.29(15)
Mn4-O81[4]=2.304(5)	O121-Mn2-O61[3]=86.56(12)	O21[2]-Mn5-O52=106.60(12)
Mn4-O82[4]=2.173(4)	O121-Mn2-O71=176.16(14)	O21[2]-Mn5-O101=148.33(14)
Mn4-O91[1]=2.056(3)	O11-Mn3-O61[3]=102.95(14)	O21[2]-Mn5-O102=92.73(14)
Mn4-O112=2.072(4)	O11-Mn3-O62[3]=94.09(16)	O21[2]-Mn5-O122=101.46(17)
Mn5-O21[2]=2.085(3)	O11-Mn3-O131=145.8(2)	O52-Mn5-O51=57.19(11)
Mn5-O51=2.377(3)	O11-Mn3-O132=96.9(3)	O52-Mn5-O101=98.48(12)
Mn5-O52=2.211(3)	O61[3]-Mn3-O131=109.47(19)	O101-Mn5-O51=83.17(15)
Mn5-O101=2.323(4)	O62[3]-Mn3-O61[3]=57.75(12)	O102-Mn5-O51=105.09(16)
Mn5-O102=2.186(4)	O62[3]-Mn3-O131=94.2(2)	O102-Mn5-O52=153.98(14)
Mn5-O122=2.091(4)	O62[3]-Mn3-O132=104.6(2)	O102-Mn5-O101=58.08(14)
	O72-Mn3-O11=95.30(15)	O122-Mn5-O51=152.18(15)
	O72-Mn3-O61[3]=92.82(13)	O122-Mn5-O52=96.06(14)
	O72-Mn3-O62[3]=150.45(14)	O122-Mn5-O101=94.66(16)
	O72-Mn3-O131=93.58(18)	O122-Mn5-O102=96.98(17)

Symmetry code: [1] -X, 1-Y, -Z; [2] X, -1+Y, Z; [3] 1+X, Y, Z; [4] 1+X, Y, -1+Z.

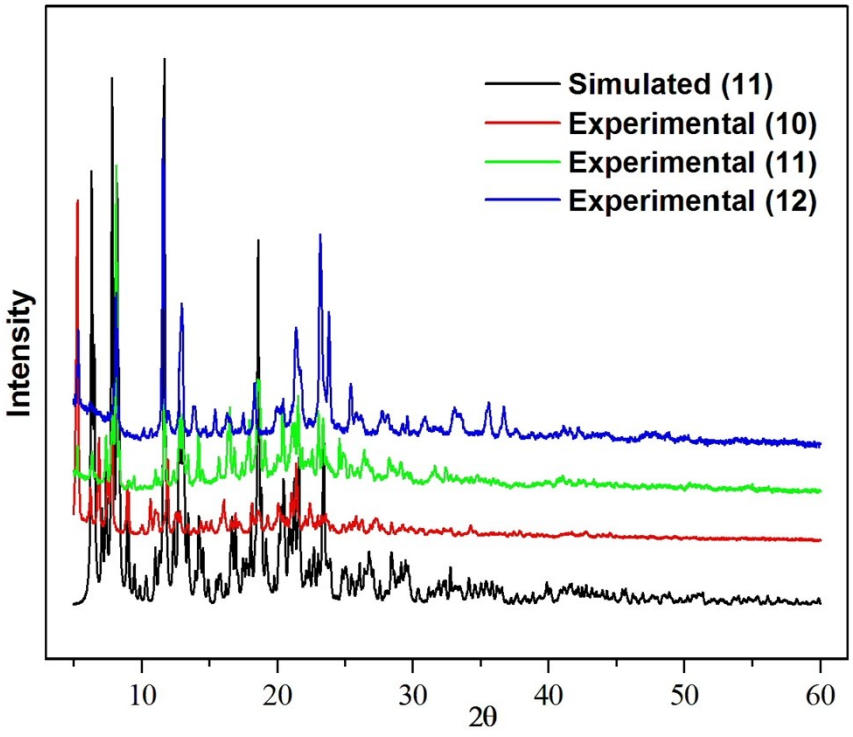


Fig. S1. Comparison of PXRD patterns of compounds **10** and **12** to those simulated and experimental PXRD patterns of compound **11**.

