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**Role of aromatic dicarboxylates in the structural diversity of cobalt(II) and copper(II) coordination polymers containing a flexible N,N'-di(3-pyridyl)octandiamide ligand**

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**ELECTRONIC SUPPLEMENTARY INFORMATION**

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

Co(1)-O(7)	2.0593(14)	Co(1)-N(1)	2.1752(17)
Co(1)-O(4)	2.0762(15)	Co(1)-N(3)	2.1988(17)
Co(1)-O(1W)	2.1345(17)	Co(1)-N(6)#1	2.2092(18)
O(7)-Co(1)-O(4)	87.70(6)	O(7)-Co(1)-O(1W)	87.30(7)
O(4)-Co(1)-O(1W)	173.94(7)	O(1W)-Co(1)-N(3)	88.53(7)
O(7)-Co(1)-N(1)	90.88(6)	N(1)-Co(1)-N(3)	173.88(6)
O(4)-Co(1)-N(1)	85.93(6)	O(7)-Co(1)-N(6)#1	177.64(6)
O(1W)-Co(1)-N(1)	90.72(7)	O(4)-Co(1)-N(6)#1	89.96(6)
O(7)-Co(1)-N(3)	95.16(6)	O(1W)-Co(1)-N(6)#1	95.01(7)
O(4)-Co(1)-N(3)	95.34(6)	N(1)-Co(1)-N(6)#1	88.67(6)
N(3)-Co(1)-N(6)#1	85.34(6)		

Symmetry code: #1 -x+1,-y-1,-z

**Table S2.** Selected bond distances (Å) and angles (deg) for compound **2**

Co(1)-N(1)	2.211(6)	Co(1)-O(1W)	2.101(6)
Co(1)-O(8)	2.074(5)	Co(1)-O(1W)#1	2.101(6)
Co(1)-O(8)#1	2.074(5)	Co(1)-N(1)#1	2.211(6)
Co(2)-O(2W)	2.129(5)	Co(2)-O(2W)#2	2.129(5)
Co(2)-O(5)	2.075(5)	Co(2)-N(5)#2	2.166(5)
Co(2)-O(5)#2	2.075(5)	Co(2)-N(5)	2.166(5)
Co(2)-O(2W)#2	2.129(5)	O(8)#1-Co(1)-O(1W)	89.8(2)

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O(8)-Co(1)-O(8)#1	179.999(2)	O(8)#1-Co(1)-N(1)#1	90.6(2)
O(8)-Co(1)-O(1W)	90.2(2)	O(1W)-Co(1)-N(1)#1	89.5(2)
O(8)-Co(1)-O(1W)#1	89.8(2)	O(1W)#1-Co(1)-N(1)#1	90.5(2)
O(8)#1-Co(1)-O(1W)#1	90.2(2)	O(8)-Co(1)-N(1)	90.6(2)
O(1W)-Co(1)-O(1W)#1	180	O(8)#1-Co(1)-N(1)	89.4(2)
O(8)-Co(1)-N(1)#1	89.4(2)	O(1W)-Co(1)-N(1)	90.5(2)
N(1)#1-Co(1)-N(1)	179.999(2)	O(1W)#1-Co(1)-N(1)	89.5(2)
O(5)#2-Co(2)-O(5)	179.999(2)	O(2W)-Co(2)-N(5)#2	86.5(2)
O(5)#2-Co(2)-O(2W)	90.9(2)	O(2W)#2-Co(2)-N(5)#2	93.5(2)
O(5)-Co(2)-O(2W)	89.1(2)	O(5)#2-Co(2)-N(5)	88.8(2)
O(5)#2-Co(2)-O(2W)#2	89.1(2)	O(5)-Co(2)-N(5)	91.2(2)
O(5)-Co(2)-O(2W)#2	90.9(2)	O(2W)-Co(2)-N(5)	93.5(2)
O(2W)-Co(2)-O(2W)#2	179.999(1)	O(2W)#2-Co(2)-N(5)	86.5(2)
O(5)#2-Co(2)-N(5)#2	91.2(2)	N(5)#2-Co(2)-N(5)	179.999(1)
O(5)-Co(2)-N(5)#2	88.8(2)		

Symmetry code: #1 -x,-y+2,-z+2 #2 -x+1,-y+1,-z+1

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**Table S3.** Selected bond distances (Å) and angles (deg) for compound **3**

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Co(1)-O(5)	2.023(2)	Co(1)-N(1)	2.162(2)
Co(1)-O(1W)	2.090(2)	Co(1)-O(2)#1	2.1735(17)
Co(1)-O(3)#1	2.158(2)	Co(1)-N(3)#2	2.3156(16)
O(5)-Co(1)-N(1)	91.86(9)	O(5)-Co(1)-O(2)#1	98.44(8)
O(1W)-Co(1)-N(1)	88.88(9)	O(1W)-Co(1)-O(2)#1	160.80(8)
O(3)#1-Co(1)-N(1)	94.81(8)	O(3)#1-Co(1)-O(2)#1	60.64(7)
O(5)-Co(1)-O(1W)	100.70(9)	O(1W)-Co(1)-N(3)#2	87.15(7)
O(5)-Co(1)-O(3)#1	158.20(8)	O(3)#1-Co(1)-N(3)#2	86.05(7)
O(1W)-Co(1)-O(3)#1	100.16(9)	N(1)-Co(1)-N(3)#2	176.03(8)
N(1)-Co(1)-O(2)#1	92.06(8)	O(2)#1-Co(1)-N(3)#2	91.74(6)
O(5)-Co(1)-N(3)#2	88.73(7)		

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Symmetry code: #1 x,y-1,z; #2 -x+1,-y+1,-z+1;

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**Table S4.** Selected bond distances (Å) and angles (deg) for compound **4**

