Electronic Supplementary Material (ESI) for CrystEngComm

Seven structural versatile coordination polymers based on a flexible bis(triazole) and polycarboxylate co-ligands: Syntheses, structures and properties

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Thermogravimetric analysis

TG experiments were carried out to explore thermal stability of seven complexes (Fig. S9). In the TG curves of **1,** the coordination and lattice water molecules were lost from 75 to 150^{o}C (Calcd.: 18.25%, found: 18.42%). The remaining substance was stable upon heating to 325^{o}C. Then the framework began to decompose slowly and stopped at 787^{o}C. The remaining weight is attributed to the formation of MnO (Calcd.: 14.99%, found: 15.02%). Compounds **2** and **3** were stable up to 350 and 370^{o}C, respectively. Then **2** and **3** exhibited the rapid decomposition at the temperature of 355 – 550 and 375 – 600^{o}C, respectively. The remaining weight is attributed to the formation of MnO (Calcd.: 10.69%, found: 11.22% for **2**; Calcd.: 13.76%, found: 14.15% for **3**). For **4**, the whole framework is stable up to 325^{o}C and then the weight loss occured, which does not end until 790^{o}C. The remaining weight is 25.05%. **5** showed that the coordination and lattice water molecule were lost from 75 to 175^{o}C (Calcd.: 10.95%, found: 10.11%). The remaining substance was thermally stable upon heating to 265^{o}C and then exhibited a rapid decomposition at the temperature of 270 – 570^{o}C and the residue may be Co_2O_3 (Calcd: 19.22%; found: 18.90 %). The lattice water molecule of **6** was lost from100 to 175 ^{o}C (Calcd.: 1.33%, found:1.25 %). The framework was stable up to 380^{o}C and then suffered a sharp weight loss, which does not end until 789^{o}C. The remaining weight corresponds to the formation of NiO (Calcd.: 11.04%, found: 12.01%). **7** showed that the first weight loss of 2.32% appeared from 150 to 235^{o}C, which corresponded to the loss of one coordination

water molecule (Calcd: 2.86%). The framework begins to decompose quickly above 330^{o}C. Finally a plateau region is observed from 560 – 780 °C with NiO as the residue (Calcd: 11.87%; found: 11.82%).

Table S1 Selected bond lengths (Å) and angles (°) for **1-7.**

		1	
Mn(1)-O(1)	2.199(3)	Mn(1)-O(2)	2.456(3)
Mn(1)-O(4)#1	2.178(3)	Mn(1)-O(6)	2.183(3)
Mn(1)-O(7)	2.160(4)	Mn(1)-N(3)	2.231(4)
O(1)-Mn(1)-O(2)	55.85(11)	O(4)#1-Mn(1)-O(1)	84.76(12)
O(6)-Mn(1)-O(1)	137.75(13)	O(7)-Mn(1)-O(1)	90.03(14)
O(1)-Mn(1)-N(3)	90.94(15)	O(4)#1-Mn(1)-O(2)	140.58(11)
O(6)-Mn(1)-O(2)	81.90(12)	O(7)-Mn(1)-O(2)	88.99(13)
N(3)-Mn(1)-O(2)	93.30(14)	O(4)#1-Mn(1)-O(6)	137.49(13)
O(7)-Mn(1)-O(4)#1	92.79(13)	O(4)#1-Mn(1)-N(3)	85.21(14)
O(7)-Mn(1)-O(6)	88.51(14)	O(6)-Mn(1)-N(3)	92.18(15)
O(7)-Mn(1)-N(3)	177.68(14)		
		2	
Mn(1)-O(1)	2.112(3)	Mn(1)-O(3)#1	2.378(3)
Mn(1)-O(4)#1	2.231(2)	Mn(1)-N(3)	2.235(3)
Mn(1)-N(6)#2	2.278(3)	Mn(1)-N(9)	2.263(3)
O(1)-Mn(1)-O(3)#1	144.51(10)	O(1)-Mn(1)-O(4)#1	88.25(10)
O(1)-Mn(1)-N(3)	132.74(11)	O(1)-Mn(1)-N(6)#2	95.35(12)
O(1)-Mn(1)-N(9)	91.27(11)	O(4)#1-Mn(1)-O(3)#1	56.89(9)
N(3)-Mn(1)-O(3)#1	82.48(10)	N(6)#2-Mn(1)-O(3)#1	91.52(11)
N(9)-Mn(1)-O(3)#1	86.88(10)	O(4)#1-Mn(1)-N(3)	138.98(10)
O(4)#1-Mn(1)-N(6)#2	90.15(11)	O(4)#1-Mn(1)-N(9)	96.66(10)
N(3)-Mn(1)-N(6)#2	85.11(11)	N(3)-Mn(1)-N(9)	85.54(11)
N(9)-Mn(1)-N(6)#2	170.65(12)		
		3	
Mn(1)-O(1)	2.172(3)	Mn(1)-O(1)#1	2.172(3)
Mn(1)-O(2)#2	2.175(3)	Mn(1)-O(2)#3	2.175(3)
Mn(1)-N(3)	2.255(4)	Mn(1)-N(3)#1	2.255(4)
O(1)#1-Mn(1)-O(1)	180.00(14)	O(1)-Mn(1)-O(2)#2	86.95(11)
O(2)#2-Mn(1)-O(2)#3	180.00(17)	O(1)-Mn(1)-N(3)	88.60(11)
N(3)-Mn(1)-N(3)#1	180.00(16)	O(2)#2-Mn(1)-N(3)	85.83(12)
		4	
Co(1)-O(1)	1.998(2)	Co(1)-O(3)#1	2.000(2)
Co(1)-O(4)#1	2.371(2)	Co(1)-N(3)	2.041(2)
Co(1)-N(6)#2	2.054(2)		
O(1)-Co(1)-O(3)#1	108.77(10)	O(1)-Co(1)-O(4)#1	165.28(9)
O(1)-Co(1)-N(3)	109.33(10)	O(1)-Co(1)-N(6)#2	91.43(9)

O(3)#1-Co(1)-O(4)#1	59.44(8)	O(3)#1-Co(1)-N(3)	116.61(9)
O(3)#1-Co(1)-N(6)#2	112.93(9)	N(3)-Co(1)-O(4)#1	84.82(8)
N(6)#2-Co(1)-O(4)#1	86.05(9)	N(3)-Co(1)-N(6)#2	114.66(10)

