Electronic supplementary information (ESI)

Cadmium(II) and zinc(II) complexes with rigid 1-(1*H*-imidazol-4-yl)-3-(4*H*-tetrazol-5-yl)benzene and varied carboxylate ligands†

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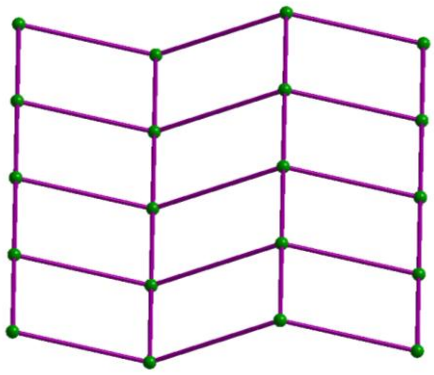


Figure S1. Schematic representation of 2D undulating network with (4, 4) topology in complex **3**.

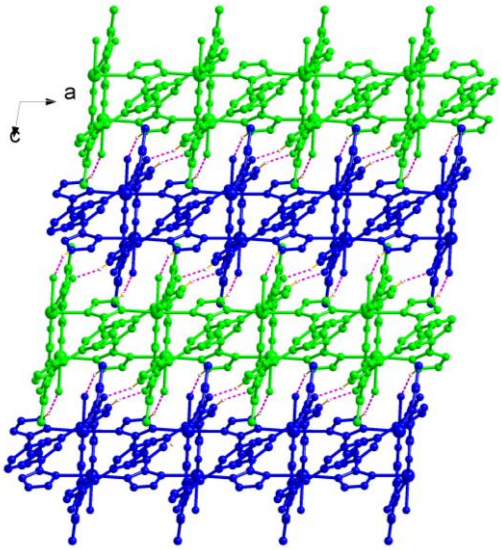


Figure S2. The 3D framework of **3** with hydrogen bonds indicated by dashed lines.

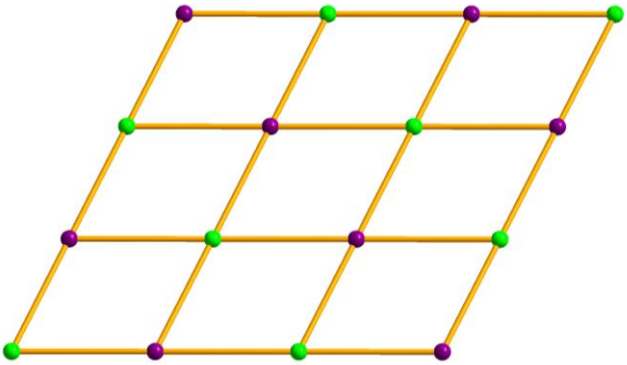


Figure S3. Schematic representation of 2D network with (4, 4) topology in complex **4** where the bright green and violet balls represent the binuclear $[Cd_2N_4]$ subunit and the centers of benzene rings of $btca^{4-}$ ligands respectively.

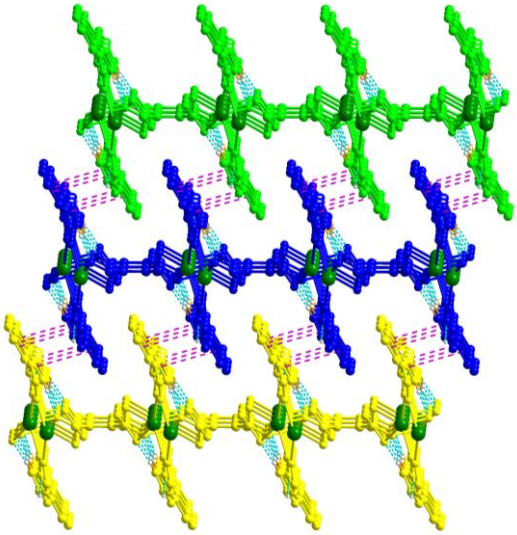


Figure S4. The 3D framework packed by π - π stacking interactions of aromatic rings highlighted by the pink dashed lines in complex **4** (the turquoise dashed lines represent intramolecular hydrogen bonds of 2D layers).

