Electronic Supplementary Information for Dalton Transactions

Supplementary information

Solvothermal syntheses, structures, and physical properties of four new coordination compounds constructed from a bent dicarboxylate ligand

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Table S1 Selected bond lengths (Å) and angles (deg) for compounds **1-4**

Compound **1**

Cd1-O8a	2.223(4)	Cd3-O7a	2.196(4)
Cd1-O10	2.225(4)	Cd3-O10	2.225(4)
Cd1-O2b	2.252(4)	Cd3-O9	2.225(4)
Cd1-O6b	2.310(4)	Cd3-O6	2.327(4)
Cd1-O3c	2.366(4)	Cd3-O5	2.447(4)
Cd1-O11	2.392(4)	Cd3-O1	2.474(4)
Cd2-O10	2.273(4)	Cd4-O9	2.156(4)
Cd2-O9	2.304(4)	Cd4-O3d	2.331(4)
Cd2-O4c	2.354(4)	Cd4-O1	2.372(4)
O8a-Cd1-O10	95.65(16)	O9-Cd3-O6	119.86(15)
O8a-Cd1-O2b	163.27(16)	O7a-Cd3-O5	90.28(16)
O10-Cd1-O2b	94.75(15)	O10-Cd3-O5	97.95(14)
O8a-Cd1-O6b	88.78(16)	O9-Cd3-O5	164.84(15)
O10-Cd1-O6b	167.56(14)	O6-Cd3-O5	54.70(14)
O2b-Cd1-O6b	83.79(15)	O7a-Cd3-O1	159.41(17)
O8a-Cd1-O3c	84.39(14)	O10-Cd3-O1	91.28(15)
O10-Cd1-O3c	87.31(15)	O9-Cd3-O1	75.54(15)
O2b-Cd1-O3c	109.18(14)	O6-Cd3-O1	78.59(15)
O6b-Cd1-O3c	81.54(14)	O5-Cd3-O1	89.32(14)
O8a-Cd1-O11	89.16(16)	O9f-Cd4-O9	180.0
O10-Cd1-O11	86.50(15)	O9-Cd4-O3d	90.85(15)
O2b-Cd1-O11	78.43(14)	O9-Cd4-O3g	89.15(15)
O6b-Cd1-O11	105.23(14)	O3d-Cd4-O3g	180.00(18)

O3c-Cd1-O11	170.58(14)	O9f-Cd4-O1	101.01(15)
O10-Cd2-O10e	180.0(3)	O9-Cd4-O1	78.99(15)
O10-Cd2-O9e	99.45(15)	O3d-Cd4-O1	97.55(15)
O10-Cd2-O9	80.55(15)	O3g-Cd4-O1	82.45(15)
O9e-Cd2-O9	180.0(2)	O1-Cd4-O1f	180.0(3)
O10-Cd2-O4d	90.46(14)	Cd4-O1-Cd3	92.29(14)
O9-Cd2-O4d	100.91(15)	Cd4h-O3-Cd1i	113.75(15)
O10-Cd2-O4c	89.54(14)	Cd1j-O6-Cd3	119.02(18)
O9-Cd2-O4c	79.09(15)	Cd4-O9-Cd3	105.83(16)
O4d-Cd2-O4c	180.00(16)	Cd4-O9-Cd2	114.94(18)
O7a-Cd3-O10	109.15(17)	Cd3-O9-Cd2	97.46(17)
O7a-Cd3-O9	103.62(17)	Cd1-O10-Cd3	111.34(17)
O10-Cd3-O9	83.36(15)	Cd1-O10-Cd2	118.05(17)
O7a-Cd3-O6	84.41(17)	Cd3-O10-Cd2	98.37(15)
O10-Cd3-O6	150.41(14)		

Compound **2**

N1-Ni1	2.079(3)	Ni1-O1	2.106(2)
Ni1-O4a	1.999(3)	Ni1-O2	2.121(3)
Ni1-O3b	2.029(2)	Ni1-N2'c	2.15(2)
Ni1-N2c	2.08(2)		
O4a-Ni1-O3b	101.66(11)	O3b-Ni1-O2	160.43(11)
O4a-Ni1-N1	94.05(12)	N1-Ni1-O2	89.14(11)
O3b-Ni1-N1	93.37(11)	N2c-Ni1-O2	88.5(7)
O4a-Ni1-N2c	88.0(6)	O1-Ni1-O2	62.11(10)
O3b-Ni1-N2c	88.3(7)	O4a-Ni1-N2'c	86.0(6)
N1-Ni1-N2c	177.1(6)	O3b-Ni1-N2'c	87.5(7)
O4a-Ni1-O1	159.29(10)	N1-Ni1-N2'c	179.2(7)

