Supporting Information

Two Unique Entangling Cd(II) Coordination Frameworks Constructed by Square Cd_4-building blocks and auxiliary N,N′-Donor Ligands

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Cryst. Growth Des. (Communication)

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1. Materials and General Methods

All solvents and reagents for synthesis and analysis were commercially available and used as received. The FT-IR spectra were recorded as KBr pellets on a FTIR Nexus spectrophotometer. Elemental analysis of C, H, and N was performed on a Perkin-Elmer 2400 Series II analyzer. X-ray powder diffraction (XRPD) patterns for microcrystalline samples were measured on a Rigaku Ultima IV diffractometer for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 2 deg/min and a step size of 0.02 deg in 2θ. The calculated PXRD patterns were obtained from the single-crystal X-ray diffraction data. Thermogravimetric (TG) analysis was taken on a NETZSCH STA 449C microanalyzer in an atmosphere of nitrogen at a heating rate of 10 ºC·min^{-1}. Solid-state fluorescent spectra were carried out on a Perkin-Elmer LS50B luminescence spectrophotometer.

2. Crystallographic Data Collection and Refinement

Single-crystal X-ray diffraction data collection for complexes **1** and **2** was carried out at room temperature on a RIGAKU RAXIS-RAPID diffractometer with Mo Ka radiation (λ = 0.71073 Å). The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least–squares methods with SHELXL.[1] Metal centers in each complex were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on F^2. The hydrogen-atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Selected bond lengths for complexes **1** and **2** are listed in Table S1.

References

(1) Sheldrick, G. M. SHELXTL NT, *Program for Solution and Refinement of Crystal Structures*, version 5.1, University of Göttingen, Germany, 1997.

Table S1 Selected bond distances (Å) and angles (deg) for complexes **1** and **2.**

Complex **1**			
Cd(1)-N(3)	2.266(4)	Cd(1)-N(1)	2.286(3)
Cd(1)-N(2)#1	2.334(4)	Cd(1)-O(4)#1	2.359(4)
Cd(1)-O(5)	2.364(3)	Cd(1)-O(1)	2.452(4)
N(3)-Cd(1)-N(1)	153.34(12)	N(3)-Cd(1)-N(2)#1	96.76(13)
N(1)-Cd(1)-N(2)#1	94.46(12)	N(3)-Cd(1)-O(4)#1	106.10(13)
N(1)-Cd(1)-O(4)#1	100.27(12)	N(2)#1-Cd(1)-O(4)#1	73.17(11)
N(3)-Cd(1)-O(5)	83.35(12)	N(1)-Cd(1)-O(5)	95.68(11)
N(2)#1-Cd(1)-O(5)	156.51(12)	O(4)#1-Cd(1)-O(5)	84.19(11)
N(3)-Cd(1)-O(1)	81.94(12)	N(1)-Cd(1)-O(1)	71.48(11)
N(2)#1-Cd(1)-O(1)	118.82(12)	O(4)#1-Cd(1)-O(1)	165.27(11)
O(5)-Cd(1)-O(1)	84.53(12)		
Complex **2**			
Cd(2)-N(3)	2.234(3)	Cd(2)-N(6)#1	2.272(3)
Cd(1)-N(4)#2	2.233(3)	Cd(2)-N(5)	2.351(3)
Cd(1)-N(2)	2.310(3)	Cd(1)-N(1)#3	2.235(3)
Cd(1)-O(8)#2	2.403(3)	Cd(1)-O(1)	2.377(2)
Cd(2)-O(9)	2.288(3)	Cd(1)-O(4)#3	2.489(3)
Cd(2)-O(5)	2.410(3)	Cd(2)-O(2)	2.455(2)
N(3)-Cd(2)-N(6)#1	162.11(11)	N(3)-Cd(2)-O(9)	95.08(11)
N(6)#1-Cd(2)-O(9)	101.06(12)	N(3)-Cd(2)-N(5)	93.00(11)
N(6)#1-Cd(2)-N(5)	92.89(11)	O(9)-Cd(2)-N(5)	96.20(11)
N(3)-Cd(2)-O(5)	72.48(10)	N(6)#1-Cd(2)-O(5)	89.65(10)
O(9)-Cd(2)-O(5)	154.42(10)	N(5)-Cd(2)-O(5)	106.49(11)
N(3)-Cd(2)-O(2)	95.50(10)	N(6)#1-Cd(2)-O(2)	79.11(10)
O(9)-Cd(2)-O(2)	82.60(9)	N(5)-Cd(2)-O(2)	171.48(10)
O(5)-Cd(2)-O(2)	76.65(9)	N(4)#2-Cd(1)-N(1)#3	157.47(11)
N(4)#2-Cd(1)-N(2)	101.82(11)	N(1)#3-Cd(1)-N(2)	96.96(10)
N(4)#2-Cd(1)-O(1)	93.40(11)	N(1)#3-Cd(1)-O(1)	104.21(10)
N(2)-Cd(1)-O(1)	72.10(9)	N(4)#2-Cd(1)-O(8)#2	72.92(10)
N(1)#3-Cd(1)-O(8)#2	90.47(10)	N(2)-Cd(1)-O(8)#2	169.03(10)
O(1)-Cd(1)-O(8)#2	98.29(10)	N(4)#2-Cd(1)-O(4)#3	93.92(10)
N(1)#3-Cd(1)-O(4)#3	71.39(9)	N(2)-Cd(1)-O(4)#3	96.90(10)
O(1)-Cd(1)-O(4)#3	167.86(10)	O(8)#2-Cd(1)-O(4)#3	93.11(11)

