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Exceptional sensitivity to synthetic approach and halogen substituent for Zn(II) coordination assemblies with 5-halonicotinic acids

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Table S1 Crystal data and structural refinement summary for complexes **1**–**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Chemical formula	$C_{12}H_6F_2N_2O_4Zn$	$C_{24}H_{26}Cl_4N_4O_{15}Zn_2$	$C_{12}H_9Cl_2N_2O_{5.5}Zn$	$C_{24}H_{14}Cl_4N_4O_9Zn_2$	$C_{26.5}H_{24}Br_4N_4O_{11.5}Zn_2$	$C_{24}H_{22}Br_4N_4O_{12}Zn$	$C_{12}H_{8.3}Br_2N_2O_{5.15}Zn$
Formula Mass	345.56	883.07	405.48	774.93	1032.88	943.47	488.10
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	12.2658(16)	14.8972(5)	7.7158(8)	12.0840(17)	14.910(3)	15.3861(15)	7.782(5)
b (Å)	20.425(3)	16.8530(4)	7.7397(8)	9.8218(14)	17.044(3)	6.8845(7)	7.787(5)
c (Å)	9.6121(16)	14.5964(5)	25.946(3)	11.9104(16)	14.696(3)	29.387(3)	26.565(17)
β (°)	90.00	119.614(5)	98.273(2)	94.035(3)	120.49	90.112(2)	96.944(13)
Unit cell volume (Å^3)	2408.1(6)	3185.92(17)	1533.3(3)	1410.1(3)	3218.4(10)	3112.9(5)	1598.0(18)
Space group	*Fdd*2	*C*2/*c*	*P*2/*c*	*C*2/*c*	*C*2/*c*	*P*2/*c*	*P*2/*c*
Z	8	4	1	2	4	4	4
μ (mm^{-1})	2.084	5.646	1.756	2.140	6.524	5.990	6.561
No. of reflections measured	4323	5918	11194	5127	9114	18502	8192
No. of independent reflections	1486	3074	3848	1756	2847	7290	3786
R_{int}	0.0434	0.0322	0.0387	0.0319	0.0428	0.0420	0.0837
Final R values ($I > 2\sigma(I)$)	0.0265	0.0417	0.0413	0.0326	0.0305	0.0431	0.1101
Final R_w (F^2) values ($I > 2\sigma(I)$)	0.0618	0.1197	0.1047	0.0780	0.0691	0.0910	0.2363
Final R values (all data)	0.0278	0.0468	0.0554	0.0413	0.0385	0.1012	0.1467
Final R_w (F^2) values (all data)	0.0623	0.1246	0.1112	0.0826	0.0717	0.1086	0.2508
Goodness of fit on F^2	1.103	1.072	1.069	1.133	1.089	1.010	1.095

Table S2 Selective bond lengths (Å) and angles (°) for complexes **1**–**7**

		1	
Zn1–O1	2.0168(19)	Zn1–N1B	2.099(2)
Zn1–O2A	2.401(2)		
O1–Zn1–O1A	150.73(12)	O1A–Zn1–N1B	101.75(9)
O1–Zn1–N1B	96.01(8)	O1A–Zn1–O2	98.58(8)
O1–Zn1–O2	58.95(8)	N1B–Zn1–O2	153.71(7)
N1C–Zn1–O2	89.36(8)	O2–Zn1–O2A	87.00(11)
N1B–Zn1–N1C	104.77(12)		
		2	
Zn1–O1	2.087(2)	Zn1–O2A	2.104(2)
Zn1–O5	2.1333(16)	Zn1–N1B	2.140(2)
Zn1–N2C	2.184(2)	Zn1–O3	2.192(2)
O1–Zn1–O2A	98.59(9)	O1–Zn1–O5	88.32(7)
O2A–Zn1–O5	90.36(9)	O1–Zn1–N1B	93.13(9)
O2A–Zn1–N1B	83.60(9)	O5–Zn1–N1B	173.93(8)
O1–Zn1–N2C	88.50(9)	O2A–Zn1–N2C	170.25(9)
O5–Zn1–N2C	96.57(9)	N1B–Zn1–N2C	89.36(9)
O1–Zn1–O3	175.30(9)	O2A–Zn1–O3	83.37(9)
O5–Zn1–O3	87.39(7)	N1B–Zn1–O3	91.33(9)
N2C–Zn1–O3	90.07(9)		
		3	
Zn1–O4A	2.027(2)	Zn1–O2	2.041(2)
Zn1–N2	2.071(2)	Zn1–N1B	2.078(2)
Zn1–O1	2.356(2)	Zn1–O3A	2.361(3)

O4A–Zn1–O2	147.76(11)	O4–Zn1–N2	94.76(9)
O2–Zn1–N2	109.94(10)	O4A–Zn1–N1B	102.40(10)
O2–Zn1–N1B	94.77(9)	N2–Zn1–N1B	97.52(9)
O4A–Zn1–O1	100.15(10)	O2–Zn1–O1	58.98(8)
N2–Zn1–O1	93.95(9)	N1B–Zn1–O1	153.68(9)
O4A–Zn1–O3A	58.51(9)	O2–Zn1–O3A	94.20(10)
N2–Zn1–O3A	153.08(9)	N1B–Zn1–O3A	91.96(10)
O1–Zn1–O3A	88.33(9)		