5

Co(1)-O(1)	2.151(4)	Co(1)-O(3)	2.094(5)
Co(1)-O(10)	2.102(4)	Co(1)-O(12)	2.086(5)
Co(1)-N(3)	2.158(5)	Co(1)-N(6)#1	2.153(5)
Co(2)-O(1)	2.185(4)	Co(2)-O(1)#2	2.185(4)
Co(2)-O(2)	2.089(4)	Co(2)-O(2)#2	2.089(4)
Co(2)-O(19)	2.053(5)	Co(2)-O(19)#2	2.053(5)
Co(3)-O(13)	2.060(5)	Co(3)-O(13)#3	2.060(5)
Co(3)-O(20)	2.103(6)	Co(3)-O(20)#3	2.103(6)
Co(3)-O(21)	2.079(7)	Co(3)-O(21)#3	2.079(7)
Co(4)-O(5)#4	2.081(4)	Co(4)-O(7)#4	2.134(4)
Co(4)-O(14)	2.062(4)	Co(4)-O(22)	2.130(4)
Co(4)-O(23)	2.046(5)	Co(4)-N(9)	2.161(5)
Co(5)-O(6)#4	2.072(4)	Co(5)-O(15)	2.070(4)
Co(5)-O(16)	2.127(4)	Co(5)-O(24)	2.135(4)
Co(5)-O(25)	2.054(5)	Co(5)-N(12)	2.132(5)
O(3)-Co(1)-O(1)	87.12(17)	O(10)-Co(1)-O(1)	93.24(16)
O(12)-Co(1)-O(1)	173.54(17)	O(1)-Co(1)-N(3)	89.58(17)
O(1)-Co(1)-N(6)#1	94.08(18)	O(3)-Co(1)-O(10)	178.88(18)
O(12)-Co(1)-O(3)	88.63(18)	O(3)-Co(1)-N(3)	93.1(2)
O(3)-Co(1)-N(6)#1	88.8(2)	O(12)-Co(1)-O(10)	91.11(17)
O(10)-Co(1)-N(3)	87.9(2)	O(10)-Co(1)-N(6)#1	90.14(19)
O(12)-Co(1)-N(3)	85.81(18)	O(12)-Co(1)-N(6)#1	90.67(19)
N(6)#1-Co(1)-N(3)	175.9(2)	O(1)#2-Co(2)-O(1)	180.000(1)
O(2)#2-Co(2)-O(2)	180.0(3)	O(19)#2-Co(2)-O(19)	180.000(1)
O(2)-Co(2)-O(1)	61.73(15)	O(19)-Co(2)-O(1)	87.46(17)
O(19)-Co(2)-O(2)	90.1(2)	O(13)-Co(3)-O(13)#3	180.0(4)
O(20)#3-Co(3)-O(20)	180.0(4)	O(21)#3-Co(3)-O(21)	180.0(4)
O(13)-Co(3)-O(20)	93.4(2)	O(13)-Co(3)-O(21)	89.5(2)
O(21)-Co(3)-O(20)	90.3(3)	O(5)#4-Co(4)-O(7)#4	85.79(17)
O(14)-Co(4)-O(5)#4	93.62(16)	O(5)#4-Co(4)-O(22)	80.58(17)
O(23)-Co(4)-O(5)#4	165.50(17)	O(5)#4-Co(4)-N(9)	100.01(17)
O(14)-Co(4)-O(7)#4	175.65(17)	O(22)-Co(4)-O(7)#4	88.92(17)
O(23)-Co(4)-O(7)#4	91.5(2)	O(7)#4-Co(4)-N(9)	87.86(17)
O(14)-Co(4)-O(22)	86.73(18)	O(23)-Co(4)-O(14)	88.0(2)
O(14)-Co(4)-N(9)	96.48(18)	O(23)-Co(4)-O(22)	85.12(18)
O(22)-Co(4)-N(9)	176.68(18)	O(23)-Co(4)-N(9)	94.12(18)
O(15)-Co(5)-O(6)#4	93.18(16)	O(6)#4-Co(5)-O(16)	176.16(16)
O(6)#4-Co(5)-O(24)	87.38(17)	O(25)-Co(5)-O(6)#4	86.84(18)
O(6)#4-Co(5)-N(12)	93.50(18)	O(15)-Co(5)-O(16)	86.43(16)
O(15)-Co(5)-O(24)	79.43(17)	O(25)-Co(5)-O(15)	166.36(16)

O(15)-Co(5)-N(12)	98.98(17)	O(16)-Co(5)-O(24)	88.80(17)
O(25)-Co(5)-O(16)	92.63(18)	O(16)-Co(5)-N(12)	90.34(18)
O(25)-Co(5)-O(24)	86.95(18)	N(12)-Co(5)-O(24)	178.2(2)
O(25)-Co(5)-N(12)	94.63(18)		

6

Ni(1)-O(1)	2.204(2)	Ni(1)-O(2)	2.1206(19)
Ni(1)-O(4)#1	2.021(2)	Ni(1)-N(3)	2.098(3)
Ni(1)-N(6)#2	2.086(3)	Ni(1)-N(9)	2.081(2)
O(2)-Ni(1)-O(1)	60.94(7)	O(4)#1-Ni(1)-O(1)	95.74(8)
N(3)-Ni(1)-O(1)	150.15(9)	N(6)#2-Ni(1)-O(1)	89.89(9)
N(9)-Ni(1)-O(1)	92.25(9)	O(4)#1-Ni(1)-O(2)	156.57(9)
N(3)-Ni(1)-O(2)	89.24(9)	N(6)#2-Ni(1)-O(2)	90.66(9)
N(9)-Ni(1)-O(2)	88.65(9)	O(4)#1-Ni(1)-N(3)	114.11(9)
O(4)#1-Ni(1)-N(6)#2	91.57(9)	O(4)#1-Ni(1)-N(9)	90.18(9)
N(6)#2-Ni(1)-N(3)	89.00(10)	N(9)-Ni(1)-N(3)	88.16(10)
N(9)-Ni(1)-N(6)#2	177.09(10)		

7a

Ni(1)-O(1)	2.045(3)	Ni(1)-O(3)#2	2.101(3)
Ni(1)-O(4)#2	2.119(3)	Ni(1)-O(6)	2.042(3)
Ni(1)-N(3)	2.083(4)	Ni(1)-N(6)#1	2.097(4)
O(1)-Ni(1)-O(3)#2	163.93(12)	O(1)-Ni(1)-O(4)#2	102.14(12)
O(6)-Ni(1)-O(1)	95.88(13)	O(1)-Ni(1)-N(3)	94.42(13)
O(1)-Ni(1)-N(6)#1	86.92(13)	O(3)#2-Ni(1)-O(4)#2	62.60(11)
O(6)-Ni(1)-O(3)#2	99.73(12)	N(3)-Ni(1)-O(3)#2	89.81(14)
N(6)#1-Ni(1)-O(3)#2	87.51(14)	O(6)-Ni(1)-O(4)#2	161.60(12)
N(3)-Ni(1)-O(4)#2	86.56(13)	N(6)#1-Ni(1)-O(4)#2	88.03(14)
O(6)-Ni(1)-N(3)	88.38(14)	O(6)-Ni(1)-N(6)#1	96.70(15)
N(3)-Ni(1)-N(6)#1	174.59(15)		

7b

Ni(1)-O(1)	2.093(6)	Ni(1)-O(2)	2.133(6)
Ni(1)-O(3)#1	2.045(6)	Ni(1)-O(6)	2.028(7)
Ni(1)-N(3)	2.065(8)	Ni(1)-N(6)#2	2.100(7)
O(1)-Ni(1)-O(2)	62.7(2)	O(3)#1-Ni(1)-O(1)	163.9(2)
O(6)-Ni(1)-O(1)	99.5(3)	O(3)#1-Ni(1)-O(2)	101.8(3)
O(6)-Ni(1)-O(2)	161.6(3)	O(6)-Ni(1)-O(3)#1	96.2(3)
N(3)-Ni(1)-O(1)	89.8(3)	N(3)-Ni(1)-O(2)	86.8(3)
O(3)#1-Ni(1)-N(3)	93.8(3)	O(6)-Ni(1)-N(3)	88.3(3)
O(1)-Ni(1)-N(6)#2	87.5(3)	N(6)#2-Ni(1)-O(2)	88.4(3)
O(3)#1-Ni(1)-N(6)#2	87.7(3)	O(6)-Ni(1)-N(6)#2	96.1(3)
N(3)-Ni(1)-N(6)#2	175.1(3)		

Symmetry transformations used to generate equivalent atoms: #1 x, y-1, z for **1**; #1 x+1, y, z; #2 x, y, z-1 for **2**; #1 -x+1, -y+1, -z; #2 -x+2, -y+1, -z; #3 x-1, y, z for **3**; #1 x, y, z+1; #2 -x+1, -y+2, -z+1 for **4**; #1 x, y+1, z; #2 -x+1, -y, -z+1; #3 -x+1, -y, -z; #4 x-1, y+1, z for **5**; #1 x+1, y, z; #2 x, y, z+1 for **6**; #1 x+1/2, -y+1/2, -z; #2 x, y+1, z for **7a;** #1 x, y-1, z; #2 x-1/2, -y+3/2, -z for **7b**.

