Employing tripodal carboxylate ligand to construct Co(II) coordination networks modulated by N-donor ligands: syntheses, structures and magnetic properties

Xue-Zhi Song,[†,‡] Shu-Yan Song,[†] Min Zhu,[†,‡] Zhao-Min Hao,[†,‡] Xing Meng,[†,‡] Shu-Na Zhao,[†,‡] Hong-Jie Zhang[*,†]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China
[‡]University of Chinese Academy of Sciences, Beijing, 100049, China

Fig. S1-S3: ORTEP drawing of the asymmetrical units in compounds **4-6**.

Fig. S4: Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of compounds **1-6**.

Fig. S5: The FT-IR spectrum of compounds **1-6**.

Fig. S6: TGA curve of compounds **1-6**.

Table S1: Selected bond lengths (Å) and angles (deg) for compounds **1-6**.

Table S2: Hydrogen bonds (lengths and angles, Å and deg) for compounds **1-6**.

Table S3: The C_{phenyl}-O-C_{phenyl} bond angles and the dihedral angles between the phenyl rings in H_3cpia ligand.

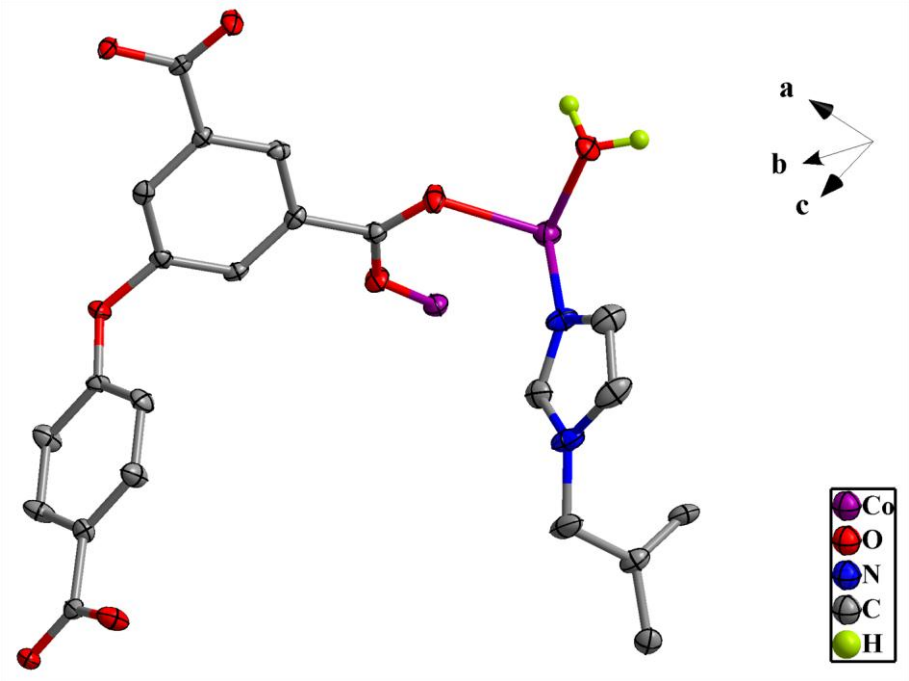

Fig. S1 ORTEP drawing of the asymmetrical unit in **4** (50% probability ellipsoids). Hydrogen atoms attached to carbon atoms are omitted for clarity.