O3b-Ni1-O1	98.48(10)	N2c-Ni1-N2'c	2.4(11)
N1-Ni1-O1	89.52(11)	O1-Ni1-N2'c	90.2(6)
N2c-Ni1-O1	87.8(6)	O2-Ni1-N2'c	90.0(6)
O4a-Ni1-O2	97.51(10)		

Compound **3**

Cu1-O5	1.888(2)	Cu1-O4	2.351(3)
Cu1-O3a	1.963(3)	Cu2-O5	1.810(2)
Cu1-O1	1.975(2)	Cu2-O2	1.945(2)
Cu1-N1	2.053(3)		
O5-Cu1-O3a	91.76(11)	O1-Cu1-O4	98.52(10)
O5-Cu1-O1	91.26(11)	N1-Cu1-O4	86.84(11)
O3a-Cu1-O1	165.91(11)	O5-Cu2-O5b	180.000(1)
O5-Cu1-N1	178.11(12)	O5-Cu2-O2b	88.65(11)
O3a-Cu1-N1	86.49(12)	O5-Cu2-O2	91.35(11)
O1-Cu1-N1	90.61(12)	O2b-Cu2-O2	180.0(2)
O5-Cu1-O4	92.62(9)	Cu2-O5-Cu1	128.13(13)
O3a-Cu1-O4	95.09(11)		

Compound **4**

Co1-O1a	1.962(3)	Co1-O6	2.039(3)
Co1-O2b	1.976(3)	Co1-O3	2.172(3)
Co1-O4c	1.999(3)	Co1-Co1c	2.9073(11)
O1a-Co1-O2b	159.54(14)	O4c-Co1-O3	160.57(13)
O1a-Co1-O4c	93.89(12)	O6-Co1-O3	91.14(12)
O2b-Co1-O4c	90.42(14)	O1a-Co1-Co1c	82.68(9)
O1a-Co1-O6	103.40(12)	O2b-Co1-Co1c	77.44(10)
O2b-Co1-O6	94.26(13)	O4c-Co1-Co1c	88.59(10)
O4c-Co1-O6	107.78(13)	O6-Co1-Co1c	161.85(9)

O1a-Co1-O3	85.72(12)	O3-Co1-Co1c	72.08(8)
O2b-Co1-O3	83.64(14)		

Symmetry codes: for **1:** (a) -*x*+1, -*y*+1, -*z*+1; (b) *x*-1, *y*, *z*; (c) *x*-1, *y*-1, *z*; (d) –*x*+1, -*y*+2, -*z*; (e) –*x*, -*y*+1, -*z*; (f) –*x*+1, -*y*+1, -*z*; (g)*x*, *y*-1, *z*; (h) *x*, *y*+1, *z*; (i) *x*+1, *y*+1, *z*; (j) *x*+1, *y*, *z*; for **2:** (a) *x*, *y*, *z*+1; (b) -*x*+2, -*y*+1, -*z*+1; (c) *x*, *y*+1, *z*; for **3**: (a) -*x*+2, -*y*, -*z*+1; (b) -*x*+2, -*y*+1, -*z*+1; for **4**: (a) –*x*+1, *y*-1, -*z*+3/2; (b) *x*, -*y*+2, *z*-1/2; (c) –*x*+1, -*y*+1, -*z*+1.

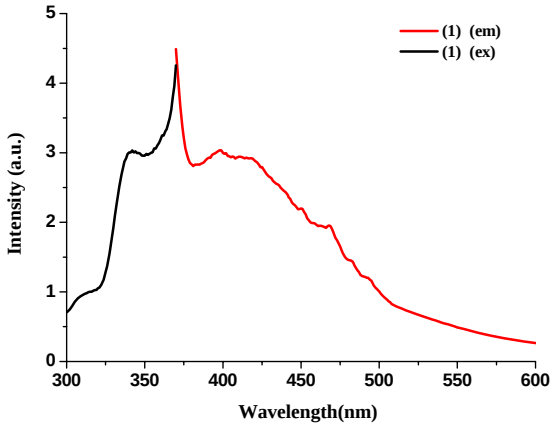

Figure S1. Excitation (left) and emission spectra (right, excited at 340 nm) of compound **1** at room temperature.

