Dinuclear complexes of Mn, Co, Zn and Cd assembled with 1,4-cyclohexanedicarboxylato: Synthesis, crystal structures and acetonitrile fluorescent sensing properties

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Supplementary information

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Table S1. Crystal data and structure refinement parameters for **1**-**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{36}H_{40}Mn_2N_4O_{10}$	$C_{36}H_{44}Co_2N_4O_{12}$	$C_{36}H_{44}N_4O_{12}Zn_2$	$C_{36}H_{44}Cd_2N_4O_{12}$
Formula weight	798.60	842.61	855.49	949.55
Temperature (K)	100(2)			
Wavelength (Å)	0.71073			
Crystal system	Monoclinic			Triclinic
Space group	$P2_1/c$			P-1
a (Å)	9.76750(10)	10.2385(4)	10.2587(5)	9.3550(4)
b (Å)	16.1090(2)	16.0725(6)	16.0646(7)	9.9500(4)
c (Å)	10.91170(10)	11.3029(4)	11.2653(5)	10.8783(5)
α (°)	90	90	90	88.0818(7)
β (°)	101.9053(4)	95.7321(6)	95.3428(10)	70.4169(7)
γ (°)	90	90	90	72.3874(7)
Volume ($Å^3$)	1679.97(3)	1850.69(12)	1848.48(15)	906.68(7)
Z	2	2	2	1
D_{calc} (Mg/m^3)	1.579	1.512	1.537	1.739
Absorption coefficient (mm^{-1})	0.819	0.965	1.367	1.243
F(000)	828	876	888	480
Crystal size (mm^3)	0.446 x 0.221 x 0.167	0.415 x 0.339 x 0.137	0.256 x 0.234 x 0.174	0.445 x 0.142 x 0.126
Theta range for data collection (°)	2.131 to 27.446	1.999 to 27.506	1.994 to 27.445	1.993 to 27.511
Index ranges	-12<=h<=12, -20<=k<=20, -14<=l<=14	-13<=h<=13, -20<=k<=20, -14<=l<=14	-13<=h<=13, -20<=k<=20, -14<=l<=13	-12<=h<=12, -12<=k<=12, -14<=l<=14
Reflections collected	18297	20364	22778	16817
Independent reflections	3837 [R(int) = 0.0284]	4253 [R(int) = 0.0255]	4222 [R(int) = 0.0310]	4159 [R(int) = 0.0242]
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	3837 / 3 / 241	4253 / 6 / 256	4222 / 6 / 256	4159 / 120 / 290
Goodness-of-fit on F^2	1.054	1.063	1.053	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0262, wR2 = 0.0645	R1 = 0.0246, wR2 = 0.0608	R1 = 0.0247, wR2 = 0.0609	R1 = 0.0183, wR2 = 0.0445
R indices (all data)	R1 = 0.0291, wR2 = 0.0664	R1 = 0.0264, wR2 = 0.0618	R1 = 0.0278, wR2 = 0.0622	R1 = 0.0189, wR2 = 0.0449
Largest diff. peak and hole e.$Å^{-3}$	0.459 and -0.239	0.389 and -0.328	0.415 and -0.270	0.643 and -0.507

Table S2. Selected bond distances (Å), angles (˚) and hydrogen bonding for **1**

Bond lengths (Å)			
Mn(1)-O(1)	2.0937(10)	Mn(1)-N(1)	2.2612(12)
Mn(1)-O(5)	2.1774(10)	Mn(1)-O(4)#1	2.2818(10)
Mn(1)-O(3)#1	2.2139(10)	Mn(1)-N(2)	2.2969(12)

Angles (˚)			
O(1)-Mn(1)-O(5)	94.17(4)	O(3)#1-Mn(1)-O(4)#1	58.48(4)
O(1)-Mn(1)-O(3)#1	111.74(4)	N(1)-Mn(1)-O(4)#1	101.87(4)
O(5)-Mn(1)-O(3)#1	90.84(4)	O(1)-Mn(1)-N(2)	160.53(4)
O(1)-Mn(1)-N(1)	90.53(4)	O(5)-Mn(1)-N(2)	84.38(4)
O(5)-Mn(1)-N(1)	105.99(4)	O(3)#1-Mn(1)-N(2)	87.71(4)
O(3)#1-Mn(1)-N(1)	151.24(4)	N(1)-Mn(1)-N(2)	71.36(4)
O(1)-Mn(1)-O(4)#1	98.27(4)	O(4)#1-Mn(1)-N(2)	92.58(4)
O(5)-Mn(1)-O(4)#1	149.29(4)		

