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pH-Dependent two novel 3D polynuclear cobalt(II) cluster-based metal-organic frameworks constructed from a tri-pyridyl-bis-amide and a polycarboxylate: assembly, structures and properties †

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ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1 Selected bond distances (Å) and angles (deg) for complexes **1**–**2**.

1			
Co(1)-O(1)#1	2.015(3)	Co(1)-O(2)#2	2.030(3)
Co(1)-O(5)#3	2.122(3)	Co(1)-O(6)#3	2.248(3)
Co(1)-N(5)	2.146(4)	Co(1)-N(3)#4	2.181(3)
Co(2)-O(3)	2.058(3)	Co(2) -O(1W)	2.124(3)
Co(2)-O(3)#6	2.058(3)	Co(2)-O(1W)#6	2.124(3)
Co(2) -N(1)	2.178(4)	Co(2)-N(1)#6	2.178(4)
O(1)#1-Co(1)-O(2)#2	118.83(11)	O(1)#1-Co(1)-O(5)#3	91.59(11)
O(2)#2-Co(1)-O(5)#3	149.14(11)	O(1)#1-Co(1)-N(5)	90.87(13)
O(2)#2-Co(1)-N(5)	94.48(12)	O(5)#3-Co(1)-N(5)	89.79(12)
O(1)#1-Co(1)-N(3)#4	83.96(13)	O(2)#2-Co(1)-N(3)#4	88.65(12)
O(5)#3-Co(1)-N(3)#4	89.66(12)	N(5)-Co(1)-N(3)#4	174.78(13)
O(1)#1-Co(1)-O(6)#3	150.52(11)	O(2)#2-Co(1)-O(6)#3	89.52(10)
O(5)#3-Co(1)-O(6)#3	59.64(10)	N(5)-Co(1)-O(6)#3	94.99(13)
N(3)#4-Co(1)-O(6)#3	89.20(12)	O(3)#6-Co(2)-O(3)	180
O(3)#6-Co(2)-O(1W)#6	90.01(12)	O(3)-Co(2)-O(1W)#6	89.99(12)
O(3)#6-Co(2)-O(1W)	89.99(12)	O(3)-Co(2)-O(1W)	90.01(12)
O(1W)#6-Co(2)-O(1W)	180	O(3)#6-Co(2)-N(1)	87.86(13)
O(3)-Co(2)-N(1)	92.14(13)	O(1W)#6-Co(2)-N(1)	90.64(14)
O(1W)-Co(2)-N(1)	89.36(14)	O(3)#6-Co(2)-N(1)#6	92.14(13)
O(3)-Co(2)-N(1)#6	87.86(13)	O(1W)#6-Co(2)-N(1)#6	89.36(14)
O(1W)-Co(2)-N(1)#6	90.64(14)	N(1)-Co(2)-N(1)#6	180

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

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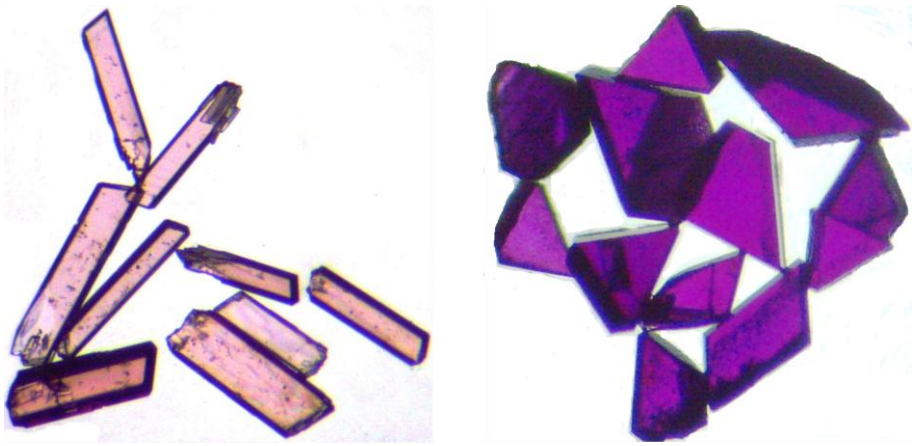
2			
Co(1)-O(1)	2.0983(18)	Co(1)-O(9)#3	2.0875(18)
Co(1)-O(6)#2	2.0800(19)	Co(1)-O(2)#1	2.1130(19)
Co(1)-O(9)	2.1420(19)	Co(1)-N(1)	2.156(2)
Co(2)-O(1)	2.286(2)	Co(2)-O(9)	1.9628(18)
Co(2)-O(3)#1	1.9616(19)	Co(2)-O(5)#4	1.9712(19)
Co(2)-N(3)#5	2.121(2)		
O(6)#2-Co(1)-O(9)#3	98.80(7)	O(6)#2-Co(1)-O(1)	171.43(7)
O(9)#3-Co(1)-O(1)	88.09(7)	O(6)#2-Co(1)-O(2)#1	85.46(7)
O(9)#3-Co(1)-O(2)#1	171.01(7)	O(1)-Co(1)-O(2)#1	87.03(7)
O(6)#2-Co(1)-O(9)	94.36(8)	O(9)#3-Co(1)-O(9)	79.68(7)
O(1)-Co(1)-O(9)	81.81(7)	O(2)#1-Co(1)-O(9)	92.15(7)
O(6)#2-Co(1)-N(1)	87.71(9)	O(9)#3-Co(1)-N(1)	97.32(8)
O(1)-Co(1)-N(1)	96.50(8)	O(2)#1-Co(1)-N(1)	90.74(9)
O(9)-Co(1)-N(1)	176.57(8)	O(3)#1-Co(2)-O(9)	106.91(8)
O(3)#1-Co(2)-O(5)#4	137.40(9)	O(9)-Co(2)-O(5)#4	113.18(8)
O(3)#1-Co(2)-N(3)#5	93.76(9)	O(9)-Co(2)-N(3)#5	100.16(9)
O(5)#4-Co(2)-N(3)#5	92.91(9)	O(3)#1-Co(2)-O(1)	84.48(8)
O(9)-Co(2)-O(1)	81.25(7)	O(5)#4-Co(2)-O(1)	87.79(7)
N(3)#5-Co(2)-O(1)	178.02(8)		