Symmetry transformations used to generate equivalent atoms: #1: y+1/2, -x+1/2, -z+1/2 for **1**; #1: -x+2, y-1/2, -z+3/2; #2: -x+1, -y+1, -z+1; #3: x+1/2, -y+1/2, -z+1 for **2**.

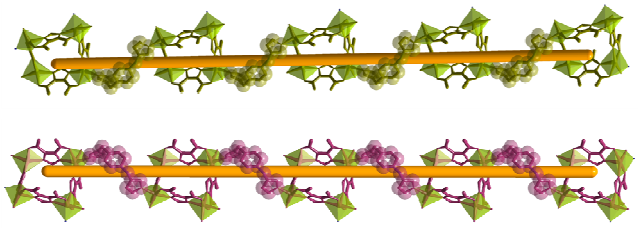


Figure S1. Left-handed (top) and right-handed (bottom) helical chains in **1** constructed from Cd4-squares and cis-bix ligands.

Figure S2. View of the 2D layer in **1** along the [010] direction.

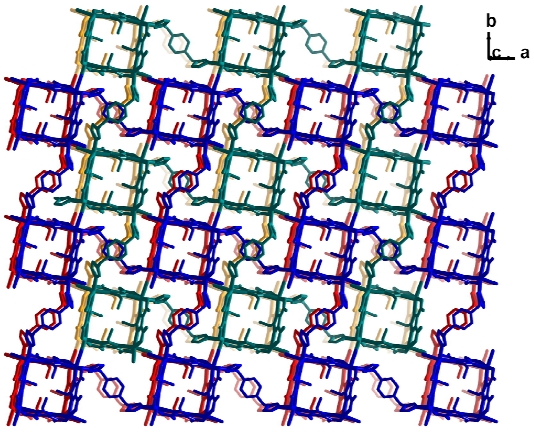


Figure S3. View of the 2D → 3D parallel polycatenate architecture in **1**.

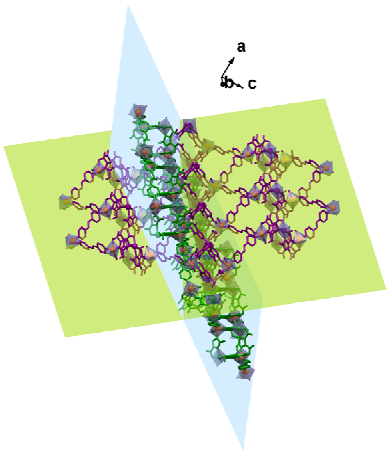


Figure S4. Two sets of layers in **2** oriented towards different directions with an angle of 71.75º.

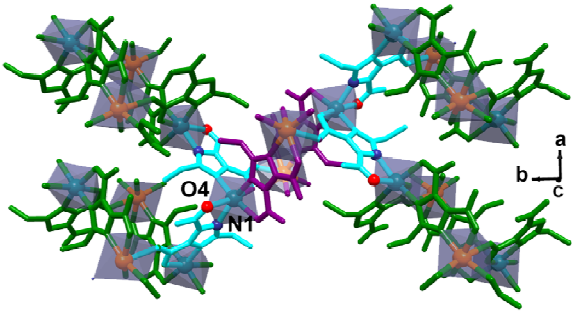


Figure S5. The linking of μ_3-HEtIDC^{2-} anions in N',O'-chelating mode in **2**.