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(2)#2	0.845(13)	1.851(14)	2.6914(15)	172.9(18)
O(5)-H(5B)...O(3)#3	0.850(13)	1.943(15)	2.6999(14)	147.8(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1 #3 x+1,y,z

Table S3. Selected bond distances (Å), angles (˚) and hydrogen bonding for **2**

Bond lengths (Å)			
Co(1)-O(1)	2.0638(10)	Co(1)-N(2)	2.1356(12)
Co(1)-N(1)	2.0808(12)	Co(1)-O(4)#1	2.1974(10)
Co(1)-O(5)	2.0977(11)		
Co(1)-O(3)#1	2.1306(10)		
Angles (˚)			
O(1)-Co(1)-N(1)	95.02(4)	O(5)-Co(1)-N(2)	88.45(4)
O(1)-Co(1)-O(5)	91.36(4)	O(3)#1-Co(1)-N(2)	92.31(4)
N(1)-Co(1)-O(5)	100.20(4)	O(1)-Co(1)-O(4)#1	93.67(4)
O(1)-Co(1)-O(3)#1	95.65(4)	N(1)-Co(1)-O(4)#1	103.28(4)
N(1)-Co(1)-O(3)#1	161.28(4)	O(5)-Co(1)-O(4)#1	155.44(4)
O(5)-Co(1)-O(3)#1	94.89(4)	O(3)#1-Co(1)-O(4)#1	60.70(4)
O(1)-Co(1)-N(2)	172.02(4)	N(2)-Co(1)-O(4)#1	89.78(4)
N(1)-Co(1)-N(2)	77.17(5)		

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(6)	0.843(14)	1.847(14)	2.6824(16)	170.6(18)
O(5)-H(5B)...O(2)	0.836(13)	1.849(14)	2.6542(15)	161.1(18)
O(6)-H(6A)...O(3)#2	0.859(14)	1.847(15)	2.6953(15)	169.1(18)
O(6)-H(6B)...O(2)#3	0.838(14)	2.029(16)	2.8216(16)	157.5(17)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x-1,y,z #3 -x,-y+1,-z+1

Table S4. Selected bond distances (Å), angles (˚) and hydrogen bonding for **3**

Bond lengths (Å)			
Zn(1)-O(1)	2.0549(11)	Zn(1)-O(5)	2.0945(11)
Zn(1)-O(3)#1	2.0888(11)	Zn(1)-N(2)	2.1765(13)
Zn(1)-N(1)	2.0894(13)	Zn(1)-O(4)#1	2.3105(12)

Angles (˚)			
O(1)-Zn(1)-O(3)#1	98.63(5)	N(1)-Zn(1)-N(2)	76.61(5)
O(1)-Zn(1)-N(1)	94.04(5)	O(5)-Zn(1)-N(2)	89.35(5)
O(3)#1-Zn(1)-N(1)	156.85(5)	O(1)-Zn(1)-O(4)#1	94.17(4)
O(1)-Zn(1)-O(5)	91.65(5)	O(3)#1-Zn(1)-O(4)#1	59.55(4)
O(3)#1-Zn(1)-O(5)	96.37(4)	N(1)-Zn(1)-O(4)#1	100.42(5)
N(1)-Zn(1)-O(5)	102.57(5)	O(5)-Zn(1)-O(4)#1	155.81(4)
O(1)-Zn(1)-N(2)	170.58(5)	N(2)-Zn(1)-O(4)#1	88.71(4)
O(3)#1-Zn(1)-N(2)	90.56(5)		

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(6)	0.839(14)	1.847(15)	2.6820(17)	173(2)
O(5)-H(5B)...O(2)	0.830(14)	1.865(14)	2.6605(16)	160.2(19)
O(6)-H(6A)...O(2)#2	0.820(14)	2.052(16)	2.8226(17)	156.4(19)
O(6)-H(6B)...O(3)#3	0.862(14)	1.841(15)	2.6936(16)	169.8(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1 #3 x-1,y,z

Table S5. Selected bond distances (Å), angles (˚) and hydrogen bonding for **4**

Bond lengths (Å)			
Cd(1)-O(5)	2.3085(11)	Cd(1)-O(4)#1	2.3973(11)
Cd(1)-O(3)#1	2.3467(11)	Cd(1)-O(1)	2.409(10)
Cd(1)-N(1)	2.3537(13)	Cd(1)-O(2)	2.580(3)
Cd(1)-N(2)	2.3574(13)		