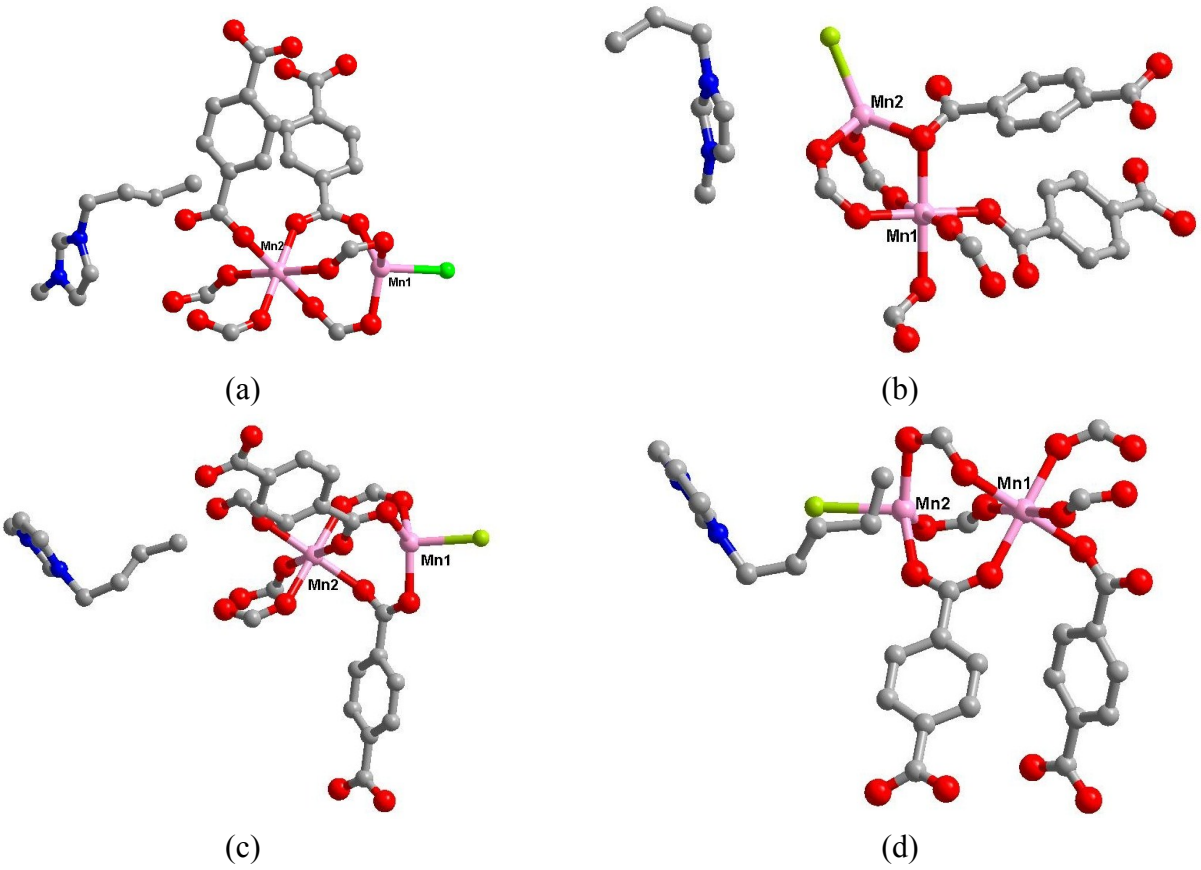