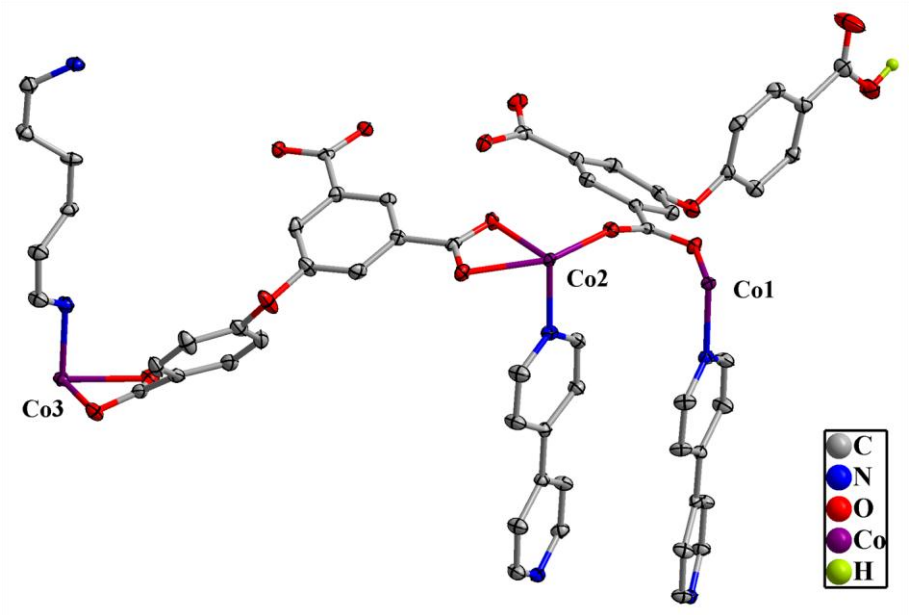

Fig. S2 ORTEP drawing of the asymmetrical unit in **5** (50% probability ellipsoids). Hydrogen atoms attached to carbon atoms are omitted for clarity.

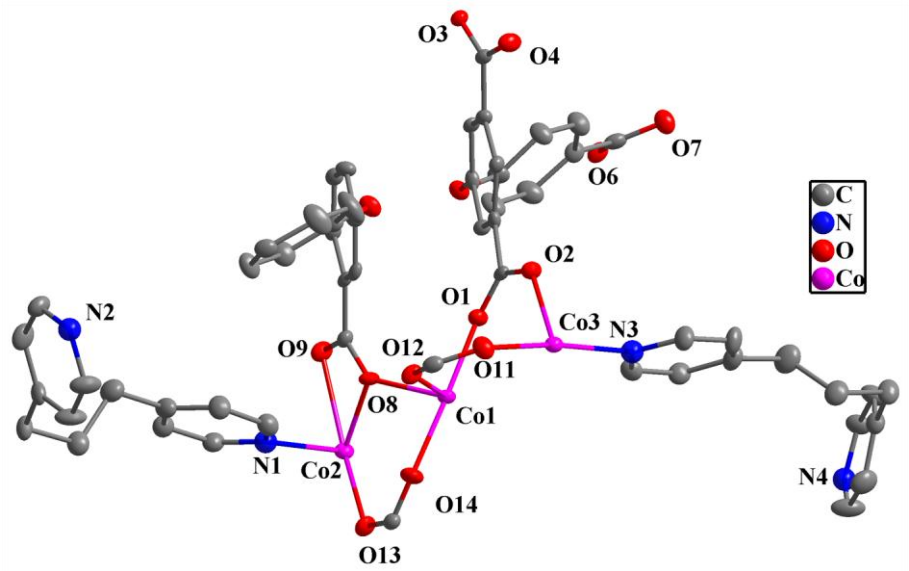

Fig. S3 ORTEP drawing of the asymmetrical unit in **6** (50% probability ellipsoids). Hydrogen atoms attached to carbon atoms are omitted for clarity.

