Supplementary Information

Interweaving of two enantiomorphic 3D heterometallic coordination polymers with homochiral unequal triple concentric helical chains

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1. Experimental procedures

1.1 Materials and Instruments.

All the chemicals were purchased commercially and used as received. Thermogravimetric analysis-mass spectrometry analysis (TGA-MS) experiments were performed using a TGA/NETZSCH STA449C instrument heated from 30–800 ºC (heating rate of 10 ºC /min, nitrogen stream). The powder X-ray diffraction (XRD) patterns were recorded on crushed single crystals in the 2θ range 5–50º using Cu-Kα radiation. The XRD were measured on a PAN alytical X'pert PRO X-Ray Diffractometer. IR spectra using the KBr pellet technique were recorded on a Spectrum-One FT-IR spectrophotometer. Elemental analyses (C, H, and N) were measured with an Elemental Vairo EL III Analyzer. Fluorescence spectra for the solid samples were performed on an Edinburgh Analytical instrument FLS920. The NLO properties of **1D** and **1L** were tested on the powder samples by the Kurtz and Perry method[1] using an Nd:YAG laser (1064 nm) with an input pulse of 350 mV.

1.2 Synthesis of $[Cd_3K_3(D\text{-}HAPA)_3(m\text{-}BDC)_6(EtOH)_3]_n$ (1D) and $[Cd_3K_3(L\text{-}HAPA)_3(m\text{-}BDC)_6(EtOH)_3]_n$ (1L). A mixture of $Cd(NO_3)_2{\cdot}4H_2O$, (0.0925 g, 0.3 mmol), KNO_3 (0.5055 g, 0.5 mmol), *m*-H_2BDC (0.1661 g, 1.0 mmol) and D-Alaninol (0.156 mL, 2.0 mmol) in CH_3CH_2OH (10 mL) was stirred at room temperature for a few minutes. The resulting slurry was transferred into a 20 mL of Teflon-lined stainless steel vessel, which was heated at 130 ºC for 12 hrs and then cooled to room temperature in two days. Colorless prism crystals of **1D** were collected (yield 70%, based on Cd). Elemental Anal. Calcd. for $Cd_3K_3C_{63}H_{72}N_3O_{30}$ (**1D**): C, 41.90; H, 4.02; N, 2.33; found: C, 41.62; H, 3.79; N, 2.57. IR (KBr, cm^{-1}): 1607s, 1558s, 1478w, 1436m, 1043w, 914w, 829w, 657vw (Fig. S10). Complex **1L** was prepared in a manner similar to that for **1D** except that L-Alaninol was used instead of D-Alaninol ((yield 64%, based on Cd). Elemental Anal. Calcd. for $Cd_3K_3C_{63}H_{72}N_3O_{30}$ (**1L**): C, 41.90; H, 4.02; N, 2.33; found: C, 41.79; H, 3.75; N, 2.41. IR (KBr, cm^{-1}): 1607s, 1558s, 1478w, 1436m, 1043w, 914w, 829w, 657vw (Fig. S10).

1.3 X-ray Crystallography.

Single-crystal X-ray diffraction data were collected on a Rigaku diffractometer with a Mercury CCD area detector (Mo Kα; λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied to the data using the Crystal Clear program.[2] The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXTL-97 program.[3] Metal atoms in each compound were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. Crystallographic data and other pertinent information are summarized in Table S1.

Reference

1. S. W. Kurtz, T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798−3813.
2. *CrystalClear*, version 1.36; Molecular Structure Corp. and Rigaku Corp.: The Woodlands, TX, and Tokyo, Japan, 2000.
3. G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany.

Table S1 Crystallographic data for compounds **1D** and **1L**

Compound	**1D**	**1L**
Formula	$C_{63}H_{72}Cd_3K_3N_3O_{30}$	$C_{63}H_{72}Cd_3K_3N_3O_{30}$
Formula mass	1805.74	1805.74
Crystal system	Hexagonal	Hexagonal
Space group	$P6_5$	$P6_1$
a (Å)	20.5909(4)	20.609(3)
b (Å)	20.5909(4)	20.609(3)
c (Å)	28.3082(9)	28.314(4)
α (º)	90	90
β (º)	90	90
γ (º)	120	120
V (Å^3)	10394.3(4)	10414(2)
Z	6	6
μ (mm^{-1})	1.183	1.181
D_{calcd} (g/cm^3)	1.731	1.728
F(000)	5472	5472
R_{int}	0.0263	0.0412
R_1[a] [I >2σ(I)]	0.0308	0.0704
wR_2[b] [I >2σ(I)]	0.0734	0.1639
GOF on F^2	1.072	1.106
Flack parameter	−0.016(14)	0.09(3)