Cu(1)-N(1)	1.999(2)	Cu(1)-O(4)	2.0055(16)
Cu(1)-N(1)#3	1.999(2)	Cu(1)-O(2)	2.492(3)
Cu(1)-O(4)#3	2.0054(16)	Cu(1)-O(2)#3	2.492(3)
N(1)#3-Cu(1)-N(1)	92.67(12)	N(1)-Cu(1)-O(4)#3	92.18(8)
N(1)#3-Cu(1)-O(4)	92.18(8)	O(4)-Cu(1)-O(4)#3	85.98(10)
N(1)-Cu(1)-O(4)	166.41(7)	O(2)-Cu(1)-O(4)#3	92.32(12)
N(1)#3-Cu(1)-O(4)#3	166.41(7)	N(1)#3-Cu(1)-O(2)	98.09(7)
O(2)-Cu(1)-O(2)#3	140.63(6)	N(1)#3-Cu(1)-O(2)#3	108.93(10)
N(1)-Cu(1)-O(2)	98.09(7)	O(2)#3-Cu(1)-O(4)	92.32(12)
N(1)-Cu(1)-O(2)#3	108.93(10)	O(2)-Cu(1)-O(4)	57.78(8)

Symmetry code: #1 -x+3/2,-y+1/2,-z+1; #2 -x+1,y,-z+1/2; #3 -x,y,-z+1/2

**Table S5.** Selected bond distances (Å) and angles (deg) for compound **5**

Cu(1)-N(1)	2.025(3)	Cu(1)-O(1)	1.995(2)
Cu(1)-O(1W)	2.328(2)	Cu(1)-O(3)	1.953(2)
Cu(1)-N(2)	2.032(3)		
O(3)-Cu(1)-O(1)	174.24(9)	O(3)-Cu(1)-N(1)	90.85(10)
O(1)-Cu(1)-N(1)	89.14(9)	O(3)-Cu(1)-N(2)	91.10(10)
O(1)-Cu(1)-N(2)	90.12(9)	N(1)-Cu(1)-N(2)	167.72(10)
O(3)-Cu(1)-O(1W)	82.50(9)	O(1)-Cu(1)-O(1W)	91.78(8)
N(1)-Cu(1)-O(1W)	97.08(9)	N(2)-Cu(1)-O(1W)	95.19(9)

**Table S6.** Selected bond distances (Å) and angles (deg) for compound **6**

Cu(1)-O(9)	1.979(3)	Cu(1)-O(7)	1.987(3)
Cu(1)-N(4)#1	1.992(4)	Cu(1)-N(1)	2.000(4)
Cu(1)-O(6)	2.550(2)	Cu(1)-O(3)	2.511(3)
Cu(2)-O(1W)	2.328(4)	Cu(2)-O(8)#2	1.929(3)
Cu(2)-O(4)	1.976(3)	Cu(2)-N(9)	2.016(4)
Cu(2)-N(7)	2.021(4)	Cu(2)-O(5)	2.667(4)
O(9)-Cu(1)-O(7)	174.00(13)	O(9)-Cu(1)-N(4)#1	91.68(15)
O(7)-Cu(1)-N(4)#1	87.90(15)	O(7)-Cu(1)-N(1)	89.31(15)

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O(6)-Cu(1)-O(3)	171.30(13)	O(9)-Cu(1)-N(1)	91.20(15)
O(6)-Cu(1)-N(1)	96.94(13)	O(6)-Cu(1)-N(4)#1	85.29(15)
O(3)-Cu(1)-N(4)#1	87.68(12)	O(3)-Cu(1)-N(1)	89.92(13)
N(4)#1-Cu(1)-N(1)	177.00(16)	O(8)#2-Cu(2)-N(9)	91.10(16)
O(8)#2-Cu(2)-O(4)	176.94(14)	O(8)#2-Cu(2)-N(7)	89.25(16)
O(4)-Cu(2)-N(9)	88.87(15)	N(9)-Cu(2)-N(7)	171.64(17)
O(4)-Cu(2)-N(7)	91.22(15)	O(4)-Cu(2)-O(1W)	91.39(14)
O(8)#2-Cu(2)-O(1W)	85.56(14)	N(7)-Cu(2)-O(1W)	95.18(16)
N(9)-Cu(2)-O(1W)	93.18(16)		
Symmetry code: #1 x,y-1,z+1 #2 x+1,y-1,z			

**Table S7.** Hydrogen-bonding geometry (Å, °) for compound **1**

D-H...A	D-H	H...A	D...A	D-H...A
N(5)-H(5)...O(6) <sup>a</sup>	0.86	2.08	2.9275	167
O(1W)-H(1WA)...O(5) <sup>b</sup>	0.82	1.93	2.7471	171
Symmetry code for (a) -x,-1+y,1/2-z; (b) x,1+y,z				

**Table S8.** Hydrogen-bonding geometry (Å, °) for compound **2**

D-H...A	D-H	H...A	D...A	D-H...A
N(2)-H(2B)...O(6) <sup>a</sup>	0.86	2.28	3.1158	165
Symmetry code for (a) 1-x,1-y,-z				

**Table S9.** Hydrogen-bonding geometry (Å, °) for compound **3**


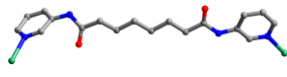


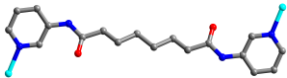
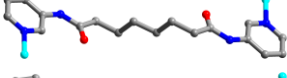
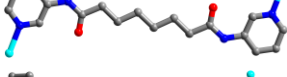
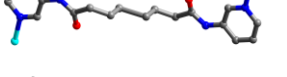
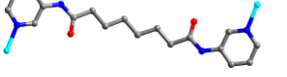
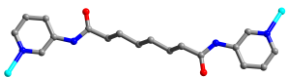
D-H...A	D-H	H...A	D...A	D-H...A
O(2W)-H(2WB)...O(4) <sup>a</sup>	0.87	2.23	2.8962	133
O(2W)-H(2WA)...O(1) <sup>a</sup>	0.77	2.05	2.8024	166
Symmetry code for (a) -1+x,y,z,				

