Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

In Situ Tetrazole Ligand Based Novel Metal-Organic Frameworks: Synthesis, Structure and Luminescence

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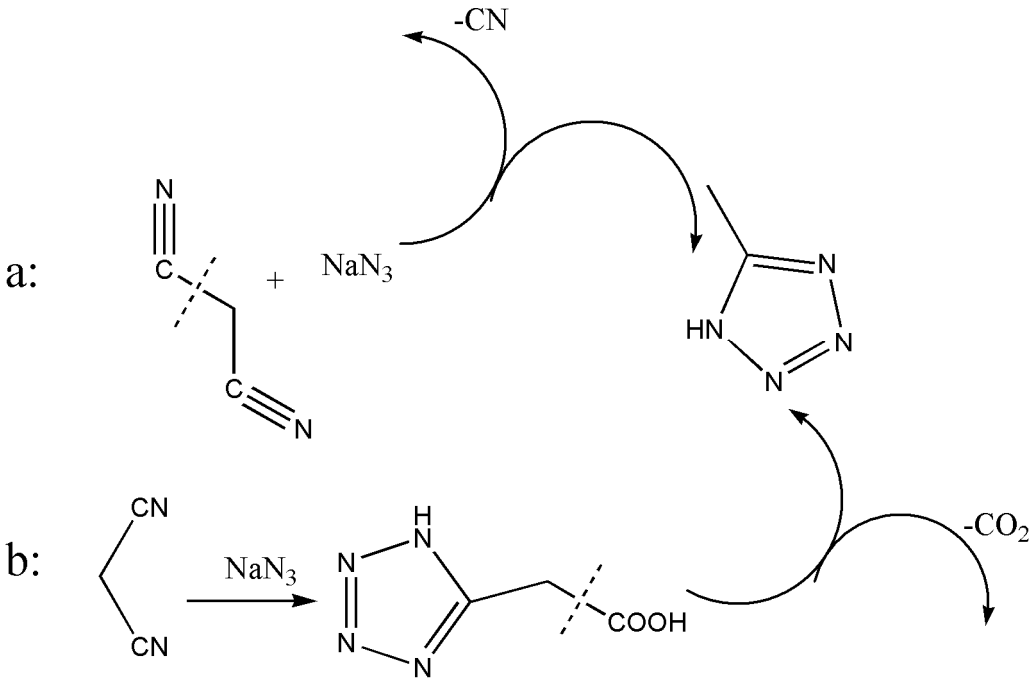

Scheme S1. Two possible routes to form 5MT *in situ* reaction.

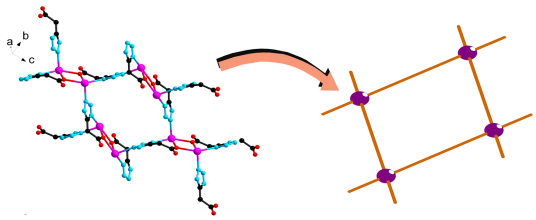

Figure S1. Perspective view of the 2D (4,4) topology by the linkage of Cd_2O_2 clusters as a four node and tetrazole ligands of the complex **1.**

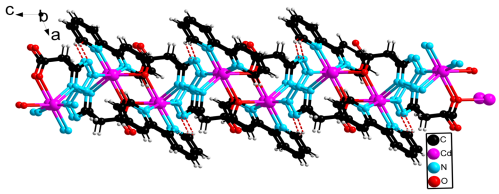

Figure S2. View of the intramolecular hydrogen bonding in complex **1.**

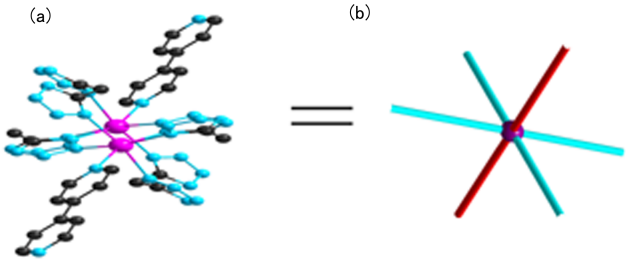

Figure S3. Ball and stick plot showing the coordination geometry around the $[CdN_2]_2$ clusters as a six connected node in complex **3**.

