Electronic Supplementary Information

Crystal engineering of cadmium coordination polymers decorated by nitro-functionalized thiophene-2,5-dicarboxylate and structurally related bis(imidazole) ligands with varying flexibility

Table S1 Selected bond distances (Å) and angles (°) for complexes **1**−**5**

Compound **1**[a]					
Cd(1)−O(1)	2.227(4)	Cd(1)−O(3)#2	2.298(4)	Cd(1)−O(7)	2.388(5)
Cd(1)−O(4)#2	2.604(4)	Cd(1)−N(1)	2.260(5)	Cd(1)−N(2)#1	2.298(5)
O(1)−Cd(1) −N(1)	101.26(17)	O(1)−Cd(1)−N(2) #2	90.6(2)	N(1)−Cd(1)−N(2)#1	106.65(18)
O(1)−Cd(1)−O(3)#2	111.41(16)	N(1)−Cd(1)−O(3)#2	144.76(15)	N(2)#1−Cd(1)−O(3)#2	86.37(16)
O(1)−Cd(1)−O(7)	87.75(19)	N(1)−Cd(1)−O(7)	87.15(17)	N(2)#1−Cd(1)−O(7)	166.14(18)
O(3)#2−Cd(1)−O(7)	81.45(16)	O(1)−Cd(1)−O(4)#2	164.17(16)	N(1)−Cd(1)−O(4)#2	93.68(14)
N(2)−Cd(1)−O(4)#2	90.10(16)	O(3)#2−Cd(1)−O(4)#2	52.87(13)	O(7)−Cd(1)−O(4)#2	87.79(16)
[a] Symmetry codes: #1x, -y+3/2, z-1/2; #2 x+1, y, z.					
Compound **2**[b]					
Cd(1)−O(1)	2.378(7)	Cd(1)−O(2)#4	2.476(7)	Cd(1)−O(3)#3	2.481(9)
Cd(1)−O(4)#3	2.323(7)	Cd(1)−N(1)	2.246(10)	Cd(1)−N(4)#2	2.221(10)
O(1)−Cd(1)−O(2)#4	164.4(3)	O(1)−Cd(1)−O(3)#3	92.9(3)	O(2)#4−Cd(1)−O(3)#3	80.4(3)
O(4)#3−Cd(1)−O(3)#3	55.4(3)	O(4)#3−Cd(1)−O(2)#4	80.3(3)	O(4)#3−Cd(1)−O(1)	84.3(3)
N(1) −Cd(1)−O(1)	92.2(3)	N(4)#2−Cd(1)−O(1)	97.7(3)	N(1)−Cd(1)−O(4)#3	143.0(3)
N(4)#2−Cd(1)−O(4)#3	103.5(3)	N(4)#2−Cd(1)−N(1)	113.5(3)	N(4)#2−Cd(1)−O(2)#2	83.6(3)
N(1)−Cd(1)−O(2)#4	101.6(3)	N(4)#2−Cd(1)−O(3)#3	155.3(3)	N(1)−Cd(1)−O(3)#3	88.1(3)
[b]Symmetry codes: #1 x-1, -y+3/2, z-1/2; #2 -x+2, -y+2, -z+1; #3 x+1, -y+3/2, z+1/2; #4 x+1, y, z.					
Compound **3**[c]					
Cd(1)−O(1)	2.359(2)	Cd(1) −O(2)#1	2.249(2)	Cd(1)−O(3)#2	2.404(2)
Cd(1)−O(4)#2	2.353(2)	Cd(1) −N(3)	2.332(3)	Cd(1)−N(4)	2.269(3)
O(2)#1−Cd(1)−N(4)	90.04(9)	O(2)#1−Cd(1)−N(3)	82.63(9)	N(4)−Cd(1)−N(3)	97.34(9)
O(2)#1−Cd(1)−O(4)#2	96.30(8)	N(4)−Cd(1)−O(4)#2	160.89(9)	N(3)−Cd(1)−O(4)#2	101.33(9)
O(2)#1−Cd(1)−O(1)	95.49(8)	N(4)−Cd(1)−O(1)	79.59(8)	N(3)-Cd(1)-O(1)	176.43(8)
O(4)#2−Cd(1)−O(1)	81.87(8)	O(2)#1-Cd(1)-O(3)#2	150.91(9)	N(4)-Cd(1)-O(3)#2	118.83(9)
N(3)-Cd(1)-O(3)#2	96.17(9)	O(4)#2-Cd(1)-O(3)#2	55.25(8)	O(1)-Cd(1)-O(3)#2	86.95(7)
[c]Symmetry codes: #1 -x+3/2,-y+1/2,-z+1; #2 -x+1,-y+1,-z+1; #3 -x+3/2,y+1/2,-z+3/2; #4 -x+3/2,y-1/2,-z+3/2.					
Compound **4**[d]					
Cd(1)−O(1)	2.260(4)	Cd(1)−O(2)	2.519(4)	Cd(1)−N(1)	2.239(3)
N(1)−Cd(1)−N(1)#1	96.84(18)	N(1)−Cd(1)−O(1)	126.30(13)	N(1)−Cd(1)−O(1)#1	93.14(14)
O(1)−Cd(1)−O(1)#1	121.7(2)	N(1)−Cd(1)−O(2)	86.12(14)	N(1)#1−Cd(1)−O(2)	136.73(15)
O(1)−Cd(1)−O(2)	53.35(13)	O(1)#1−Cd(1)−O(2)	96.42(15)	O(2)−Cd(1)−O(2)#1	120.3(2)
[d]Symmetry codes: #1 x+1, -y+3/2, z+1/2.					
Compound **5**[e]					
Cd(1)−O(1)	2.342(2)	Cd(1)−O(2)	2.448(2)	Cd(1)−O(3)	2.288(2)
Cd(1)−O(4)	2.591(3)	Cd(1)−N(1)	2.238(2)	Cd(1)#1− N(4)	2.241(2)