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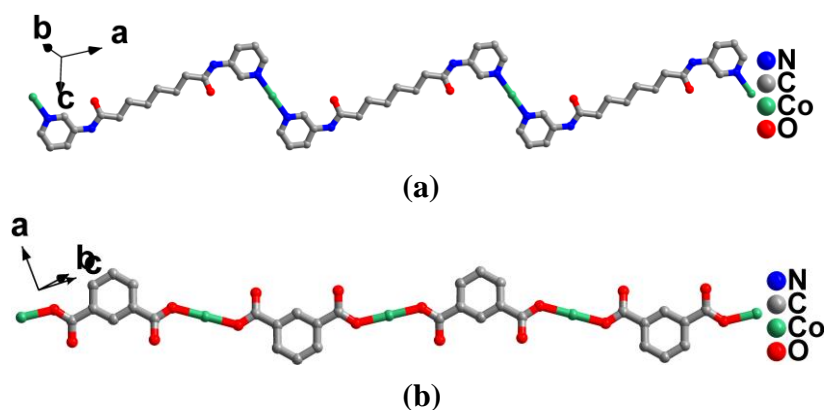
**Table S10.** Hydrogen-bonding geometry (Å, °) for compound **4**

D–H···A	D–H	H···A	D···A	D–H···A
N(2)–H(2)···O(4) <sup>a</sup>	0.86	2.14	2.9752	164
Symmetry code for (a) x, -y, -1/2+z				

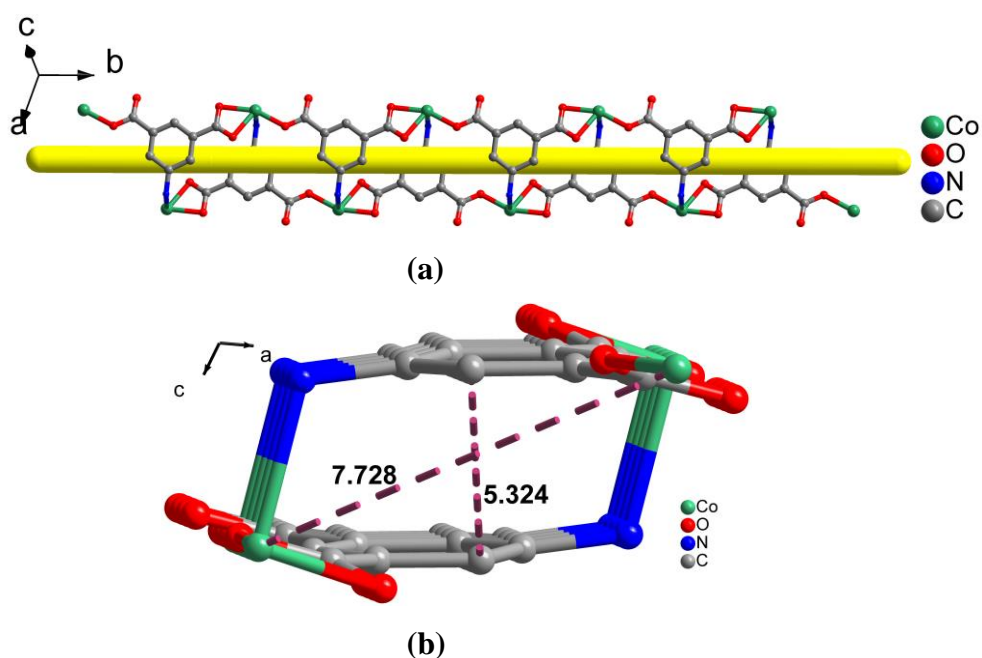
**Table S11.** Conformations of ligand **L** and corresponding angles for compounds **1–6**

Compounds	Diagram	Torsion angle/°	Conformation
<b>1</b>		<b>L<sup>a</sup></b> 178.64,-179.11,-180,179.11,-178.64	AAAAA trans
		<b>L<sup>b</sup></b> 173.86,174.97,178.14,177.61,179.16	AAAAA trans
<b>2</b>		<b>L</b> 177.61,178.57,-180.00,-178.57,-177.61	AAAAA trans
<b>3</b>		<b>L</b> 179.38,-177.76,-180.00,177.76,-179.38	AAAAA trans
<b>4</b>		<b>L</b> -175.28,-171.17,180.00,171.17,-175.28	AAAAA trans
<b>5</b>		<b>L<sup>a</sup></b> 75.43,176.98,-180.00,-176.98,-75.43	GAAAG trans
		<b>L<sup>b</sup></b> -177.88,-178.91,-180.00,178.91,177.88	AAAAA trans
<b>6</b>		<b>L<sup>a</sup></b> 58.97, 167.04,-180.00,-167.04,-58.97	GAAAG trans
		<b>L<sup>b</sup></b> 175.96, -175.54, 170.59,-166.78,-169.31	AAAAA trans
		<b>L<sup>c</sup></b> -176.22,-178.90,-180.00,178.90,176.22	AAAAA trans