4

Zn1–O2A	2.041(5)	Zn1–O1B	2.351(5)
Zn1–N1	2.099(4)		
O2A–Zn1–O2B	156.1(3)	O2A–Zn1–N1	94.86(18)
O2B–Zn1–N1	101.28(19)	N1C–Zn1–N1	94.9(2)
O2A–Zn1–O1B	103.4(2)	N1–Zn1–O1B	90.54(17)
O2A–Zn1–O1A	59.33(19)	N1–Zn1–O1A	154.20(17)
O1B–Zn1–O1A	95.4(2)		

5

Zn1–O4A	2.095(2)	Zn1–O3B	2.220(3)
Zn1–O5	2.116(2)	Zn1–N2	2.132(3)
Zn1–N1	2.175(3)	Zn1–O2C	2.220(3)
O4A–Zn1–O3B	99.51(10)	O4A–Zn1–O5	87.97(8)
O3B–Zn1–O5	90.15(10)	O4A–Zn1–N2	93.69(11)
O3B–Zn1–N2	83.63(11)	O5–Zn1–N2	173.74(11)
O4A–Zn1–N1	88.40(11)	O3B–Zn1–N1	169.59(10)
O5–Zn1–N1	96.93(11)	N2–Zn1–N1	89.15(12)
O4A–Zn1–O2C	174.21(10)	O3B–Zn1–O2C	82.95(10)
O5–Zn1–O2C	86.78(8)	N2–Zn1–O2C	91.78(11)
N1–Zn1–O2C	89.81(11)		

6

Zn1–O5	2.046(3)	Zn1–O6	2.071(3)
Zn1–N1	2.239(3)	Zn2–N2	2.176(3)
Zn2–O8	2.106(3)	Zn2–O7	2.111(3)
O5–Zn1–O5A	89.94(19)	O5A–Zn1–O6	177.43(12)
O5–Zn1–O6	90.05(16)	O6A–Zn1–O6	90.1(3)
O5–Zn1–N1A	89.67(12)	O5–Zn1–N1	92.88(13)
O6–Zn1–N1	87.77(13)	O6A–Zn1–N1	89.68(13)
N1A–Zn1–N1	176.40(19)	O8–Zn2–O7	91.94(12)
N2–Zn2–O7	88.07(12)	O8–Zn2–N2	92.15(12)

7

Zn1–O4B	2.026(9)	Zn1–O2A	2.358(9)
Zn1–N2	2.101(8)	Zn1–N1	2.089(10)
Zn1–O1A	2.063(9)	Zn1–O3B	2.409(11)
O4B–Zn1–O1A	147.9(4)	O4B–Zn1–N1	95.2(4)
O1A–Zn1–N1	109.7(4)	O4B–Zn1–N2	103.1(4)
O1A–Zn1–N2	94.2(3)	N2–Zn1–N1	96.3(4)
O4B–Zn1–O2A	99.3(4)	O2A–Zn1–O1A	59.7(3)
N1–Zn1–O2A	95.0(4)	N2–Zn1–O2A	153.8(3)
O4B–Zn1–O3B	58.5(4)	O1A–Zn1–O3B	95.1(4)
N1–Zn1–O3B	153.7(4)	N2–Zn1–O3B	90.5(4)
O2A–Zn1–O3B	89.7(4)		

Symmetry codes: A = $-x + 1/2, -y + 1/2, z$; B = $x + 1/2, y, z + 1/2$; C = $-x, -y + 1/2, z + 1/2$ for **1**; A = $-x + 1, y, -z + 1/2$; B = $x, -y, z + 1/2$; C = $x - 1/2, -y + 1/2, z - 1/2$ for **2**; A = $x + 1, y, z$; B = $x, y - 1, z$ for **3**; A = $x + 1/2, y + 1/2, z$; B = $-x + 1/2, y + 1/2, -z + 1/2$; C = $-x + 1, y, -z + 1/2$ for **4**; A = $x - 1/2, -y + 1/2, z - 1/2$; B = $-x + 1/2, -y + 1/2, -z + 1$; C = $x, -y, z + 1/2$ for **5**; A = $-x, y, -z + 3/2$ for **6**; A = $x, y + 1, z$; B = $x - 1, y, z$ for **7**.