Table S2 Hydrogen bonds (Å and °) for **1.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(5)-H(5)···O(8)#4	0.83	1.83	2.640(6)	166.1
O(6)-H(1W)···O(3)#5	0.870(19)	1.84(2)	2.708(4)	177(5)
O(6)-H(2W)···O(5)#6	0.887(19)	1.929(19)	2.813(5)	175(4)
O(7)-H(3W)···O(9)	0.889(19)	1.83(2)	2.697(5)	164(4)
O(7)-H(4W)···O(4)#7	0.879(19)	1.95(2)	2.797(5)	162(5)
O(8)-H(5W)···O(7)#5	0.901(19)	2.53(4)	3.099(5)	122(4)
O(8)-H(6W)···O(2)	0.921(19)	1.79(3)	2.662(5)	157(6)
O(9)-H(7W)···O(6)#8	0.93(2)	2.25(3)	3.068(7)	146(5)
O(9)-H(8W)···O(10)	0.958(19)	1.83(4)	2.658(8)	143(5)

Symmetry transformations used to generate equivalent atoms: #4 x-1, y, z; #5 -x+1, -y+1, -z; #6 x+1, y, z; #7 -x, -y+1, -z; #8 -x+1, -y, -z.

Table S3 Hydrogen bonds (Å and °) for **5.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(19)-H(1W)···O(10)	0.84(2)	2.00(3)	2.745(6)	147(5)
O(19)-H(2W)···O(26)	0.84(2)	1.86(2)	2.698(7)	172(7)
O(20)-H(3W)···O(12)	0.847(19)	2.10(4)	2.709(7)	129(4)
O(20)-H(4W)···O(13)#3	0.85(2)	2.57(4)	2.856(7)	101(3)
O(21)-H(5W)...O(28)	0.86(2)	1.76(2)	2.618(10)	176(9)
O(21)-H(6W)...O(27)	0.86(2)	2.04(5)	2.830(10)	152(9)
O(22)-H(7W)...O(27)#9	0.86(2)	2.42(3)	3.246(9)	162(6)
O(22)-H(8W)...O(7)#3	0.84(2)	1.92(3)	2.744(6)	166(7)
O(23)-H(9W)...O(8)#3	0.85(2)	1.93(2)	2.780(7)	173(8)
O(23)-H(10W)...O(11)#1	0.85(2)	1.78(4)	2.575(6)	156(8)
O(24)-H(11W)...O(15)	0.838(19)	2.40(3)	2.687(6)	101(2)
O(24)-H(12W)...O(16)#10	0.849(19)	1.821(18)	2.666(6)	174(3)
O(25)-H(13W)...O(4)#9	0.84(2)	1.83(3)	2.651(6)	166(7)
O(25)-H(14W)...O(17)#10	0.85(2)	1.91(3)	2.730(6)	163(7)
O(26)-H(15W)...O(4)#2	0.85(2)	2.01(3)	2.837(8)	164(8)
O(26)-H(16W)...O(17)#6	0.85(2)	2.18(5)	2.896(7)	142(7)
O(27)-H(17W)...O(8)#1	0.86(2)	2.32(5)	3.052(9)	143(8)
O(27)-H(18W)...O(11)#3	0.86(2)	2.14(6)	2.838(8)	138(7)
O(28)-H(19W)...O(3)	0.86(2)	2.14(2)	2.949(8)	157(7)
O(28)-H(20W)...O(6)#1	0.87(2)	2.11(5)	2.869(7)	146(7)

Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z; #2 -x+1, -y, -z+1; #3 -x+1, -y, -z; #6 x, y-1, z; #9 x-1, y, z; #10 -x, -y+1, -z+1.

Table S4 Hydrogen bonds for **7a.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(6)-H(1W)···O(4)#5	0.855(18)	2.15(4)	2.841(4)	138(4)
O(6)-H(1W)···O(2)	0.855(18)	2.37(4)	2.838(5)	115(4)
O(6)-H(2W)···O(1)#4	0.860(19)	1.87(3)	2.682(5)	156(5)

Symmetry transformations used to generate equivalent atoms: #4 x-1/2, -y+1/2, -z; #5 x-1/2, -y-1/2, -z.

Table S5 Hydrogen bonds for **7b.**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(6)-H(1W)···O(3)#5	0.91(2)	1.85(4)	2.696(9)	154(7)
O(6)-H(2W)···O(2)#4	0.90(2)	2.24(3)	2.885(9)	128(3)

Symmetry transformations used to generate equivalent atoms: #4 x+1/2, -y+3/2, -z; #5 x+1/2, -y+5/2, -z .

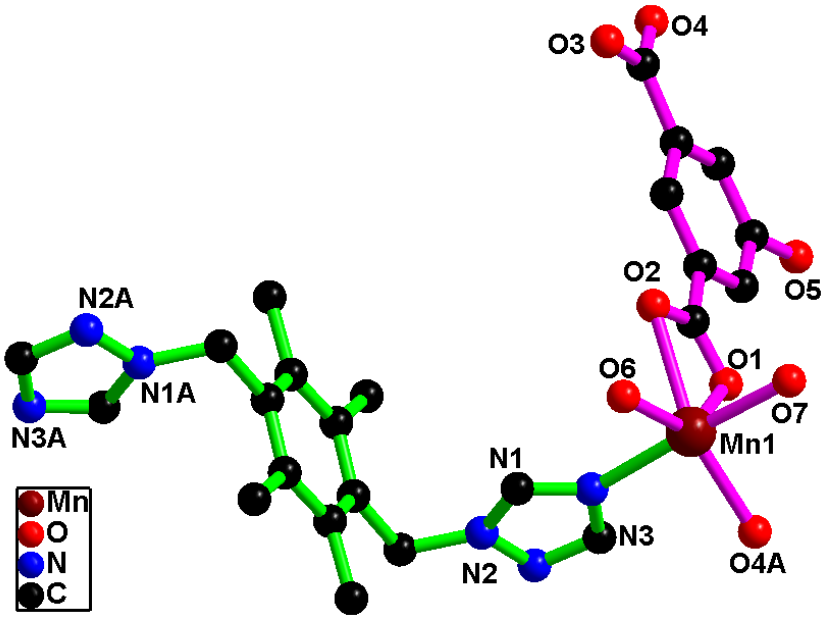

Fig. S1 The coordination environment of the Mn(II) atom in **1** (Symmetry codes: A x, y-1, z).