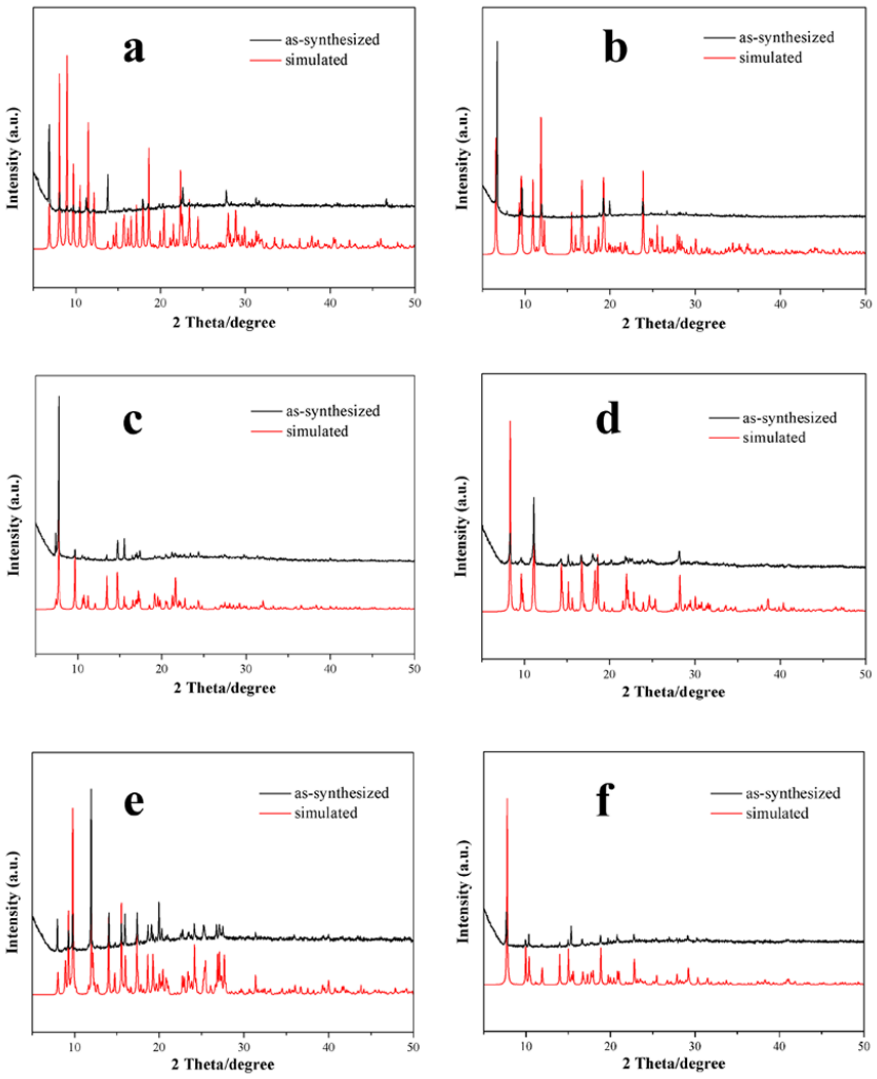

Fig. S4 Simulated (red) and experimental as-synthesized (black) powder X-ray diffraction (PXRD) patterns of **1**(a), **2**(b), **3**(c), **4**(d), **5**(e) and **6**(f).

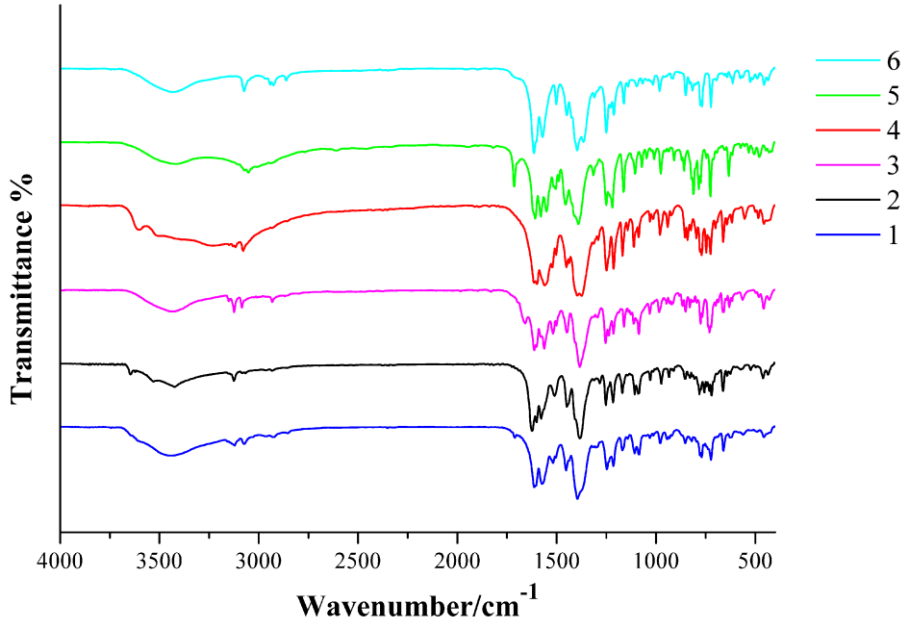

Fig. S5 The FT-IR spectrum of compounds **1-6**.