Angles (˚)			
O(5)-Cd(1)-O(3)#1	145.41(4)	O(3)#1-Cd(1)-O(1)	94.9(3)
O(5)-Cd(1)-N(1)	122.22(4)	N(1)-Cd(1)-O(1)	83.1(2)
O(3)#1-Cd(1)-N(1)	92.30(4)	N(2)-Cd(1)-O(1)	149.22(19)
O(5)-Cd(1)-N(2)	91.08(4)	O(4)#1-Cd(1)-O(1)	126.7(2)
O(3)#1-Cd(1)-N(2)	100.00(4)	O(5)-Cd(1)-O(2)	76.35(14)
N(1)-Cd(1)-N(2)	69.56(5)	O(3)#1-Cd(1)-O(2)	80.90(14)
O(5)-Cd(1)-O(4)#1	94.04(4)	N(1)-Cd(1)-O(2)	134.09(8)
O(3)#1-Cd(1)-O(4)#1	55.40(4)	N(2)-Cd(1)-O(2)	156.34(8)
N(1)-Cd(1)-O(4)#1	133.90(4)	O(4)#1-Cd(1)-O(2)	77.51(7)
N(2)-Cd(1)-O(4)#1	83.59(4)	O(1)-Cd(1)-O(2)	52.74(18)
O(5)-Cd(1)-O(1)	91.7(3)		

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(4)#2	0.842(5)	1.810(6)	2.6500(15)	175.7(17)
O(5)-H(5B)...O(2)	0.842(6)	2.310(17)	3.029(4)	143(2)
O(5)-H(5C)...O(6)#3	0.842(5)	1.965(11)	2.7623(18)	158(3)
O(6)-H(6A)...O(1)	0.842(5)	1.848(13)	2.637(9)	155(2)
O(6)-H(6A)...O(1A)	0.842(5)	2.114(14)	2.880(9)	151.1(19)
O(6)-H(6B)...O(5)#3	0.842(5)	1.977(12)	2.7623(18)	155(3)
O(6)-H(6C)...O(6)#3	0.842(5)	1.962(11)	2.783(3)	165(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x,y-1,z #3 -x+1,-y,-z+2

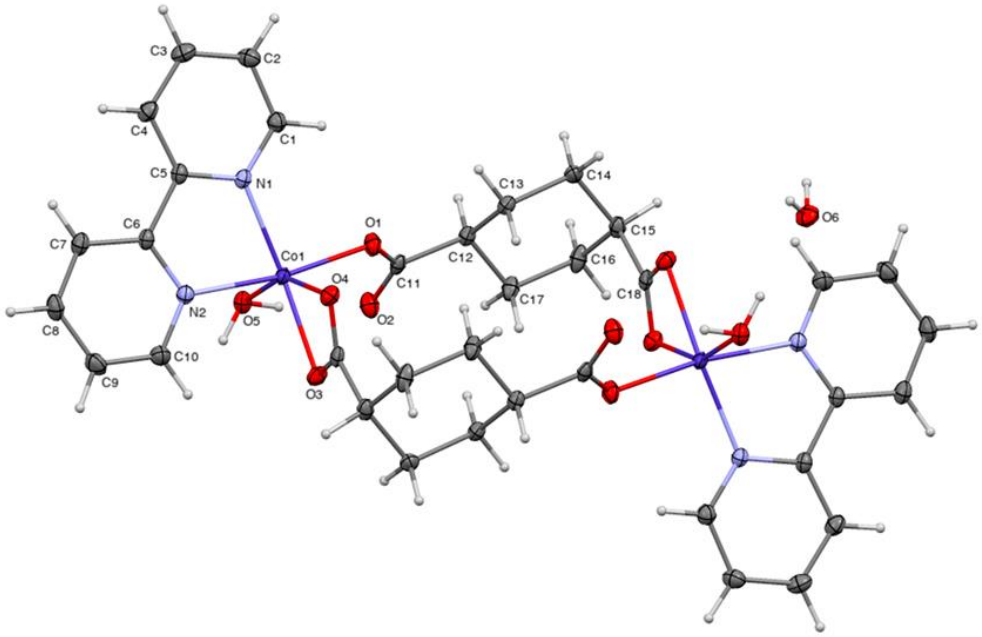

Figure S1. Molecular structure of **2** (ellipsoids shown at 50% probability).