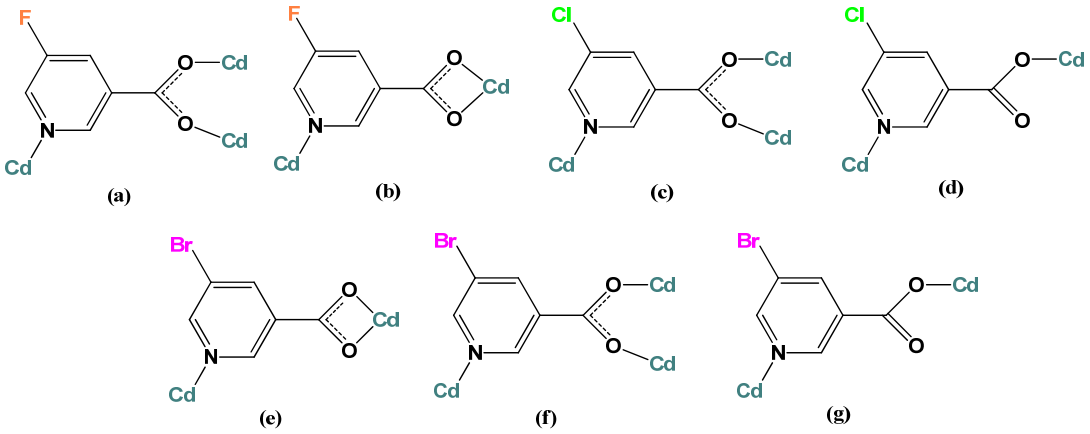
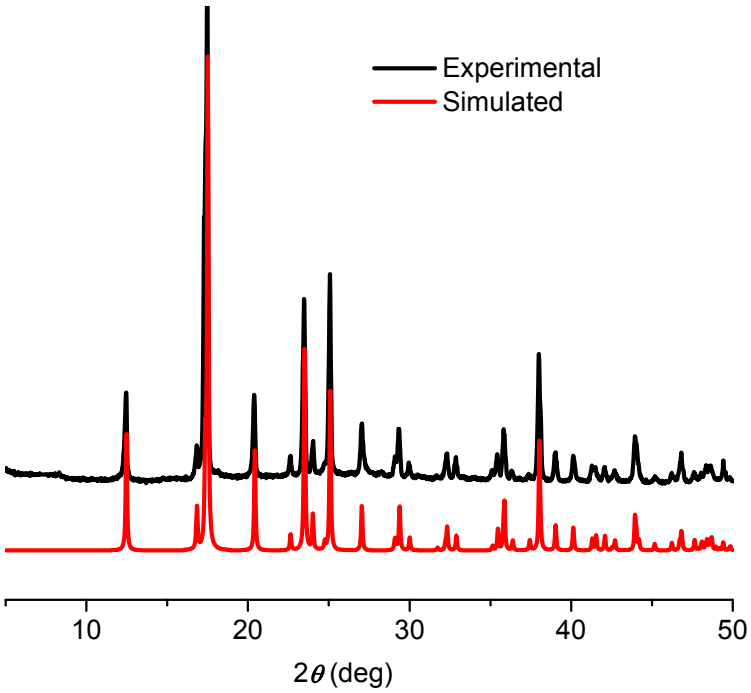
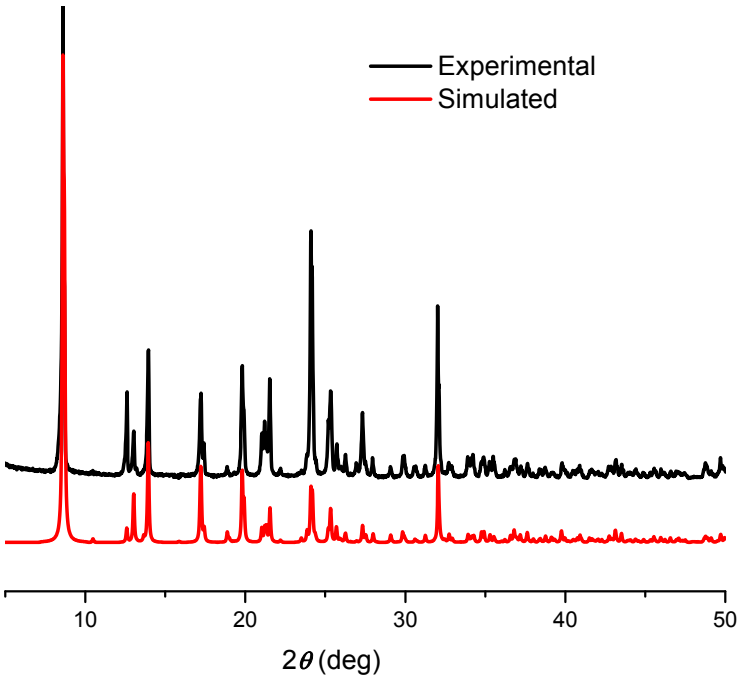


Chart S1 Coordination modes of HL-X ligands in reported Cd(II) complexes.


