Supporting Information

Structures and multiple properties of two polar metal-organic frameworks based on achiral N,O-coordinated ligands: toward multifunctional materials

Guang-Ning Liu,*[,a] Ming-Jian Zhang,[b] Wan-Qing Liu,[a] Hui Sun,[a] Xin-Yu Li,[a] Ke Li,[a] Cai-Ze Ren,[a] Zhen-Wei Zhang,[a] and Cuncheng Li*[,a]

[a]*Key Laboratory of Chemical Sensing & Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan, Shandong 250022, P. R. China*

[b]*School of Advanced Materials, Shenzhen Graduate School, Peking University, Shenzhen 518055, P. R. China*

Table S1. Selected Bond Distances (Å) and Angles (°) for **1**–**2**.

1			
Bond	(Å)	Bond	(Å)
Cd(1)-O(13)#1	2.215(3)	O(33)-Cd(1)#4	2.275(3)
Cd(1)-N(32)#2	2.271(3)	O(33)-Cd(2)#6	2.542(3)
Cd(1)-O(33)#3	2.275(3)	O(34)-C(35)	1.295(5)
Cd(1)-O(34)#2	2.363(3)	O(34)-Cd(1)#6	2.363(3)
Cd(1)-N(11)	2.377(3)	O(34)-Cd(2)#6	2.371(3)
Cd(1)-O(12)	2.385(3)	N(11)-N(12)	1.291(5)
Cd(2)-N(31)#4	2.236(3)	N(11)-C(12)	1.348(5)
Cd(2)-O(23)#5	2.245(3)	N(12)-C(14)	1.337(5)
Cd(2)-N(21)	2.355(3)	N(21)-C(22)	1.331(5)
Cd(2)-O(34)#2	2.371(3)	N(21)-N(22)	1.339(5)
Cd(2)-O(22)	2.421(3)	N(22)-C(24)	1.311(5)
Cd(2)-O(33)#2	2.542(3)	N(31)-C(32)	1.347(5)
Cd(3)-O(21)	2.261(3)	N(31)-N(32)	1.347(4)
Cd(3)-O(1W)	2.320(4)	N(31)-Cd(2)#3	2.236(3)

Cd(3)-O(12)	2.370(3)	N(32)-C(34)	1.335(5)
Cd(3)-O(31)	2.373(3)	N(32)-Cd(1)#6	2.271(3)
Cd(3)-O(11)	2.391(3)	C(11)-C(12)	1.485(5)
Cd(3)-O(32)	2.407(3)	C(12)-C(13)	1.379(6)
Cd(3)-O(22)	2.547(3)	C(13)-C(14)	1.396(6)
Cd(3)-C(11)	2.714(4)	C(14)-C(15)	1.500(6)
Cd(3)-C(31)	2.722(4)	C(21)-C(22)	1.490(5)
Cd(3)-C(21)	2.733(4)	C(22)-C(23)	1.389(5)
O(11)-C(11)	1.224(5)	C(23)-C(24)	1.370(6)
O(12)-C(11)	1.260(4)	C(24)-C(25)	1.487(6)
O(13)-C(15)	1.257(6)	C(31)-C(32)	1.464(5)
O(13)-Cd(1)#5	2.215(3)	C(32)-C(33)	1.385(6)
O(14)-C(15)	1.197(5)	C(33)-C(34)	1.415(5)
O(21)-C(21)	1.274(5)	C(34)-C(35)	1.445(5)
O(22)-C(21)	1.239(4)	O(31)-C(31)	1.262(6)
O(23)-C(25)	1.269(5)	O(32)-C(31)	1.269(6)
O(23)-Cd(2)#1	2.245(3)	O(33)-C(35)	1.238(5)
O(24)-C(25)	1.242(6)		

Angle	(°)	Angle	(°)
O(13)#1-Cd(1)-N(32)#2	118.29(12)	C(21)-O(22)-Cd(3)	85.0(2)
O(13)#1-Cd(1)-O(33)#3	98.74(12)	Cd(2)-O(22)-Cd(3)	150.78(12)
N(32)#2-Cd(1)-O(33)#3	80.03(11)	C(25)-O(23)-Cd(2)#1	111.4(3)
O(13)#1-Cd(1)-O(34)#2	92.65(12)	Cd(3)-O(12)-Cd(1)	147.05(12)
N(32)#2-Cd(1)-O(34)#2	71.01(10)	C(21)-O(22)-Cd(2)	116.7(2)
O(33)#3-Cd(1)-O(34)#2	150.90(10)	C(31)-O(31)-Cd(3)	91.7(3)
O(13)#1-Cd(1)-N(11)	141.76(12)	C(31)-O(32)-Cd(3)	90.0(2)
N(32)#2-Cd(1)-N(11)	99.95(12)	C(35)-O(33)-Cd(1)#4	144.8(3)
O(33)#3-Cd(1)-N(11)	87.19(11)	C(35)-O(33)-Cd(2)#6	91.0(2)

O(34)#2-Cd(1)-N(11)	100.26(11)	Cd(1)#4-O(33)-Cd(2)#6	121.26(11)
O(13)#1-Cd(1)-O(12)	76.46(10)	C(35)-O(34)-Cd(1)#6	114.4(2)
N(32)#2-Cd(1)-O(12)	153.22(10)	C(35)-O(34)-Cd(2)#6	97.5(2)
O(33)#3-Cd(1)-O(12)	121.77(10)	Cd(1)#6-O(34)-Cd(2)#6	147.35(13)
O(34)#2-Cd(1)-O(12)	86.88(10)	N(12)-N(11)-C(12)	105.7(3)
N(11)-Cd(1)-O(12)	68.57(10)	N(12)-N(11)-Cd(1)	137.6(3)
N(31)#4-Cd(2)-O(23)#5	110.13(12)	C(12)-N(11)-Cd(1)	116.5(3)
N(31)#4-Cd(2)-N(21)	94.05(12)	N(11)-N(12)-C(14)	114.0(3)
O(23)#5-Cd(2)-N(21)	146.86(11)	C(22)-N(21)-N(22)	106.0(3)
N(31)#4-Cd(2)-O(34)#2	131.78(10)	C(22)-N(21)-Cd(2)	115.6(3)
O(23)#5-Cd(2)-O(34)#2	86.83(11)	N(22)-N(21)-Cd(2)	137.7(2)
N(21)-Cd(2)-O(34)#2	93.76(11)	C(24)-N(22)-N(21)	111.1(3)
N(31)#4-Cd(2)-O(22)	141.36(10)	C(32)-N(31)-N(32)	108.4(3)
O(23)#5-Cd(2)-O(22)	77.47(9)	C(32)-N(31)-Cd(2)#3	126.4(2)
N(21)-Cd(2)-O(22)	69.57(10)	N(32)-N(31)-Cd(2)#3	124.8(2)
O(34)#2-Cd(2)-O(22)	85.34(9)	C(34)-N(32)-N(31)	108.7(3)
N(31)#4-Cd(2)-O(33)#2	80.04(10)	C(34)-N(32)-Cd(1)#6	116.1(2)
O(23)#5-Cd(2)-O(33)#2	116.07(10)	N(31)-N(32)-Cd(1)#6	133.7(2)
N(21)-Cd(2)-O(33)#2	89.54(10)	O(11)-C(11)-O(12)	122.5(4)
O(34)#2-Cd(2)-O(33)#2	52.53(9)	O(11)-C(11)-C(12)	120.3(3)
O(22)-Cd(2)-O(33)#2	132.17(9)	O(12)-C(11)-C(12)	117.1(3)
O(21)-Cd(3)-O(1W)	91.73(14)	O(11)-C(11)-Cd(3)	61.7(2)
O(21)-Cd(3)-O(12)	104.14(10)	O(12)-C(11)-Cd(3)	60.78(19)
O(1W)-Cd(3)-O(12)	83.37(12)	C(12)-C(11)-Cd(3)	177.9(3)
O(21)-Cd(3)-O(31)	87.19(12)	N(11)-C(12)-C(13)	110.0(3)
O(1W)-Cd(3)-O(31)	133.13(12)	N(11)-C(12)-C(11)	117.3(3)
O(12)-Cd(3)-O(31)	142.05(11)	C(13)-C(12)-C(11)	132.6(4)
O(21)-Cd(3)-O(11)	151.32(10)	C(12)-C(13)-C(14)	105.0(4)
O(1W)-Cd(3)-O(11)	102.93(14)	N(12)-C(14)-C(13)	105.2(3)