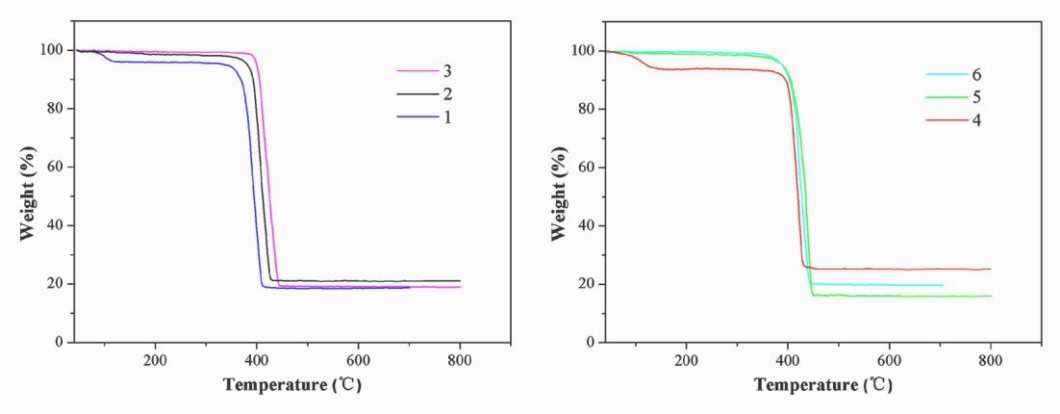

Fig. S6: TGA curve of compounds **1-6**.

Table S1: Selected bond lengths (Å) and angles (deg) for compounds **1-6**.

		Compound **1**	
Co(1)-O(2)	2.141(3)	Co(2)-N(1)	2.167(3)
Co(1)-O(4)#4	2.019(3)	Co(2)-O(1)	2.368(3)
Co(1)-O(4)#5	2.019(3)	Co(2)-O(2)	2.113(3)
Co(1)-O(6)#6	2.062(3)	Co(2)-O(7)#7	2.073(3)
Co(1)-O(6)#7	2.062(3)	Co(2)-N(3)#9	2.085(3)
Co(1)-O(2)#8	2.141(3)	Co(2)-O(3)#5	2.093(3)
O(4)#4-Co(1)-O(4)#5	180.00(14)	O(6)#6-Co(1)-O(2)#8	93.23(10)
O(4)#4-Co(1)-O(6)#6	94.04(11)	O(6)#7-Co(1)-O(2)#8	86.77(10)
O(4)#5-Co(1)-O(6)#6	85.96(11)	O(4)#4-Co(1)-O(2)	94.98(10)
O(4)#4-Co(1)-O(6)#7	85.96(11)	O(4)#5-Co(1)-O(2)	85.02(10)
O(4)#5-Co(1)-O(6)#7	94.04(11)	O(6)#6-Co(1)-O(2)	86.77(10)
O(6)#6-Co(1)-O(6)#7	180.00(16)	O(6)#7-Co(1)-O(2)	93.23(10)
O(4)#4-Co(1)-O(2)#8	85.02(10)	O(2)#8-Co(1)-O(2)	180.000(1)
O(4)#5-Co(1)-O(2)#8	94.98(10)	N(3)#9-Co(2)-N(1)	99.64(13)
O(7)#7-Co(2)-N(3)#9	85.75(12)	O(3)#5-Co(2)-N(1)	84.15(12)
O(7)#7-Co(2)-O(3)#5	93.24(12)	O(2)-Co(2)-N(1)	86.66(11)
N(3)#9-Co(2)-O(3)#5	97.08(12)	O(7)#7-Co(2)-O(1)	87.45(11)
O(7)#7-Co(2)-O(2)	89.43(11)	N(3)#9-Co(2)-O(1)	94.91(11)
N(3)#9-Co(2)-O(2)	152.91(12)	O(3)#5-Co(2)-O(1)	168.01(11)
O(3)#5-Co(2)-O(2)	109.81(11)	O(2)-Co(2)-O(1)	58.21(10)
O(7)#7-Co(2)-N(1)	174.25(12)	N(1)-Co(2)-O(1)	94.04(11)
		Compound **2**	
Co(1)-N(1)	2.170(2)	Co(2)-O(1)	2.1155(16)
Co(1)-O(2)	2.0528(16)	Co(2)-O(6)	2.0269(17)
Co(1)-O(5)	2.1651(18)	Co(2)-O(8)	1.9931(16)
Co(1)-O(8)	2.0890(16)	Co(2)-O(3)#3	1.9946(16)
Co(1)-O(4)#6	2.0345(16)	Co(2)-O(8)#5	2.1451(16)
Co(1)-N(3)#2	2.141(2)	O(5)-Co(1)-N(1)	86.91(7)
O(4)#6-Co(1)-O(2)	171.41(7)	O(2)-Co(1)-O(5)	88.24(7)
O(4)#6-Co(1)-O(8)	94.16(6)	O(8)-Co(1)-O(5)	93.89(7)
O(2)-Co(1)-O(8)	94.30(7)	N(3)#2-Co(1)-O(5)	174.08(7)
O(4)#6-Co(1)-N(3)#2	94.50(8)	O(4)#6-Co(1)-N(1)	84.85(7)
O(2)-Co(1)-N(3)#2	86.99(8)	O(2)-Co(1)-N(1)	86.71(7)
O(8)-Co(1)-N(3)#2	90.00(7)	O(8)-Co(1)-N(1)	178.73(7)
O(4)#6-Co(1)-O(5)	89.68(7)	N(3)#2-Co(1)-N(1)	89.27(8)
O(8)-Co(2)-O(3)#3	134.27(7)	O(8)-Co(2)-O(6)	117.23(7)
O(3)#3-Co(2)-O(6)	108.48(7)	O(8)-Co(2)-O(8)#5	79.99(7)
O(8)-Co(2)-O(1)	97.86(7)	O(3)#3-Co(2)-O(8)#5	98.11(6)
O(3)#3-Co(2)-O(1)	83.51(6)	O(6)-Co(2)-O(8)#5	91.48(7)
O(6)-Co(2)-O(1)	89.35(7)	O(1)-Co(2)-O(8)#5	177.84(6)
		Compound **3**	
Co(1)-O(1)	2.087(4)	Co(2)-O(2)	2.057(4)