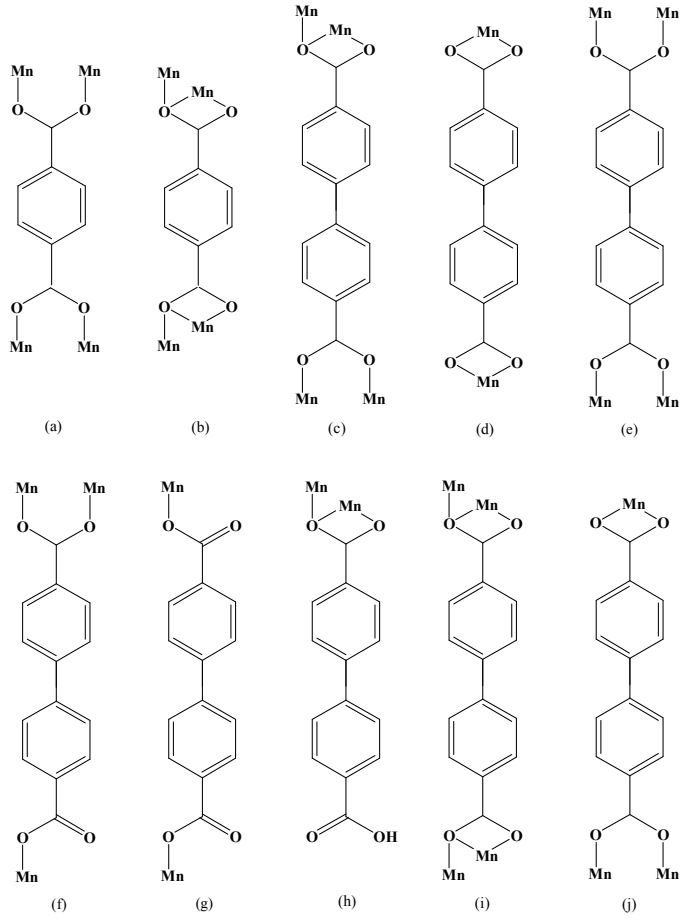