O(12)-Cd(3)-O(11)	54.41(9)	N(12)-C(14)-C(15)	123.9(4)
O(31)-Cd(3)-O(11)	99.84(12)	C(13)-C(14)-C(15)	130.7(4)
O(21)-Cd(3)-O(32)	116.78(11)	O(14)-C(15)-O(13)	125.3(4)
O(1W)-Cd(3)-O(32)	84.36(12)	O(14)-C(15)-C(14)	118.1(4)
O(12)-Cd(3)-O(32)	137.49(11)	O(13)-C(15)-C(14)	116.6(4)
O(31)-Cd(3)-O(32)	55.37(11)	O(22)-C(21)-O(21)	123.0(4)
O(11)-Cd(3)-O(32)	89.42(11)	O(22)-C(21)-C(22)	118.2(3)
O(21)-Cd(3)-O(22)	54.28(9)	O(21)-C(21)-C(22)	118.8(3)
O(1W)-Cd(3)-O(22)	134.64(12)	O(22)-C(21)-Cd(3)	68.2(2)
O(12)-Cd(3)-O(22)	78.30(9)	O(21)-C(21)-Cd(3)	55.2(2)
O(31)-Cd(3)-O(22)	79.70(10)	C(22)-C(21)-Cd(3)	169.6(3)
O(11)-Cd(3)-O(22)	99.34(10)	N(21)-C(22)-C(23)	110.0(3)
O(32)-Cd(3)-O(22)	135.07(10)	N(21)-C(22)-C(21)	118.4(3)
O(21)-Cd(3)-C(11)	129.12(11)	C(23)-C(22)-C(21)	131.6(3)
O(1W)-Cd(3)-C(11)	94.36(13)	C(24)-C(23)-C(22)	104.4(3)
O(12)-Cd(3)-C(11)	27.64(10)	N(22)-C(24)-C(23)	108.5(3)
O(31)-Cd(3)-C(11)	121.84(12)	N(22)-C(24)-C(25)	122.6(4)
O(11)-Cd(3)-C(11)	26.79(10)	C(23)-C(24)-C(25)	128.9(3)
O(32)-Cd(3)-C(11)	114.08(12)	O(24)-C(25)-O(23)	123.7(4)
O(22)-Cd(3)-C(11)	88.16(10)	O(24)-C(25)-C(24)	120.0(4)
O(21)-Cd(3)-C(31)	102.08(13)	O(23)-C(25)-C(24)	116.2(4)
O(1W)-Cd(3)-C(31)	108.85(14)	O(31)-C(31)-O(32)	122.7(4)
O(12)-Cd(3)-C(31)	150.65(12)	O(31)-C(31)-C(32)	118.5(4)
O(31)-Cd(3)-C(31)	27.62(13)	O(32)-C(31)-C(32)	118.8(4)
O(11)-Cd(3)-C(31)	96.37(12)	O(31)-C(31)-Cd(3)	60.6(2)
O(32)-Cd(3)-C(31)	27.80(13)	O(32)-C(31)-Cd(3)	62.2(2)
O(22)-Cd(3)-C(31)	107.29(12)	C(32)-C(31)-Cd(3)	172.3(3)
C(11)-Cd(3)-C(31)	123.06(13)	N(31)-C(32)-C(33)	109.9(3)
O(21)-Cd(3)-C(21)	27.54(10)	N(31)-C(32)-C(31)	119.2(4)

O(1W)-Cd(3)-C(21)	113.59(14)	C(33)-C(32)-C(31)	130.8(4)
O(12)-Cd(3)-C(21)	89.69(11)	C(32)-C(33)-C(34)	103.6(4)
O(31)-Cd(3)-C(21)	84.27(12)	N(32)-C(34)-C(33)	109.4(3)
O(11)-Cd(3)-C(21)	124.95(11)	N(32)-C(34)-C(35)	118.5(3)
O(32)-Cd(3)-C(21)	132.31(12)	C(33)-C(34)-C(35)	132.1(4)
O(22)-Cd(3)-C(21)	26.84(9)	O(33)-C(35)-O(34)	118.7(4)
C(11)-Cd(3)-C(21)	108.31(11)	O(33)-C(35)-C(34)	123.2(4)
C(31)-Cd(3)-C(21)	108.25(13)	O(34)-C(35)-C(34)	118.1(3)
C(11)-O(11)-Cd(3)	91.5(2)	C(15)-O(13)-Cd(1)#5	112.7(3)
C(11)-O(12)-Cd(3)	91.6(2)	C(21)-O(21)-Cd(3)	97.3(2)
C(11)-O(12)-Cd(1)	119.3(2)		

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z; #2 x, y+1, z; #3 x, -y+1, z+1/2; #4 x, -y+1, z-1/2; #5 x-1, y, z; #6 x, y-1, z.

2[a]			
Bond	(Å)	Bond	(Å)
Co(1)-O(21)	1.889(3)	O(31)-C(31)	1.221(6)
Co(1)-O(32)	1.895(3)	O(32)-C(31)	1.289(6)
Co(1)-O(12)	1.900(3)	O(33)-C(37)	1.267(7)
Co(1)-N(31)	1.923(4)	O(34)-C(37)	1.236(6)
Co(1)-N(21)	1.925(4)	N(11)-C(16)	1.332(6)
Co(1)-N(11)	1.941(4)	N(11)-C(12)	1.337(6)
Co(2)-O(13)#1	2.047(4)	N(21)-C(26)	1.320(6)
Co(2)-O(13)#2	2.047(4)	N(21)-C(22)	1.359(5)
Co(2)-O(24)#3	2.090(3)	N(31)-C(32)	1.333(6)
Co(2)-O(24)	2.090(3)	N(31)-C(36)	1.346(6)
Co(2)-O(2W)	2.115(4)	C(11)-C(12)	1.484(7)
Co(2)-O(1W)	2.168(4)	C(12)-C(13)	1.367(7)
Co(3)-O(14)#4	2.062(3)	C(13)-C(14)	1.399(7)

Co(3)-O(14)#5	2.062(3)	C(14)-C(15)	1.390(7)
Co(3)-O(34)#6	2.102(3)	C(15)-C(16)	1.387(7)
Co(3)-O(34)	2.102(3)	C(15)-C(17)	1.499(7)
Co(3)-O(1W)#7	2.115(5)	C(21)-C(22)	1.482(7)
Co(3)-O(3W)	2.133(5)	C(22)-C(23)	1.368(6)
O(11)-C(11)	1.238(6)	C(23)-C(24)	1.383(7)
O(12)-C(11)	1.298(6)	C(24)-C(25)	1.404(6)
O(13)-C(17)	1.230(6)	C(25)-C(26)	1.395(6)
O(13)-Co(2)#8	2.047(4)	C(25)-C(27)	1.503(7)
O(14)-C(17)	1.248(6)	C(31)-C(32)	1.499(6)
O(14)-Co(3)#7	2.062(3)	C(32)-C(33)	1.395(7)
O(21)-C(21)	1.293(6)	C(33)-C(34)	1.347(7)
O(22)-C(21)	1.214(6)	C(34)-C(35)	1.399(7)
O(23)-C(27)	1.250(6)	C(35)-C(36)	1.362(7)
O(24)-C(27)	1.238(6)	C(35)-C(37)	1.498(7)
Co(1)-O(21)	1.889(3)	O(1W)-Co(3)#5	2.115(5)