Co(1)-O(3)	2.116(4)	Co(2)-O(3)	2.105(4)
Co(1)-O(6)#4	2.048(4)	Co(2)-O(5)#4	2.051(4)
Co(1)-O(6)#5	2.048(4)	Co(2)-N(3)#3	2.129(6)
Co(1)-O(1)#6	2.087(4)	Co(2)-N(1)	2.079(6)
Co(1)-O(3)#6	2.116(4)	O(3)-Co(1)-O(3)#6	180.000(1)
O(6)#4-Co(1)-O(6)#5	180.0	O(6)#4-Co(1)-O(1)	95.17(17)
O(6)#5-Co(1)-O(1)	84.83(17)	O(6)#5-Co(1)-O(1)#6	95.17(17)
O(6)#4-Co(1)-O(1)#6	84.83(17)	O(1)-Co(1)-O(1)#6	180.0
O(6)#4-Co(1)-O(3)	89.98(17)	O(6)#5-Co(1)-O(3)	90.02(17)
O(1)-Co(1)-O(3)	85.27(16)	O(1)#6-Co(1)-O(3)	94.73(16)
O(6)#4-Co(1)-O(3)#6	90.02(17)	O(6)#5-Co(1)-O(3)#6	89.98(17)
O(1)-Co(1)-O(3)#6	94.73(16)	O(1)#6-Co(1)-O(3)#6	85.27(16)
O(5)#4-Co(2)-O(2)	94.94(17)	O(5)#4-Co(2)-N(1)	89.6(2)
O(2)-Co(2)-N(1)	89.0(2)	O(5)#4-Co(2)-O(3)	105.39(17)
O(2)-Co(2)-O(3)	89.97(18)	N(1)-Co(2)-O(3)	164.95(19)
O(5)#4-Co(2)-N(3)#3	95.47(19)	O(2)-Co(2)-N(3)#3	168.8(2)
N(1)-Co(2)-N(3)#3	95.2(2)	O(3)-Co(2)-N(3)#3	83.33(19)
		Compound **4**	
Co(1)-O(2)#1	2.035(3)	Co(2)-O(6)#2	1.994(3)
Co(1)-O(2)	2.035(3)	Co(2)-N(1)	2.083(3)
Co(1)-O(7)#2	2.080(3)	Co(2)-O(1)	2.088(3)
Co(1)-O(7)#3	2.080(3)	Co(2)-O(1W)	2.104(3)
Co(1)-O(3)#4	2.128(2)	Co(2)-O(3)#4	2.117(3)
Co(1)-O(3)#5	2.128(2)	O(2)-Co(1)-O(3)#4	88.14(11)
O(2)#1-Co(1)-O(2)	180.00(17)	O(7)#2-Co(1)-O(3)#4	91.14(10)
O(2)#1-Co(1)-O(7)#2	83.58(11)	O(7)#3-Co(1)-O(3)#4	88.86(10)
O(2)-Co(1)-O(7)#2	96.42(11)	O(2)#1-Co(1)-O(3)#5	88.14(11)
O(2)#1-Co(1)-O(7)#3	96.42(11)	O(2)-Co(1)-O(3)#5	91.86(11)
O(2)-Co(1)-O(7)#3	83.58(11)	O(7)#2-Co(1)-O(3)#5	88.86(10)
O(7)#2-Co(1)-O(7)#3	180.000(1)	O(7)#3-Co(1)-O(3)#5	91.14(10)
O(2)#1-Co(1)-O(3)#4	91.86(11)	O(3)#4-Co(1)-O(3)#5	180.0
O(6)#2-Co(2)-N(1)	168.59(14)	O(6)#2-Co(2)-O(3)#4	93.59(11)
O(6)#2-Co(2)-O(1)	94.13(13)	N(1)-Co(2)-O(3)#4	87.55(12)
N(1)-Co(2)-O(1)	96.20(14)	O(1)-Co(2)-O(3)#4	109.29(11)
O(6)#2-Co(2)-O(1W)	86.66(11)	O(1W)-Co(2)-O(3)#4	165.01(11)
N(1)-Co(2)-O(1W)	89.32(13)	O(1)-Co(2)-O(1W)	85.62(11)
		Compound **5**	
Co(1)-N(3)	2.154(2)	Co(2)-O(8)	2.2434(17)
Co(1)-O(1)	2.0492(16)	Co(2)-O(9)	2.1474(17)
Co(1)-O(11)#5	2.0299(17)	Co(2)-N(1)	2.139(2)
Co(1)-O(3)#5	2.1143(17)	Co(2)-O(2)	2.0444(17)
Co(1)-N(4)#3	2.132(2)	Co(2)-O(10)#5	2.0530(16)
Co(1)-O(4)#5	2.3968(19)	Co(2)-N(2)#3	2.145(2)
Co(3)-N(5)	2.203(3)	Co(3)-O(13)#1	2.0648(17)