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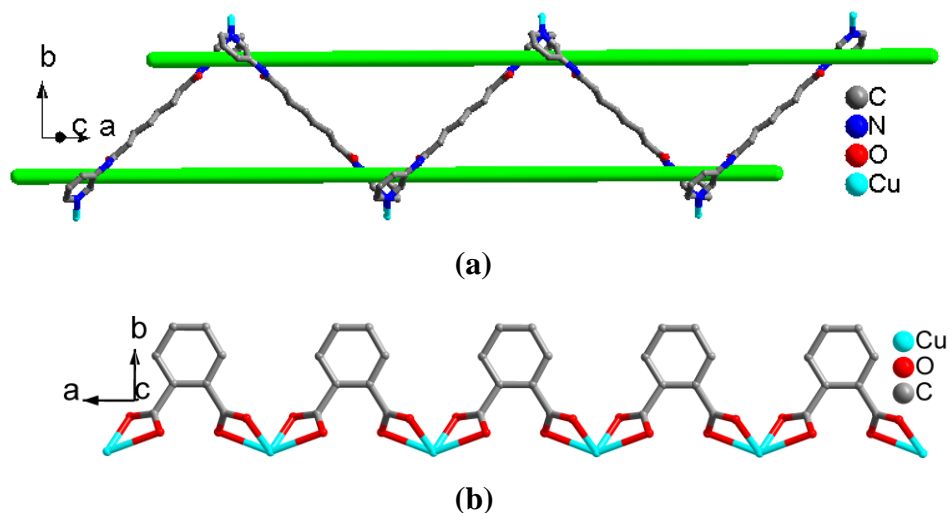


**Fig. S1.** (a) The 1D zigzag chain connected by L ligands in compound 2. (b) The 1D linear chain connected by bridging 1,3-BDC ligand 2.

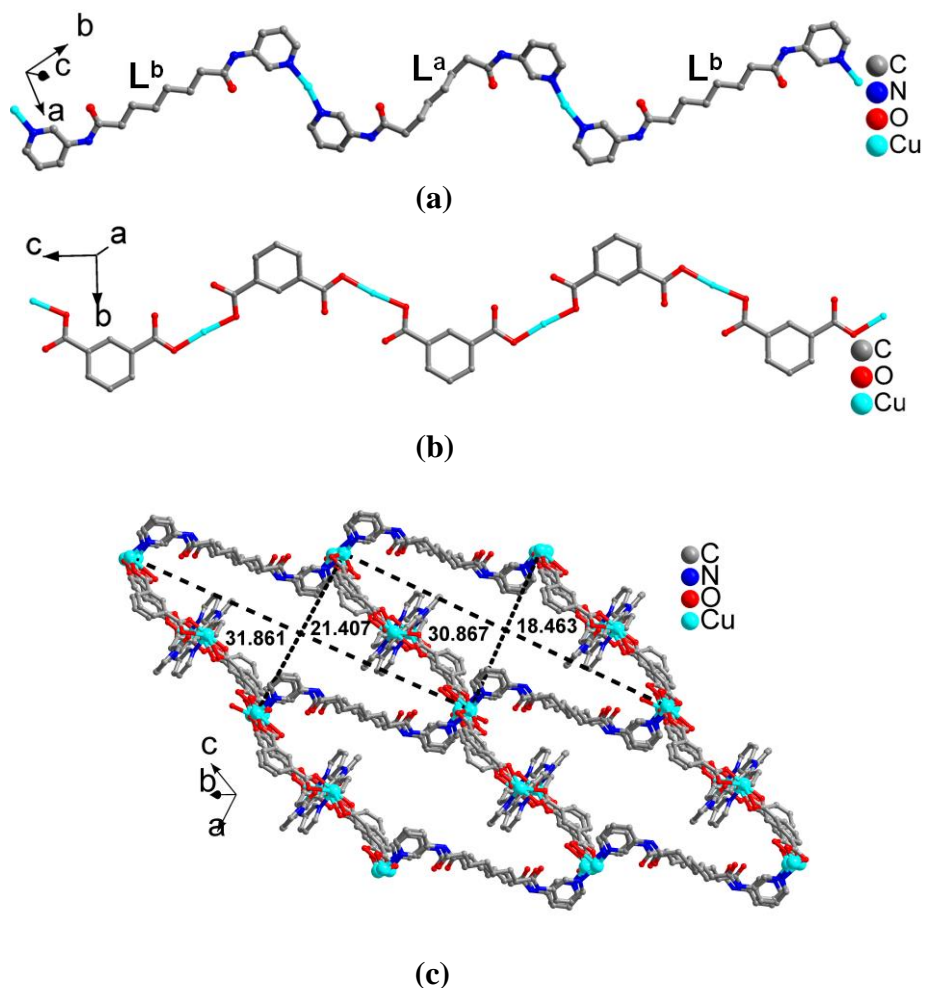


**Fig. S2.** (a) 5-AIP anions connect adjacent Co<sup>II</sup> ions to form a 1D [Co-5-AIP]<sub>2n</sub> channel-like chain in compound 3. (b) The 1D [Co-5-AIP]<sub>2n</sub> channel-like chain with tunnel size of 7.728×5.324 Å<sup>2</sup> in compound 3.

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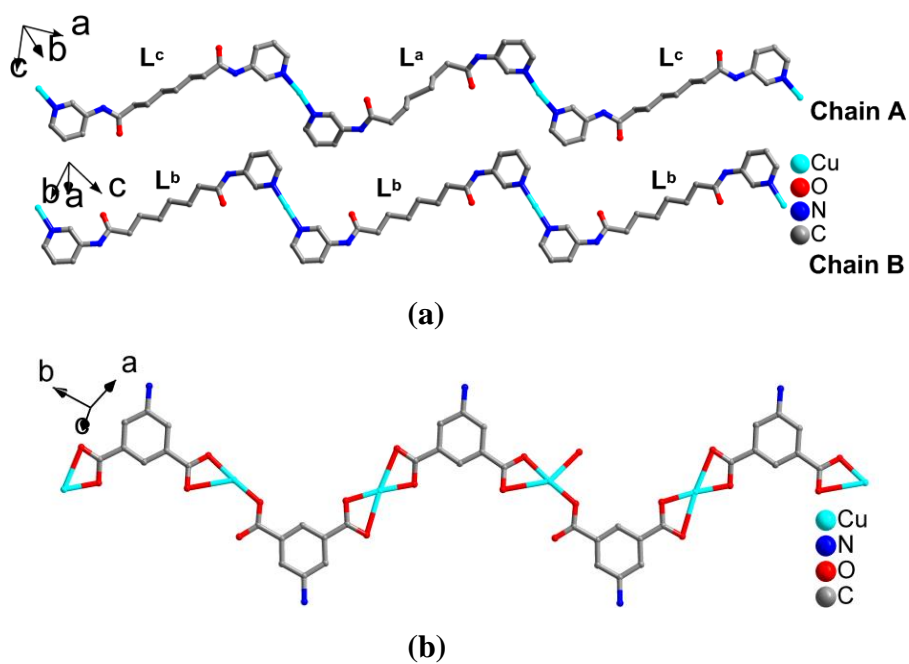