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$

Table S2 Bond lengths (Å) and angles (º) for complexes **1D** and **1L**

1D			
Cd(1)−O(1A)	2.701(3)	Cd(3)−O(21)	2.494(3)
Cd(1)−O(2A)	2.283(2)	Cd(3)−O(22)	2.358(3)
Cd(1)−O(3)	2.309(3)	K(1)−O(7)	2.833(3)
Cd(1)−O(4)	2.517(2)	K(1)−O(9)	2.713(3)
Cd(1)−O(7)	2.751(3)	K(1)−O(15F)	3.255(3)
Cd(1)−O(8)	2.285(2)	K(1)−O(18F)	2.710(3)
Cd(1)−O(9)	2.305(3)	K(1)−O(21F)	2.718(3)
Cd(1)−O(10)	2.526(3)	K(1)−O(25)	2.831(4)
Cd(2)−O(5C)	2.337(3)	K(1)−O(26)	2.958(3)
Cd(2)−O(6C)	2.459(3)	K(2)−O(11B)	2.689(3)
Cd(2)−O(11)	2.761(4)	K(2)−O(13D)	3.037(3)
Cd(2)−O(12)	2.309(3)	K(2)−O(23B)	2.634(3)
Cd(2)−O(13D)	2.511(3)	K(2)−O(24)	2.611(3)
Cd(2)−O(14D)	2.337(3)	K(2)−O(27)	2.787(4)
Cd(2)−O(23)	2.432(3)	K(2)−O(28)	2.914(3)
Cd(2)−O(24)	2.354(3)	K(3)−O(1D)	2.786(3)
Cd(3)−O(15)	2.401(2)	K(3)−O(3E)	2.662(3)
Cd(3)−O(16)	2.395(3)	K(3)-O(16)	2.730(3)
Cd(3)−O(17)	2.436(2)	K(3)−O(17)	3.035(3)
Cd(3)−O(18)	2.374(3)	K(3)−O(19B)	2.746(3)
Cd(3)−O(19B)	2.510(3)	K(3)−O(29)	2.809(5)
Cd(3)−O(20B)	2.363(3)	K(3)−O(30)	3.026(4)
O(1A)−Cd(1)−O(7)	108.43(8)	O(20B)−Cd(3)−O(15)	86.56(9)
O(2A)−Cd(1)−O(1A)	51.78(9)	O(20B)−Cd(3)−O(16)	93.80(10)
O(2A)−Cd(1)−O(3)	137.25(9)	O(20B)−Cd(3)−O(17)	139.93(9)
O(2A)−Cd(1)−O(4)	161.13(9)	O(20B)−Cd(3)−O(18)	165.00(9)
O(2A)−Cd(1)−O(7)	74.61(9)	O(20B)−Cd(3)−O(19B)	53.43(9)
O(2A)−Cd(1)−O(8)	82.02(9)	O(20B)−Cd(3)−O(21)	86.73(9)
O(2A)-Cd(1)−O(9)	96.23(9)	O20(B)−Cd(3)−O(22)	87.65(10)
O(2A)−Cd(1)−O(10)	79.47(9)	O(22)−Cd(3)−O(15)	141.11(9)
O(3)−Cd(1)−O(1A)	86.30(9)	O(22)−Cd(3)−O(16)	164.28(9)
O(3)−Cd(1)−O(4)	54.11(8)	O(22)−Cd(3)−O(17)	84.74(10)
O(3)−Cd(1)−O(7)	135.70(9)	O(22)−Cd(3)−O(18)	91.42(10)
O(3)−Cd(1)−O(10)	90.67(9)	O(22)−Cd(3)−O(19B)	87.16(10)
O(4)−Cd(1)−O(1A)	131.04(9)	O(22)−Cd(3)−O(21)	53.92(9)
O(4)−Cd(1)−O(7)	87.95(8)	O(7)−K(1)−O(15F)	95.94(8)
O(4)−Cd(1)−O(10)	118.27(9)	O(7)−K(1)−O(26)	82.63(9)
O(8)−Cd(1)−O(1A)	75.41(10)	O(9)−K(1)−O(7)	79.12(9)
O(8)−Cd(1)−O(3)	96.56(10)	O(9)−K(1)−O(15F)	70.35(7)
O(8)−Cd(1)−O(4)	81.38(9)	O(9)−K(1)−O(21F)	136.59(9)

O(8)−Cd(1)−O(7)	51.03(9)	O(9)−K(1)−O(25)	138.40(10)
O(8)−Cd(1)−O(10)	159.20(10)	O(9)−K(1)−O(26)	74.87(8)
O(8)−Cd(1)−O(9)	138.39(10)	O(18F)−K(1)−O(7)	157.81(8)
O(9)−Cd(1)−O(1A)	134.49(9)	O(18F)−K(1)−O(9)	102.32(9)
O(9)−Cd(1)−O(3)	111.21(10)	O(18F)−K(1)−O(15F)	64.57(7)
O(9)−Cd(1)−O(4)	90.27(9)	O(18F)−K(1)−O(21F)	70.99(9)
O(9)−Cd(1)−O(7)	88.21(9)	O(18F)−K(1)−O(25)	83.17(9)
O(9)−Cd(1)−O(10)	53.88(9)	O(18F)−K(1)−O(26)	119.31(9)
O(10)−Cd(1)−O(1A)	85.68(9)	O(21F)−K(1)−O(7)	92.55(9)
O(10)−Cd(1)−O(7)	130.86(9)	O(21F)−K(1)−O(15F)	68.28(8)
O(5C)−Cd(2)−O(6C)	54.76(8)	O(21F)−K(1)−O(25)	84.51(10)
O(5C)−Cd(2)−O(11)	85.68(9)	O(21F)−K(1)−O(26)	146.80(9)
O(5C)−Cd(2)−O(13D)	127.72(10)	O(25)−K(1)−O(7)	110.70(9)
O(5C)−Cd(2)−O(23)	88.47(9)	O(25)−K(1)−O(15F)	142.77(8)
O(5C)−Cd(2)−O(24)	117.47(10)	O(25)−K(1)−O(26)	66.96(10)
O(6C)−Cd(2)−O(11)	139.27(9)	O(26)−K(1)−O(15F)	144.78(8)
O(6C)−Cd(2)−O(13D)	86.07(10)	O(11B)−K(2)−O(13D)	86.68(10)
O(12)−Cd(2)−O(5C)	135.75(10)	O(11B)−K(2)−O(27)	86.18(12)
O(12)−Cd(2)−O(6C)	165.99(10)	O(11B)−K(2)−O(28)	150.14(11)
O(12)−Cd(2)−O(11)	50.11(10)	O(23B)−K(2)−O(11B)	77.36(10)
O(12)−Cd(2)−O(13D)	79.92(11)	O(23B)−K(2)−O(13D)	154.15(10)
O(12)−Cd(2)−O(14D)	84.19(11)	O(23B)−K(2)−O(27)	79.88(10)
O(12)−Cd(2)−O(23)	85.15(11)	O(23B)−K(2)−O(28)	114.08(10)
O(12)−Cd(2)−O(24)	93.41(10)	O(24)−K(2)−O(11B)	125.15(10)
O(13D)−Cd(2)−O(11)	116.48(9)	O(24)−K(2)−O(13D)	74.03(9)
O(14D)−Cd(2)−O(5C)	87.71(10)	O(24)−K(2)−O(23B)	98.63(10)
O(14D)−Cd(2)−O(6C)	87.45(10)	O(24)−K(2)−O(27)	147.85(12)
O(14D)−Cd(2)−O(11)	81.07(10)	O(24)−K(2)−O(28)	81.87(9)
O(14D)−Cd(2)−O(13D)	54.01(10)	O(27)−K(2)−O(13D)	119.61(10)
O(14D)−Cd(2)−O(24)	143.04(10)	O(27)−K(2)−O(28)	69.94(11)
O(14D)−Cd(2)−O(23)	160.34(10)	O(28)−K(2)−O(13D)	89.79(9)
O(23)−Cd(2)−O(6C)	105.93(10)	O(1D)−K(3)−O(17)	97.40(8)
O(23)−Cd(2)−O(11)	79.42(10)	O(1D)−K(3)−O(29)	111.39(11)
O(23)−Cd(2)−O(13D)	139.43(10)	O(1D)−K(3)−O(30)	78.75(9)
O(24)−Cd(2)−O(6C)	86.54(10)	O(3E)−K(3)−O(1D)	78.22(9)
O(24)−Cd(2)−O(11)	124.63(10)	O(3E)−K(3)−O(16)	105.22(9)
O(24)−Cd(2)−O(13D)	89.20(10)	O(3E)−K(3)−O(17)	72.10(8)
O(24)−Cd(2)−O(23)	54.13(9)	O(3E)−K(3)−O(19B)	142.12(9)
O(15)−Cd(3)−O(17)	122.31(8)	O(3E)−K(3)−O(29)	132.54(14)
O(15)−Cd(3)−O(19B)	118.83(9)	O(3E)−K(3)−O(30)	73.77(9)
O(15)−Cd(3)−O(21)	87.36(9)	O(16)−K(3)−O(1D)	162.36(9)
O(16)−Cd(3)−O(15)	54.60(8)	O(16)−K(3)−O(17)	68.05(8)
O(16)−Cd(3)−O(17)	84.10(9)	O(16)−K(3)−O(19B)	71.34(9)
O(16)−Cd(3)−O(19B)	81.20(10)	O(16)−K(3)−O(29)	79.40(11)