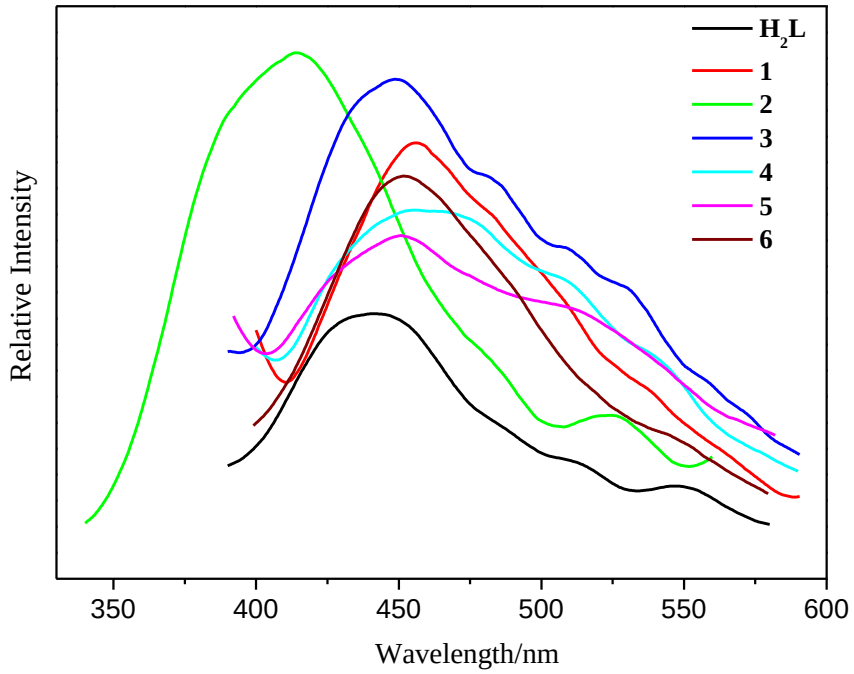


Figure S5. Emission spectra of H_2L ligand and complexes **1** - **6**.

Table S1 Selected bond lengths [Å] and bond angles [°] for complexes **1** - **6**

1

Cd(1)-N(4)	2.451(3)	Cd(1)-N(6)#1	2.208(2)
Cd(1)-N(1)#2	2.266(2)	Cd(1)-O(1)	2.241(2)
Cd(1)-O(2)	2.586(3)	Cd(1)-O(3)	2.426(3)
N(6)#1-Cd(1)-O(1)	138.64(9)	N(6)#1-Cd(1)-N(1)#2	104.34(8)
O(1)-Cd(1)-N(1)#2	117.00(8)	N(6)#1-Cd(1)-O(3)	100.87(11)
O(1)-Cd(1)-O(3)	81.17(11)	N(1)#2-Cd(1)-O(3)	86.68(13)
N(6)#1-Cd(1)-N(4)	94.82(8)	O(1)-Cd(1)-N(4)	87.93(8)
N(1)#2-Cd(1)-N(4)	88.22(9)	O(3)-Cd(1)-N(4)	164.26(10)

2

Cd(1)-N(1)	2.467(3)	Cd(1)-N(6)#3	2.216(2)
Cd(1)-N(4)#4	2.275(2)	Cd(1)-O(2)	2.284(2)
Cd(1)-O(3)	2.351(3)	Cd(1)-O(1)	2.527(2)
N(6)#3-Cd(1)-N(4)#4	109.48(9)	N(6)#3-Cd(1)-O(2)	140.78(9)
N(4)#4-Cd(1)-O(2)	109.38(9)	N(6)#3-Cd(1)-O(3)	91.72(11)
N(4)#4-Cd(1)-O(3)	88.77(10)	O(2)-Cd(1)-O(3)	83.99(12)
N(6)#3-Cd(1)-N(1)	95.46(9)	N(4)#4-Cd(1)-N(1)	90.66(9)
O(2)-Cd(1)-N(1)	89.20(9)	O(3)-Cd(1)-N(1)	172.56(11)
N(6)#3-Cd(1)-O(1)	88.56(9)	N(4)#4-Cd(1)-O(1)	160.19(9)
O(2)-Cd(1)-O(1)	54.07(8)	O(3)-Cd(1)-O(1)	99.11(11)
N(1)-Cd(1)-O(1)	79.18(9)		