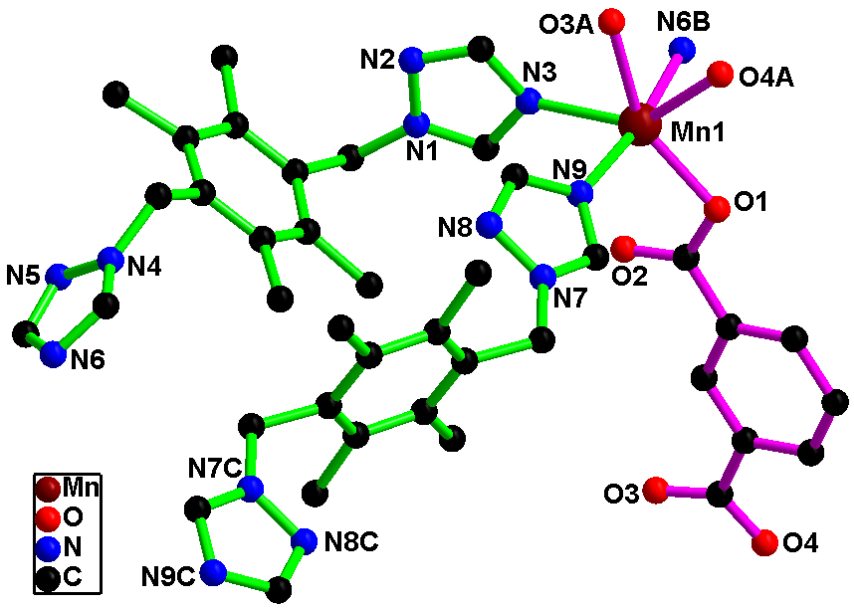

Fig. S2 The coordination environment of the Mn(II) atom in **2** (Symmetry codes: A x+1, y, z; B x, y, z-1).

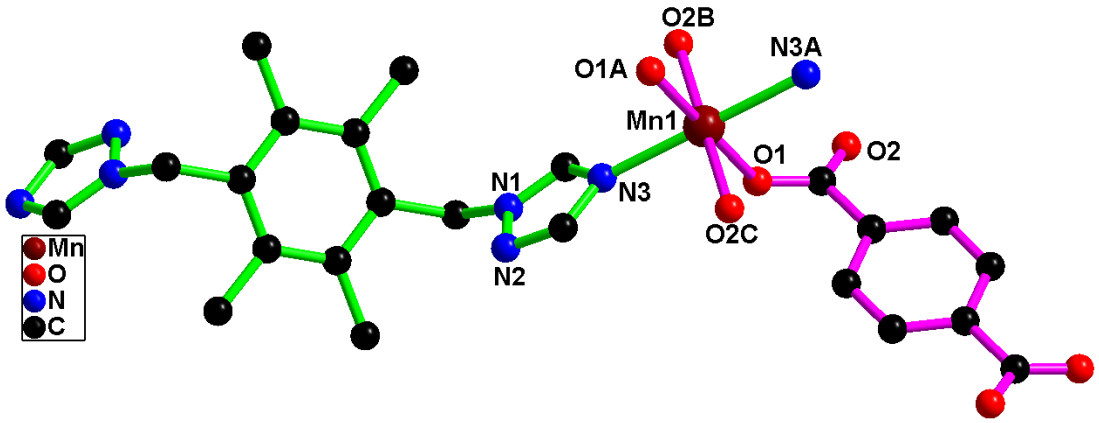

Fig. S3 The coordination environment of the Mn(II) atom in **3** (Symmetry codes: A -x+1, -y+1, -z; B -x+2, -y+1, -z; C x-1, y, z).

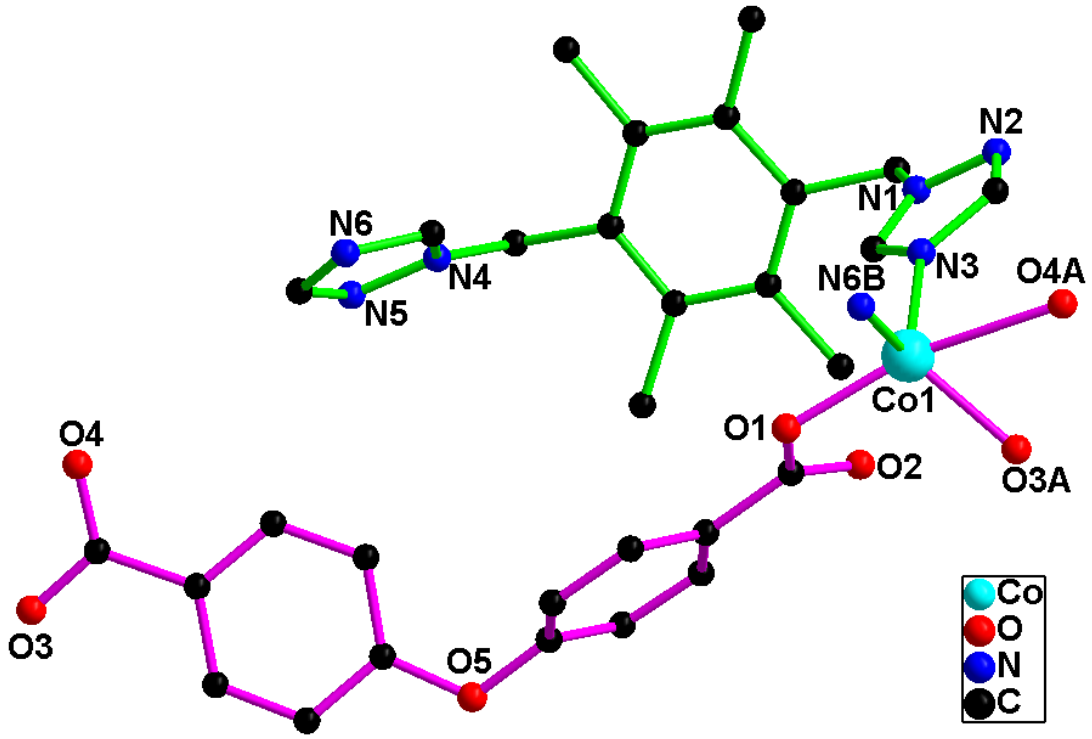

Fig. S4 (a) The coordination environment of the Co(II) atom in **4** (Symmetry codes: A x, y, z+1; B -x+1, -y+2, -z+1).

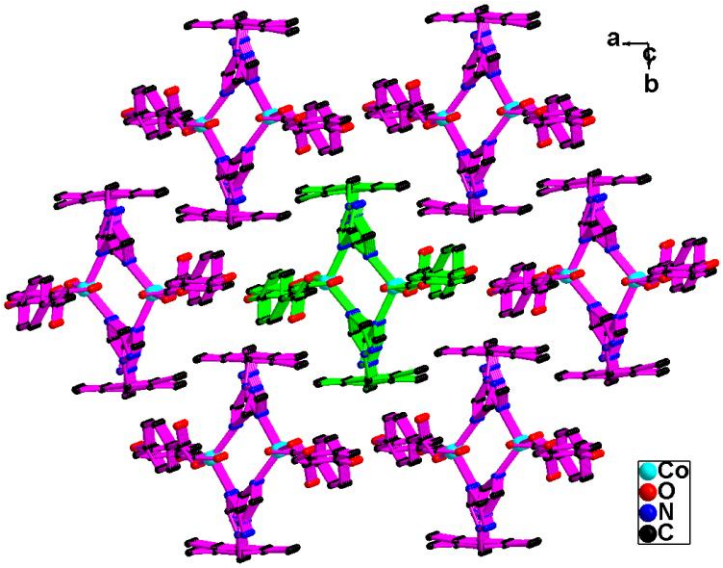

Fig. S4 (b) The stacking plot of the 1D tubular-like chains in **4**.