Co(3)-O(13)	2.0648(17)	Co(3)-N(6)#2	2.100(3)
Co(3)-O(14)	2.2192(18)	Co(3)-O(14)#1	2.2192(18)
O(11)#5-Co(1)-O(1)	121.90(7)	O(11)#5-Co(1)-O(4)#5	151.05(6)
O(11)#5-Co(1)-O(3)#5	93.17(7)	O(1)-Co(1)-O(4)#5	87.05(6)
O(1)-Co(1)-O(3)#5	144.85(7)	O(3)#5-Co(1)-O(4)#5	57.88(6)
O(11)#5-Co(1)-N(4)#3	90.96(7)	N(4)#3-Co(1)-O(4)#5	88.28(7)
O(1)-Co(1)-N(4)#3	92.16(7)	N(3)-Co(1)-O(4)#5	94.09(7)
O(3)#5-Co(1)-N(4)#3	89.21(7)	O(3)#5-Co(1)-N(3)	92.83(7)
O(11)#5-Co(1)-N(3)	87.41(7)	N(4)#3-Co(1)-N(3)	177.45(8)
O(1)-Co(1)-N(3)	87.05(7)	N(1)-Co(2)-O(9)	94.51(7)
O(2)-Co(2)-O(10)#5	121.31(7)	O(2)-Co(2)-N(1)	91.81(7)
O(10)#5-Co(2)-N(1)	90.63(7)	N(2)#3-Co(2)-O(9)	88.99(7)
O(2)-Co(2)-N(2)#3	87.52(7)	O(2)-Co(2)-O(8)	151.11(7)
O(10)#5-Co(2)-N(2)#3	86.75(7)	O(10)#5-Co(2)-O(8)	87.59(6)
N(1)-Co(2)-N(2)#3	176.46(8)	N(1)-Co(2)-O(8)	87.62(7)
O(2)-Co(2)-O(9)	91.40(7)	N(2)#3-Co(2)-O(8)	94.65(7)
O(10)#5-Co(2)-O(9)	146.73(7)	O(9)-Co(2)-O(8)	59.89(6)
O(13)-Co(3)-O(13)#1	166.45(10)	N(5)-Co(3)-O(14)	83.91(5)
O(13)-Co(3)-N(6)#2	96.78(5)	O(13)-Co(3)-O(14)#1	117.23(7)
O(13)#1-Co(3)-N(6)#2	96.78(5)	O(13)#1-Co(3)-O(14)#1	61.14(7)
O(13)-Co(3)-N(5)	83.22(5)	N(6)#2-Co(3)-O(14)#1	96.09(5)
O(13)#1-Co(3)-N(5)	83.22(5)	N(5)-Co(3)-O(14)#1	83.91(5)
N(6)#2-Co(3)-N(5)	180.000(2)	O(14)-Co(3)-O(14)#1	167.82(9)
O(13)-Co(3)-O(14)	61.14(7)	N(6)#2-Co(3)-O(14)	96.09(5)
O(13)#1-Co(3)-O(14)	117.23(7)		
		Compound **6**	
O(8)-Co(1)	2.109(3)	O(12)-Co(1)	2.077(3)
O(14)-Co(1)	2.057(3)	O(1)-Co(1)	2.036(3)
Co(1)-O(6)#5	2.076(3)	Co(1)-O(4)#3	2.103(3)
N(1)-Co(2)	2.164(4)	O(8)-Co(2)	2.086(3)
O(13)-Co(2)	2.063(3)	Co(2)-O(7)#5	2.047(3)
Co(2)-N(4)#4	2.098(4)		
N(3)-Co(3)	2.164(4)	O(2)-Co(3)	2.074(3)
Co(3)-O(4)#3	2.107(3)	Co(3)-N(2)#2	2.111(4)
Co(3)-O(3)#3	2.369(3)	O(11)-Co(3)	2.033(3)
O(1)-Co(1)-O(14)	177.38(13)	O(1)-Co(1)-O(12)	97.78(13)
O(14)-Co(1)-O(12)	82.79(13)	O(1)-Co(1)-O(6)#5	82.06(13)
O(14)-Co(1)-O(6)#5	97.41(13)	O(12)-Co(1)-O(6)#5	179.28(12)
O(1)-Co(1)-O(4)#3	89.19(12)	O(14)-Co(1)-O(4)#3	93.36(13)
O(12)-Co(1)-O(4)#3	90.67(12)	O(6)#5-Co(1)-O(4)#3	88.62(12)
O(1)-Co(1)-O(8)	90.58(12)	O(14)-Co(1)-O(8)	86.84(12)
O(12)-Co(1)-O(8)	92.20(12)	O(6)#5-Co(1)-O(8)	88.47(12)
O(4)#3-Co(1)-O(8)	177.09(13)		
O(7)#5-Co(2)-O(13)	95.73(14)	O(8)-Co(2)-N(4)#4	151.79(14)