3

Cd(1)-N(1)	2.390(2)	Cd(1)-N(4)#6	2.357(2)
Cd(1)-O(1)	2.2336(16)	Cd(1)-O(5)	2.3206(18)
Cd(1)-O(3)#5	2.3447(16)	Cd(1)-O(4)#5	2.4110(19)
O(1)-Cd(1)-O(5)	92.05(7)	O(1)-Cd(1)-O(3)#5	162.34(6)
O(5)-Cd(1)-O(3)#5	105.34(6)	O(1)-Cd(1)-N(4)#6	95.64(6)
O(5)-Cd(1)-N(4)#6	88.31(7)	O(3)#5-Cd(1)-N(4)#6	88.04(7)
O(1)-Cd(1)-N(1)	93.34(7)	O(5)-Cd(1)-N(1)	85.91(7)
O(3)#5-Cd(1)-N(1)	85.03(7)	N(4)#6-Cd(1)-N(1)	169.49(7)
O(1)-Cd(1)-O(4)#5	107.74(6)	O(5)-Cd(1)-O(4)#5	160.19(7)
O(3)#5-Cd(1)-O(4)#5	54.84(6)	N(4)#6-Cd(1)-O(4)#5	90.48(7)

N(1)-Cd(1)-O(4)#5	91.98(7)		
4			
Cd(1)-N(2)	2.313(3)	Cd(1)-N(1)#7	2.304(3)
Cd(1)-O(1)	2.236(2)	Cd(1)-O(5)	2.326(3)
Cd(1)-O(4)#8	2.364(2)	Cd(1)-O(3)#8	2.465(2)
O(1)-Cd(1)-N(1)#7	101.56(10)	O(1)-Cd(1)-N(2)	101.07(10)
N(1)#7-Cd(1)-N(2)	117.07(9)	O(1)-Cd(1)-O(5)	178.63(10)
N(1)#7-Cd(1)-O(5)	79.18(11)	N(2)-Cd(1)-O(5)	79.54(13)
O(1)-Cd(1)-O(4)#8	84.99(10)	N(1)#7-Cd(1)-O(4)#8	150.21(9)
N(2)-Cd(1)-O(4)#8	89.50(9)	O(5)-Cd(1)-O(4)#8	93.80(12)
O(1)-Cd(1)-O(3)#8	94.20(9)	N(1)#7-Cd(1)-O(3)#8	96.41(8)
N(2)-Cd(1)-O(3)#8	138.92(9)	O(5)-Cd(1)-O(3)#8	84.56(12)
O(4)#8-Cd(1)-O(3)#8	53.91(8)		
5			
Zn(1)-N(1)	2.005(2)	Zn(1)-N(5)#9	1.975(2)
Zn(1)-O(1)	1.988(2)	Zn(1)-O(2)#10	2.014(2)
N(5)#9-Zn(1)-O(1)	113.40(9)	N(5)#9-Zn(1)-N(1)	110.13(9)
O(1)-Zn(1)-N(1)	99.19(9)	N(5)#9-Zn(1)-O(2)#10	112.81(9)
O(1)-Zn(1)-O(2)#10	95.67(8)	N(1)-Zn(1)-O(2)#10	123.59(9)
6			
Zn(1)-N(12)	1.976(3)	Zn(1)-O(2)	1.980(2)
Zn(1)-O(6)#11	1.983(2)	Zn(1)-N(4)	2.005(3)
Zn(2)-O(10)	1.980(2)	Zn(2)-N(5)#12	1.986(3)
Zn(2)-N(7)#13	2.004(3)	Zn(2)-O(5)	2.015(2)
Zn(3)-N(18)	1.965(3)	Zn(3)-O(1)	1.972(2)
Zn(3)-N(16)#14	2.000(3)	Zn(3)-O(9)#15	2.003(2)
N(12)-Zn(1)-O(2)	111.92(11)	N(12)-Zn(1)-O(6)#11	116.81(11)
O(2)-Zn(1)-O(6)#11	98.09(10)	N(12)-Zn(1)-N(4)	108.41(12)
O(2)-Zn(1)-N(4)	121.66(11)	O(6)#11-Zn(1)-N(4)	99.40(11)
O(10)-Zn(2)-N(5)#12	114.68(11)	O(10)-Zn(2)-N(7)#13	101.91(11)
N(5)#12-Zn(2)-N(7)#13	108.51(12)	O(10)-Zn(2)-O(5)	92.97(9)
N(5)#12-Zn(2)-O(5)	110.68(11)	N(7)#13-Zn(2)-O(5)	126.79(11)