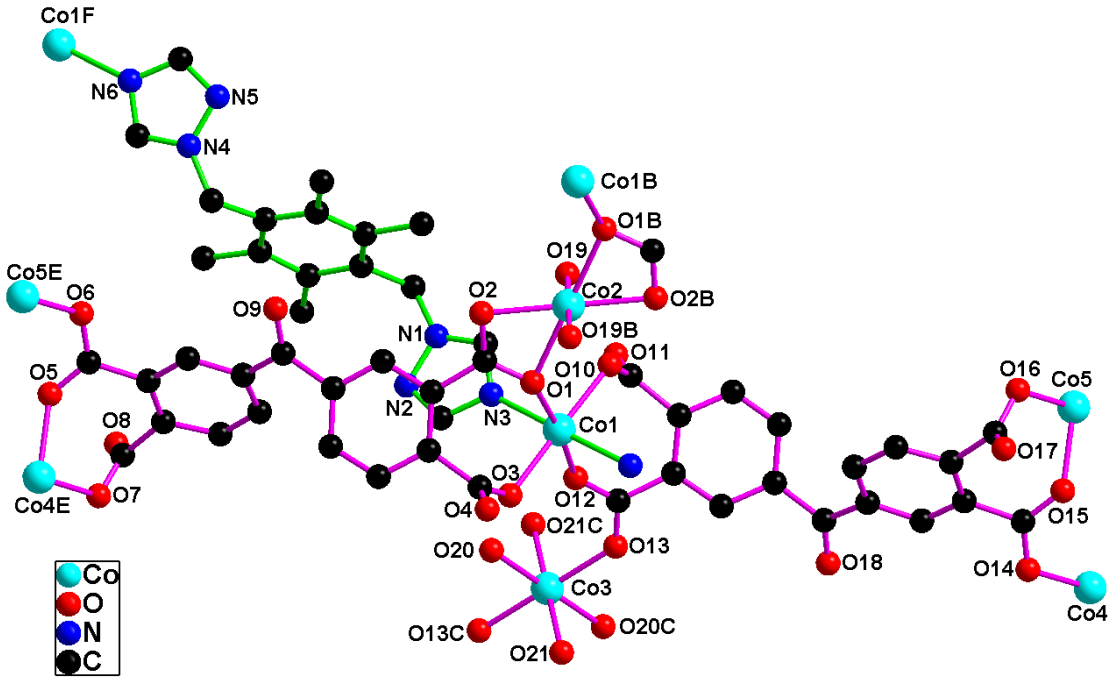

Fig. S5 (a) The coordination environments of the Co(II) atoms in **5** (Symmetry codes: A x, y+1, z; B -x+1, -y, -z+1; C -x+1, -y, -z; E x+1, y-1, z; F x, y-1, z).

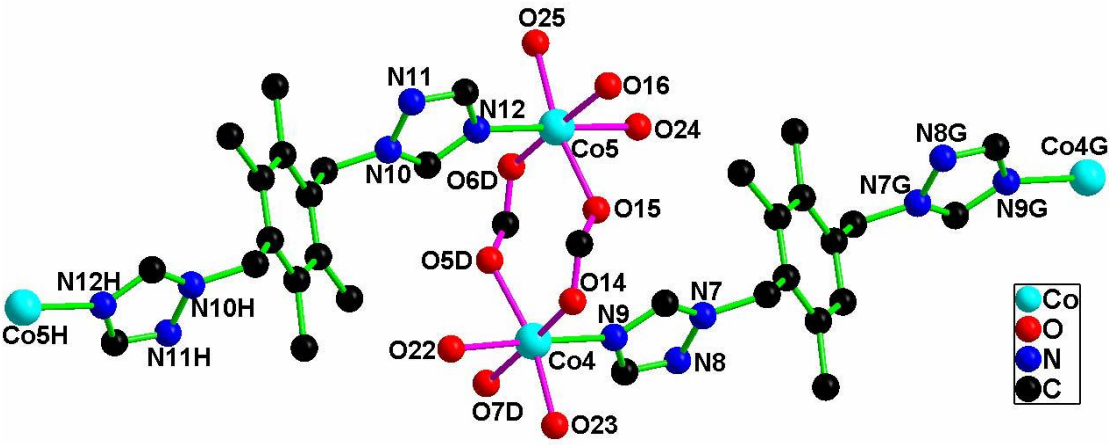

Fig. S5 (b) The coordination environments of the Co(II) atoms in **5** (Symmetry codes: D x-1, y+1, z; H -x, -y, -z; G –x, -y+2, -z+1).

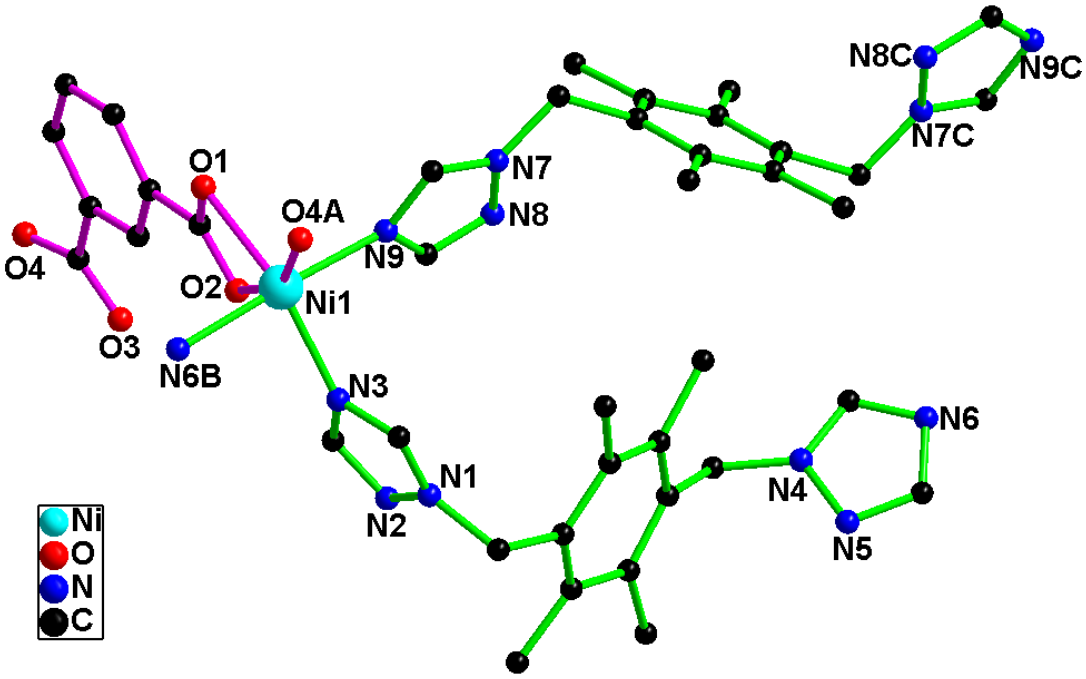

Fig. S6 (a) The coordination environment of the Ni(II) atom in **6** (Symmetry codes: A x+1, y, z; B x, y, z+1).