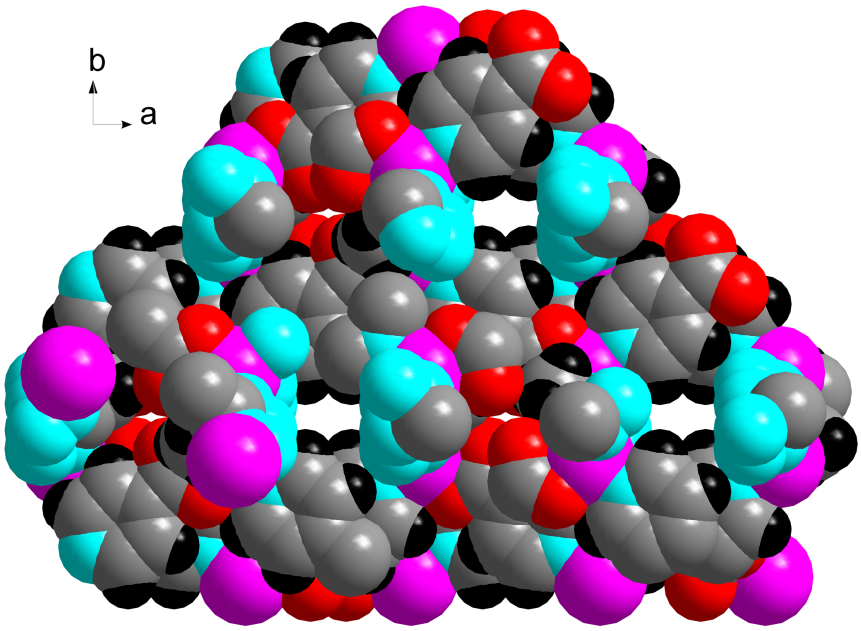

Figure S4. Perspective view of A space-filling model of 3D complex **4**

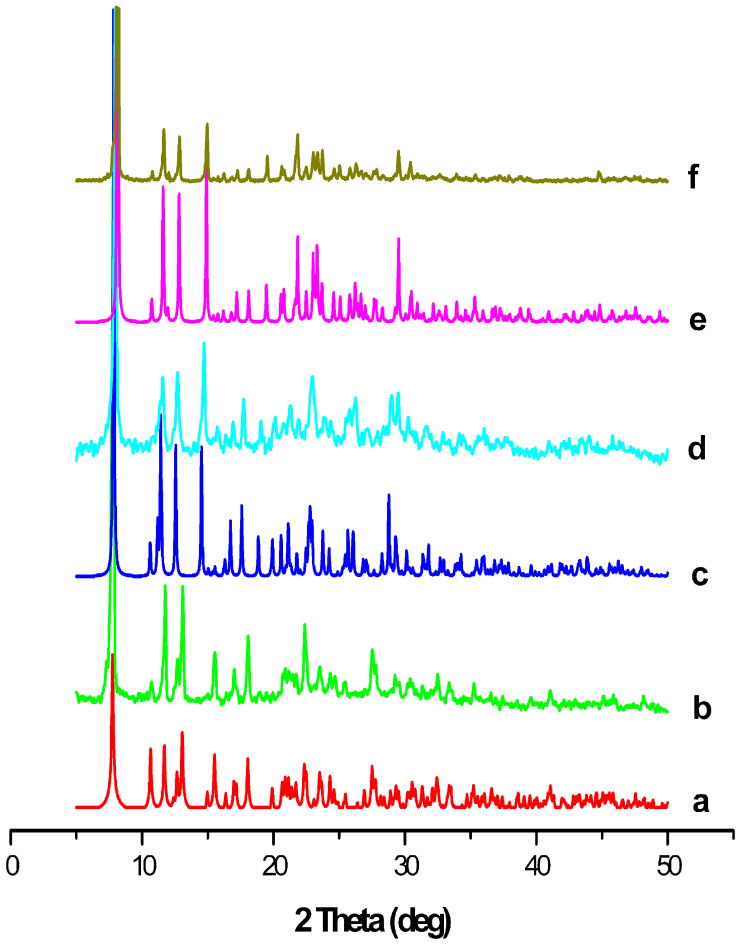

Figure S5 (a), (c) and (e) are simulated PXRD patterns based on the X-ray single-crystal diffraction data of **1**, **2a**, **2b**, respectively. (b), (d) and (f) are for as-synthesized **1**, **2a**, **2b**.