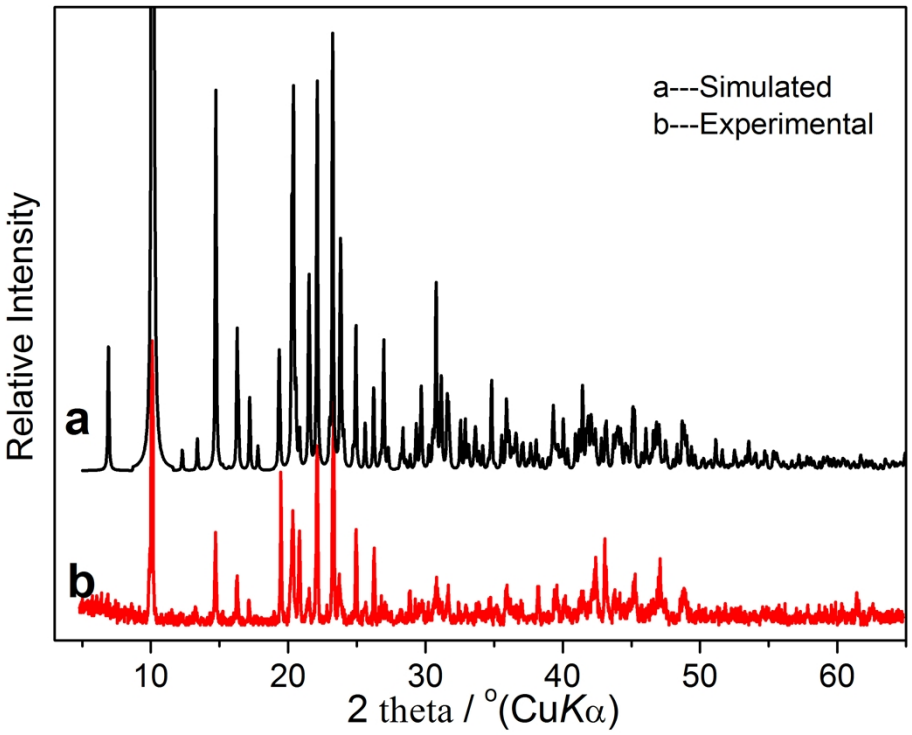
Angle	(°)	Angle	(°)
O(21)-Co(1)-O(32)	175.99(15)	C(16)-N(11)-Co(1)	129.3(3)
O(21)-Co(1)-O(12)	89.28(14)	C(12)-N(11)-Co(1)	111.1(3)
O(32)-Co(1)-O(12)	93.75(14)	C(26)-N(21)-C(22)	119.1(4)
O(21)-Co(1)-N(31)	92.93(16)	C(26)-N(21)-Co(1)	130.0(3)
O(32)-Co(1)-N(31)	84.66(15)	C(22)-N(21)-Co(1)	110.8(3)
O(12)-Co(1)-N(31)	86.06(16)	C(32)-N(31)-C(36)	119.1(4)
O(21)-Co(1)-N(21)	85.14(14)	C(32)-N(31)-Co(1)	111.5(3)
O(32)-Co(1)-N(21)	91.86(14)	C(36)-N(31)-Co(1)	128.7(3)
O(12)-Co(1)-N(21)	174.36(15)	O(11)-C(11)-O(12)	125.5(5)
N(31)-Co(1)-N(21)	95.05(16)	O(11)-C(11)-C(12)	120.3(5)
O(21)-Co(1)-N(11)	92.21(16)	O(12)-C(11)-C(12)	114.1(4)

O(32)-Co(1)-N(11)	90.69(15)	N(11)-C(12)-C(13)	122.3(4)
O(12)-Co(1)-N(11)	84.67(15)	N(11)-C(12)-C(11)	114.8(4)
N(31)-Co(1)-N(11)	169.34(15)	C(13)-C(12)-C(11)	122.9(4)
N(21)-Co(1)-N(11)	94.69(15)	C(12)-C(13)-C(14)	119.2(4)
O(13)#1-Co(2)-O(13)#2	92.1(2)	C(15)-C(14)-C(13)	118.1(4)
O(13)#1-Co(2)-O(24)#3	175.64(14)	C(16)-C(15)-C(14)	119.1(4)
O(13)#2-Co(2)-O(24)#3	87.17(15)	C(16)-C(15)-C(17)	121.2(4)
O(13)#1-Co(2)-O(24)	87.17(15)	C(14)-C(15)-C(17)	119.7(4)
O(13)#2-Co(2)-O(24)	175.64(14)	N(11)-C(16)-C(15)	121.8(4)
O(24)#3-Co(2)-O(24)	93.25(19)	O(13)-C(17)-O(14)	128.3(5)
O(13)#1-Co(2)-O(2W)	88.77(14)	O(13)-C(17)-C(15)	115.2(4)
O(13)#2-Co(2)-O(2W)	88.77(14)	O(14)-C(17)-C(15)	116.5(4)
O(24)#3-Co(2)-O(2W)	86.93(14)	O(22)-C(21)-O(21)	124.3(5)
O(24)-Co(2)-O(2W)	86.93(14)	O(22)-C(21)-C(22)	121.6(5)
O(13)#1-Co(2)-O(1W)	91.58(13)	O(21)-C(21)-C(22)	114.1(4)
O(13)#2-Co(2)-O(1W)	91.58(13)	N(21)-C(22)-C(23)	122.1(4)
O(24)#3-Co(2)-O(1W)	92.73(13)	N(21)-C(22)-C(21)	114.8(4)
O(24)-Co(2)-O(1W)	92.73(13)	C(23)-C(22)-C(21)	123.1(4)
O(2W)-Co(2)-O(1W)	179.50(19)	C(22)-C(23)-C(24)	119.4(4)
O(14)#4-Co(3)-O(14)#5	94.3(2)	C(23)-C(24)-C(25)	118.9(4)
O(14)#4-Co(3)-O(34)#6	84.51(14)	C(26)-C(25)-C(24)	118.0(4)
O(14)#5-Co(3)-O(34)#6	178.55(16)	C(26)-C(25)-C(27)	121.3(4)
O(14)#4-Co(3)-O(34)	178.55(15)	C(24)-C(25)-C(27)	120.5(4)
O(14)#5-Co(3)-O(34)	84.51(14)	N(21)-C(26)-C(25)	122.5(4)
O(34)#6-Co(3)-O(34)	96.6(2)	O(24)-C(27)-O(23)	126.6(5)
O(14)#4-Co(3)-O(1W)#7	93.91(13)	O(24)-C(27)-C(25)	117.3(4)
O(14)#5-Co(3)-O(1W)#7	93.91(13)	O(23)-C(27)-C(25)	116.0(4)
O(34)#6-Co(3)-O(1W)#7	87.05(13)	O(31)-C(31)-O(32)	125.8(4)
O(34)-Co(3)-O(1W)#7	87.05(13)	O(31)-C(31)-C(32)	121.3(5)

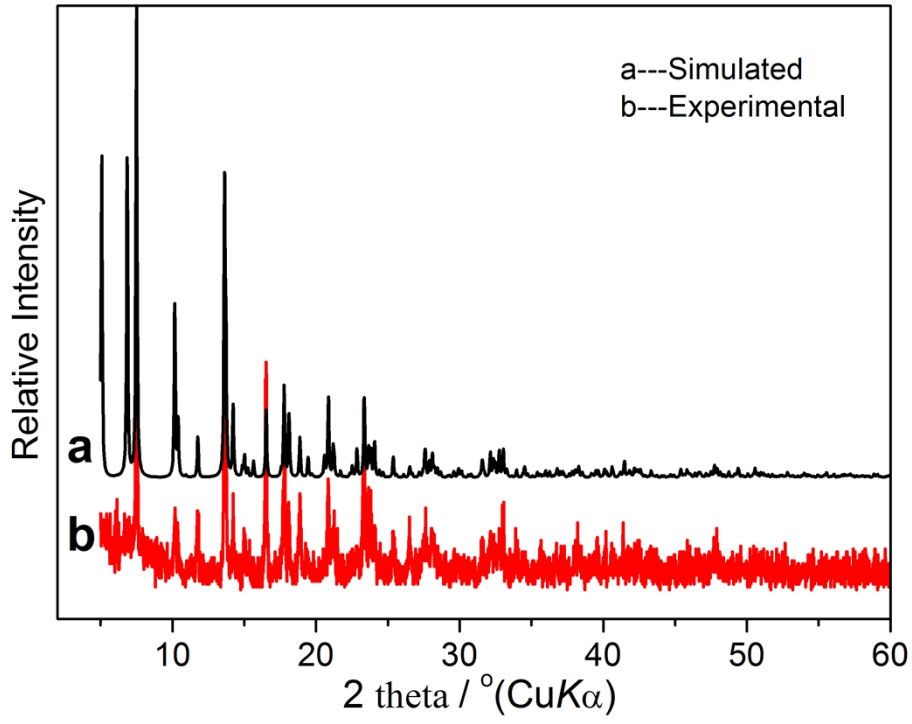
O(14)#4-Co(3)-O(3W)	86.22(13)	O(32)-C(31)-C(32)	112.9(4)
O(14)#5-Co(3)-O(3W)	86.22(13)	N(31)-C(32)-C(33)	121.6(4)
O(34)#6-Co(3)-O(3W)	92.83(13)	N(31)-C(32)-C(31)	115.1(4)
O(34)-Co(3)-O(3W)	92.83(13)	C(33)-C(32)-C(31)	123.3(4)
O(1W)#7-Co(3)-O(3W)	179.82(16)	C(34)-C(33)-C(32)	118.9(4)
C(11)-O(12)-Co(1)	113.9(3)	C(33)-C(34)-C(35)	119.9(5)
C(17)-O(13)-Co(2)#8	136.6(3)	C(36)-C(35)-C(34)	118.3(5)
C(17)-O(14)-Co(3)#7	132.3(3)	C(36)-C(35)-C(37)	122.0(5)
C(21)-O(21)-Co(1)	115.0(3)	C(34)-C(35)-C(37)	119.6(5)
C(27)-O(24)-Co(2)	125.5(3)	N(31)-C(36)-C(35)	122.2(4)
C(31)-O(32)-Co(1)	115.4(3)	O(34)-C(37)-O(33)	126.1(5)
C(37)-O(34)-Co(3)	127.0(4)	O(34)-C(37)-C(35)	118.8(5)
C(16)-N(11)-C(12)	119.5(4)	O(33)-C(37)-C(35)	115.1(5)
O(21)-Co(1)-O(32)	175.99(15)	Co(3)#5-O(1W)-Co(2)	114.12(18)