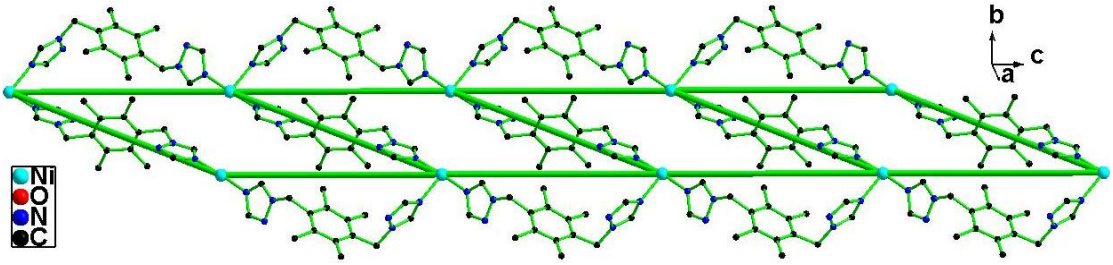

Fig. S6 (b) The $[Ni(tmtz)_{1.5}]_n$ 1D ladder in **6**.

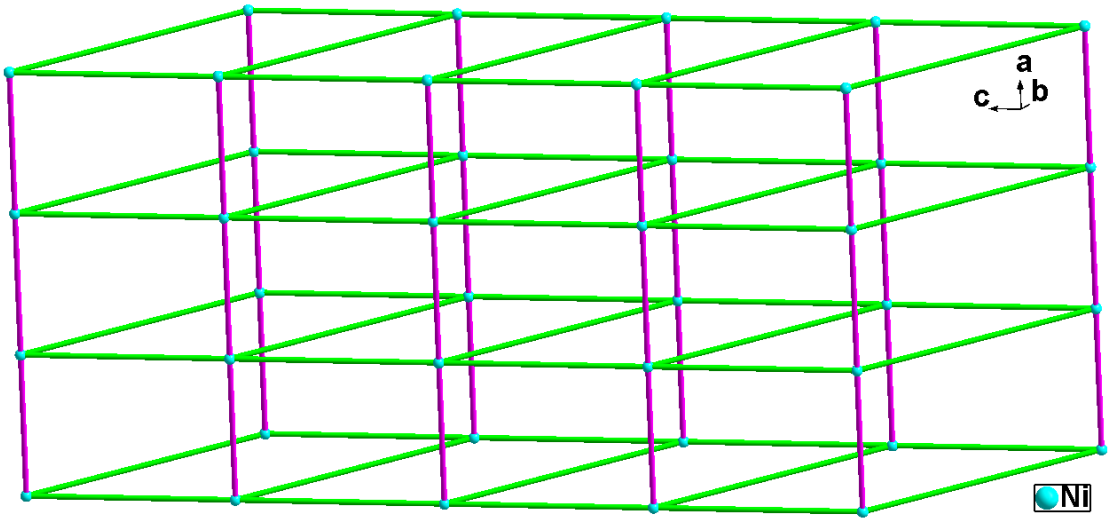

Fig. S6 (c) Schematic plot of the 5-connected 2D network in **6**. The bright green and pink sticks

present the tmtz and 1,3-bdc ligands, respectively. The turquiose balls show the Ni(II) atoms.

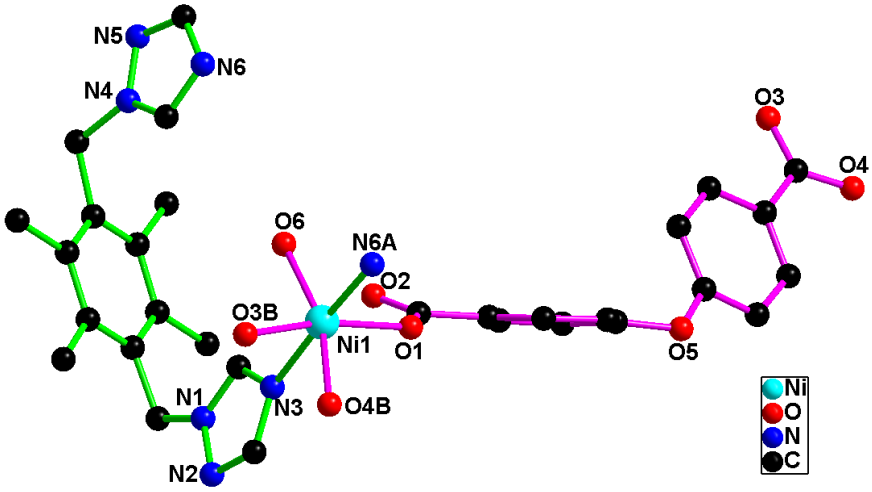

Fig. S7 (a) The coordination environment of the Ni(II) atom in 7a (Symmetry codes: A x+1/2, -y+1/2, -z; B x, y+1, z).

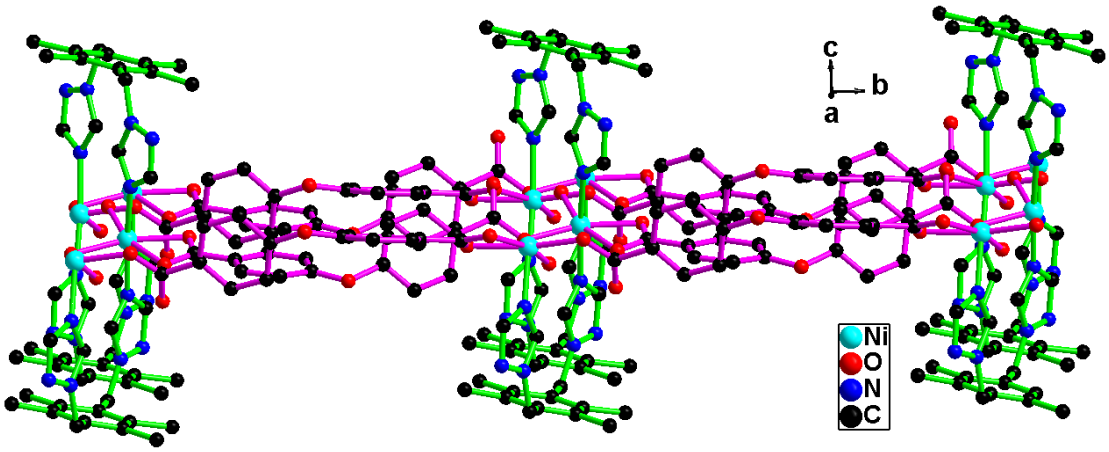

Fig. S7 (b) View the 2D (4,4) network along the a-axis direction in **7a**.