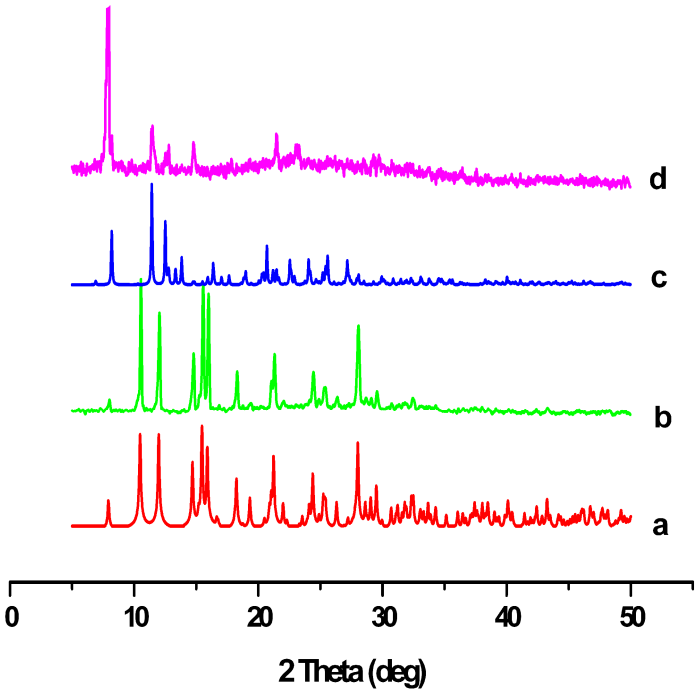

Figure S6 The PXRD patterns (a) simulated based on the X-ray single-crystal diffraction data of **4**, (b) for as-synthesized **4**, (c) simulated based on X-ray single-crystal diffraction data of **5**, (d) for as-synthesized **5**

Table S1 Selected bond lengths (Å) and angles (º) for **1**–**5**.

Complex 1			
Cd(1)-N(4)	2.312(6)	N(4)-Cd(1)-N(1)	164.3(2)
Cd(1)-N(6)#1	2.327(7)	N(6)#1-Cd(1)-N(1)	90.6(2)
Cd(1)-N(2)	2.345(7)	N(2)-Cd(1)-N(1)	69.8(2)
Cd(1)-N(1)	2.138(2)	N(4)-Cd(1)-O(1)#2	100.7(2)
Cd(1)-O(1)#2	2.372(7)	N(6)#1-Cd(1)-O(1)#2	142.2(3)
Cd(1)-O(1)#1	2.400(8)	N(2)-Cd(1)-O(1)#2	121.8(2)
N(6)-Cd(1)#3	2.327(7)	N(1)-Cd(1)-O(1)#2	86.3(2)
O(1)-Cd(1)#4	2.372(7)	N(4)-Cd(1)-O(1)#1	101.4(2)
O(1)-Cd(1)#3	2.400(8)	N(6)#1-Cd(1)-O(1)#1	77.2(2)
N(4)-Cd(1)-N(6)#1	92.3(3)	N(2)-Cd(1)-O(1)#1	160.9(2)
N(4)-Cd(1)-N(2)	94.7(2)	N(1)-Cd(1)-O(1)#1	94.3(2)
N(6)#1-Cd(1)-N(2)	91.9(3)	O(1)#2-Cd(1)-O(1)#1	65.4(3)
Complex 2a			
N(1)-Cd(1)	2.332(3)	N(9)#1-Cd(1)-N(7)	90.2(2)
N(2)-Cd(1)	2.371(3)	N(1)-Cd(1)-N(7)	90.42(17)
Cd(1)-N(3)	2.320(6)	N(3)-Cd(1)-N(2)	97.81(17)
Cd(1)-N(9)#1	2.326(6)	N(9)#1-Cd(1)-N(2)	164.1(2)
Cd(1)-N(7)	2.356(6)	N(1)-Cd(1)-N(2)	70.43(7)
Cd(1)-N(4)#2	2.391(6)	N(7)-Cd(1)-N(2)	98.96(17)