Symmetry transformations used to generate equivalent atoms: #1 x, y, z+1; #2 -x, y, z+1; #3 -x, y, z; #4 x+1/2, -y+3/2, z+1/2; #5 -x+1/2, -y+3/2, z+1/2; #6 -x+1, y, z; #7 -x+1/2, -y+3/2, z-1/2; #8 x, y, z-1.

[a] From the Difference Fourier map of **2**, number of diffuse scattered peaks with electron density were observed, which can be attributed to the disordered water molecules. PLATON/SQUEEZE was used to refine the structure further. The molecular formula of **2** was calculated and confirmed by the elemental analysis data and thermogravimetric analyses.



(a)



(b)

Fig. S1 The experimental PXRD patterns of single crystals of **1** (a) and **2** (b) are in good agreement with the simulated PXRD patterns calculated from single-crystal X-ray data of **1** and **2**, respectively.

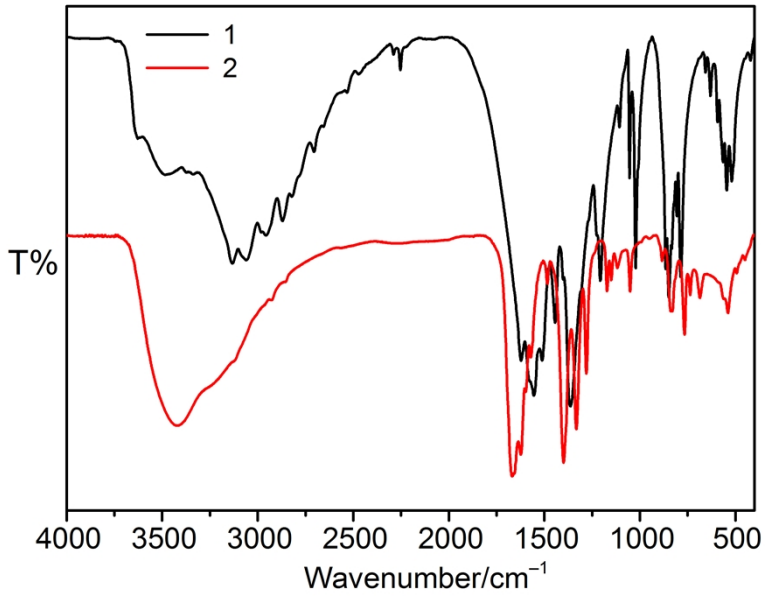


Fig. S2 IR spectra of **1** and **2**.

In the IR spectra of **1** and **2**, the strong bands at about 1556 and 1364 cm^{-1} for **1**, and 1665 and 1400 cm^{-1} for **2** are associated with the asymmetry and symmetry stretching vibration of the coordinated carboxylato group COO^{-}, respectively.[1] The broad bands in the range 3490–3405 cm^{-1} for **1** and **2** are assigned to the stretching of water since there are coordinated and lattice water molecules in both structures.

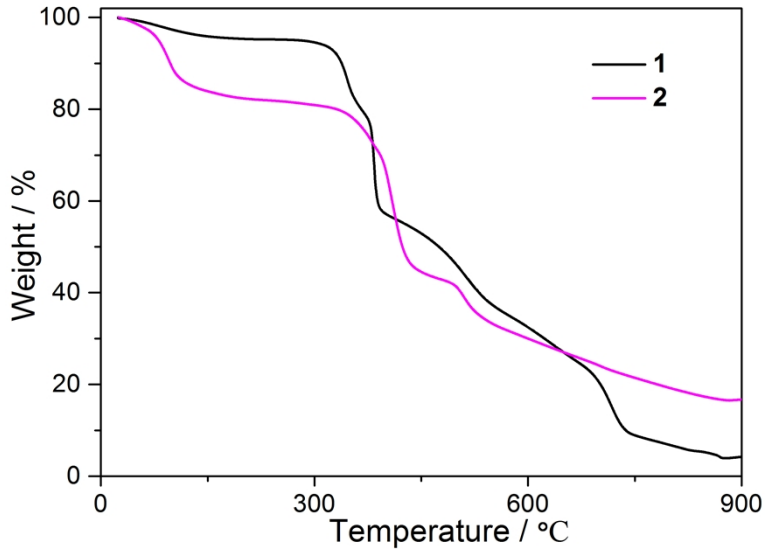


Fig. S3 TGA curves of **1** and **2**.

The thermal stabilities of **1** and **2** were examined by thermogravimetric analyses (TGA) in a N_2 atmosphere from 30 to 900 °C. For **1**, the weight loss of 4.5% in the temperature range of 30–178 °C is close to losing one coordinated water molecule and one lattice water molecule per formula with a calculated value of 4.31%. The second weight loss start from 326 °C can be attributed to the collapse of the structure. For **2**, a weight loss of 18.0% between 30 and 249 °C corresponds to the removal of three coordinated and twelve lattice water molecules per formula (theoretical value of 17.99%). The following significant weight loss is attributed to the collapse of the structure.

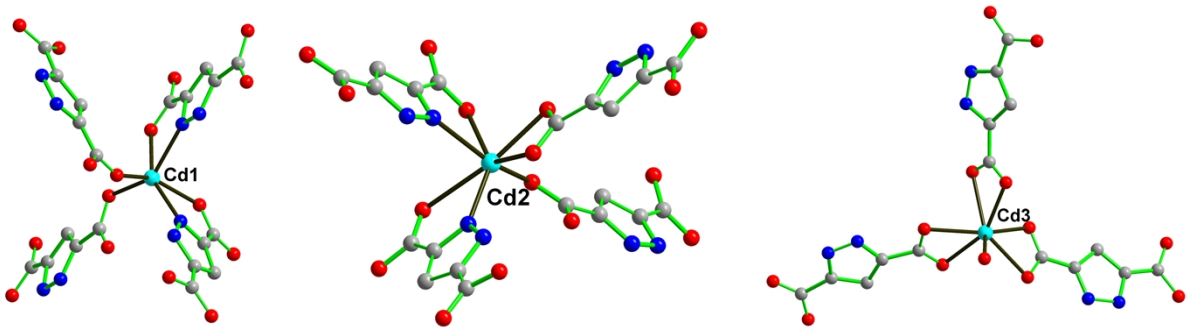
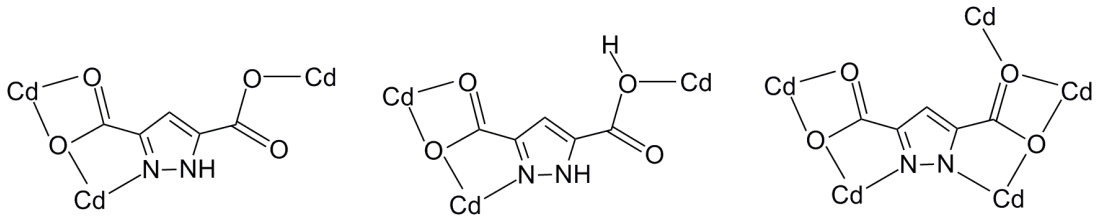


Fig. S4 The coordination mode of three crystallographically distinct Cd(II) ions in **1**.



u_3-Hpadc^{2-} u_3-H$_2$padc^{-} u_5-padc^{3-}

Fig. S5 The coordination modes of the H_2padc^{-}, $Hpadc^{2-}$, and $padc^{3-}$ ligands in **1**.