Experimental
Simulated
10
20
30
40
50
2θ (deg)

(a)


Experimental
Simulated
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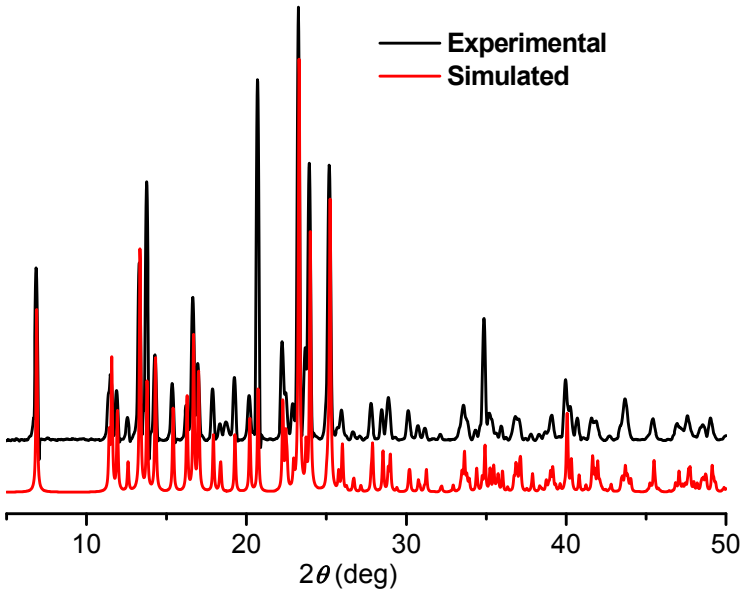
20
30
40
50
2θ (deg)

(b)


Experimental
Simulated
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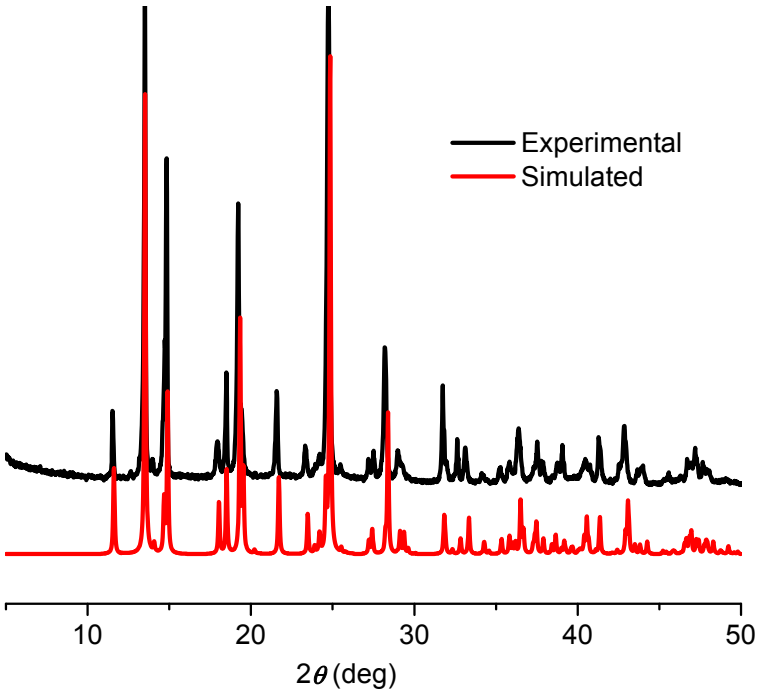
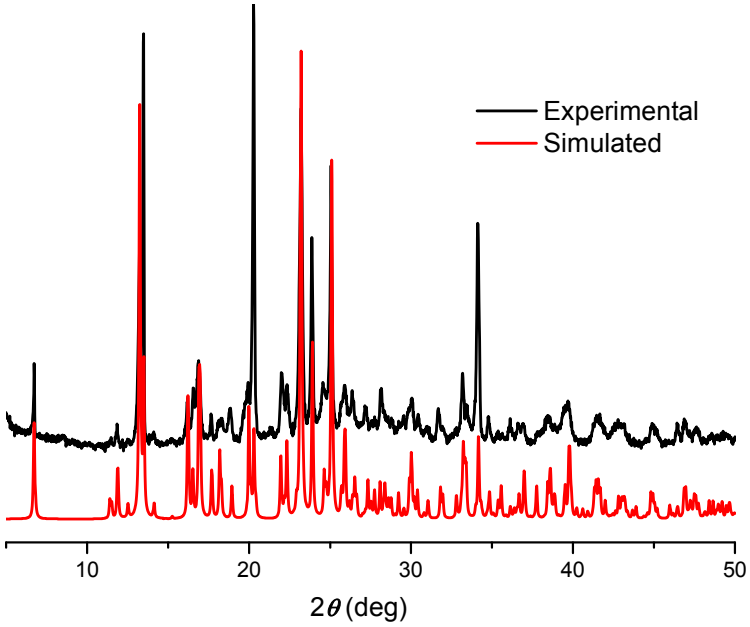
20
30
40
50
2θ (deg)

(c)


Experimental
Simulated
10
20
30
40
50
2θ (deg)

(d)