O(7)#5-Co(2)-O(8)	93.71(13)	O(7)#5-Co(2)-N(1)	172.32(15)
O(13)-Co(2)-O(8)	111.43(13)	O(13)-Co(2)-N(1)	91.93(14)
O(7)#5-Co(2)-N(4)#4	86.12(14)	O(8)-Co(2)-N(1)	82.95(13)
O(13)-Co(2)-N(4)#4	96.62(15)	N(4)#4-Co(2)-N(1)	93.54(15)
O(11)-Co(3)-O(2)	96.99(14)	O(11)-Co(3)-O(4)#3	92.03(13)
O(2)-Co(3)-O(4)#3	108.10(12)	O(11)-Co(3)-N(2)#2	85.42(14)
O(2)-Co(3)-N(2)#2	90.26(14)	O(4)#3-Co(3)-N(2)#2	161.64(14)
O(11)-Co(3)-N(3)	172.36(15)	O(4)#3-Co(3)-N(3)	85.20(13)
O(2)-Co(3)-N(3)	90.64(14)	N(2)#2-Co(3)-N(3)	94.97(15)
O(11)-Co(3)-O(3)#3	89.04(13)	O(2)-Co(3)-O(3)#3	165.14(12)
O(4)#3-Co(3)-O(3)#3	57.93(11)	N(2)#2-Co(3)-O(3)#3	103.79(14)
N(3)-Co(3)-O(3)#3	83.46(13)		