N(18)-Zn(3)-O(1)	113.92(11)	N(18)-Zn(3)-N(16)#14	109.27(11)
O(1)-Zn(3)-N(16)#14	99.28(11)	N(18)-Zn(3)-O(9)#5	113.02(11)
O(1)-Zn(3)-O(9)#15	95.40(9)	N(16)#14-Zn(3)-O(9)#15	124.08(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z+1, #2 -x+2,y+1/2,-z+1/2, #3 -x+1/2,-y+3/2,-z+1, #4 -x+1/2,y-1/2,-z+1/2, #5 -x+3/2,y+1/2,-z+3/2, #6 x-1,y,z, #7 -x+1,-y+2,-z+1, #8 -x+1,-y+2,-z, #9 -x+1/2,-y+1,z+1/2, #10 -x+1/2,y-1/2,z, #11 -x+1,-y+1,-z, #12 x,-y+3/2,z-1/2, #13 x,-y+1/2,z-1/2, #14 -x+2,y+1/2,-z+1/2, #15 -x+2,-y+1,-z.

Table S2 Hydrogen bonding data for complexes **1 - 6**

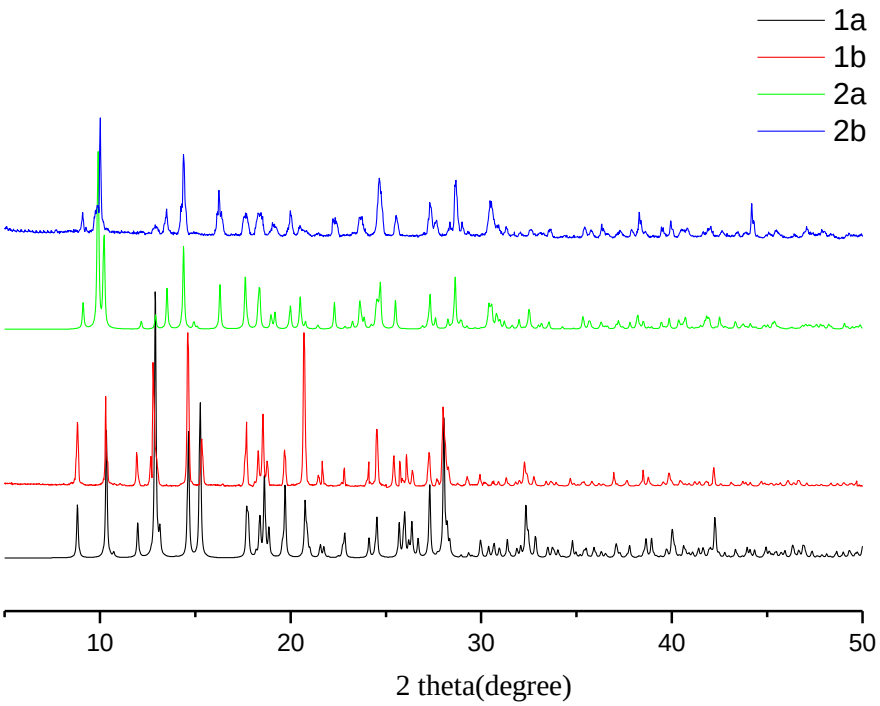
D-H···A	d(D···A) (Å)	∠D-H···A (°)
	Compound **1**	
N5-H5···N3#1	2.916(3)	172
C6-H6···N3#1	3.515(4)	169
C10-H10···N2#2	3.245(4)	130
	Compound **2**	
N5-H5A···N2#3	2.933(5)	169
C9-H9···O5#4	3.458(10)	161
	Compound **3**	
N3-H3A···O5#5	2.919(3)	159
N5-H5···O2#6	2.673(3)	145
C2-H2···O1#7	3.137(3)	159
C6-H6···O4#8	3.317(3)	170
C9-H9···O4#8	3.261(3)	132
C10-H10···N2#9	3.308(3)	144
	Compound **4**	
N4-H4A···O7	3.121(7)	157
N5-H5···O4#10	2.711(5)	177
C9-H9···O1#10	3.426(4)	172
C10-H10···N3#11	3.134(5)	132
	Compound **5**	