Experimental
Simulated
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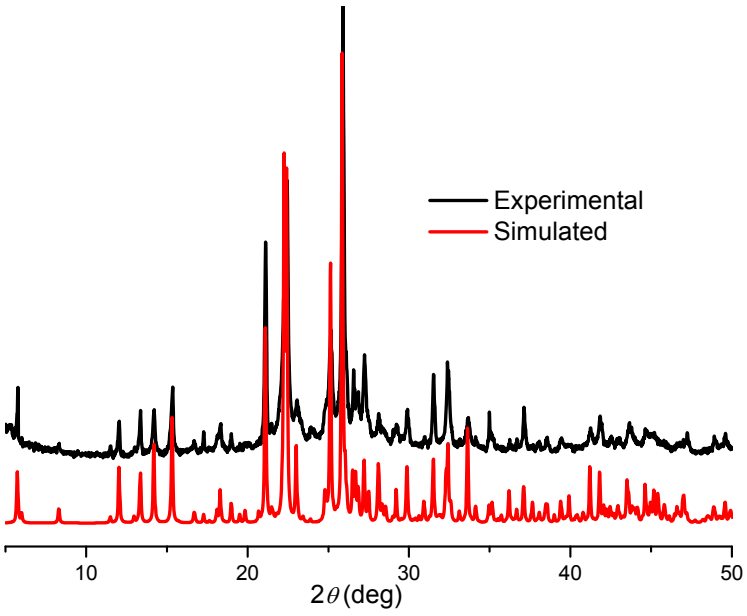
20
30
40
50
2θ (deg)

(e)


Experimental
Simulated
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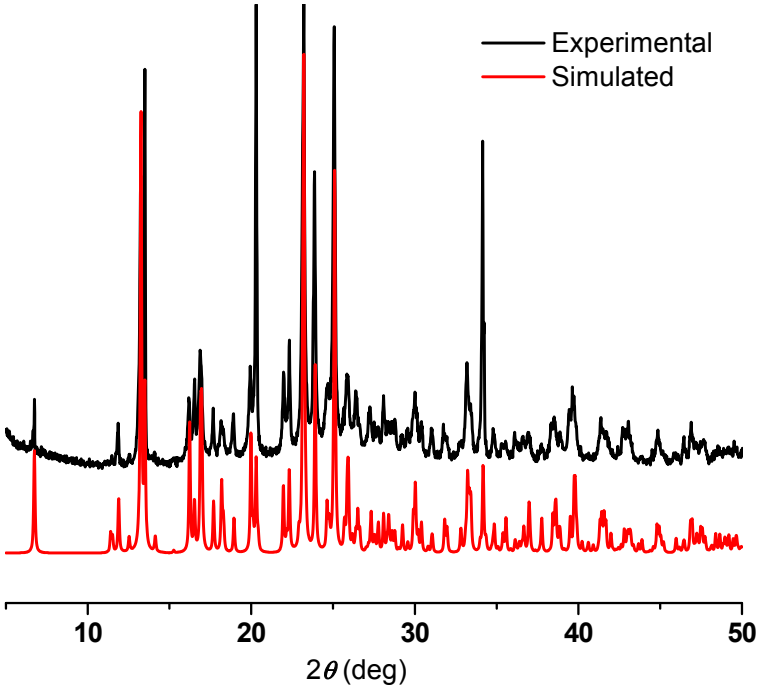
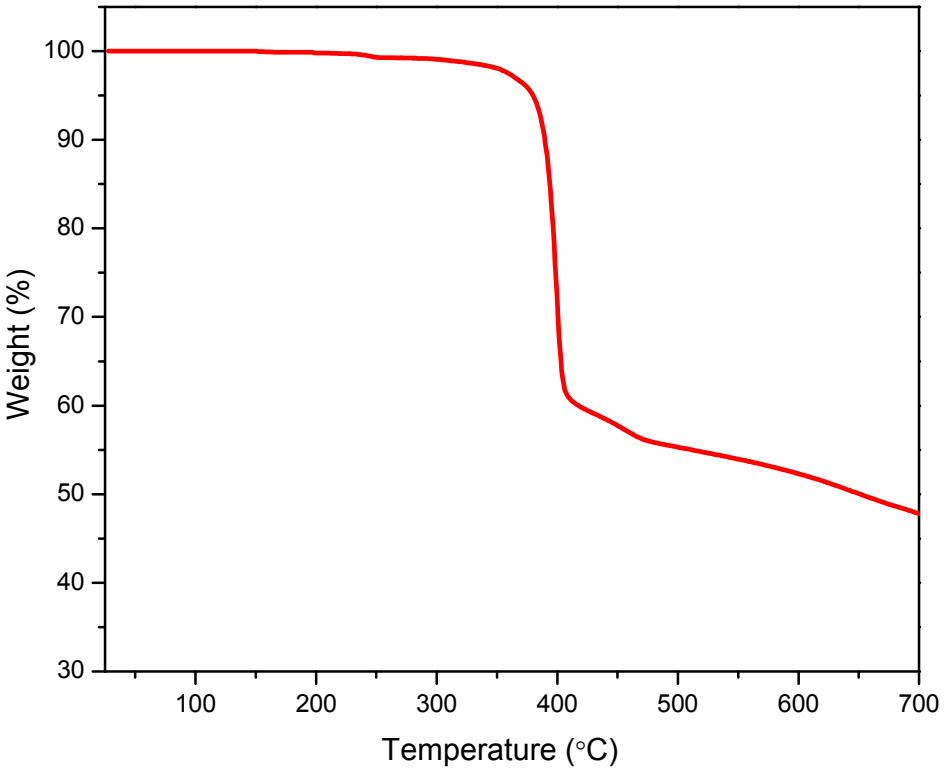
20
30
40
50
2θ (deg)

(f)



(g)

Fig. S1 Powder X-ray diffraction (PXRD) patterns for complexes **1**–**7** (a–g).