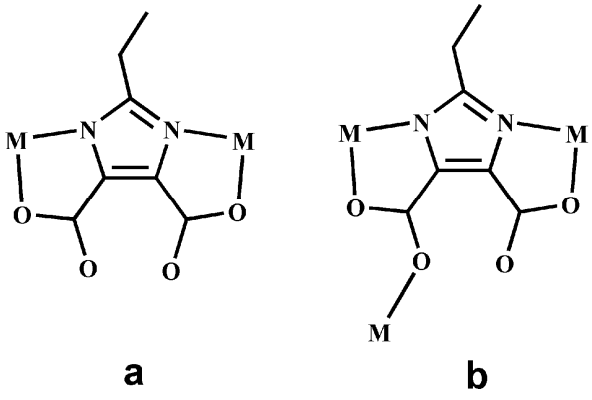
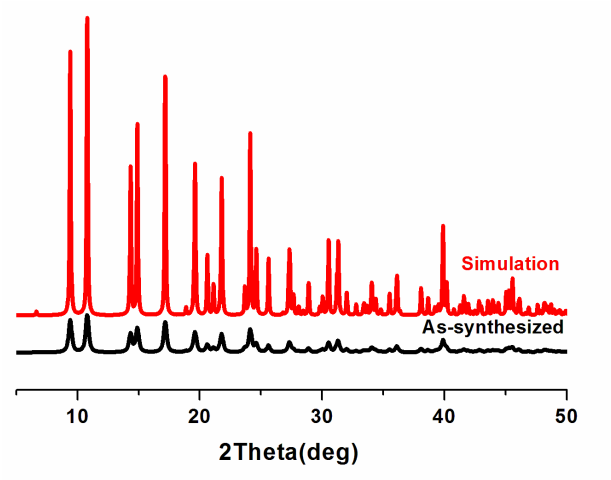
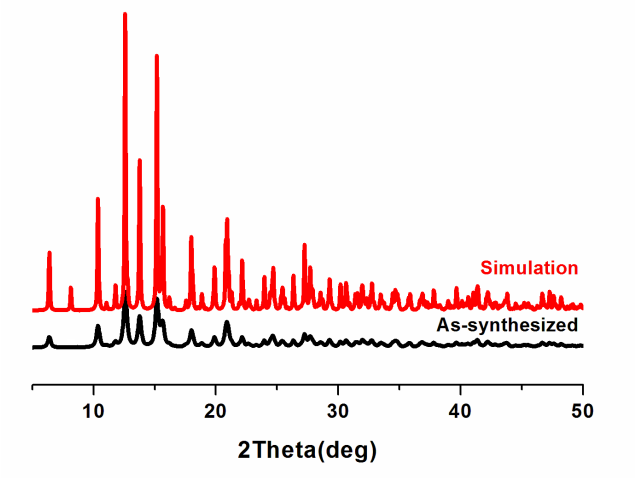


Figure 5. Coordination modes of HEtIDC^{2-} anions. (a) μ_2-κN,O:κN',O'; (b) μ_3-κN,O:κO:κN',O'.



(a)



(b)

Figure S6. Simulated and experimental PXRD patterns for complexes **1** (a) and **2** (b).

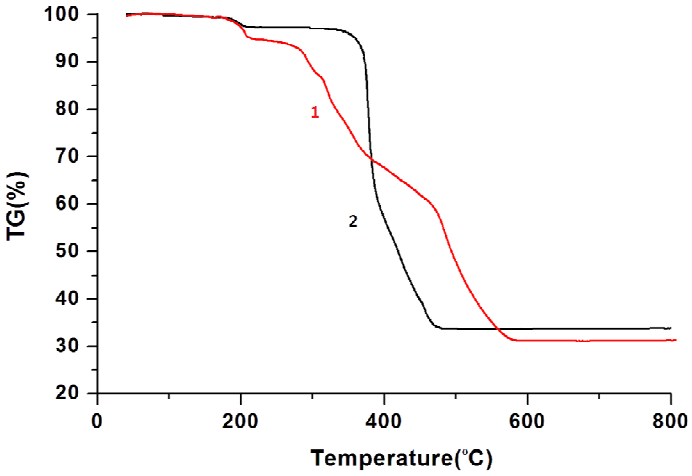


Figure S7. TG curves of complexes **1** and **2**.

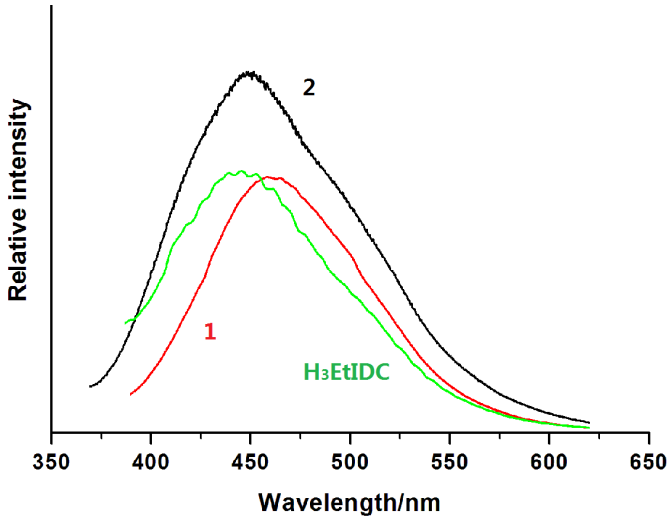


Figure S8. Solid-state emission spectra of **1** and **2** and the free ligand H_3EtIDC.