O(16)−Cd(3)−O(21)	141.77(9)	O(16)−K(3)−O(30)	118.89(9)
O(17)−Cd(3)−O(19B)	86.88(8)	O(19B)−K(3)−O(1D)	95.14(9)
O(17)−Cd(3)−O(21)	118.79(9)	O(19B)−K(3)−O(17)	71.89(8)
O(18)−Cd(3)−O(15)	84.79(9)	O(19B)−K(3)−O(29)	84.82(14)
O(18)−Cd(3)−O(16)	91.14(10)	O(19B)−K(3)−O(30)	142.12(10)
O(18)−Cd(3)−O(17)	54.71(8)	O(29)−K(3)−O(17)	144.48(10)
O(18)−Cd(3)−O(19B)	141.50(9)	O(29)−K(3)−O(30)	63.73(12)
O(18)−Cd(3)−O(21)	80.67(9)	O(30)−K(3)−O(17)	145.70(9)
O(19B)−Cd(3)−O(21)	126.83(8)		

Symmetry transformations used to generate equivalent atoms:
A $y + 1, -x + y + 1, z + 1/6$, B $x - y + 1, x, z - 1/6$, C $-x + y + 2, -x + 2, z + 1/3$, D $-x + y + 1, -x + 1, z + 1/3$, E $y, -x + y + 1, z + 1/6$, F $y, -x + y, z + 1/6$

1L

Cd(1)−O(1A)	2.694(9)	Cd(3)−O(21)	2.519(8)
Cd(1)−O(2A)	2.294(5)	Cd(3)−O(22)	2.356(7)
Cd(1)−O(3)	2.305(6)	K(1)−O(7)	2.831(6)
Cd(1)−O(4)	2.512(6)	K(1)−O(9)	2.712(7)
Cd(1)−O(7)	2.729(7)	K(1)−O(15F)	3.264(7)
Cd(1)−O(8)	2.269(6)	K(1)−O(18F)	2.697(7)
Cd(1)−O(9)	2.286(6)	K(1)−O(21F)	2.732(7)
Cd(1)−O(10)	2.533(7)	K(1)−O(25)	2.774(10)
Cd(2)−O(5C)	2.329(6)	K(1)−O(26)	2.978(8)
Cd(2)−O(6C)	2.462(7)	K(2)−O(11B)	2.703(9)
Cd(2)−O(11)	2.698(10)	K(2)−O(13D)	3.058(10)
Cd(2)−O(12)	2.306(7)	K(2)−O(23B)	2.631(8)
Cd(2)−O(13D)	2.531(9)	K(2)−O(24)	2.579(9)
Cd(2)−O(14D)	2.348(7)	K(2)−O(27)	2.815(11)
Cd(2)−O(23)	2.439(8)	K(2)−O(28)	2.905(9)
Cd(2)−O(24)	2.369(7)	K(3)−O(1D)	2.803(7)
Cd(3)−O(15)	2.398(6)	K(3)−O(3E)	2.613(9)
Cd(3)−O(16)	2.379(7)	K(3)−O(16)	2.748(7)
Cd(3)−O(17)	2.409(7)	K(3)−O(17)	3.071(7)
Cd(3)−O(18)	2.395(7)	K(3)−O(19B)	2.759(7)
Cd(3)−O(19B)	2.497(8)	K(3)−O(29)	2.815(11)
Cd(3)−O(20B)	2.360(6)	K(3)−O(30)	2.998(10)
O(1A)−Cd(1)−O(7)	109.0(2)	O(20B)−Cd(3)−O(15)	86.3(2)
O(2A)−Cd(1)−O(1A)	52.1(2)	O(20B)−Cd(3)−O(16)	92.9(3)
O(2A)−Cd(1)−O(3)	137.8(2)	O(20B)−Cd(3)−O(17)	140.9(2)
O(2A)−Cd(1)−O(4)	161.1(2)	O(20B)−Cd(3)−O(18)	164.6(2)
O(2A)−Cd(1)−O(7)	75.2(2)	O(20B)−Cd(3)−O(19B)	53.7(2)
O(2A)−Cd(1)−O(10)	79.6(2)	O(20B)−Cd(3)−O(21)	86.0(2)
O(3)−Cd(1)−O(1A)	86.4(2)	O(20B)−Cd(3)−O(22)	87.0(3)
O(3)−Cd(1)−O(4)	54.5(2)	O(22)−Cd(3)−O(15)	140.9(2)
O(3)−Cd(1)−O(7)	134.8(2)	O(22)−Cd(3)−O(16)	164.3(3)