Weight (%)
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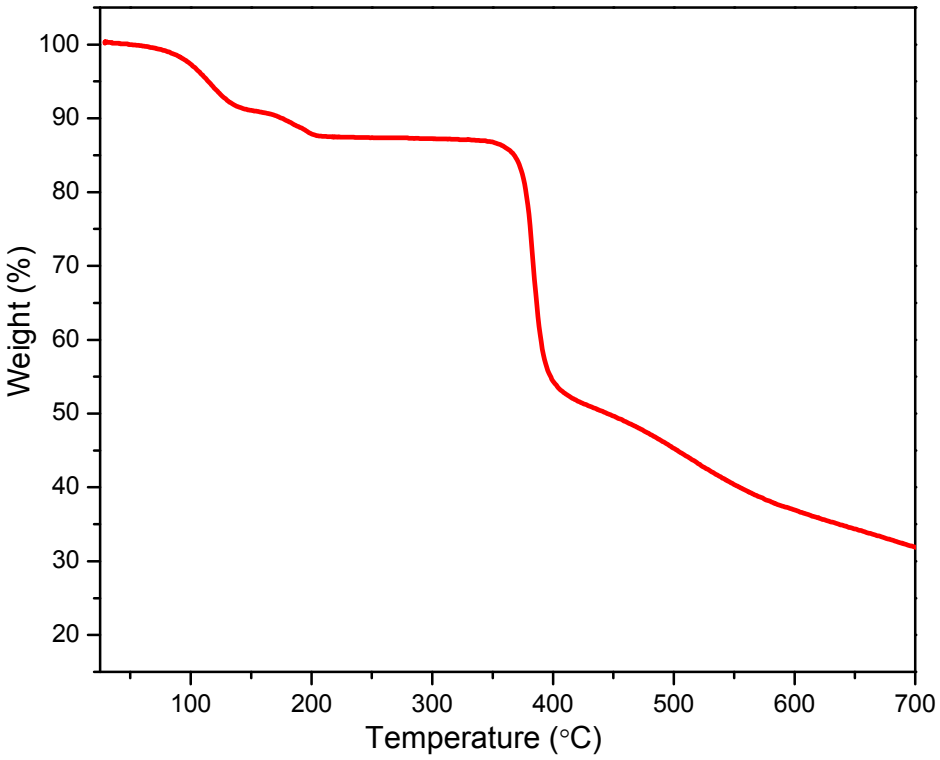
90
80
70
60
50
40
30
100
200
300
400
500
600
700
Temperature (°C)

(a)


Weight (%)
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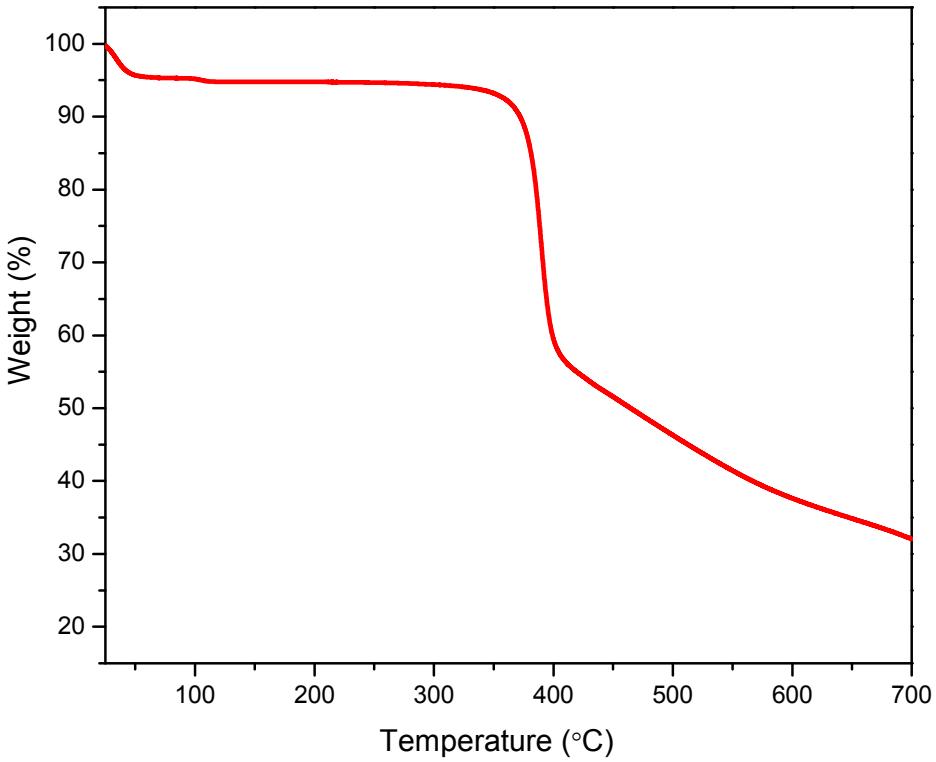
60
50
40
30
20
100
200
300
400
500
600
700
Temperature (°C)