Symmetry codes: Compound **1**: #4 = -x,-y,-z+1; #5 = x+1,y,z; #6 = -x,-y+1,-z+1; #7 = x+1,y-1,z; #8 = -x+1,-y,-z+1; #9 = x,y-1,z; **2**: #2 = -x+1,-y+1,-z; #3 = -x,-y+1,-z+1; #5 = -x+1,-y+2,-z+1; #6 = x+1,y+1,z; **3**: #3 = x,y-1,z; #4 = x+1,y,z; #5 = -x,-y+1,-z; #6 = -x+1,-y+1,-z; **4**: #1 = -x,-y+2,-z; #2 = x,y,z-1; #3 = -x,-y+2,-z+1; #4 = x-1,y,z; #5 = -x+1,-y+2,-z; **5**: #1 = -x,y,-z+3/2; #2 = x,y+1,z; #3 = x,y-1,z; #5 = x,-y+1,z-1/2; **6**: #2 = -x,-y+1,-z+1; #3 = x+1,y,z; #4 = -x+1,-y+1,-z; #5 = -x,-y+1,-z.

Table S2: Hydrogen bonds (lengths and angles, Å and deg) for compounds **1-6**.

D-H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Compound **1**				
O(1W)-H(1WA)...O(3)	0.87	2.06	2.851(5)	150.5
O(1W)-H(1WB)...O(2W')#9	0.87	2.04	2.729(17)	135.8
O(1W)-H(1WB)...O(5)#4	0.87	2.57	3.065(5)	117.4
Compound **2**				
O(8)-H(8)...O(1W)#5	0.870(17)	2.263(18)	3.094(3)	160(2)
O(1W)-H(1WB)...O(6)	0.87	1.97	2.816(3)	163.2
Compound **4**				
O(1W)-H(1WA)...O(2W)	0.89	1.92	2.771(5)	158.6
O(1W)-H(1WB)...O(4)#9	0.89	1.77	2.664(4)	177.4
O(2W)-H(2WA)...O(1)	0.87	2.63	3.231(5)	126.9
O(2W)-H(2WB)...O(1W)#9	0.87	2.30	2.995(5)	136.7
O(2W)-H(2WB)...O(1)#9	0.87	2.62	3.404(5)	151.2
Compound **5**				
O(7)-H(7)...O(13)#6	0.886(17)	1.711(17)	2.591(3)	172(3)
O(1W)-H(1WB)...O(9)	0.87	2.07	2.830(2)	145.4
O(2W)-H(2WA)...O(3W)#7	0.84	1.91	2.751(5)	179.3
O(2W)-H(2WB)...O(4)	0.84	2.18	3.026(3)	179.3
O(3W)-H(3WA)...O(1W)	0.87	1.90	2.736	160.5
O(3W)-H(3WB)...O(2W)	0.85	1.88	2.733	179.9
Compound **6**				
O(1W)-H(1WB)...O(7)	0.85	2.18	3.014(9)	169.0

Symmetry codes: Compound **1**: #4 = -x,-y,-z+1; #9 = x,y-1,z; Compound **2**: #5 = -x+1,-y+2,-z+1; Compound **4**: #9 = -x+1,-y+1,-z; Compound **5**: #6 = x+1/2,y-1/2,z; #7 = -x+1/2,-y+1/2,-z+1.

Table S3: The C_{phenyl}-O-C_{phenyl} bond angles and the dihedral angles between the phenyl rings in H_3cpia ligand.

Compound	C_{phenyl}-O-C_{phenyl} bond angle	dihedral angle between the phenyl rings
1	118.33°	80.48°
2	117.75°	65.38°
3	119.54°	76.80°
4	117.70°	81.54°
5	119.04° 116.39°	85.33° 63.66°
6	119.21° 120.42°	61.78° 67.22°