O(3)−Cd(1)−O(10)	90.7(3)	O(22)−Cd(3)−O(17)	85.6(3)
O(4)−Cd(1)−O(1A)	131.9(2)	O(22)−Cd(3)−O(18)	91.7(3)
O(4)−Cd(1)−O(7)	86.9(2)	O(22)−Cd(3)−O(19B)	85.7(3)
O(4)−Cd(1)−O(10)	117.8(2)	O(22)−Cd(3)−O(20B)	86.9(3)
O(8)−Cd(1)−O(1A)	75.5(3)	O(22)−Cd(3)−O(21)	54.0(2)
O(8)−Cd(1)−O(2A)	82.3(2)	O(7)−K(1)−O(15F)	95.64(18)
O(8)−Cd(1)−O(3)	96.2(3)	O(7)−K(1)−O(26)	83.6(2)
O(8)−Cd(1)−O(4)	81.7(2)	O(9)−K(1)−O(7)	78.2(2)
O(8)−Cd(1)−O(7)	51.1(2)	O(9)−K(1)−O(15F)	69.95(17)
O(8)−Cd(1)−O(9)	138.3(2)	O(9)−K(1)−O(21F)	135.8(2)
O(8)−Cd(1)−O(10)	159.4(3)	O(9)−K(1)−O(25)	139.8(3)
O(9)−Cd(1)−O(1A)	134.4(2)	O(9)−K(1)−O(26)	75.7(2)
O(9)−Cd(1)−O(2A)	95.7(2)	O(18F)−K(1)−O(7)	158.1(2)
O(9)−Cd(1)−O(3)	111.4(3)	O(18F)−K(1)−O(9)	102.7(2)
O(9)−Cd(1)−O(4)	89.5(2)	O(18F)−K(1)−O(15F)	64.99(18)
O(9)−Cd(1)−O(7)	87.9(2)	O(18F)−K(1)−O(21F)	71.7(2)
O(9)−Cd(1)−O(10)	54.5(2)	O(18F)−K(1)−O(25)	82.4(2)
O(10)−Cd(1)−O(1A)	85.6(2)	O(18F)−K(1)−O(26)	118.0(2)
O(10)−Cd(1)−O(7)	131.5(2)	O(21F)−K(1)−O(7)	92.2(2)
O(5C)−Cd(2)−O(6C)	55.3(2)	O(21F)−K(1)−O(15F)	68.21(19)
O(5C)−Cd(2)−O(11)	85.8(3)	O(21F)−K(1)−O(25)	84.0(3)
O(5C)−Cd(2)−O(13D)	128.2(3)	O(21F)−K(1)−O(26)	146.8(2)
O(5C)−Cd(2)−O(14D)	87.9(3)	O(25)−K(1)−O(7)	111.3(2)
O(5C)−Cd(2)−O(23)	88.6(3)	O(25)−K(1)−O(15F)	142.0(2)
O(5C)−Cd(2)−O(24)	117.4(3)	O(25)−K(1)−O(26)	67.2(2)
O(6C)−Cd(2)−O(11)	139.9(2)	O(26)−K(1)−O(15F)	145.0(2)
O(6C)−Cd(2)−O(13D)	86.1(3)	O(11B)−K(2)−O(13D)	86.9(3)
O(12)−Cd(2)−O(5C)	136.0(3)	O(11B)−K(2)−O(27)	86.5(4)
O(12)−Cd(2)−O(6C)	166.0(3)	O(11B)−K(2)−O(28)	150.7(3)
O(12)−Cd(2)−O(11)	50.2(3)	O(23B)−K(2)−O(11B)	77.1(3)
O(12)−Cd(2)−O(13D)	80.0(3)	O(23B)−K(2)−O(13D)	156.1(3)
O(12)−Cd(2)−O(14D)	84.8(3)	O(23B)−K(2)−O(27)	79.5(3)
O(12)−Cd(2)−O(23)	84.9(3)	O(23B)−K(2)−O(28)	113.4(3)
O(12)−Cd(2)−O(24)	92.4(3)	O(24)−K(2)−O(11B)	127.1(3)
O(13D)−Cd(2)−O(11)	116.3(3)	O(24)−K(2)−O(13D)	74.8(2)
O(14D)−Cd(2)−O(6C)	87.8(2)	O(24)−K(2)−O(23B)	100.7(3)
O(14D)−Cd(2)−O(11)	80.9(3)	O(24)−K(2)−O(27)	145.9(3)
O(14D)−Cd(2)−O(13D)	54.3(3)	O(24)−K(2)−O(28)	79.4(2)
O(14D)−Cd(2)−O(23)	161.2(3)	O(27)−K(2)−O(13D)	117.5(3)
O(14D)−Cd(2)−O(24)	143.4(3)	O(27)−K(2)−O(28)	69.7(3)
O(23)−Cd(2)−O(6C)	105.2(3)	O(28)−K(2)−O(13D)	89.1(2)
O(23)−Cd(2)−O(11)	80.4(3)	O(1D)−K(3)−O(17)	97.0(2)
O(23)−Cd(2)−O(13D)	138.5(3)	O(1D)−K(3)−O(29)	112.2(3)
O(24)−Cd(2)−O(6C)	86.5(2)	O(1D)−K(3)−O(30)	80.3(2)