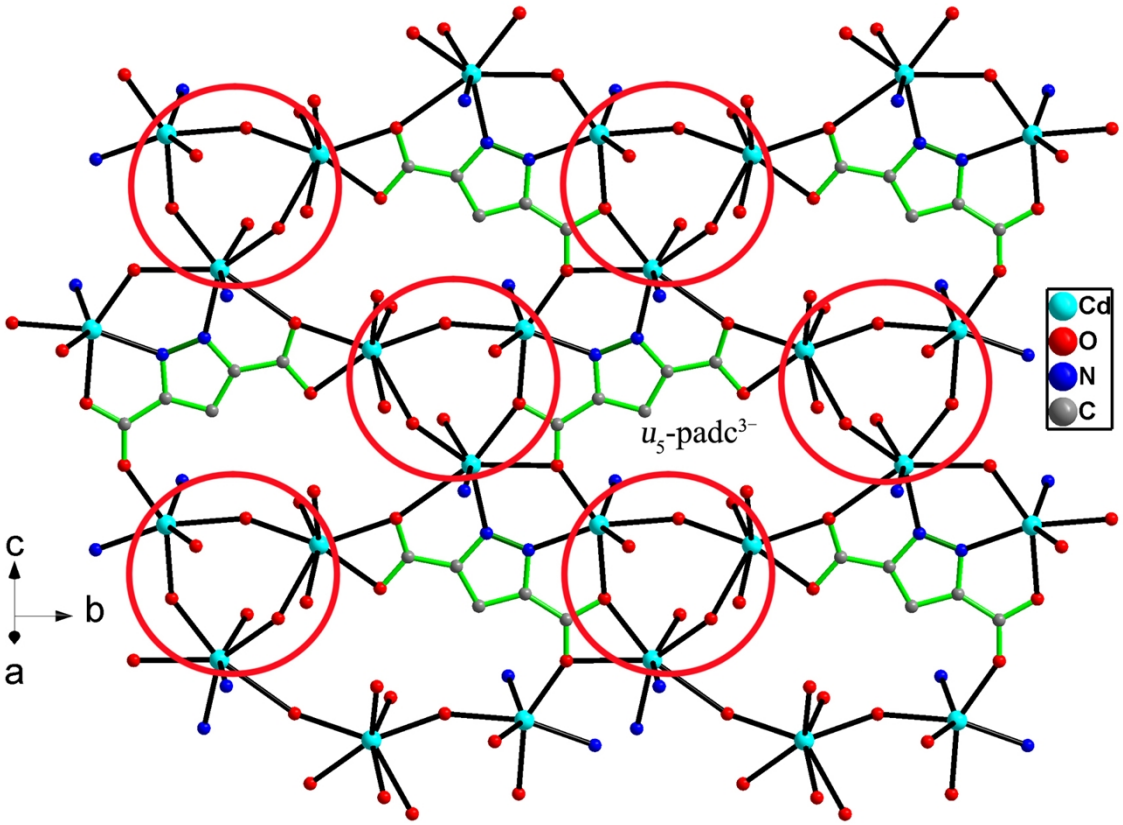


Fig. S6 The 2-D layer structure of **1** formed via the μ_5-padc^{3-} ligand connecting the trinuclear $[Cd]_3$ unit in the *bc* plane. The trinuclear $[Cd]_3$ units are marked with red rings.

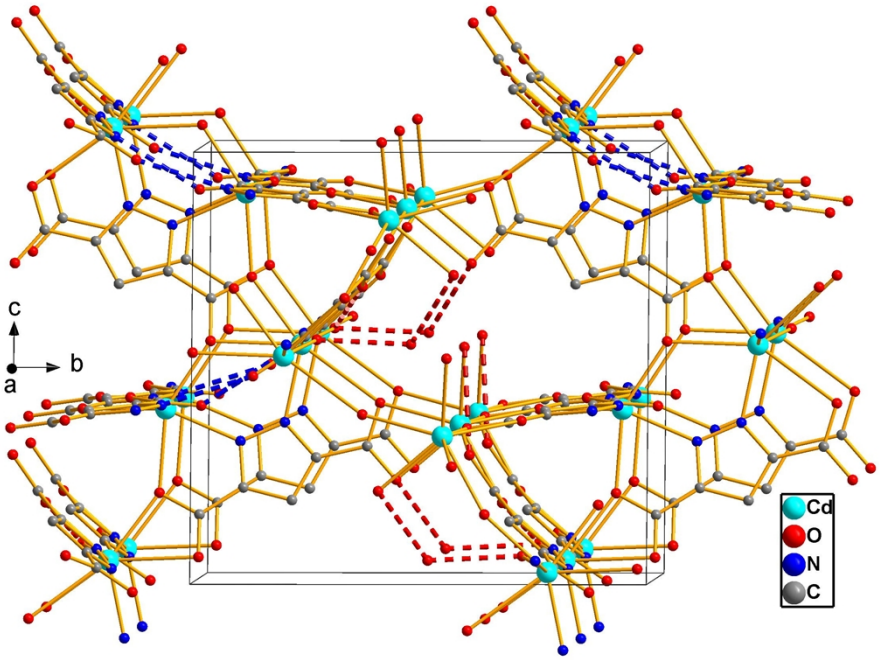
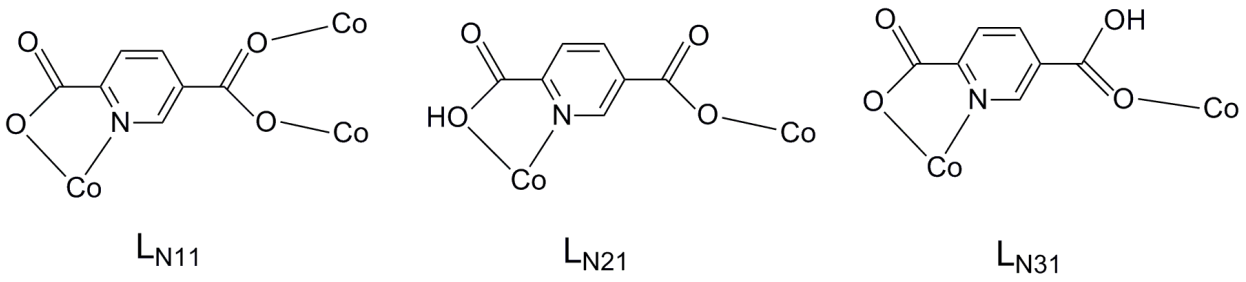


Fig. S7 View of the O–H···O (red dashed lines) and N–H···O (blue dashed lines) hydrogen bonds of **1**.

Table S2. Selected Hydrogen Bonds Data for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
O23-H23B···O2W[a]	0.85	1.96	2.645(1)	136.4
O23-H23B···O22[a]	0.85	2.44	2.923(1)	116.9
N22-H22A···O14[b]	0.86	1.96	2.789(2)	162.2
N12-H12A···O24[c]	0.86	1.89	2.716(2)	159.8
O2W-H2WA···O31	0.85	2.16	2.884(2)	143.1
O1W-H1WA···O21	0.85	2.65	3.288(2)	133.1

Symmetry codes: a (1+x, y, z); b (1+x, 2-y, -1/2+z); c (-1+x, 2-y, 1/2+z).



L_{N11} L_{N21} L_{N31}

Fig. S8 The coordination modes of the L_{N11}, L_{N21}, and L_{N31} ligands in **2**.