Fig. S2. The coordination spheres of Mn(III) centers in compounds **2** (a), **3** (b), **4** (c), **and 5** (d).



Scheme S1. The coordination fashions of BPDC^{2-} and BDC^{2-} ligands in compound **1-12**.

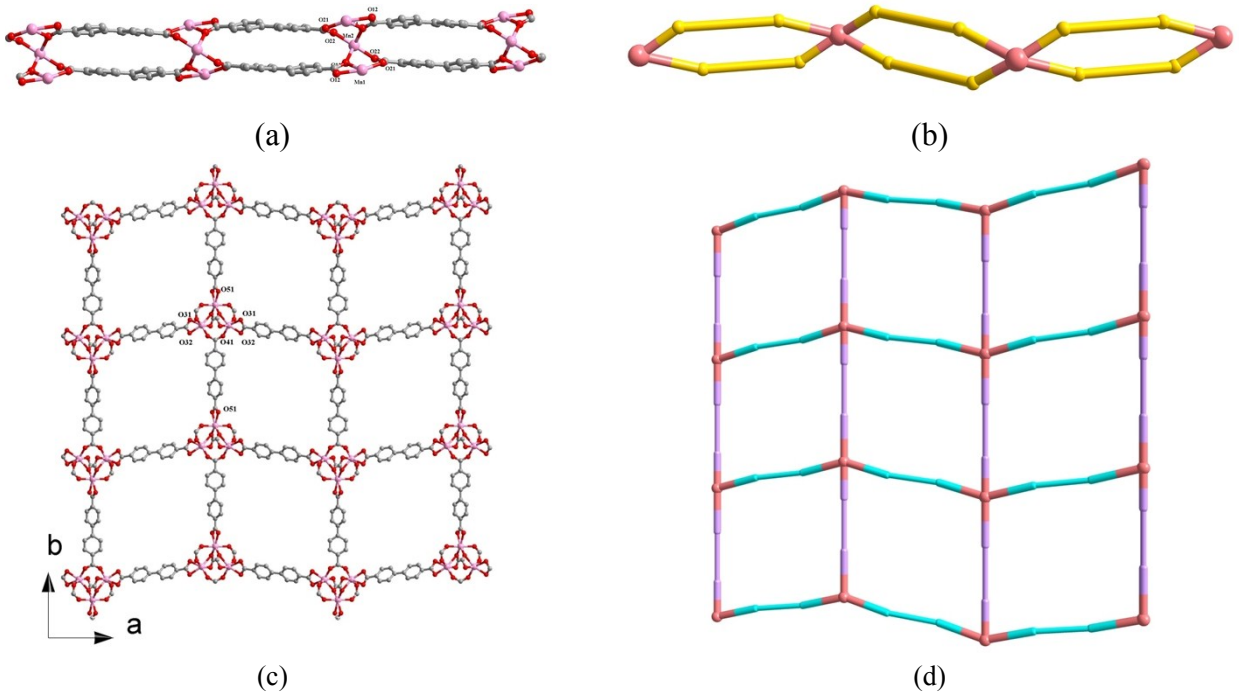


Fig. S3. The 1D chain (a) and topological (b) and 2D layer along the *ab*-plane (c) and topological (d) of compound **6**.

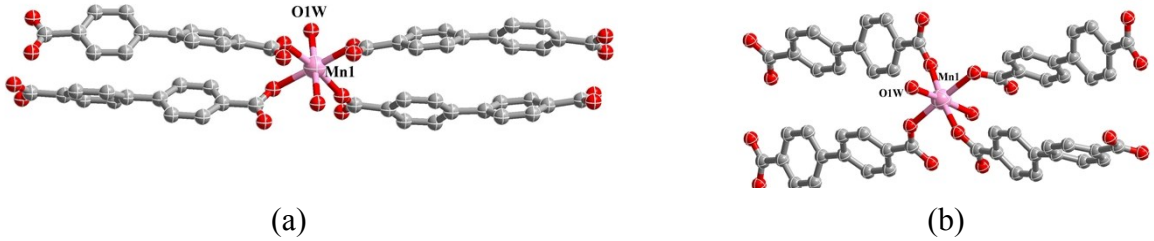


Fig. S4. The coordination spheres of Mn(III) centers in compounds **8** (a) and **9** (b).