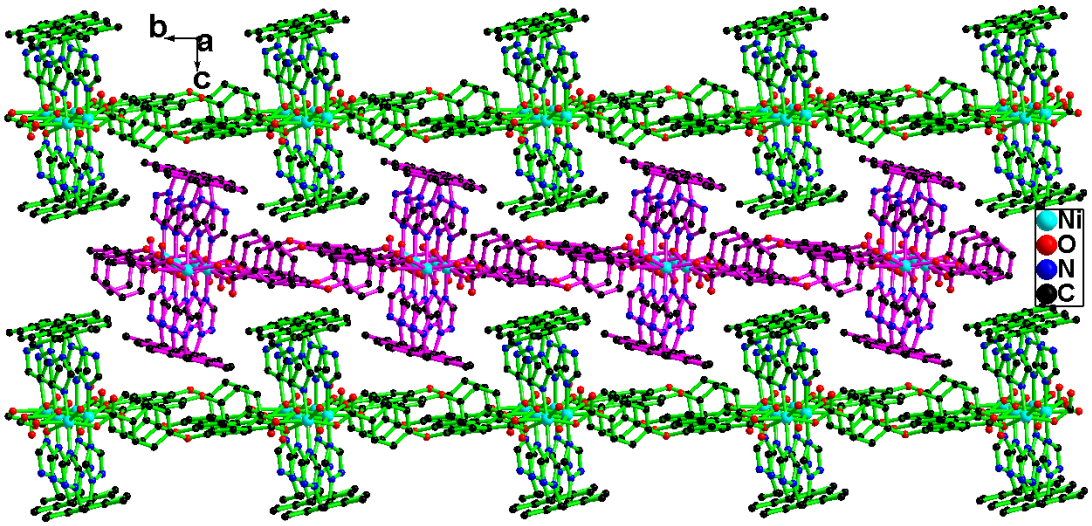

Fig. S7 (c) The stacking plot of the 2D (4,4) networks in **7a**.

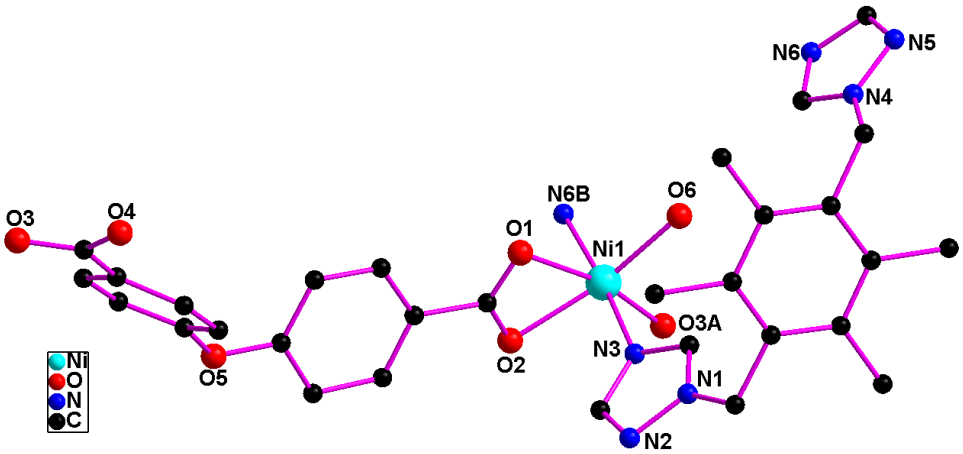

Fig. S8 The coordination environment of the Ni(II) atom in **7b** (Symmetry codes: A x, y-1, z; B x-1/2, -y+3/2, -z).

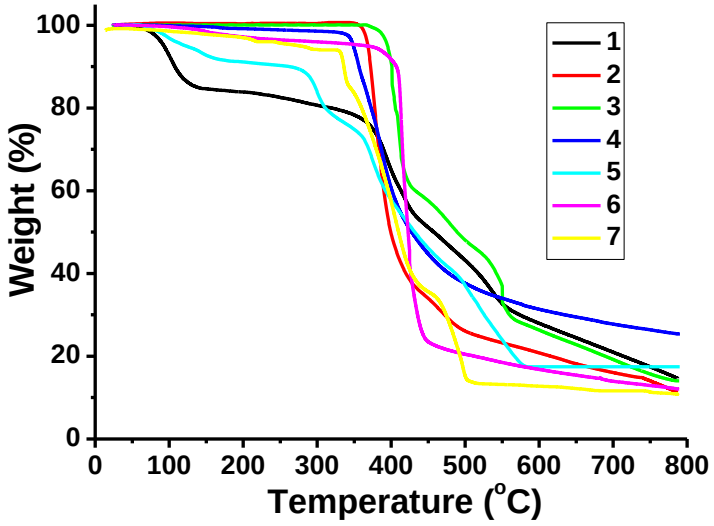

Fig. S9 The TG curves of **1-7**.

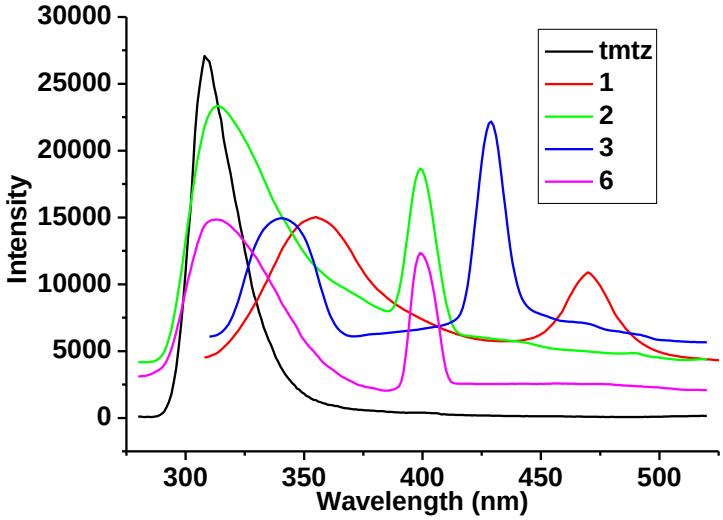

Fig. S10 The luminescent emissions of complexes and free tmtz ligand in the solid state at room temperature.

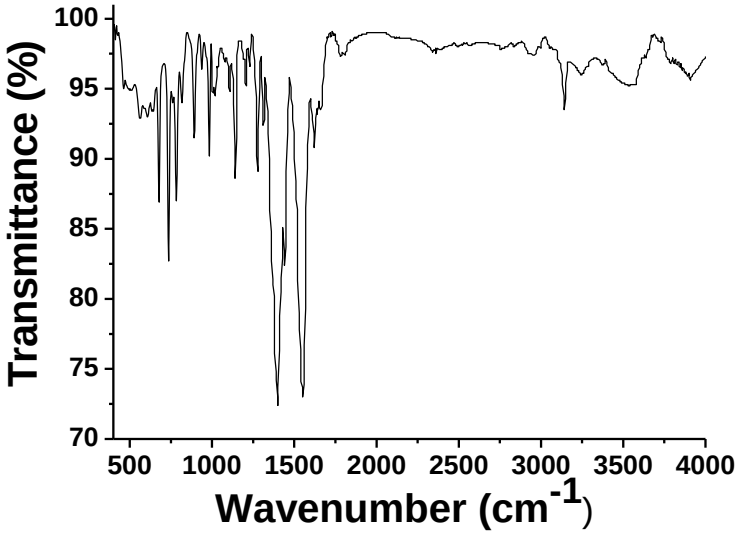

Fig. S11 (a) IR spectrum of **1**.

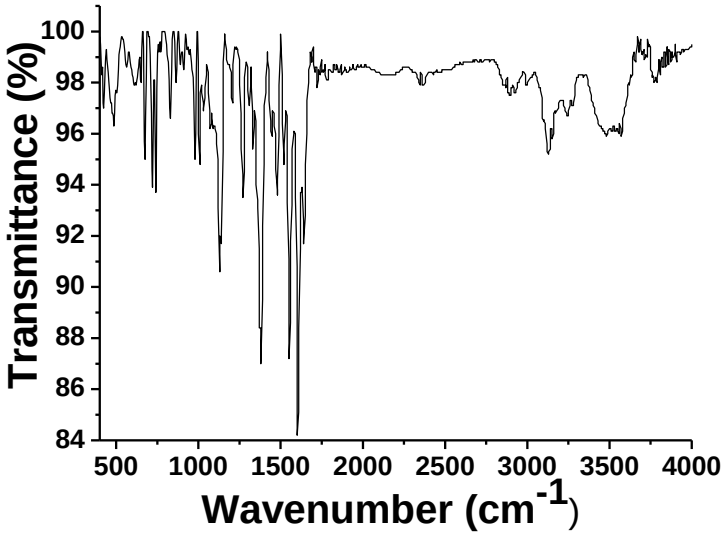

Fig. S11 (b) IR spectrum of **2**.