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



(a) **(b)**

Fig. S1 (a) The photo of complex **1**. (b) The photo of complex **2**.

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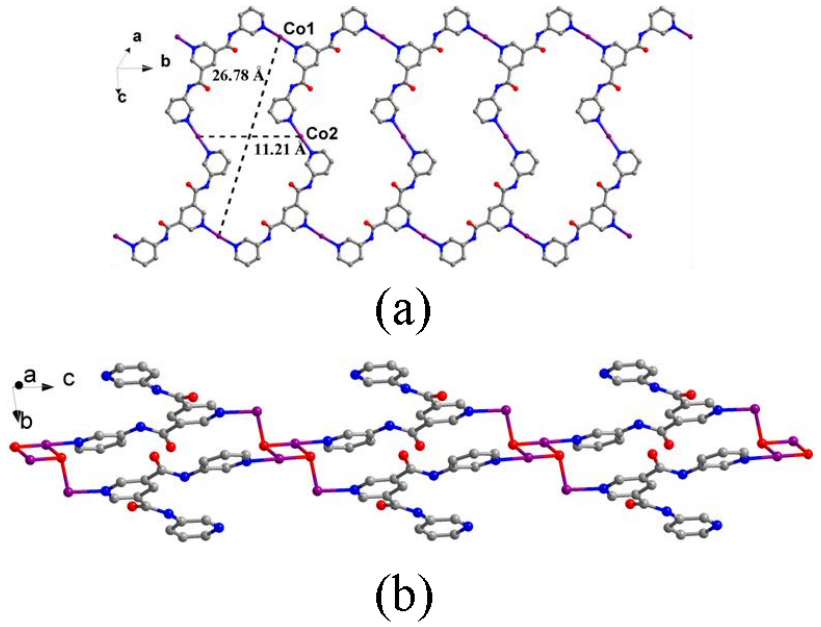

Fig. S2 (a) The $Co_4(\mathbf{L})_4$ 50-membered ring in the 1D ladder structure for complex **1**. (b) The 1D chain for complex **2**.

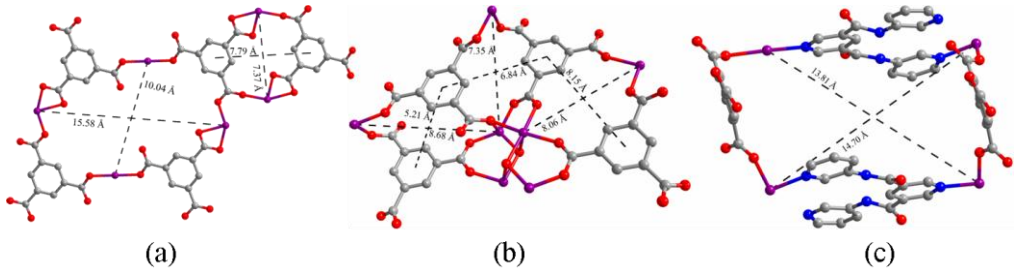

Fig. S3 (a) Two kinds of loops $Co_2(BTC)_2$ and $Co_4(BTC)_4$ in the 2D layer for complex **1**. (b) Three types of 16-membered rings of $Co_2(BTC)_2$ in the 2D layer in complex **2**. (c) The macro ring composed by L ligands and BTC anions in complex **2**.