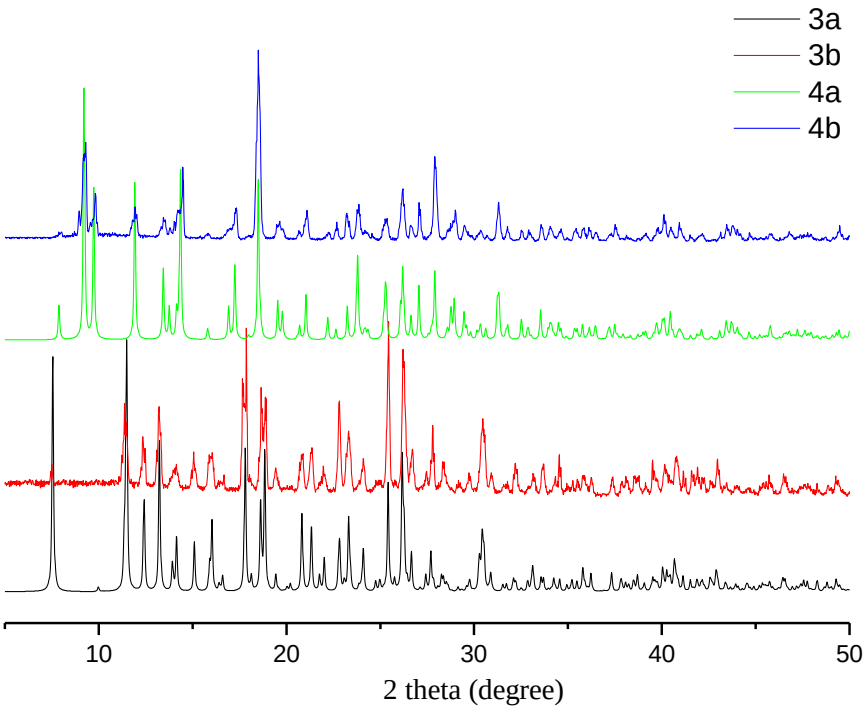
N4-H4A···O4#12	2.799(3)	155
N6-H6A···N2#13	3.364(3)	146
N6-H6A···N3#13	2.886(3)	168
C6-H6···O3#12	3.375(3)	158
C8-H8···O3#12	3.051(3)	140

Compound **6**

N1-H1A···O8#14	2.786(4)	152
N6-H6···N2#15	2.931(4)	171
N10-H10A···O4	2.792(4)	154
N11-H11A···N9#16	2.919(4)	173
N13-H13A···O12#17	2.779(4)	152
N17-H17···N14#18	2.847(4)	166
N17-H17···N15#18	3.314(4)	144
C5-H5···O7#14	3.272(5)	144
C9-H9···O7#14	3.002(5)	130
C10-H10···N8#19	3.207(5)	123
C15-H15···O3	3.308(5)	148
C19-H19···O3	3.026(4)	141
C20-H20···N3	3.230(5)	123
C25-H25···O11#17	3.363(4)	157
C29-H29···O11#17	3.028(4)	139

Symmetry transformations used to generate equivalent atoms: #1 2-x,-1/2+y,1/2-z; #2 x,1/2-y,1/2+z; #3 1/2-x,1/2+y,1/2-z; #4 x,1-y,1/2+z; #5 2-x,1-y,1-z; #6 -1/2+x,1/2-y,1/2+z; #7 1+x,y,z; #8 3/2-x,1/2+y,3/2-z; #9 3/2-x,-1/2+y,3/2-z; #10 1-x,2-y,1-z; #11 x,y,1+z; #12 x,3/2-y,-1/2+z; #13 1/2+x,y,1/2-z; #14 x,3/2-y,1/2+z; #15 x,3/2-y,-1/2+z; #16 x,1/2-y,1/2+z; #17 2-x,1-y,-z; #18 x,1/2-y,-1/2+z; #19 x,1+y,z.