O(24)−Cd(2)−O(11)	124.1(3)	O(3E)−K(3)−O(1D)	78.6(2)
O(24)−Cd(2)−O(13D)	89.3(3)	O(3E)−K(3)−O(16)	105.5(3)
O(24)−Cd(2)−O(23)	52.8(2)	O(3E)−K(3)−O(17)	72.3(2)
O(15)−Cd(3)−O(17)	122.5(2)	O(3E)−K(3)−O(19B)	140.0(3)
O(15)−Cd(3)−O(19B)	119.7(2)	O(3E)−K(3)−O(29)	133.9(3)
O(15)−Cd(3)−O(21)	87.1(2)	O(3E)−K(3)−O(30)	73.6(2)
O(16)−Cd(3)−O(15)	54.3(2)	O(16)−K(3)−O(1D)	160.3(2)
O(16)−Cd(3)−O(17)	84.5(3)	O(16)−K(3)−O(17)	66.9(2)
O(16)−Cd(3)−O(18)	92.5(3)	O(16)−K(3)−O(19B)	70.9(2)
O(16)−Cd(3)−O(19B)	81.8(3)	O(16)−K(3)−O(29)	79.2(3)
O(16)−Cd(3)−O(21)	141.3(2)	O(16)−K(3)−O(30)	119.4(2)
O(17)−Cd(3)−O(19B)	86.0(2)	O(19B)−K(3)−O(1D)	93.4(2)
O(17)−Cd(3)−O(21)	120.0(2)	O(19B)−K(3)−O(17)	69.9(2)
O(18)−Cd(3)−O(15)	85.0(2)	O(19B)−K(3)−O(29)	85.5(3)
O(18)−Cd(3)−O(17)	55.8(2)	O(19B)−K(3)−O(30)	144.3(3)
O(18)−Cd(3)−O(19B)	141.8(2)	O(29)−K(3)−O(17)	142.9(3)
O(18)−Cd(3)−O(21)	80.6(2)	O(29)−K(3)−O(30)	65.2(3)
O(19B)−Cd(3)−O(21)	125.8(2)	O(30)−K(3)−O(17)	145.6(2)

Symmetry transformations used to generate equivalent atoms:

A $y-1, -x+y-1, z-1/6$, B $x-y+1, x+1, z+1/6$, C $-x+y-1, -x, z-1/3$, D $-x+y-2, -x, z-1/3$, E $y-1, -x+y, z-1/6$, F $y-2, -x+y-1, z-1/6$

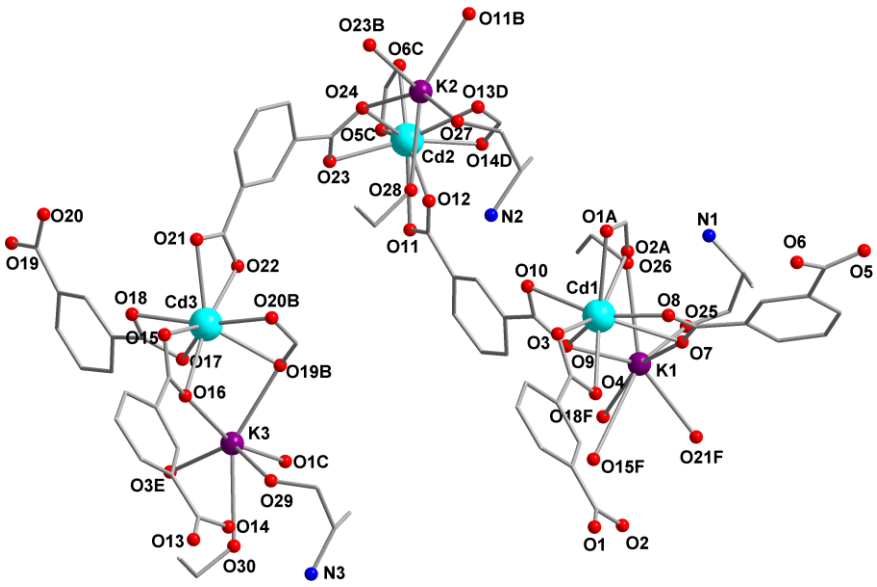

Fig. S1 Coordination environment for the metal ions in **1L**. Hydrogen atoms and the labels of carbon atoms are omitted for clarity. (Symmetry code: A $y-1, -x+y-1, z-1/6$, B $x-y+1, x+1, z+1/6$, C $-x+y-1, -x, z-1/3$, D $-x+y-2, -x, z-1/3$, E $y-1, -x+y, z-1/6$, F $y-2, -x+y-1, z-1/6$.

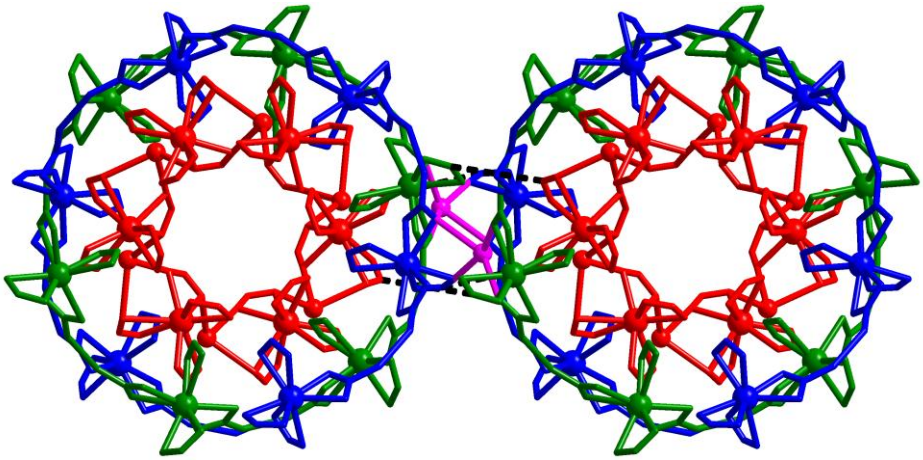

Fig. S2 The connection between two adjacent triple helical units of **ABC** viewed from the *c*-axis (pink: K3, black dotted lines: benzene rings).