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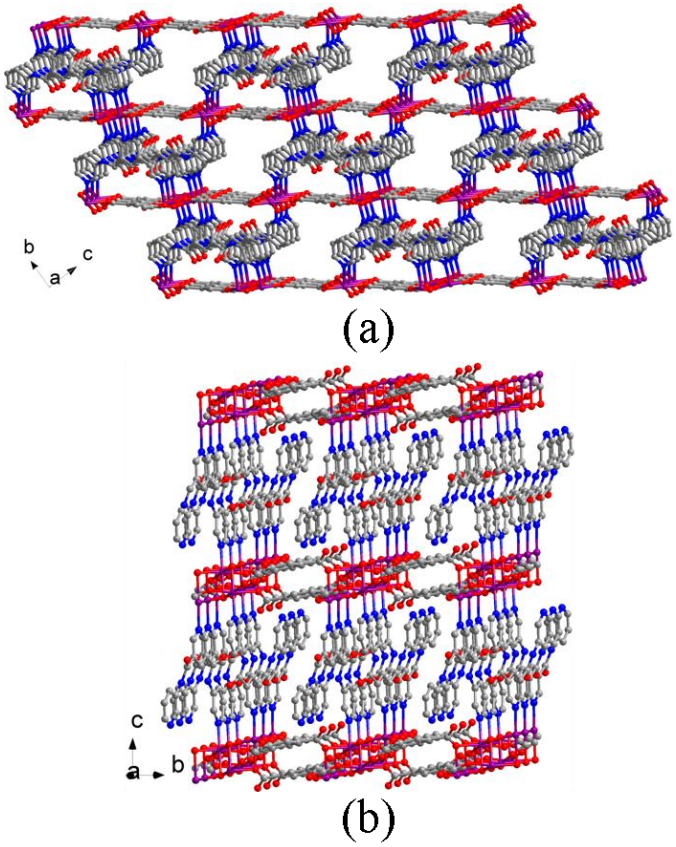

Fig. S4 (a) 3D packing structure of complex **1**. (b) 3D packing structure of complex **2**.

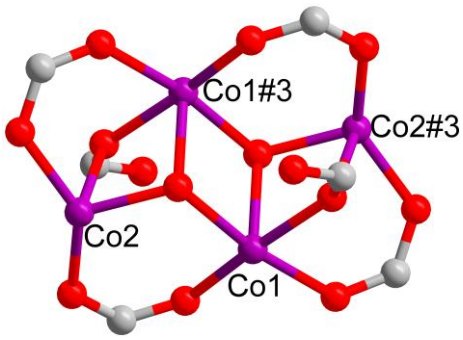

Fig. S5 Perspective view of tetranuclear cobalt cluster in complex **2**. Symmetry codes: #3 $-x + 1$, $-y + 2$, $-z$.

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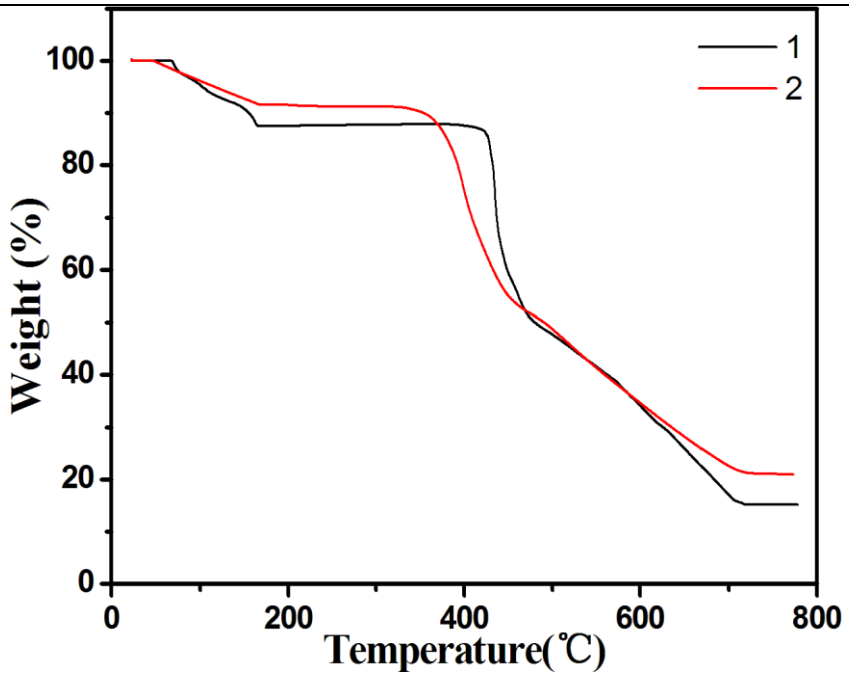

Fig.S6 The TG curves of complexes **1**–**2**.