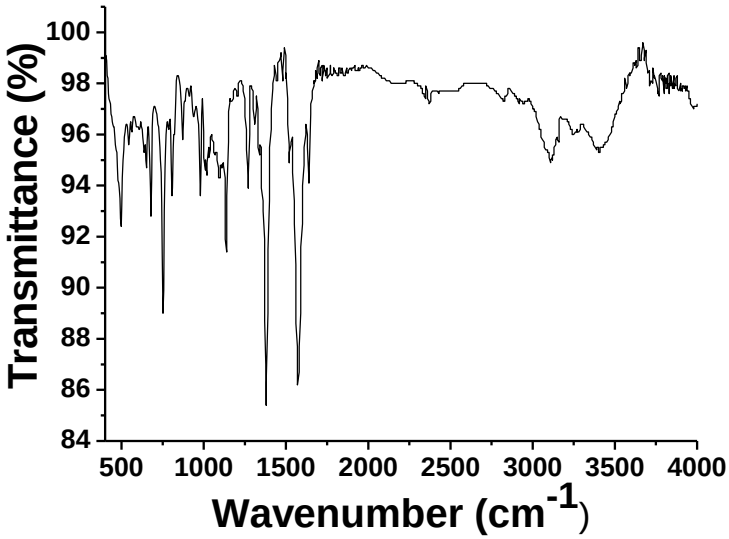

Fig. S11 (c) IR spectrum of **3**.

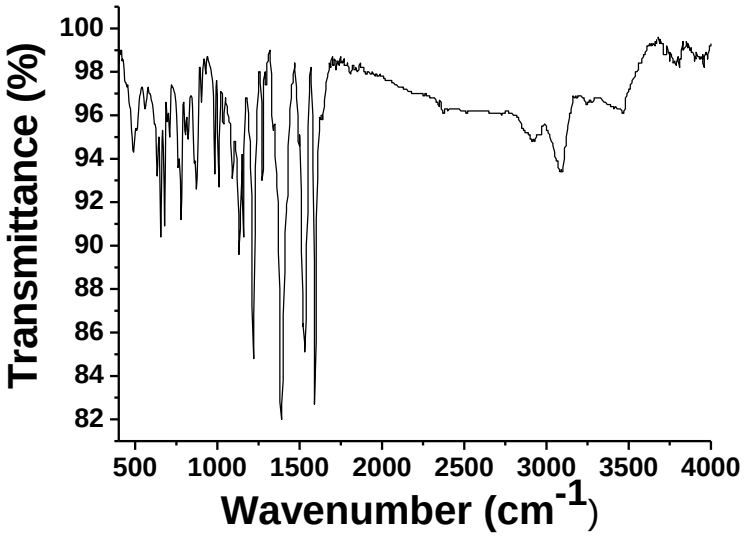

Fig. S11 (d) IR spectrum of **4**.

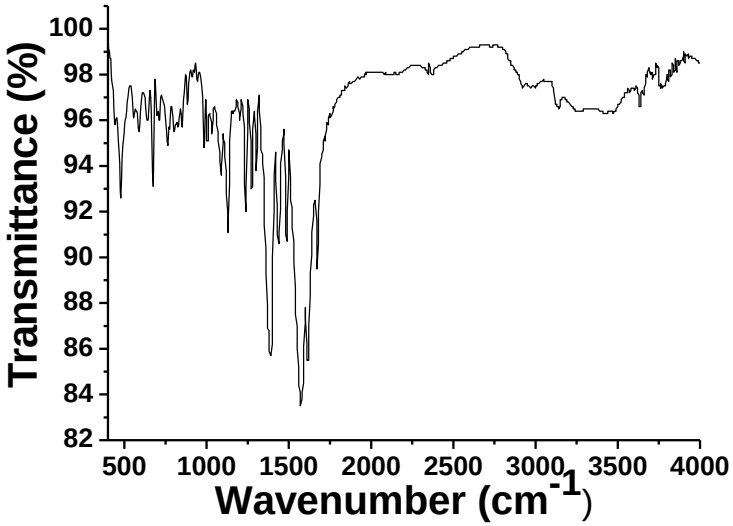

Fig. S11 (e) IR spectrum of **5**.

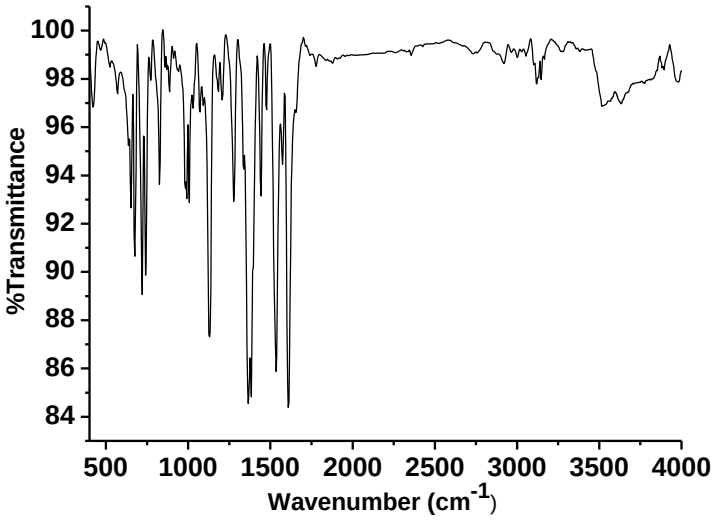

Fig. S11 (f) IR spectrum of **6**.

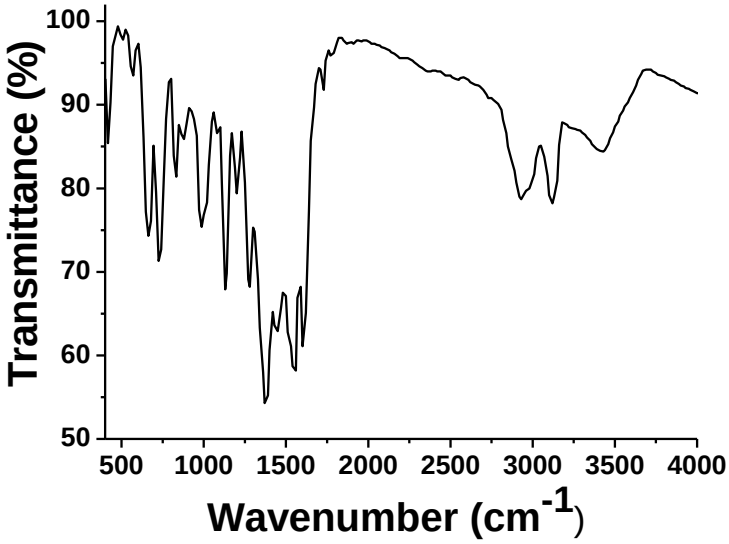

Fig. S11 (g) IR spectrum of **7**.