N(1)−Cd(1)−N(4)#2	99.29(7)	N(1)−Cd(1)−O(4)	135.62(8)	N(4)#2−Cd(1)−O(3)	100.96(9)
N(1)−Cd(1)−O(1)	97.96(8)	N(4)#2−Cd(1)−O(1)	143.46(8)	O(3)−Cd(1)−O(1)	88.52(9)
N(1)−Cd(1)−O(2)	134.27(8)	N(4)#2−Cd(1)−O(2)	91.25(7)	O(3)−Cd(1)−O(2)	84.25(8)
O(1)−Cd(1)−O(2)	54.33(7)	N(1)−Cd(1)−O(4)	84.05(8)	N(4)#2−Cd(1)−O(4)	108.85(9)
O(3)−Cd(1)−O(4)	52.08(8)	O(1)−Cd(1)−O(4)	104.78(9)	O(2)−Cd(1)−O(4)	133.98(7)

[e]Symmetry codes: #1-x+2, y+1/2, -z+1/2; #2 -x+2, y-1/2, -z+1/2.

Table S2 Hydrogen Bond Lengths (Å) and Bond Angles (°) in Complexes **1, 2** and **5**.

Compound **1**[a]				
D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O(7)−H(1W)···O(2)[i]	0.85	2.11	2.919(7)	157.7
O(7)−H(2W)···O(3)[ii]	0.85	1.93	2.740(6)	159.5
O(8)−H(3W)···O(2)[iii]	0.85	2.46	3.206(14)	146.4
O(8)−H(4W)···O(4)[iv]	0.85	2.48	3.311(15)	167.7
[a]Symmetry codes: (i) -x+1, -y+2, -z+2; (ii) -x, -y+2, -z+2; (iii) -x+1, y-1/2, -z+3/2; (iv) x+1, y, z.				
Compound **2**[b]				
D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O(7)−H(1W)···O(4)[i]	0.85	2.17	3.015(12)	179.2
O(7)−H(2W)···S(1)	0.85	2.95	3.353(9)	111.3
O(7)−H(2W)···O(3)	0.85	2.15	2.998(13)	179.4
[b]Symmetry codes: (i) x, -y+3/2, z-1/2.				

Compound **5**[c]				
D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)
O(9)−H(1W)···O(4)	0.85	2.12	2.923(4)	156.3
O(9)−H(2W)···O(6)[i]	0.85	2.38	3.233(4)	179.4
[c] Symmetry codes: (i) x+1, -y+1/2, z+1/2.				

Fig. S1 Coordination environment of Cd^{2+} ion in **1.** All water and hydrogen atoms are omitted for clarity. Symmetry transformation used to generate equivalent atoms: (A) 1 + x, y, z; (B) x, 1.5 − y, −0.5 + z.

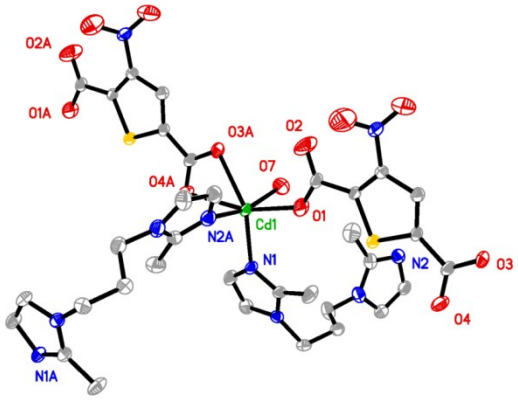

Fig. S2 Coordination environment of Cd^{2+} ion in **2.** All water and hydrogen atoms are omitted for clarity. Symmetry transformation used to generate equivalent atoms: (A) 1 + x, 1.5 − y, 0.5 + z; (B) 1 + x, y, z; (C) 2 − x, 2 − y, 1 − z.