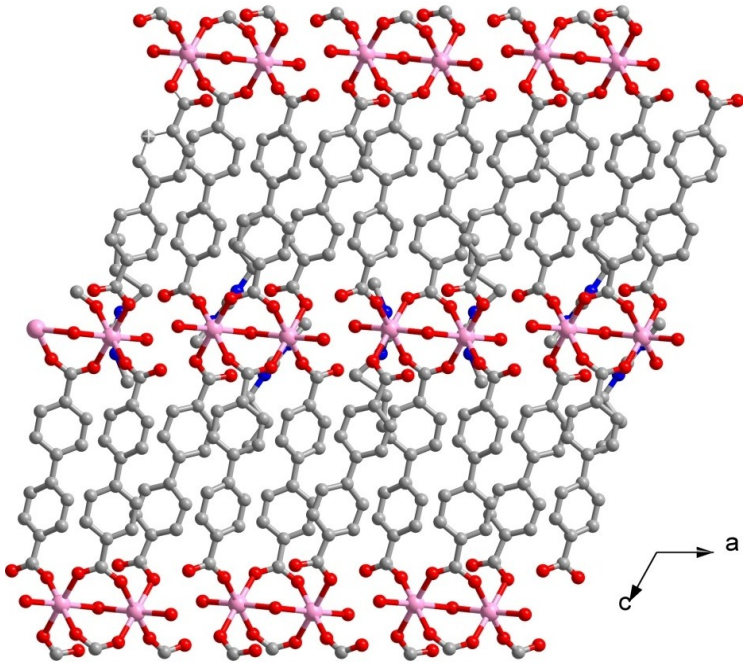


Fig. S5. The 2D layer of compound 7**.**