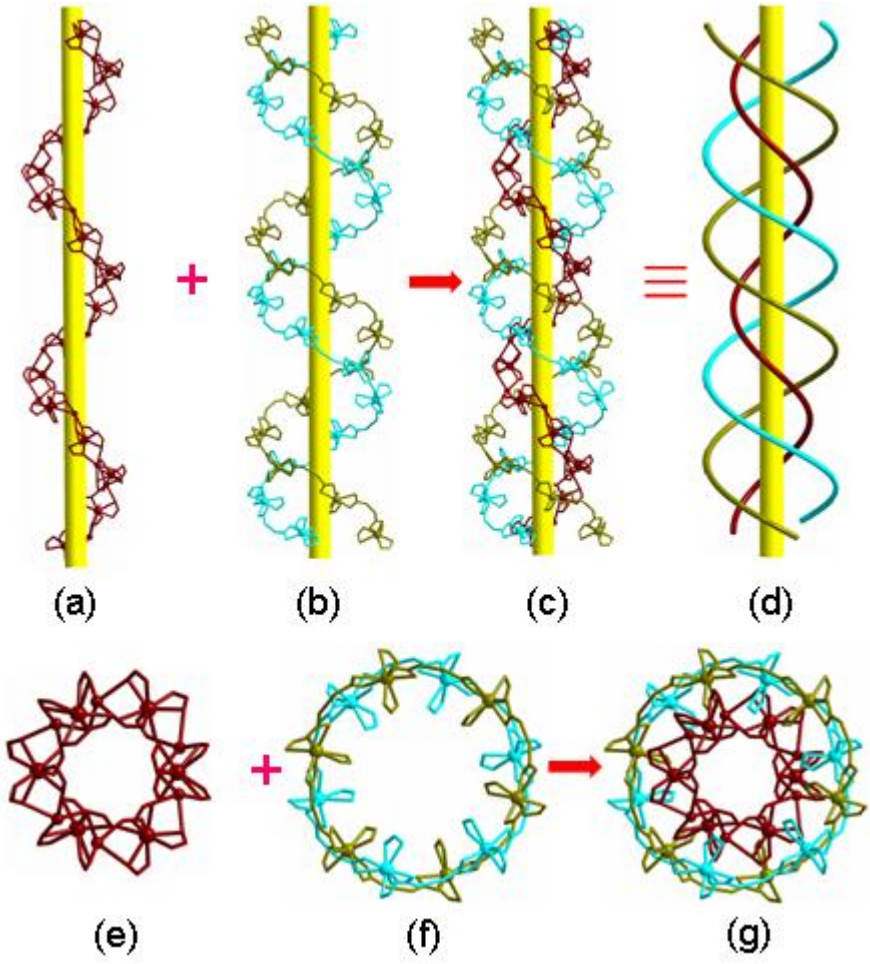

Fig. S3 (a) $\{K1Cd3K3{-}BDC\}_n$ single-helical chain (helix **F**). (b) View of unequal double-helical chains **D** and **E**. Two different chains are marked as dark-yellow $\{Cd1Cd2{-}BDC\}_n$ (**D**) and turquoise $\{Cd2Cd3{-}BDC\}_n$ (**E**), respectively. (c) View of the hierarchical assembly of the triple concentric helical system **DEF** in **1D**. (d) The idealized mode of the triple helical system. (e, f, g) View of the helical chains from the *c*-axis. Phenyl rings were omitted for charity.

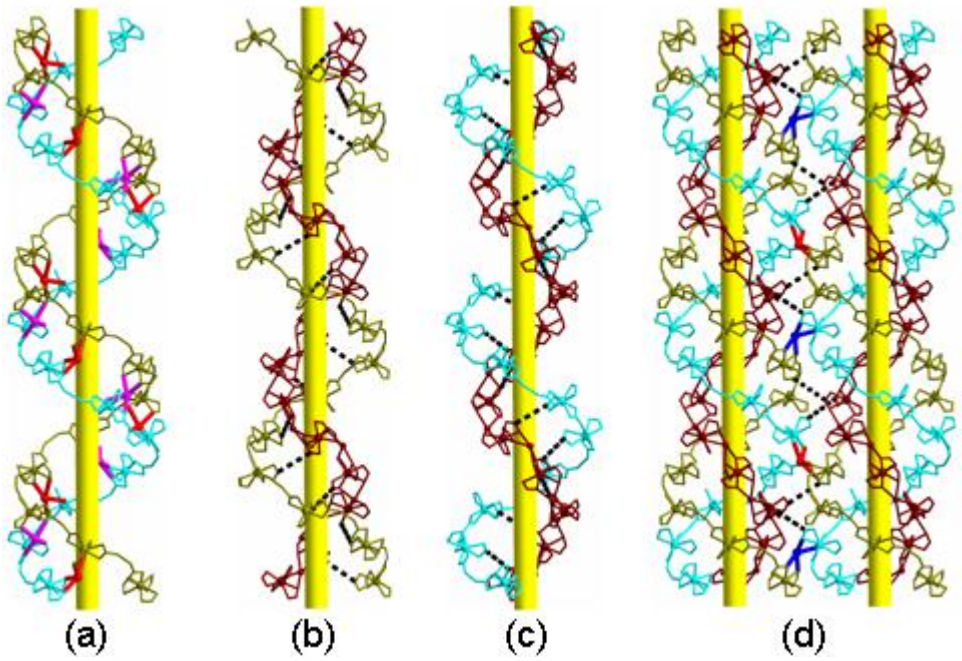

Fig. S4 (a) View of **DE** with K2 (red) and K3 (pink) linkages. (b, c) The connection of **F** with **D** and **E** through *m*-BDC^{2-} bridges (black dot lines represent benzene rings). (d) The connection between two adjacent triple-helical units (blue: K1, red: K2, black dotted lines: benzene rings).

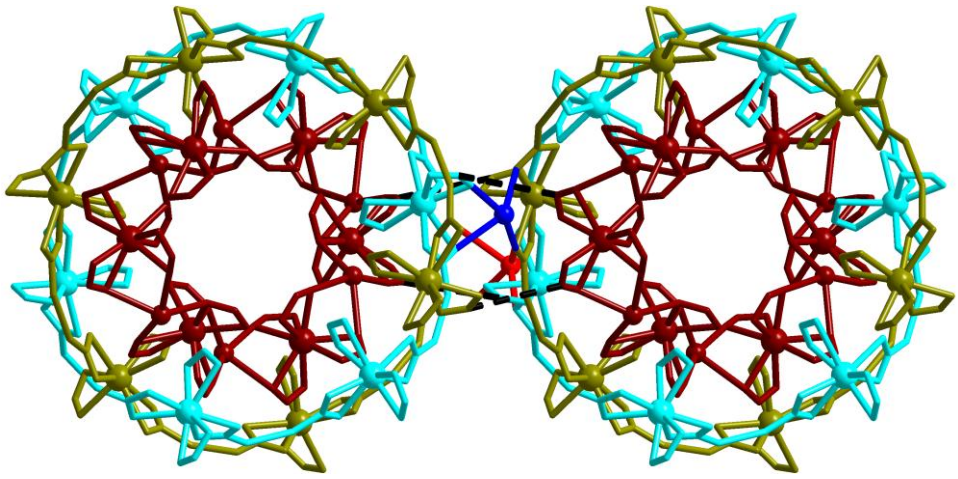

Fig. S5 The connection between two adjacent triple helical units of **DEF** viewed from the *c*-axis (blue: K1, red: K2, black dotted lines: benzene rings).