**Fig. S3.** (a) The meso-helical chain formed by ligands **L** and Cu<sup>II</sup> ions in **4**. (b) The 1D [Cu-1,2-BDC]<sub>n</sub> chain in **4**.

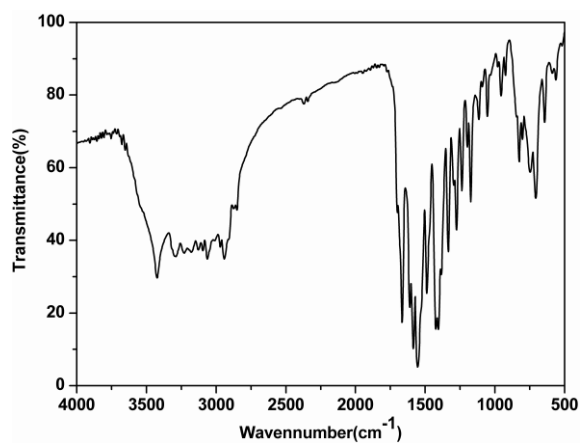


**Fig. S4.** (a) The 1D [Cu-L]<sub>n</sub> zigzag chain of **5**; (b) The 1D [Cu-1,3-BDC]<sub>n</sub> 'V'-like chain in **5**. (c) The 3D framework of **5**.

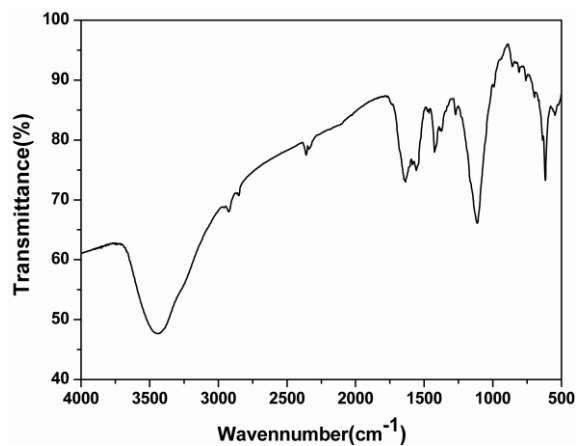
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**Fig. S5.** (a) The two types of 1D  $[\text{Cu-L}]_n$  chains formed by L ligands showing three different conformations in **6**; (b) The 1-D  $[\text{Cu-5-AIP}]_n$  chain in **6**.



**Fig. S6.** The IR spectrum of compound **1**.

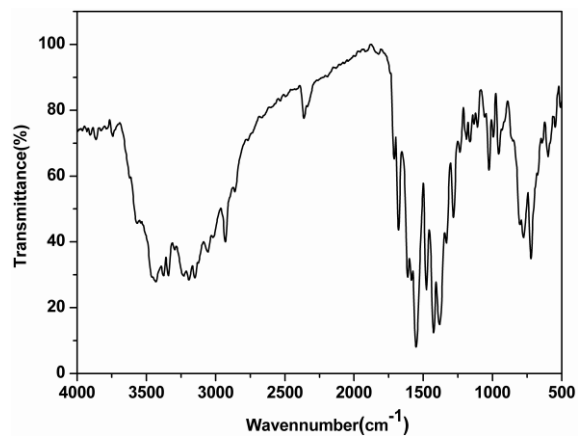


**Fig. S7.** The IR spectrum of compound **2**.

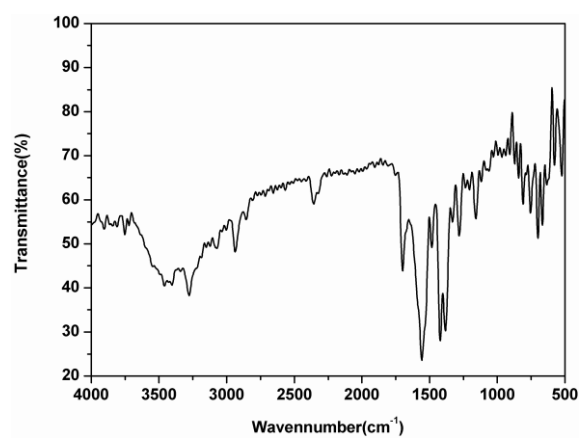


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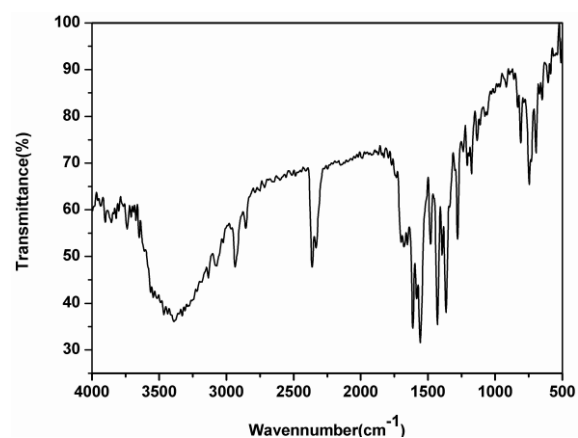
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**Fig. S8.** The IR spectrum of compound **3**.