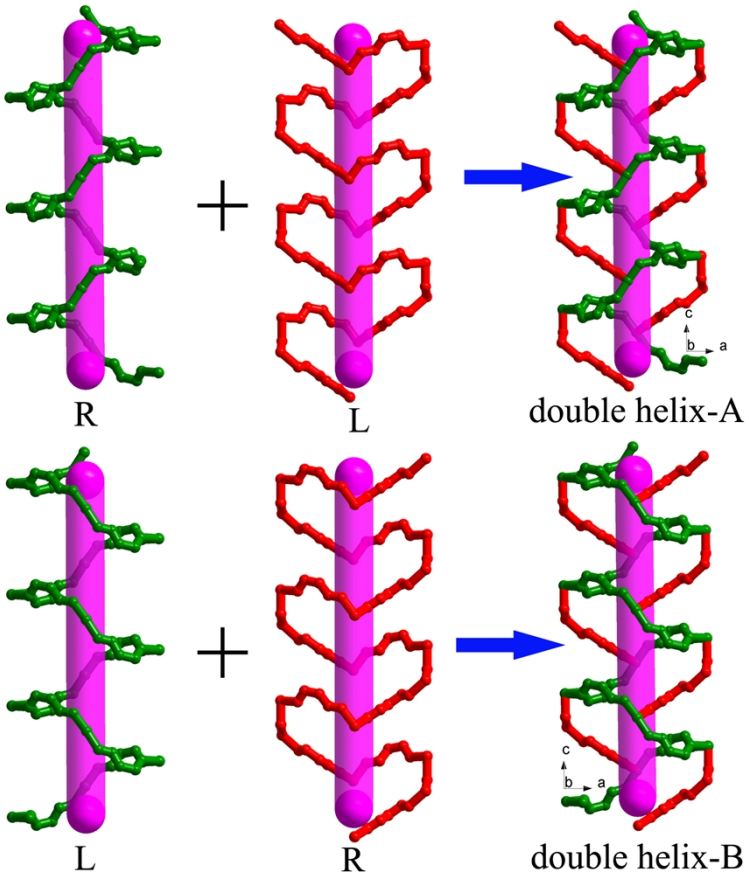


Fig. S9 The double helix tubes formed by the weaving of two single helixes with reverse helical orientation through sharing Co vertices.

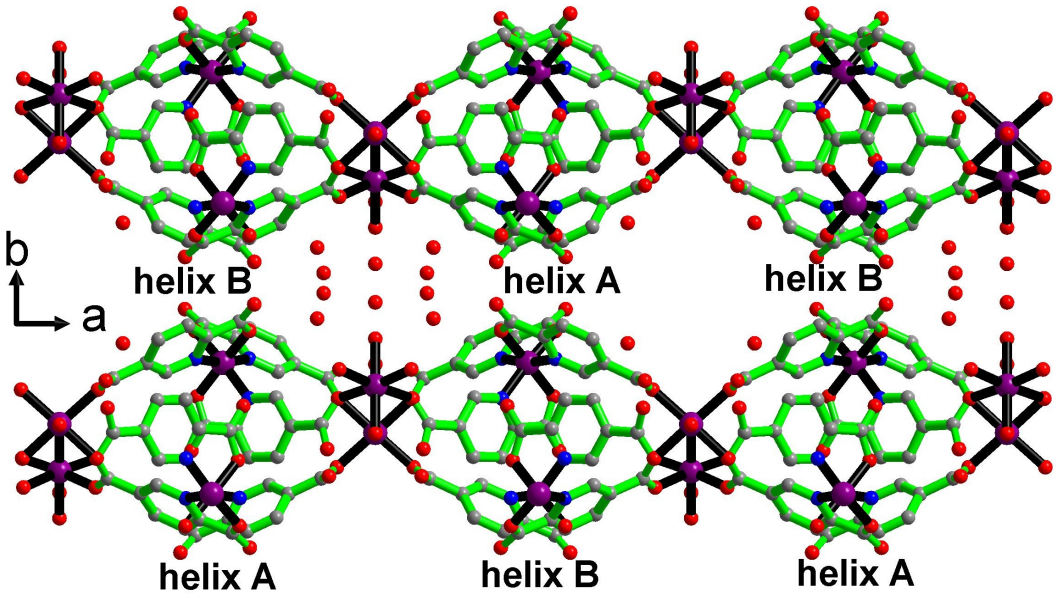


Fig. S10 The 3-D packing diagram of **2**.

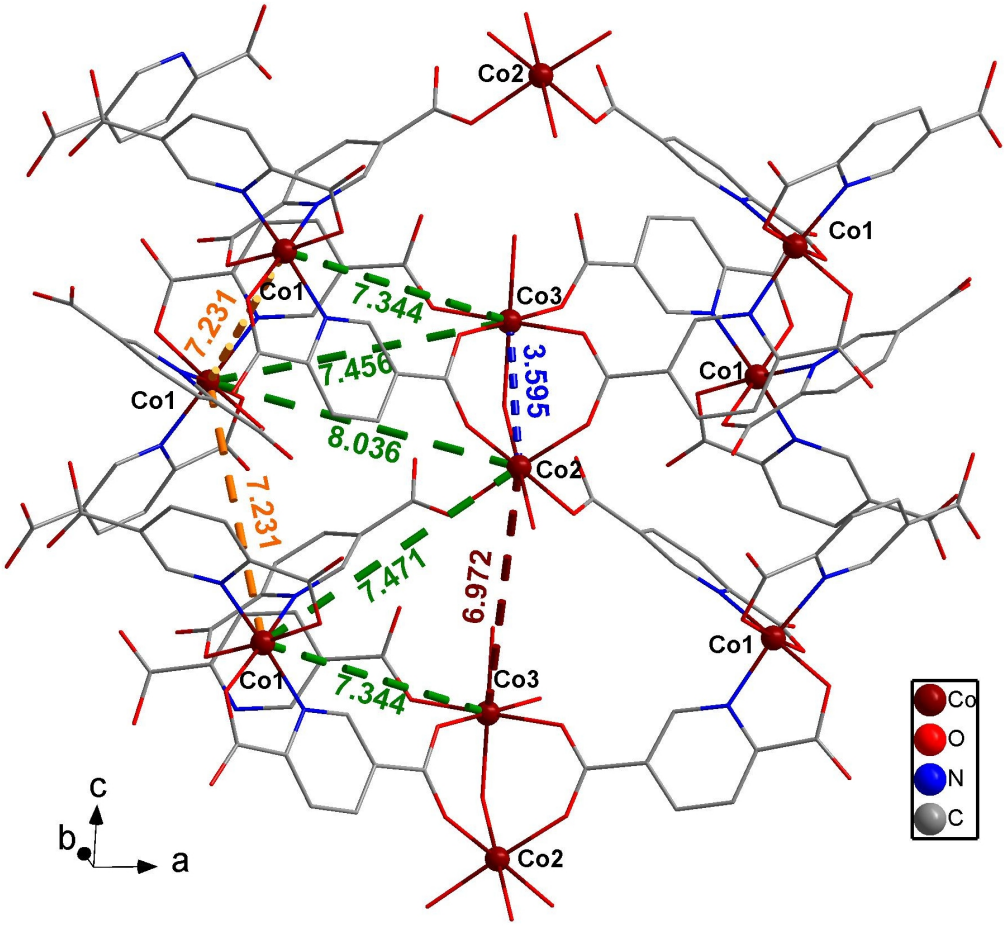


Fig. S11 The possible magnetic pathway in **2**.

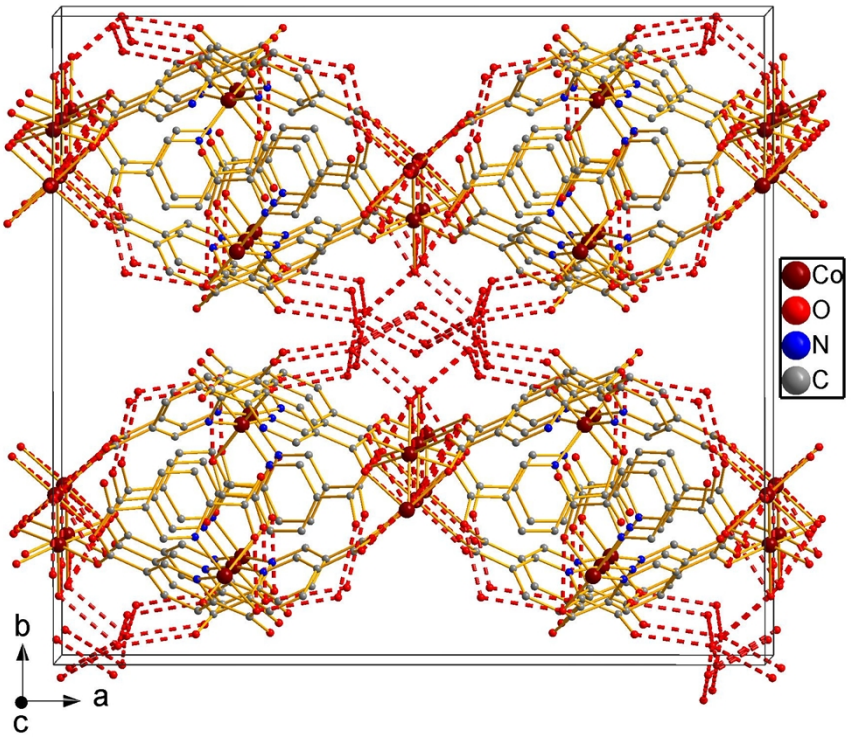


Fig. S12 View of the O–H···O hydrogen bonds (red dashed lines) of **2**.