(b)


Weight (%)
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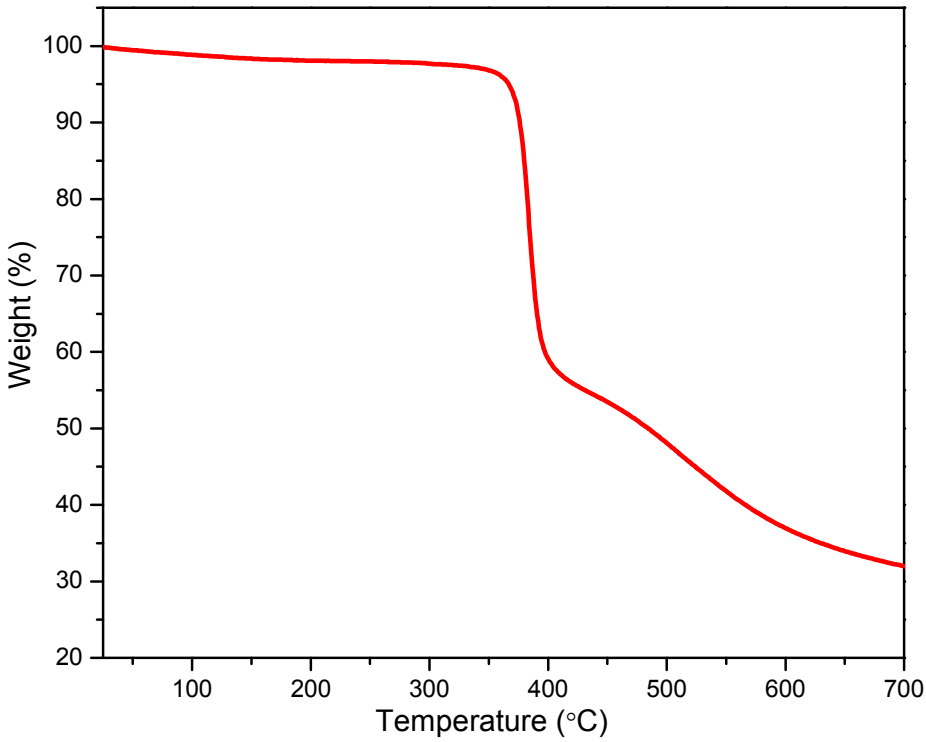
70
60
50
40
30
20
100
200
300
400
500
600
700
Temperature (°C)

(c)