N(4)-Cd(1)#2	2.391(6)	N(3)-Cd(1)-N(4)#2	93.0(2)
N(9)-Cd(1)#3	2.326(6)	N(9)#1-Cd(1)-N(4)#2	90.2(2)
N(3)-Cd(1)-N(9)#1	96.4(2)	N(1)-Cd(1)-N(4)#2	96.07(18)
N(3)-Cd(1)-N(1)	163.95(18)	N(7)-Cd(1)-N(4)#2	173.4(2)
N(9)#1-Cd(1)-N(1)	96.76(19)	N(2)-Cd(1)-N(4)#2	82.2(2)
N(3)-Cd(1)-N(7)	80.5(2)		

Complex 2b

N(1)-Zn(1)	2.1970(19)	N(3)-Zn(1)#1	2.1818(19)
N(5)-Zn(1)	2.1368(19)	N(6)-Zn(1)#2	2.232(2)
N(9)-Zn(1)	2.165(2)	N(10)-Zn(1)	2.196(2)
Zn(1)-N(3)#3	2.1818(19)	Zn(1)-N(6)#2	2.232(2)
N(5)-Zn(1)-N(9)	167.21(7)	N(5)-Zn(1)-N(3)#3	95.49(7)
N(9)-Zn(1)-N(3)#3	94.19(8)	N(5)-Zn(1)-N(10)	96.88(7)
N(9)-Zn(1)-N(10)	74.81(7)	N(3)#3-Zn(1)-N(10)	165.46(8)
N(5)-Zn(1)-N(1)	84.57(7)	N(9)-Zn(1)-N(1)	86.69(7)
N(3)#3-Zn(1)-N(1)	92.49(7)	N(10)-Zn(1)-N(1)	96.27(7)
N(5)-Zn(1)-N(6)#2	93.07(7)	N(9)-Zn(1)-N(6)#2	95.22(7)
N(3)#3-Zn(1)-N(6)#2	90.24(7)	N(10)-Zn(1)-N(6)#2	81.49(8)
N(1)-Zn(1)-N(6)#2	176.55(7)		

Complex 3

Cd(1)-N(9)	2.33(2)	Cd(1)-N(1)	2.294(19)
Cd(1)-N(4)#2	2.322(19)	Cd(1)-N(6)#3	2.391(19)
Cd(1)-N(8)#4	2.428(19)	Cd(1)-N(5)	2.526(19)
N(4)-Cd(1)#5	2.322(19)	N(6)-Cd(1)#3	2.391(19)
N(8)-Cd(1)#6	2.428(19)	N(9)-Cd(1)-N(1)	94.8(7)
N(9)-Cd(1)-N(4)#2	98.5(7)	N(1)-Cd(1)-N(4)#2	94.5(7)
N(9)-Cd(1)-N(6)#3	101.5(7)	N(1)-Cd(1)-N(6)#3	163.4(7)
N(4)#2-Cd(1)-N(6)#3	79.8(7)	N(9)-Cd(1)-N(8)#4	82.5(7)
N(1)-Cd(1)-N(8)#4	98.2(7)	N(4)#2-Cd(1)-N(8)#4	167.1(7)
N(6)#3-Cd(1)-N(8)#4	87.4(7)	N(9)-Cd(1)-N(5)	157.2(7)
N(1)-Cd(1)-N(5)	79.2(6)	N(4)#2-Cd(1)-N(5)	103.9(6)
N(6)#3-Cd(1)-N(5)	87.0(6)	N(8)#4-Cd(1)-N(5)	76.7(6)

Complex 4

Zn(1)-O(2)	1.947(2)	Zn(1)-N(1)#1	1.991(3)
Zn(1)-N(4)	2.000(3)	Zn(1)-N(5)#2	2.045(3)
N(5)-Zn(1)#3	2.045(3)	N(1)-Zn(1)#4	1.991(3)
O(2)-Zn(1)-N(1)#1	121.36(11)	O(2)-Zn(1)-N(4)	117.38(11)
N(1)#1-Zn(1)-N(4)	106.33(11)	O(2)-Zn(1)-N(5)#2	96.73(11)
N(1)#1-Zn(1)-N(5)#2	106.80(11)	N(4)-Zn(1)-N(5)#2	106.29(11)