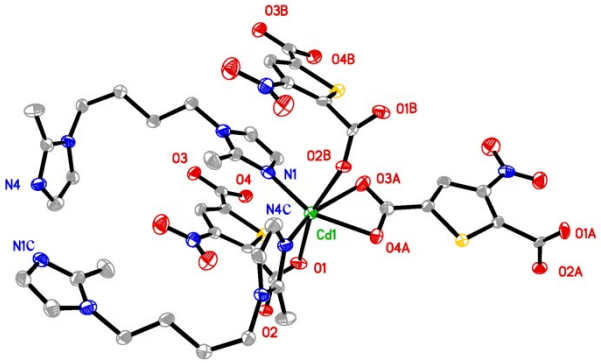

Fig. S3 Coordination environment of Cd^{2+} ion in **3**. All water and hydrogen atoms are omitted for clarity Symmetry transformation used to generate equivalent atoms (A) 1.5 − x, 0.5 − y, 1.5 − z; (B) 1.5 − x, 0.5 + y, 1.5 − z.

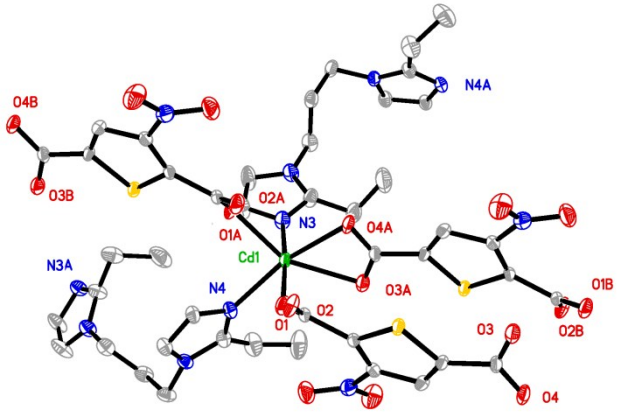

Fig. S4 Coordination environment of Cd^{2+} ion in **4**. All water and hydrogen atoms are omitted for clarity Symmetry transformation used to generate equivalent atoms (A) x, 1.5 − y, 0.5 − z; (B) −0.5 − x, 1 − y, z; (C) −0.5 − x, 0.5 + y, 0.5 − z; (D) 1 − x, 1 − y, 1 − z.

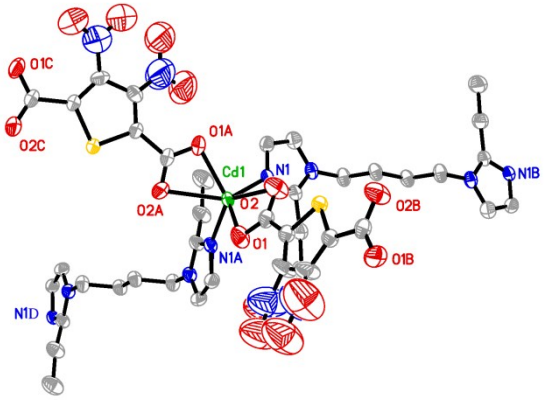

Fig. S5 Coordination environment of Cd^{2+} ion in **5.** All water and hydrogen atoms are omitted for clarity. Symmetry transformation used to generate equivalent atoms: (A) 2 − x, −0.5 + y, 0.5 − z.

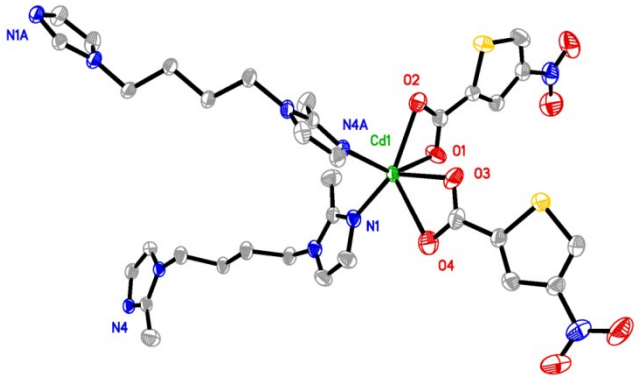

Fig. S6 ^{1}H NMR spectrum of H_2ntdc and Hntc ligands.