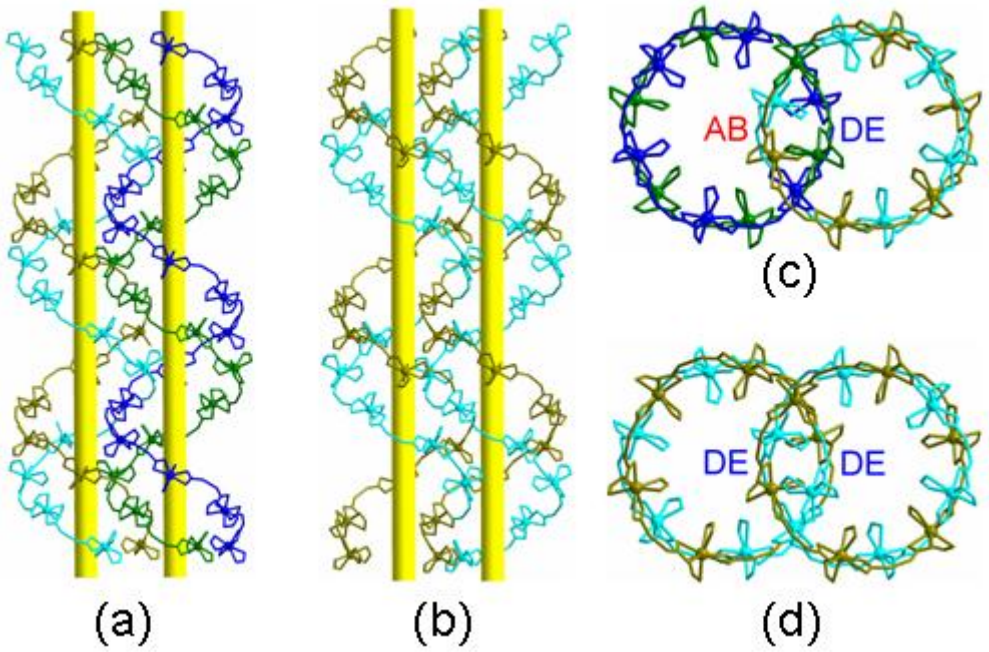

Fig. S6 View of the interweaving of **AB** and **DE** (a) and of two **DE** (b). View of the interweaving of **AB** and **DE** (c) and of two **DE** (d) viewed from the *c*-axis.

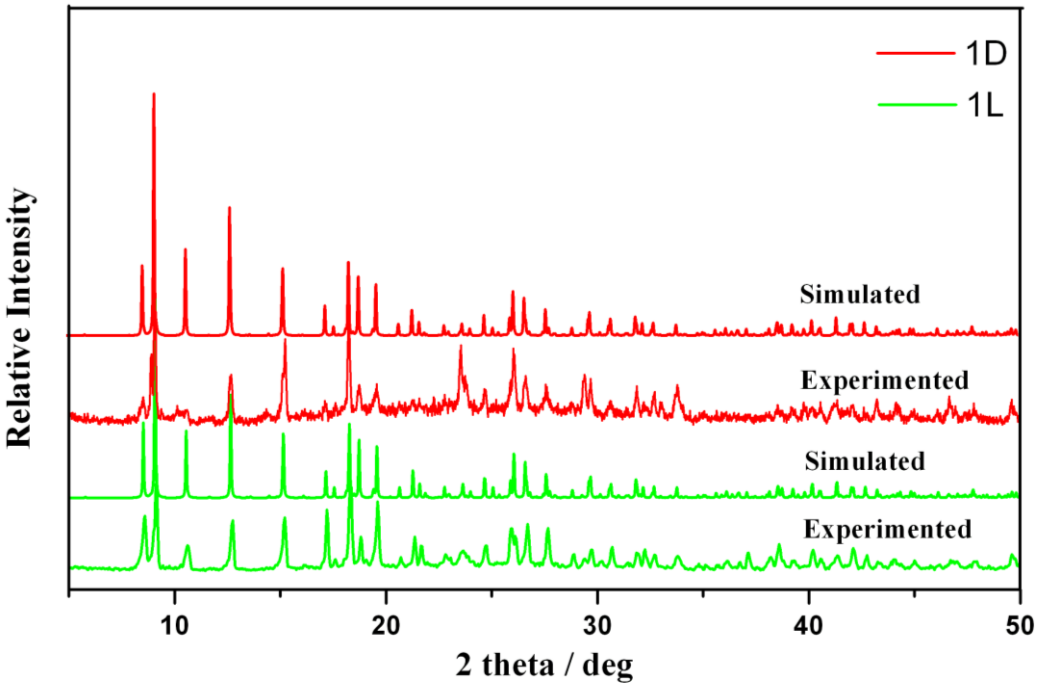

Fig. S7 Simulated and experimental XRD powder patterns of **1D** (red) and **1L** (green).