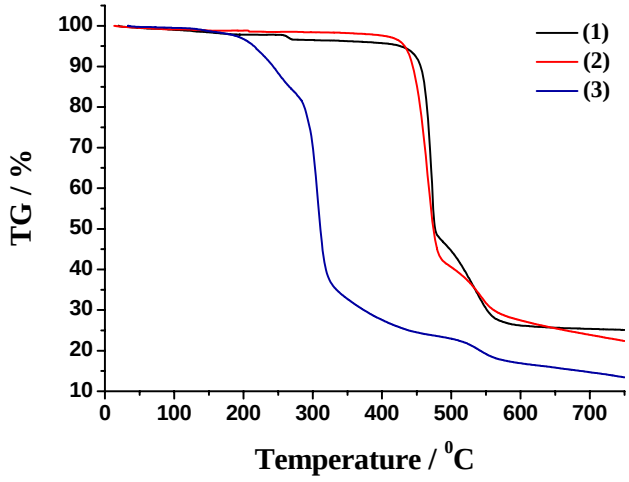

Figure S2. TGA curves of compounds **1** - **3**.

Thermal analysis and PXRD measurements

To characterize the compounds more fully in terms of thermal stability, their thermal behaviors were studied by TGA (Fig. S2). For compound **1**, a little weight loss is observed from 20 to 261 °C which is attributed to the loss of the coordinated water and the lattice water, with a weight loss of 2.97 % (calcd 3.03 %), then the structure was decomposed since 430 °C. The TGA curve of **2** shows the network of compound **2** was decomposed quickly after 420 °C. Comparably, compound **3** is less stable with the weight loss of two lattice DMF and one bipy molecules 22.9% (calcd 23.1%) between 180 °C and 291 °C, and then the framework was decomposed. To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments were carried out for **1** - **3**. The PXRD experimental and computer-simulated patterns of the corresponding compounds are shown in the Supporting Information, Figures S3-S5, and they show that the bulk synthesized materials and the measured single crystals are the same.

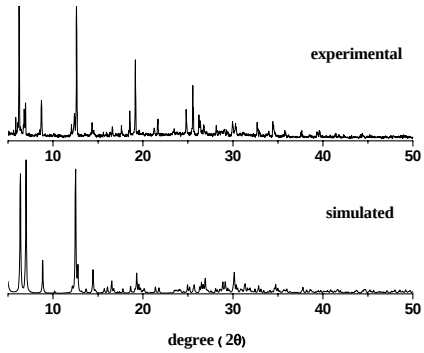

Figure S3. Powder X-ray diffraction patterns of compound **1**

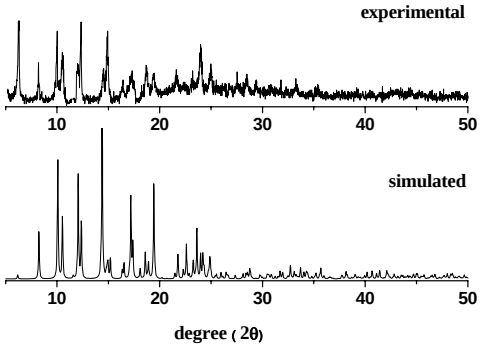

Figure S4. Powder X-ray diffraction patterns of compound **2**

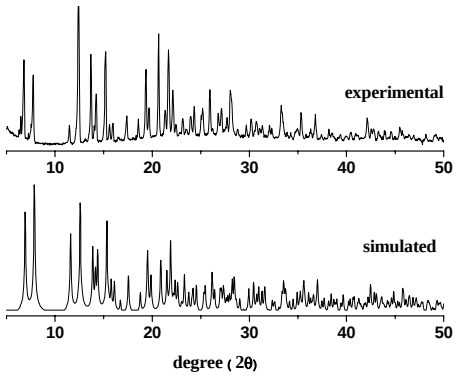

Figure S5. Powder X-ray diffraction patterns of compound **3**