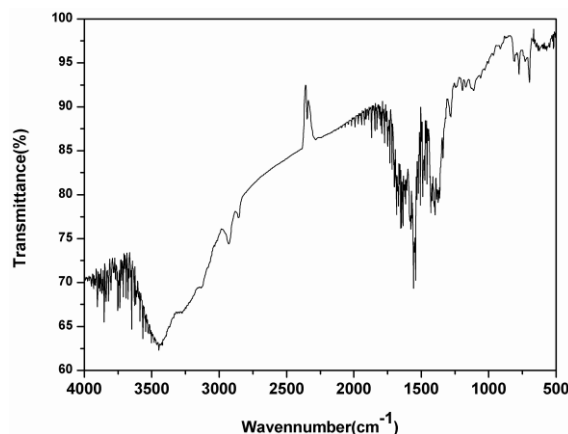
**Fig. S9.** The IR spectrum of compound **4**.



**Fig. S10.** The IR spectrum of compound **5**.

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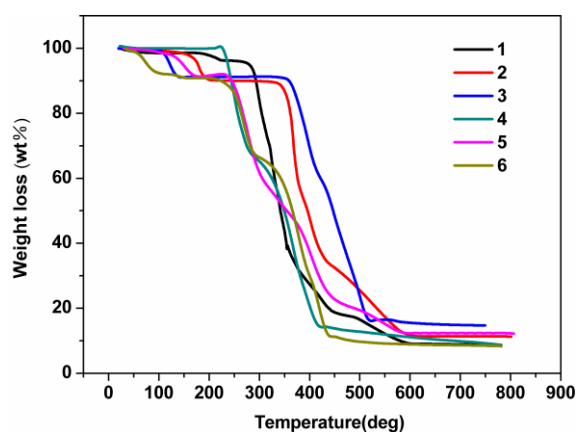
**Fig. S11.** The IR spectrum of compound **6**.

### Thermal stability analyses

Thermal gravimetric (TG) analyses were carried out to examine the thermal stabilities of compounds **1–6**. The samples were performed in the temperature range of 20–800 °C under N<sub>2</sub> atmosphere (heating rate 10 °C·min<sup>-1</sup>). For compounds **1-3**, **5** and **6**, the TG curves show obvious two-step weight loss process, while TG curve of **4** exhibits a one-step weight loss process (**Fig. S12**). For compound **1**, the first weight loss begins at 186 °C up to 222 °C, giving a weight loss of about 2.43%, which can be attributed to the loss of the coordinated water molecules (calc. 2.46%). The second weight loss of 87.29% between 276 °C and 588 °C corresponds to the loss of **L** and 1,2-BDC ligands (calc. 87.28%). The remaining residue is presumed to be CoO (obs. 10.28%, calc. 10.26%). For complex **2**, the first weight loss of 8.92% (calc. 8.95%) occurred from 147 °C to 192 °C, corresponding to the release of the lattice water and coordinated water molecules. The residual framework decomposes in the temperature range of 338–593 °C, corresponding to the loss of ligands **L** and 1,3-BDC (obs. 78.68%, calc. 78.63%) with CoO of 12.40% (calc. 12.42%) as residue. For compound **3**, the lattice and coordinated water molecules are lost between 89 to 140 °C in the first step (obs. 11.84%, calc. 11.86%). The second weight loss (obs. 71.25%, calc. 71.24%) in the range of 346 – 524 °C can be attributed to the decomposition of ligands **L** and 5-AIP, and the residue is CoO (obs. 16.91%, calc. 16.90%). For **4**, the TG curve displays only one weight loss in the range of 230 to 420 °C and corresponds to the loss of the organic ligands **L** and 1,2-BDC. The remaining weight (14.38%) corresponds to the percentage 14.44% of Cu and O components, implying that the remaining residue is CuO. In compound **5**, the first weight loss from 78 to 175 °C is about 11.48%, corresponding to the loss of coordinated water and lattice molecules (calc. 11.50%). The second weight

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loss of 75.77% occurred in the temperature range of 230–590 °C, corresponding to the decomposition of organic ligand **L** and 1,3-BDC (calc. 75.72%). The residual product weight of 12.75% for **5** was found in the temperature above 692°C, corresponding to the formation of CuO (calc. 12.78%). For compound **6**, lattice and coordinated water molecules are lost in the first step, and the weight loss of 9.95% is in correspondence with the calculated value 9.97% in the range of 62 to 146 °C. The second weight loss of 77.42% between 229 °C to 440 °C can be attributed to the decomposition of **L** and 5-AIP ligands (calc. 77.37%), leading to the formation of CuO (obs. 12.63%, calc. 12.66%).