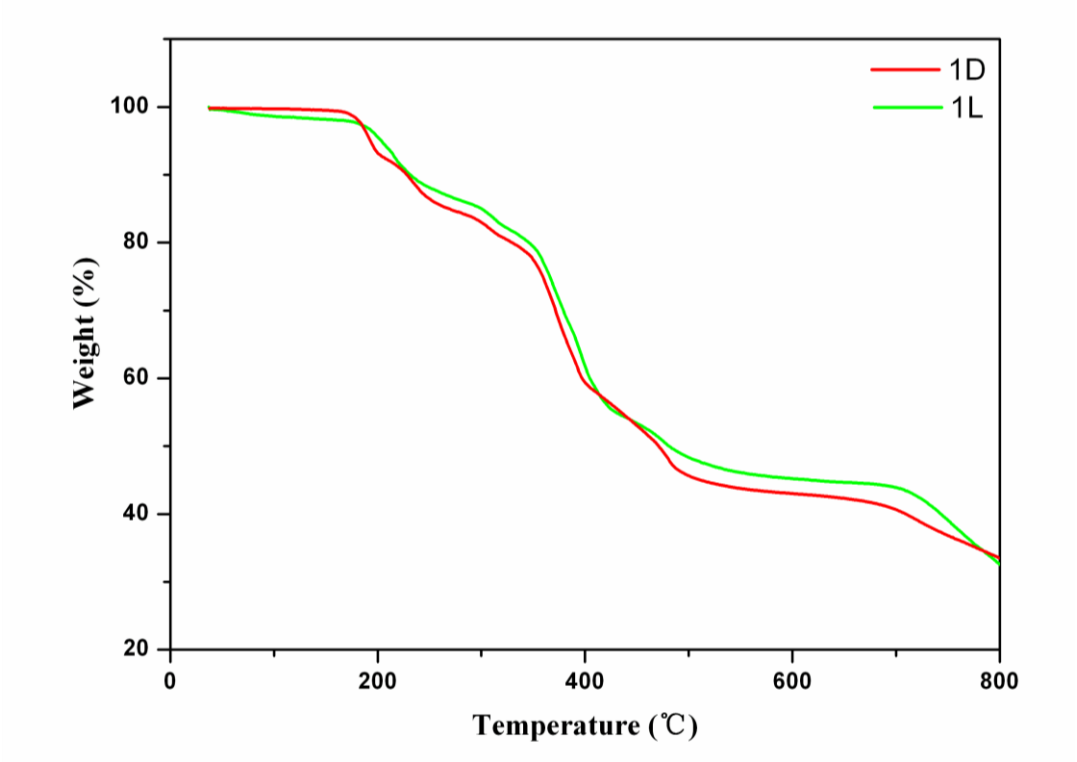

Fig. S8 TGA curves of **1D** (red) and **1L** (green).

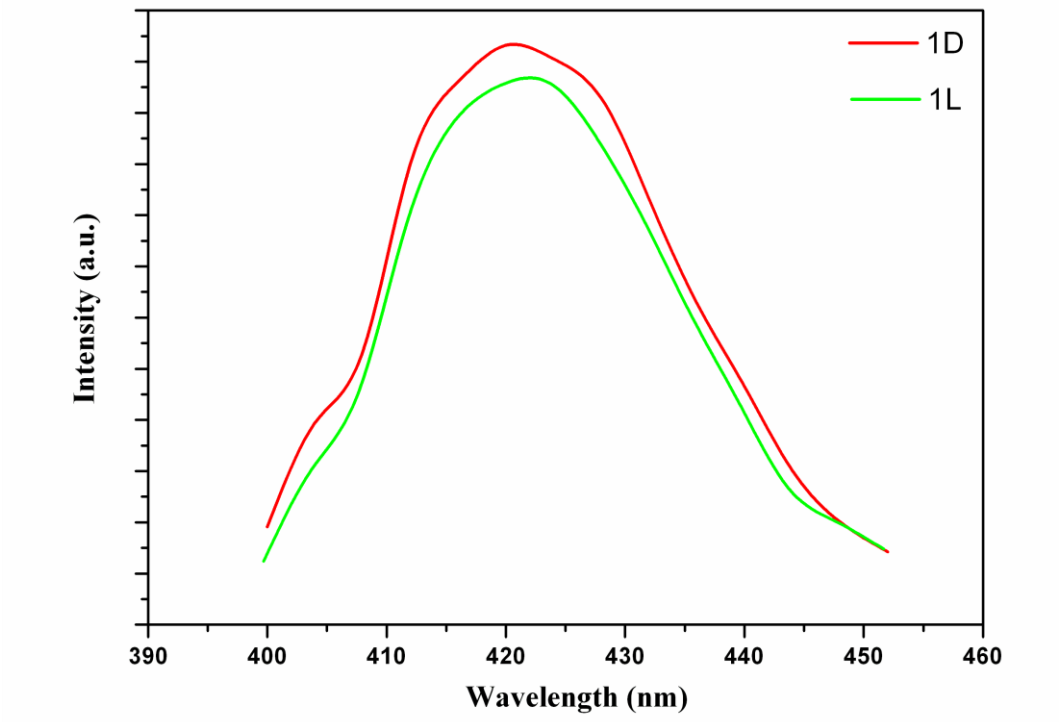

Fig. S9 Luminescent spectra at room temperature of **1D** (red) and **1L** (green).

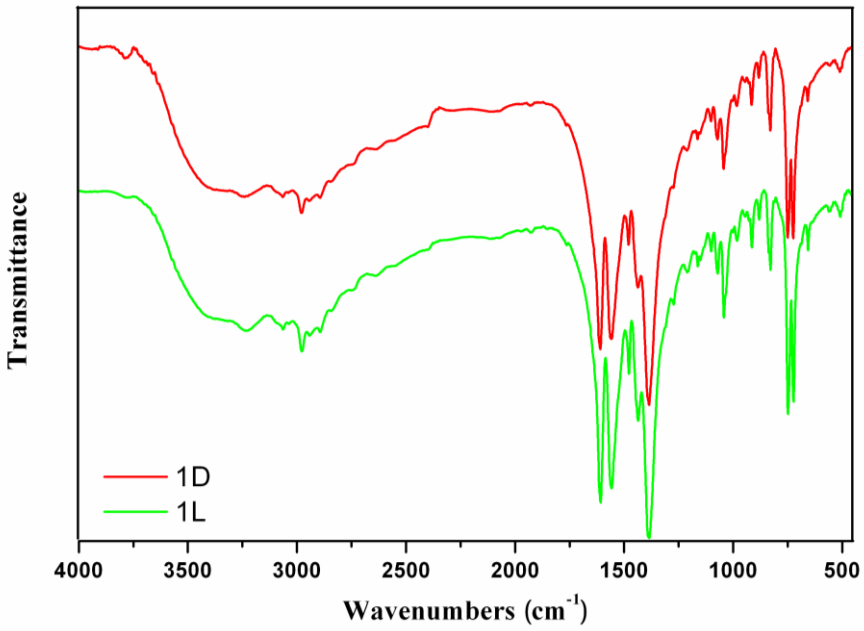

Fig. S10 IR spectra of **1D** (red) and **1L** (green).