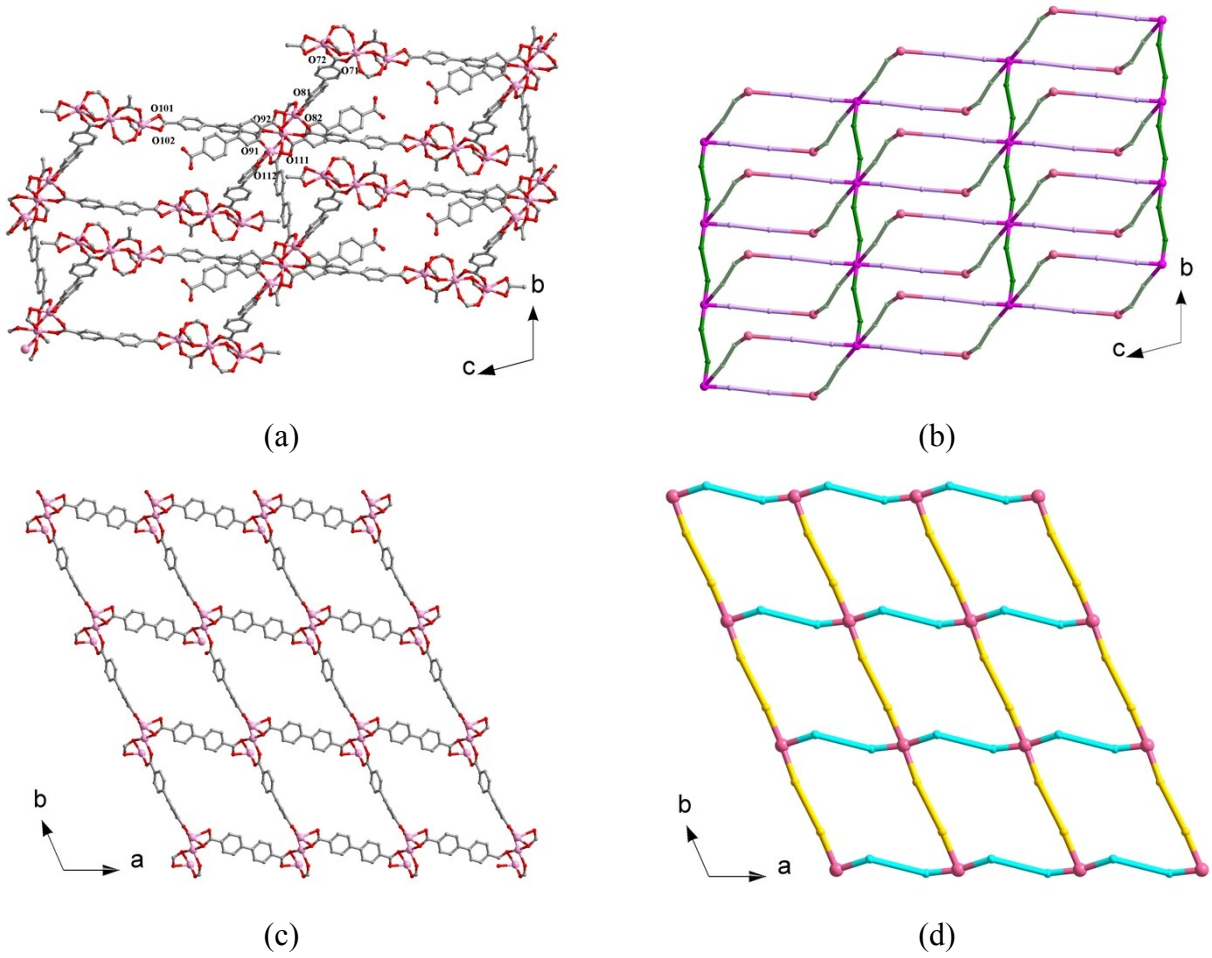
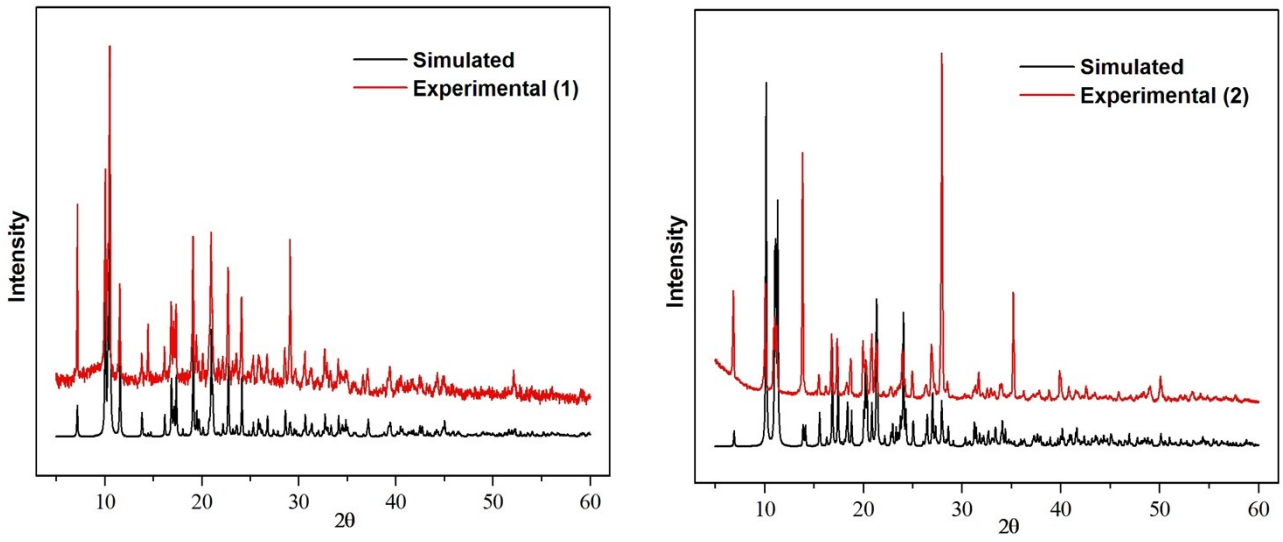