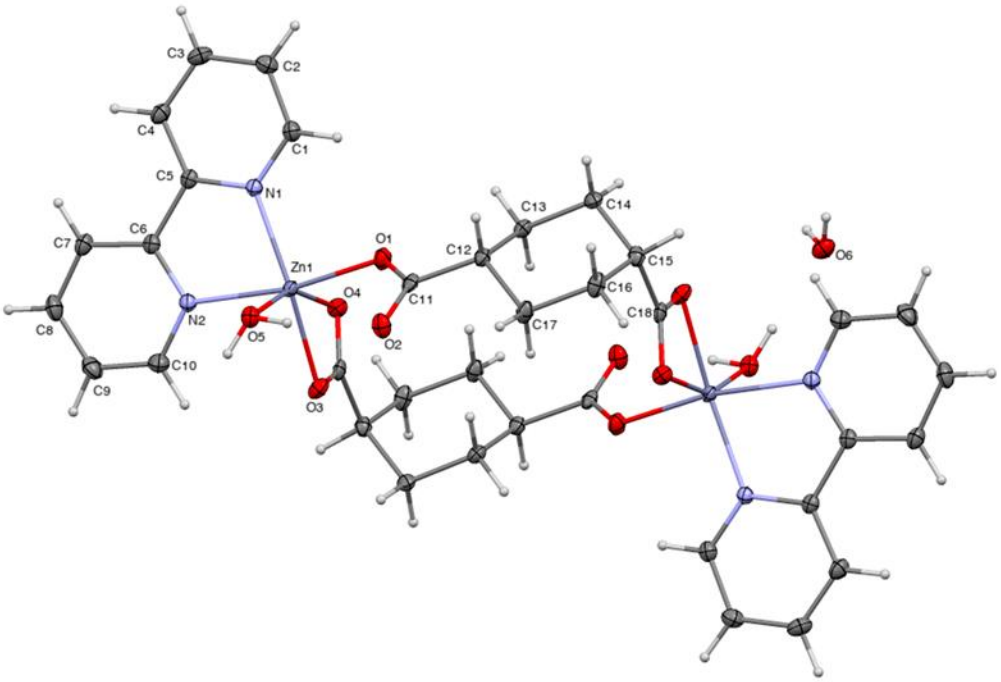

Figure S2. Molecular structure of **3** (ellipsoids shown at 50% probability).

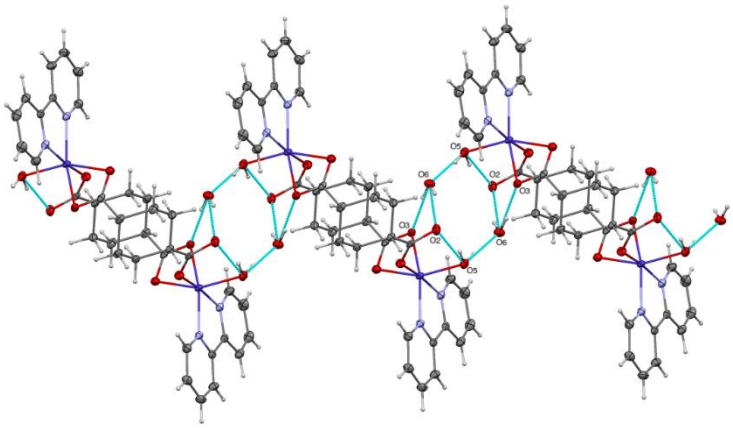

Figure S3. Supramolecular 1-D zig-zag chain of **2** formed by hydrogen-bonding interactions (ellipsoids shown at 50% probability).

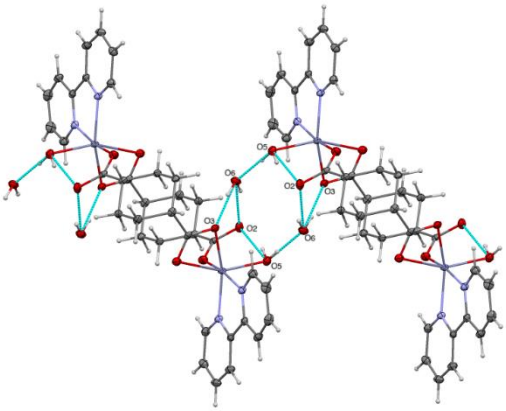

Figure S4. Supramolecular 1-D zig-zag chain of **3** formed by hydrogen-bonding interactions (ellipsoids shown at 50% probability).