Table S3. Selected Hydrogen Bonds Data for **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
O33-H33B···O3W	0.86	1.78	2.617(5)	167
C36-H36A···O21	0.93	2.53	2.993(6)	111.3
O21-H21A···O12	0.85	2.28	2.663(4)	108
C26-H26A···O32	0.93	2.51	2.973(5)	111.3
O3W-H3WA···O33[a]	0.84	2.20	2.617(5)	110.7
O3W-H3WA···O33	0.84	2.20	2.617(5)	110.7
O3W-H3WB···O5W	0.85	2.19	2.846(9)	135
O2W-H2WA···O5W[b]	0.85	2.29	3.047(11)	148.3
O2W-H2WA···O24[c]	0.85	2.40	2.893(5)	117.4
O2W-H2WA···O24	0.85	2.40	2.893(5)	117.4
O2W-H2WB···O4W[c]	0.85	2.38	2.807(6)	111.7
O2W-H2WB···O4W	0.85	2.38	2.807(6)	111.7
O1W-H1WA···O34[d]	0.85	2.24	2.904(5)	135.1
O1W-H1WA···O34[e]	0.85	2.24	2.904(5)	135.1
O1W-H1WB···O13[f]	0.85	2.33	3.022(5)	139.5
O1W-H1WB···O14[f]	0.85	2.59	3.053(5)	115.1
O1W-H1WB···O14[g]	0.85	2.59	3.053(5)	115.1
O1W-H1WB···O13[g]	0.85	1.78	3.022(5)	139.5

Symmetry codes: a (1-x, y, z); b (1/2-x, 3/2-y, -1/2+z); c (-x, y, z); d (1/2-x, 3/2-y, 1/2+z); e (-1/2+x, 3/2-y, 1/2+z); f (x, y, 1+z); g (-x, y, 1+z); h (x, 2-y, 1/2+z); i (1/2+x, 3/2-y, 1/2+z); j (x, 2-y, -1/2+z); k (1/2-x, 3/2-y, -1/2+z); l (-x, y, z); m (1/2-x, 3/2-y, 1/2+z).

Considering that the hydrogen atoms of the lattice water molecules of **2** were not added, the possible hydrogen bonds between lattice water molecules were tentatively assigned by evaluating the O···O distances. The distances of O4W···O6W[h] (2.818(11) Å), O4W···O2W (2.807(6) Å), O4W···O6W (2.994(12) Å), O4W···O7W (2.935(10) Å), O4W···O31 (2.861(6) Å), O5W···O6W[d] (3.006(9) Å), O5W···O6W[i] (3.006(9) Å), O6W···O4W[j] (2.818(11) Å), O6W···O5W[k] (3.006(9) Å), O6W···O4W (2.994(12) Å), O6W···O32 (2.931(8) Å),

O7W···O4W[l] (2.935(10) Å), O7W···O4W (2.935(10) Å), O8W···O12[m] (2.995(14) Å), O8W···O23 (2.786(11) Å) are all shorter than the sum of the van der waals's radii of two O atoms of 3.04 Å, which indicate that there are possible hydrogen bonds.

Table S4. Calculated Dipole Moments for Polar Units in **1** and **Ref. 2**.[a]

Polar unit	($Cd1O_4N_2$)			($Cd2O_5N_2$)			($Cd3O_7$)		
Dipole moment	x	y	z	x	y	z	x	y	z
(Deybe)	0.145	0.035	0.135	-0.253	0.058	-0.103	0.075	-0.092	0.186
Magnitude (Deybe)		0.201			0.279			0.220	

Polar unit	(ZnO_2N_2) in **Ref. 2**		
Dipole moment (Deybe)	x	y	z
	0.098	0.384	-0.121
Magnitude (Deybe)		0.403	

[a] The calculation was performed using a bond-valence approach proposed by Poeppelmerier et al.

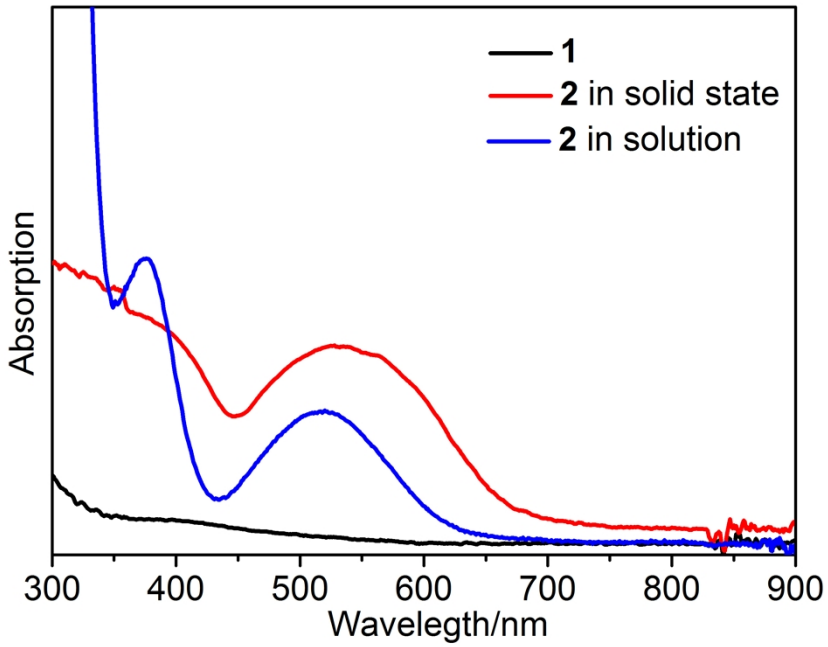


Fig. S13 The absorption spectra of **1** in solid state (black), and **2** in solid state (red) and in aqueous solution (blue) in the visible light.

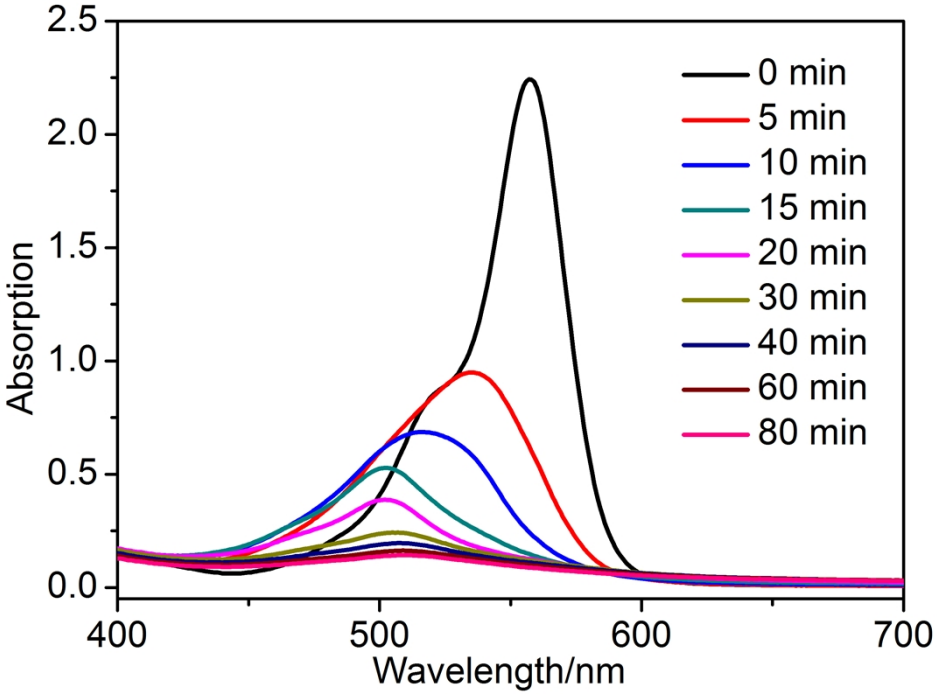


Fig. S14 Time-dependent UV/Vis spectra of RhB over **2**.