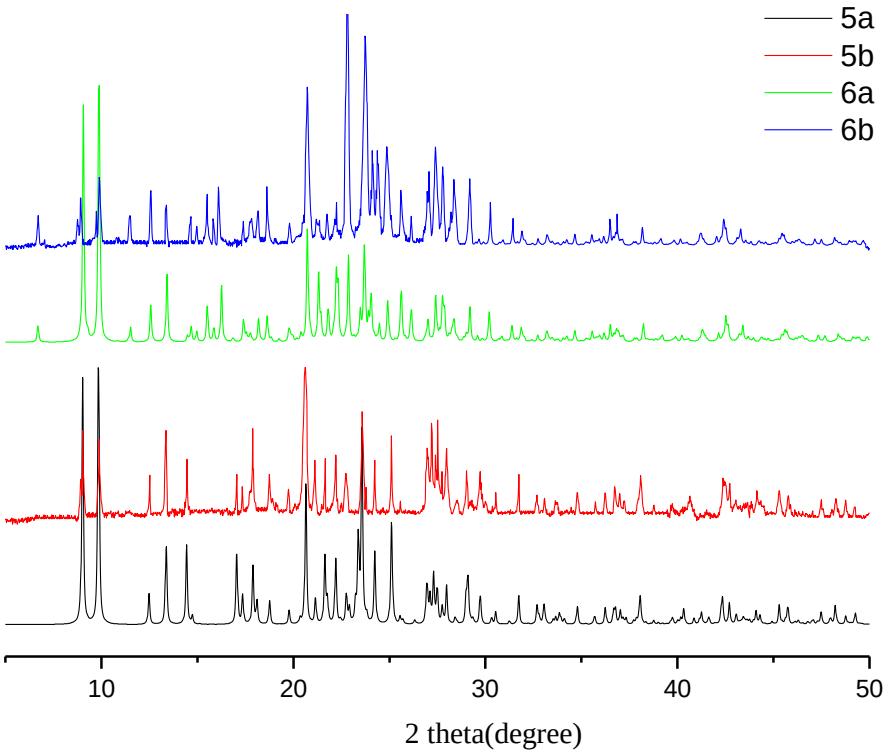


Figure S6. The X-ray powder diffraction patterns of **1** - **6:** a – simulated; b – as-synthesized**.**

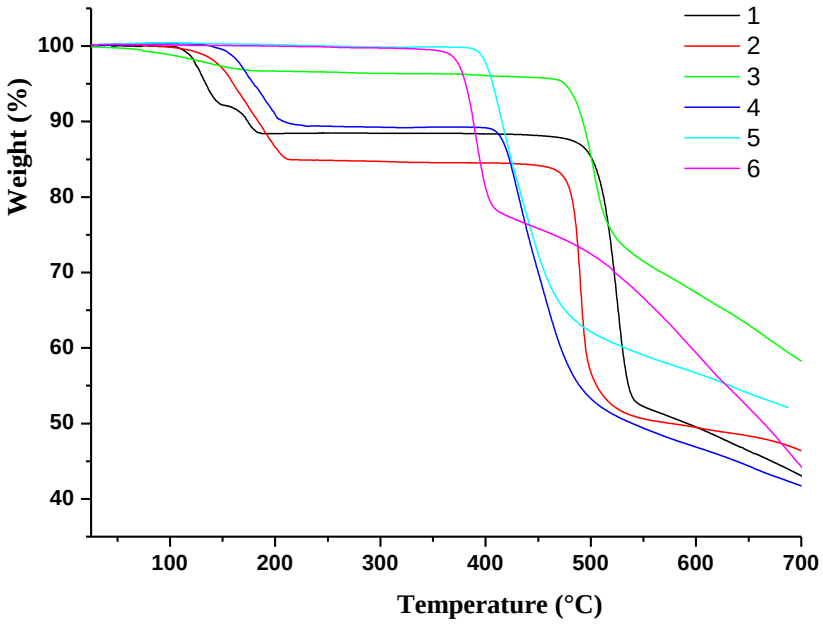


Figure S7. The TG curves of **1 - 6**.