Weight (%)
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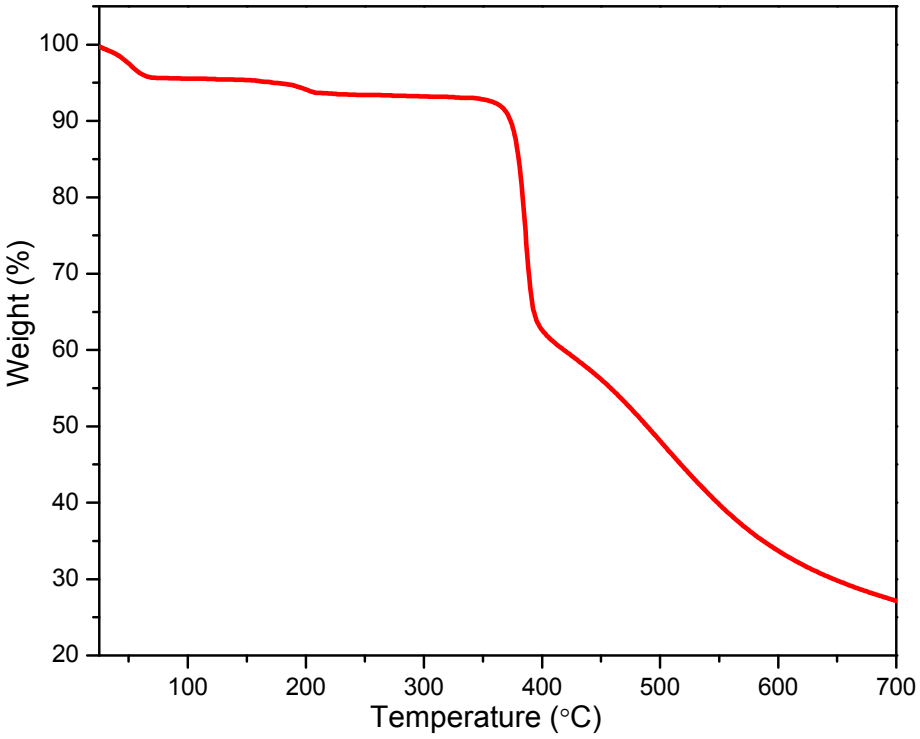
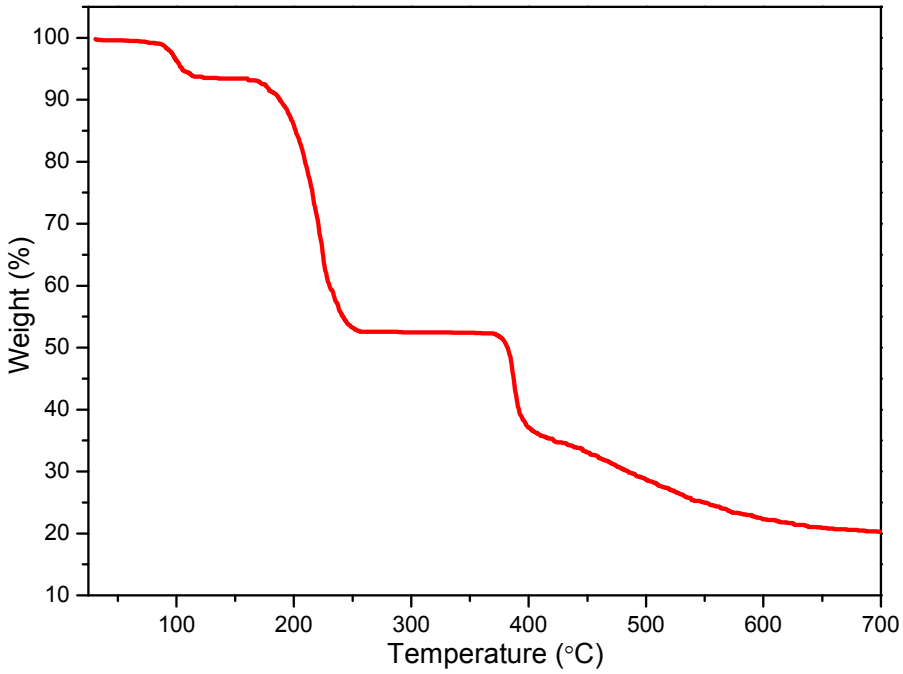
70
60
50
40
30
20
100
200
300
400
500
600
700
Temperature (°C)

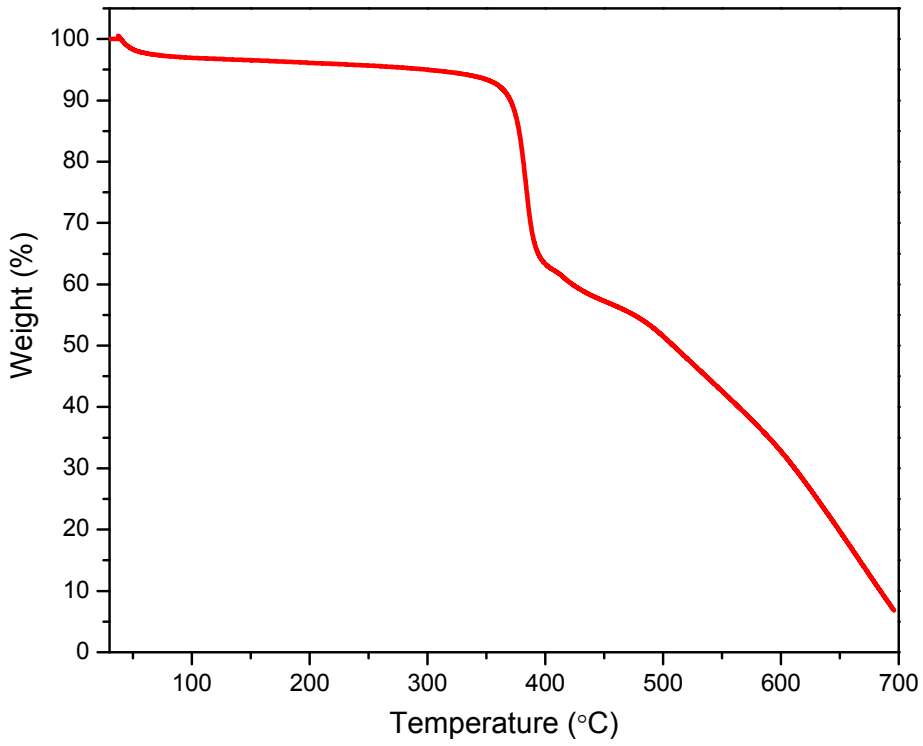
(d)


Weight (%)
Temperature (°C)
100
90
80
70
60
50
40
30
20
100
200
300
400
500
600
700

(e)


Weight (%)
Temperature (°C)
100
90
80
70
60
50
40
30
20
10
100
200
300
400
500
600
700

(f)



(g)

Fig. S2 Thermogravimetric analysis (TGA) curves for complexes **1**–**7** (a–g).