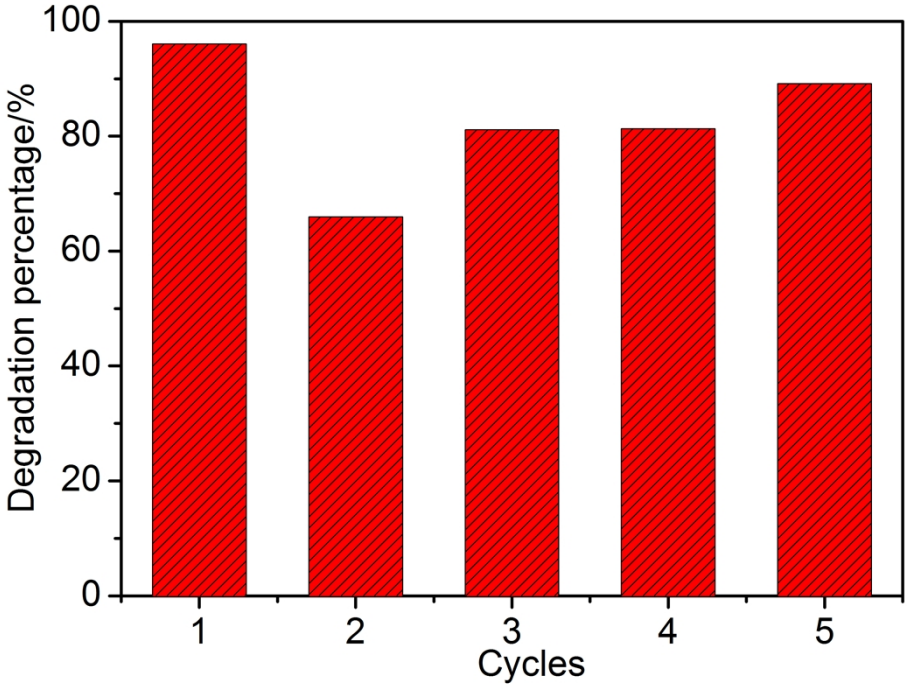
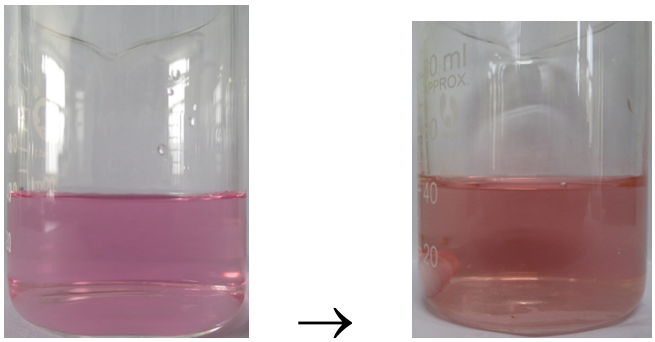


Fig. S15 Cycling tests of photocatalytic activity of the aqueous solution of **2**. The degradation percentage was obtained after each photocatalysis experiment conducted for 80 min.

The cycling tests were performed as follows: 20 mg of compound **2** was dissolved in 40 mL water to obtain a violet solution (Fig. S16a), and then 0.2 mL of 2.0×10^3 mg/L RhB aqueous solution was added. The concentration of the RhB solution was finally calculated as 10.0 mg/L. Then, five drops of hydrogen peroxide solution (H_2O_2, 30%) were added and the pH value was adjusted to 3 with sulfuric acid (H_2SO_4, 0.5 mol/L). The solution was stirred under visible light irradiation. At different time intervals, analytical samples were withdrawn and analyzed by UV/Vis spectroscopy. After each UV/Vis analysis, the sample was pour back into the reactor. The changes in the absorption spectra of the extracted RhB solution at 0 min and 80 min were used to calculate the degradation percentage. After each photocatalysis cycle, 0.2 mL of 2.0×10^3 mg/L RhB aqueous solution was added.



(a) (b)

Fig. S16 The photograph of the aqueous solution of **2** (a), and the solution after five photocatalysis cycles (b).

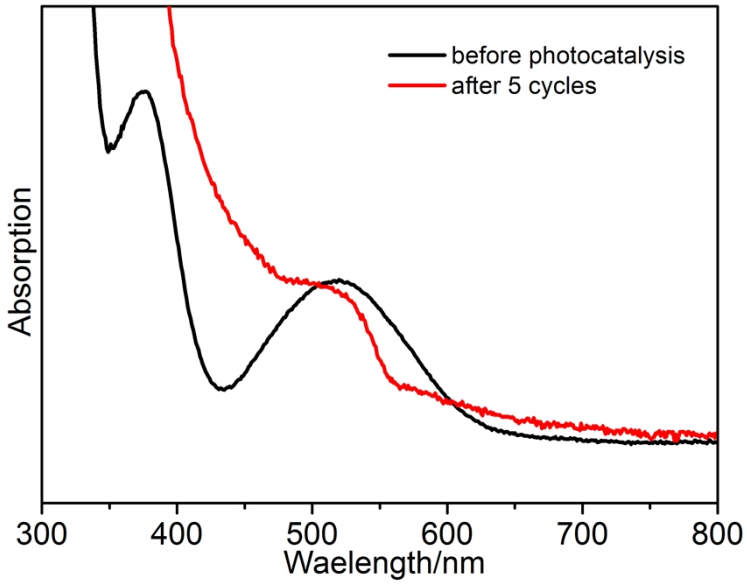


Fig. S17 The absorption spectra of the aqueous solution of **2** before and after photocatalysis experiments.

The solution after cycle 5 was further irradiated under visible light for another three hours to obtain the thorough degradation of the organic dye. Then, the absorption spectrum of the solution was tested, which is in basic agreement with that of the solution before photocatalysis experiment (Fig. S17). This result and the good recyclability of **2** as photocatalyst imply the stability of aqueous solution of **2** during the photocatalytic reactions.

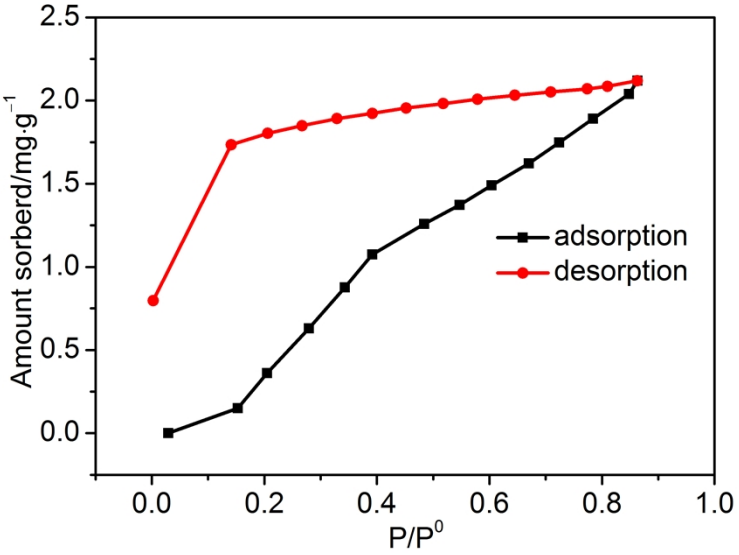


Fig. S18 Water sorption isotherm at 298 K. P° is the saturated vapor pressure at 298 K (26.70 millibars for water).

To study the adsorption property, the water adsorption isotherm of compound **1** was measured at 298 K. Before the measurement, the sample was heated at 80 °C under high vacuum to remove the guest water molecules. As shown in Fig. S18, type II behavior is observed for the water vapor adsorption isotherm of **1**, which represents unrestricted monolayer-multilayer adsorption.[3] The water vapor capacity at 0.86 P/P^o is 2.1 mg/g. Reduction of the pressure after saturation of the sample leads to a non-closing hysteresis loop, which is usually associated with narrow slit-like pores.[3] Specifically, for **1** this phenomenon may be probably due to the relatively small total volume (380 $Å^3$ per unit cell after removal of guest water molecules, which is 28% of the total crystal volume).

References:

1 Z.-L. Lv, W. Chen, J.-Q. Xu, L.-J. Zhang, C.-L. Pan and T.-G. Wang, *Inorg. Chem. Commun.*, 2003, **6,** 244.

2 J.-S. Guo, G. Xu, X.-M. Jiang, M.-J. Zhang, B.-W. Liu and G.-C. Guo, *Inorg. Chem.,* 2014, **53,** 4278.

3 T.-F. Liu, J. Lv, X. Lin and R. Cao, *Chem. Comm.,* 2010, **46,** 8439.