Fig. S6. The 2D layers of compound **11** along the *bc*-plane (a and b) and the *ab*-plane (c and d).



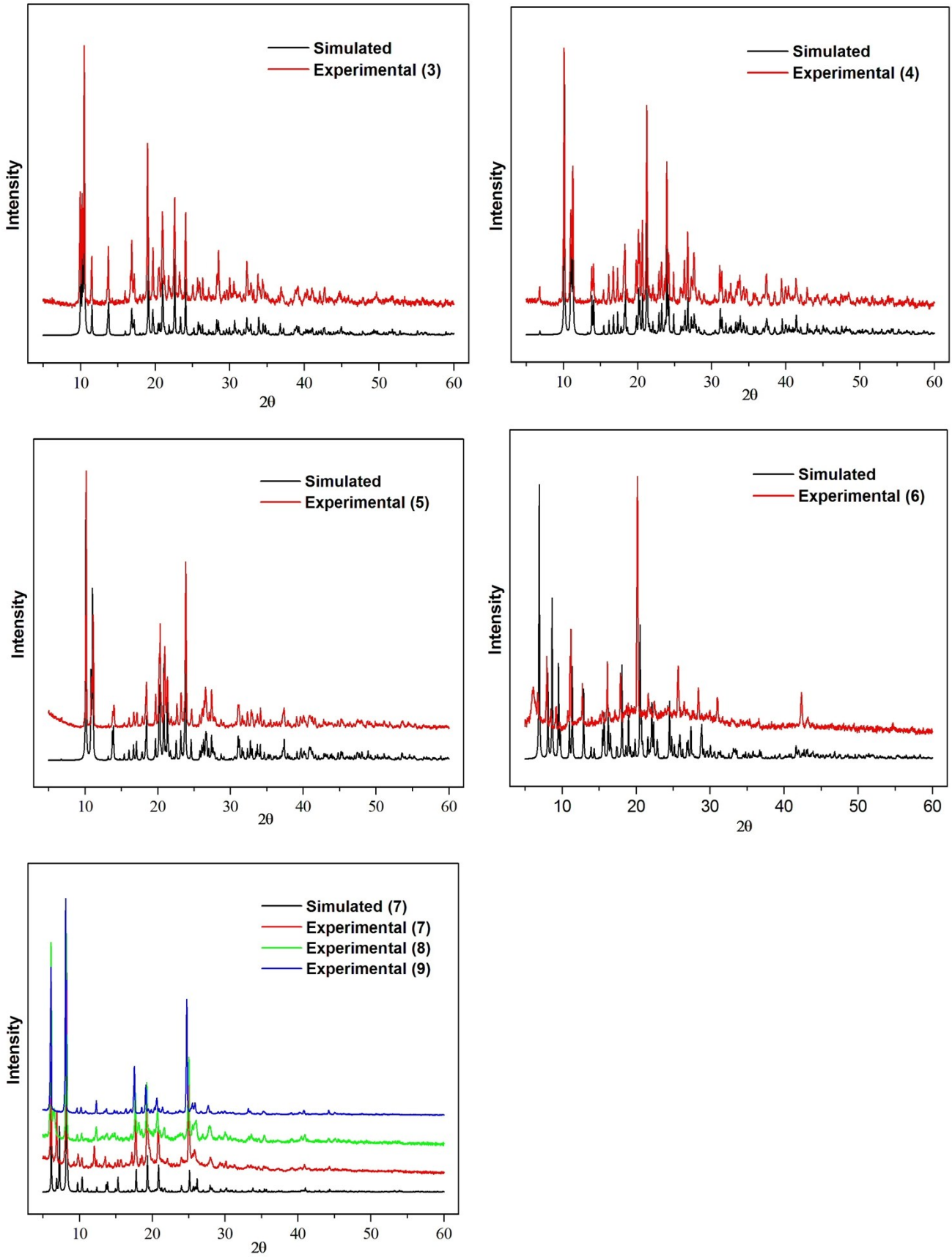


Fig. S7. Comparison of PXRD patterns of compounds **1-9** to those simulated from single crystal structure data.

Table S6. The main IR characteristic absorption peaks for compounds **1**–**12**.

compounds	$\upsilon_{as}(COO^-)/cm^{-1}$	$\upsilon s(COO^-)/cm^{-1}$	$\delta(C^-H)(MI)/cm^{-1}$	$\delta(C^-N)(MI)/cm^{-1}$	$\delta(C^-H)/(CH_3CH_2)cm^{-1}$
1	1639, 1563	1506, 1391	3146, 3108	1167	2967,2879
2	1639, 1559	1501, 1392	3146, 3098	1165	2962,2872
3	1595, 1567	1501, 1391	3146, 3102	1171	2962,2880
4	1615, 1569	1501, 1391	3146, 3098	1159	2952,2864
5	1632, 1559	1508, 1391	3146, 3090	1159	2960,2860
6	1699, 1577	1523, 1391	3154, 3102	1165	2980, 2931
7	1717,1581	1532, 1391	3140, 3106	1169	2968, 2880
8	1707,1587	1535, 1393	3152, 3110	1169	2960, 2936
9	1628, 1585	1537, 1391	3154, 3102	1166	2958, 2928
10	1714, 1605	1534, 1397	3154, 3114	1172	2966, 2928
11	1713, 1605	1541, 1396	3146, 3106	1172	2960, 2928
12	1687, 1604	1536, 1396	3146, 3106	1170	2960, 2928