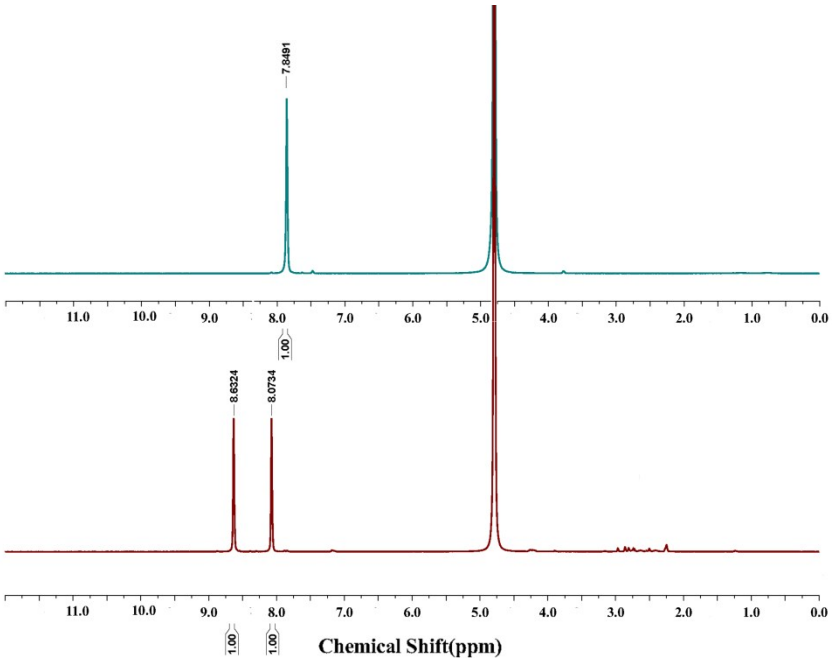

Fig. S7 PXRD patterns of as-synthesized and simulated **1-5**.

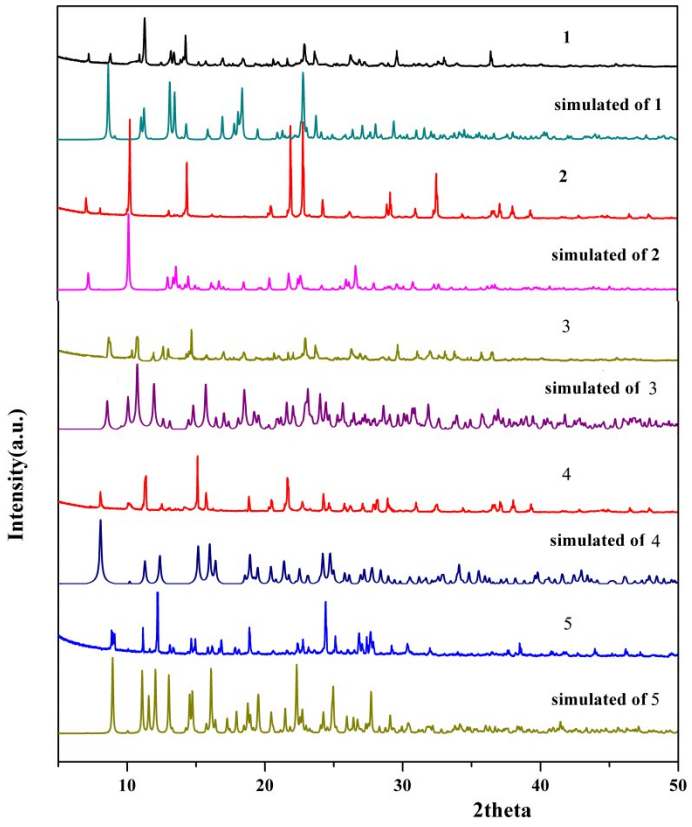

Fig. S8 TG curves of complexes **1-5**.

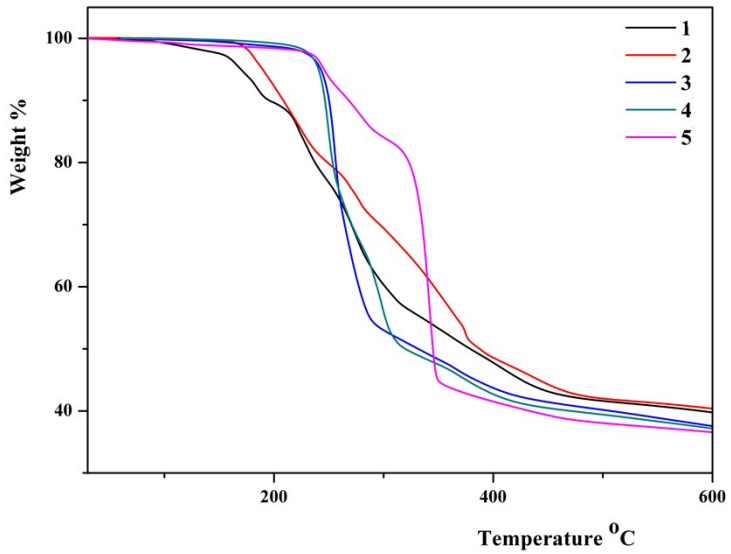

Fig. S9 Solid-state emission spectra of **1-4**.