**Fig. S12.** TG curves for compounds **1–6**.

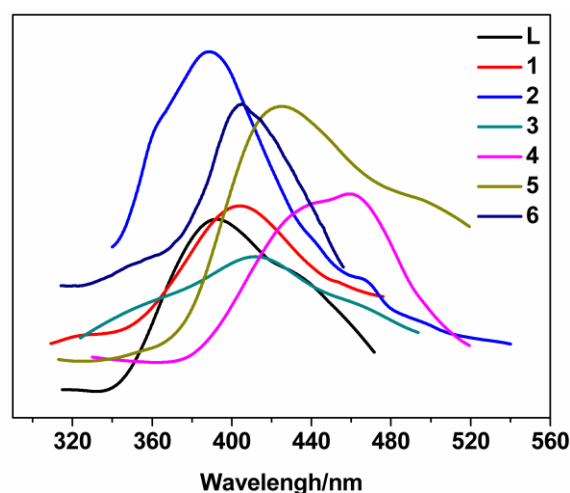
### Fluorescent properties

The transition metal complexes are interesting owing to their ability to enhance, shift and quench luminescent emission of organic ligands by metal coordination<sup>1</sup>. These crystalline solids usually display photoluminescence properties. As shown in **Fig. S16**, the solid state luminescent spectra of compounds **1–6** and the free ligand **L** have been determined at room temperature. The ligand **L** exhibits a luminescent emission at about 392 nm ( $\lambda_{ex}$  = 240 nm), which may probably be ascribed to the intraligand  $\pi \rightarrow \pi^*$  transitions<sup>2</sup>. For compounds **1–6**, the emission bands were observed at 403 nm, 388 nm, 413 nm, 459 nm, 425 nm and 404 nm, respectively, when they are excited at 260 nm. Comparing with the emission of free ligand **L**, the red shift of ca. 11 nm, 21 nm, 67 nm, 33 nm, and 12 nm for compounds **1** and **3–6**, respectively, blue shift of ca. 4 nm for **2**, which may be attributed to metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer transitions<sup>3</sup>. Six new cobalt(II) and copper(II) coordination

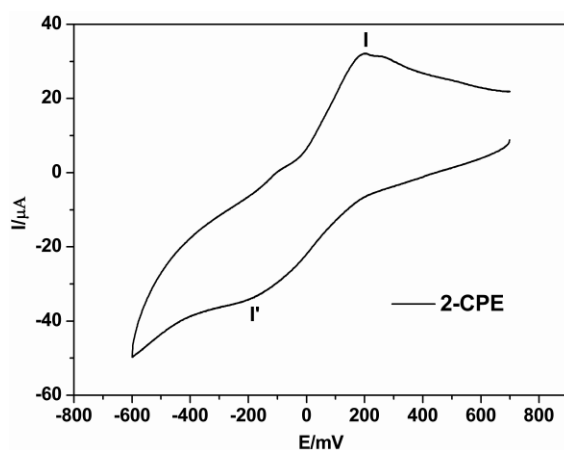
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polymers with the same N-containing ligand show different luminescence behaviors, which are probably attributed to different composition and architectures of the title compounds <sup>4</sup>.

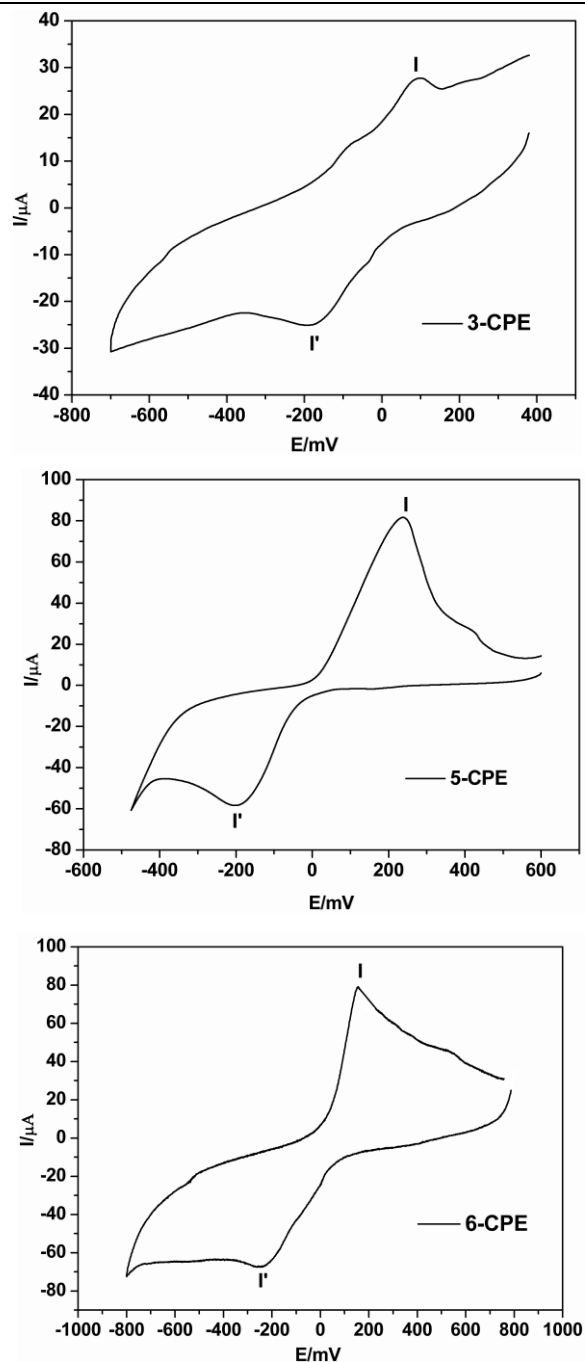
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**Fig. S13.** The emission spectra of the compounds **1-6** and free **L** ligand in solid state at room temperature.