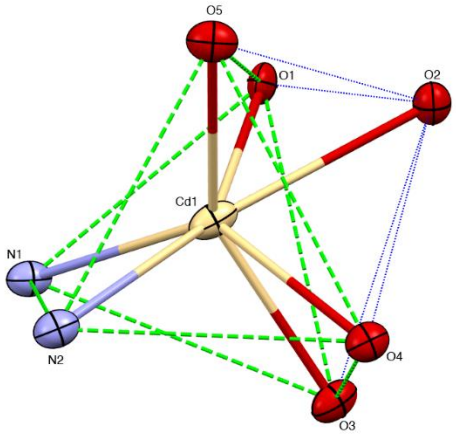

Figure S5. Distorted-monocapped trigonal prismatic geometry of Cd(II) in **4** (only coordinated atoms are shown for clarity; ellipsoids shown at 50% probability).

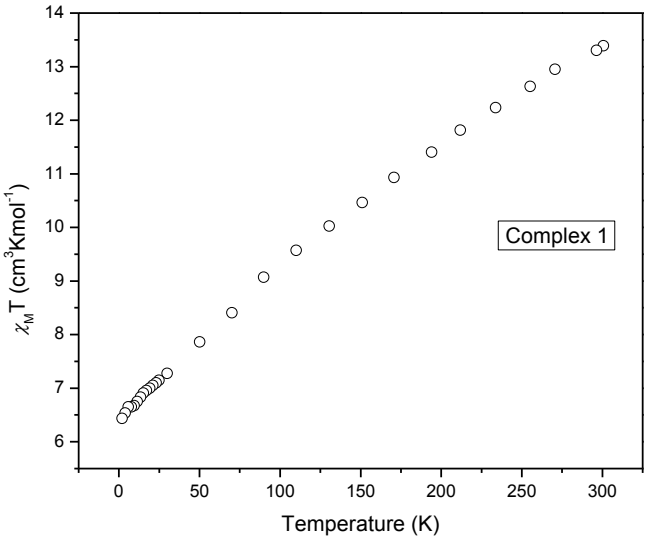

Figure S6. χT vs. T plot for **1**.

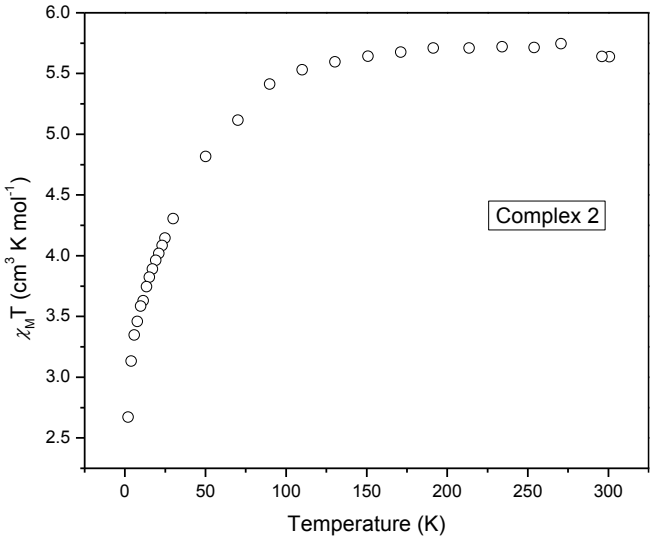

Figure S7. χT vs. T plot for **2**.

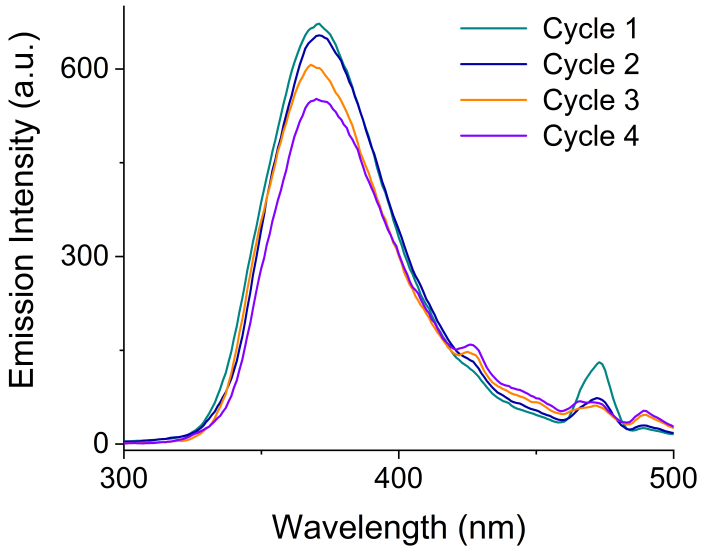

Figure S8. Changes of the initial luminescent intensity of **4** (50 μM) during four cycles of CH_3CN detection-activation