Complex 5

Mn(1)-N(10)#1	2.237(3)	Mn(1)-N(14)	2.237(3)
Mn(1)-N(15)	2.244(3)	Mn(1)-N(20)	2.257(3)
Mn(1)-N(19)	2.301(3)	Mn(1)-N(17)#2	2.305(3)
Mn(2)-N(1)	2.213(3)	Mn(2)-N(3)#3	2.215(3)

Mn(2)-N(4)	2.246(3)	Mn(2)-N(11)	2.261(3)
Mn(2)-N(7)#3	2.273(3)	Mn(2)-N(2)	2.316(3)
N(3)-Mn(2)#3	2.215(3)	N(7)-Mn(2)#3	2.273(3)
N(10)-Mn(1)#4	2.237(3)	N(17)-Mn(1)#5	2.305(3)
N(10)#1-Mn(1)-N(14)	172.62(11)	N(10)#1-Mn(1)-N(15)	91.43(11)
N(14)-Mn(1)-N(15)	81.34(11)	N(10)#1-Mn(1)-N(20)	89.53(11)
N(14)-Mn(1)-N(20)	97.84(10)	N(15)-Mn(1)-N(20)	164.09(11)
N(10)#1-Mn(1)-N(19)	85.29(11)	N(14)-Mn(1)-N(19)	96.48(11)
N(15)-Mn(1)-N(19)	92.67(11)	N(20)-Mn(1)-N(19)	71.58(11)
N(10)#1-Mn(1)-N(17)#2	93.16(11)	N(14)-Mn(1)-N(17)#2	86.48(11)
N(15)-Mn(1)-N(17)#2	98.62(11)	N(20)-Mn(1)-N(17)#2	97.19(11)
N(19)-Mn(1)-N(17)#2	168.65(11)	N(1)-Mn(2)-N(3)#3	165.48(12)
N(1)-Mn(2)-N(4)	92.36(11)	N(3)#3-Mn(2)-N(4)	93.31(11)
N(1)-Mn(2)-N(11)	94.18(12)	N(3)#3-Mn(2)-N(11)	97.34(12)
N(4)-Mn(2)-N(11)	104.44(11)	N(1)-Mn(2)-N(7)#3	90.10(11)
N(3)#3-Mn(2)-N(7)#3	82.15(11)	N(4)-Mn(2)-N(7)#3	170.05(11)
N(11)-Mn(2)-N(7)#3	84.99(11)	N(1)-Mn(2)-N(2)	71.34(12)
N(3)#3-Mn(2)-N(2)	95.24(11)	N(4)-Mn(2)-N(2)	90.51(11)
N(11)-Mn(2)-N(2)	159.80(11)	N(7)#3-Mn(2)-N(2)	81.14(11)

[a]Symmetry codes for **1**: #1 -x+1/2, y+1/2,-z+1/2; #2 x,-y,z-1/2; #3 -x+1/2,y-1/2,-z+1/2; #4 x,-y,z+1/2; for **2a**: #1 -x+1/2, y-1/2, -z+1/2; #2 -x+1/2,-y+1/2,-z; #3 -x+1/2,y+1/2,-z+1/2; for **2b**: #1 -x+1/2,y+1/2,-z+1/2 ; #2 -x+1/2,-y+1/2,-z; #3 -x+1/2, y-1/2,-z+1/2; for **3**: #1 -x,-y+1,-z+1; #2 x,-y-1/2,z-1/2; #3 -x+1,-y,-z+1; #4 -x+1,y+1/2,-z+3/2; #5 x,-y-1/2,z+1/2; #6 -x+1,y-1/2,-z+3/2; for **4**: #1 x,-y+1,z+1/2; #2 x+1/2,-y+1/2,z+1/2; #3 x-1/2,-y+1/2,z-1/2; #4 x,-y+1,z-1/2; for **5**: #1 x-1/2,-y+3/2,z+1/2; #2 -x+3/2,y+1/2,-z+1/2; #3 -x+2,-y+2,-z; #4 x+1/2,-y+3/2,z-1/2; #5 -x+3/2,y-1/2,-z+1/2;