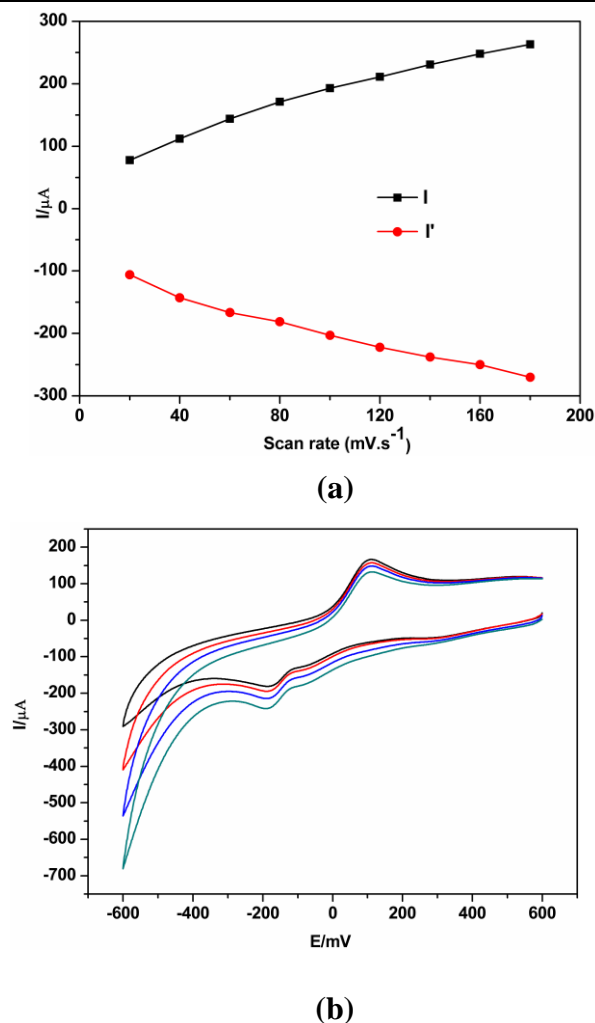


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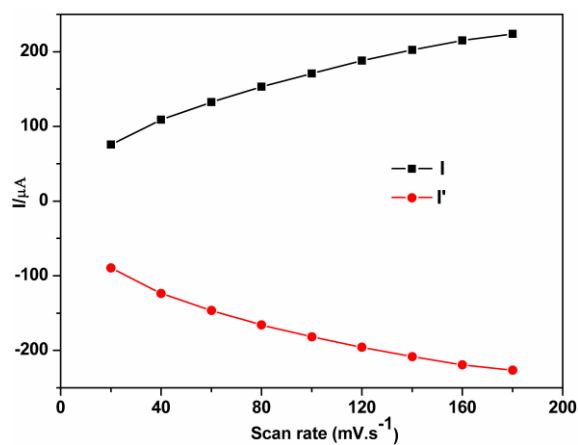


**Fig. S14.** Cyclic voltammograms of **2-CPE** (700 to -600 mV), **3-CPE** (400 to -700 mV), **5-CPE** (600 to -500 mV), **6-CPE** (800 to -800 mV) in 0.01 M  $\text{H}_2\text{SO}_4$  + 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution. Scan rate:  $20 \text{ mV s}^{-1}$  for **2-3** and  $100 \text{ mV s}^{-1}$  for **5-6**.

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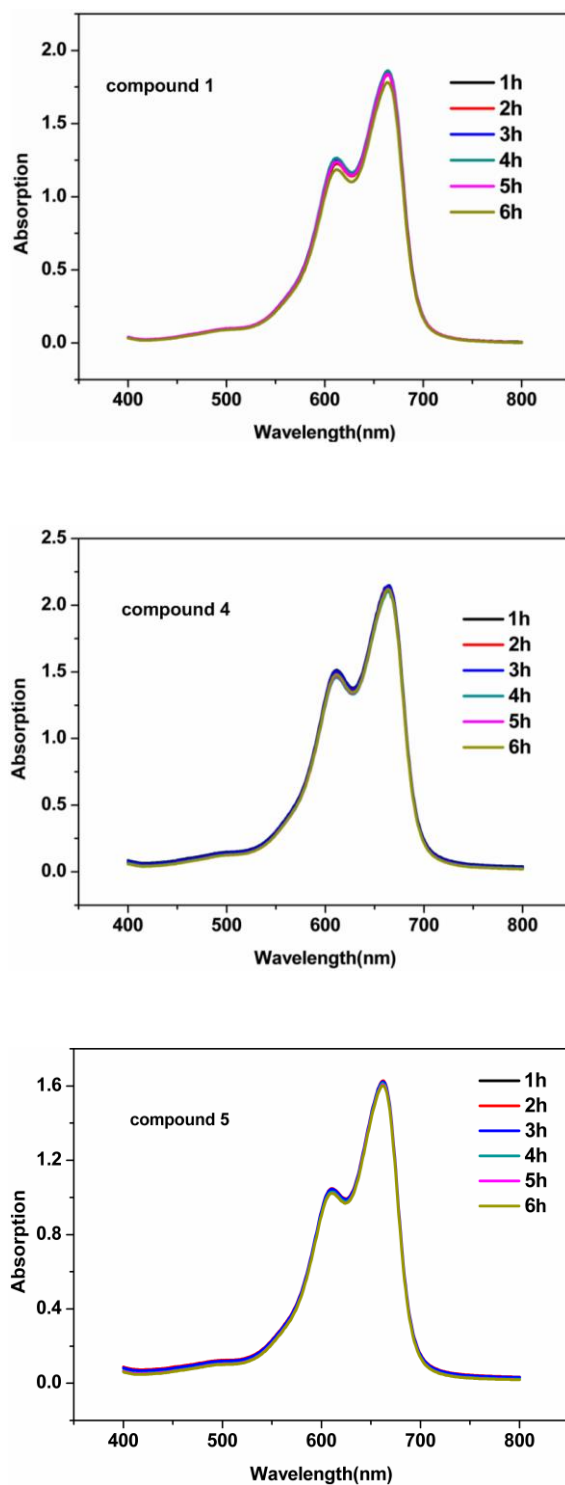


**Fig. S15.** (a) The plot of the anodic and cathodic peak currents against scan rates for the **1**-CPE (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180 mVs<sup>-1</sup>). (b) Cyclic voltammograms of the **1**-CPE in 0.01 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution containing: 1.0, 2.0, 3.0, 4.0 mM KNO<sub>2</sub>. Scan rate: 100 mVs<sup>-1</sup>.



**Fig.S16.** The plot of the anodic and cathodic peak currents against scan rates for the **4**-CPE (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180 mVs<sup>-1</sup>).

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**Fig. S17.** Absorption spectra of the MB solution during the decomposition reaction under UV light irradiation with the use of compounds **1**, **4**, **5**.