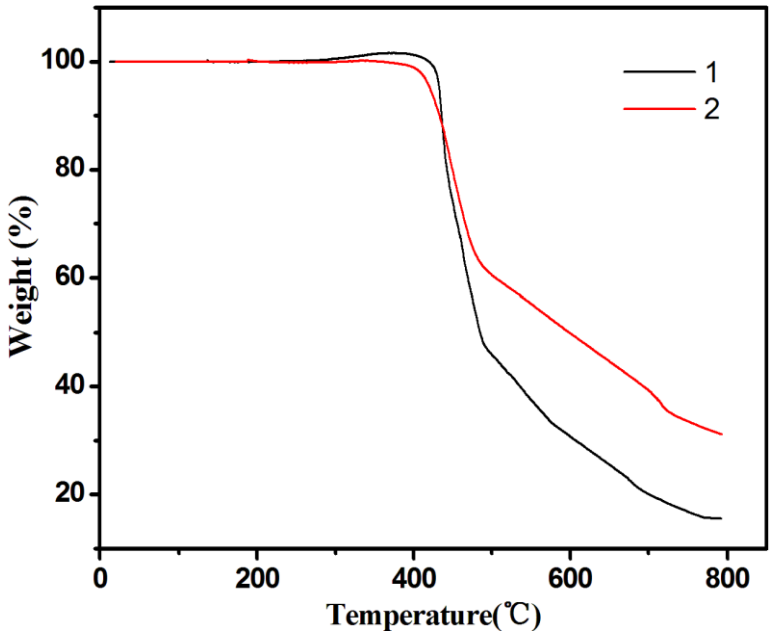

Fig. S7 The TG curves of complexes **1**–**2** after heated at 170 ^{o}C.

Preparation of the 1-CPE and 2-CPE

Complexes **1** and **2** bulk-modified carbon paste electrodes (**1**-CPE and **2**-CPE) were fabricated as follows: 0.55 g graphite powder and 0.035 g complex **1** or **2** were mixed and ground together by agate mortar and pestle for about 45 min, and then 0.2 mL paraffin oil was added with stirring.

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The homogenized mixture was pack into a glass tube (3 mm inner diameter) to a length of 8 mm. The electrical contact was established with the copper rod, and the surface of the **1**-CPE or **2**-CPE was polished by weighing paper. The same procedure was used for preparation of the bare CPE without title complex.

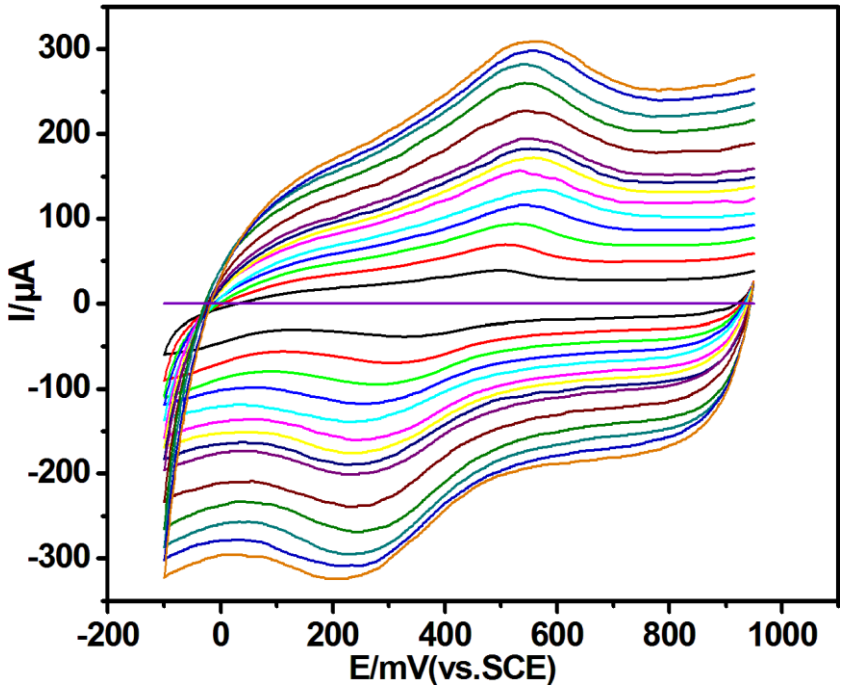

Fig. S8 Cyclic voltammograms of the **1**-CPE in 0.5 M Na_2SO_4 aqueous solution (pH = 3 adjusted by H_2SO_4) at different scan rates (from inner to outer: the bare CPE, 20, 40, 60, 80, 100, 120, 140, 180, 200, 250, 300, 350, 400, 450 $mV \cdot s^{-1}$).

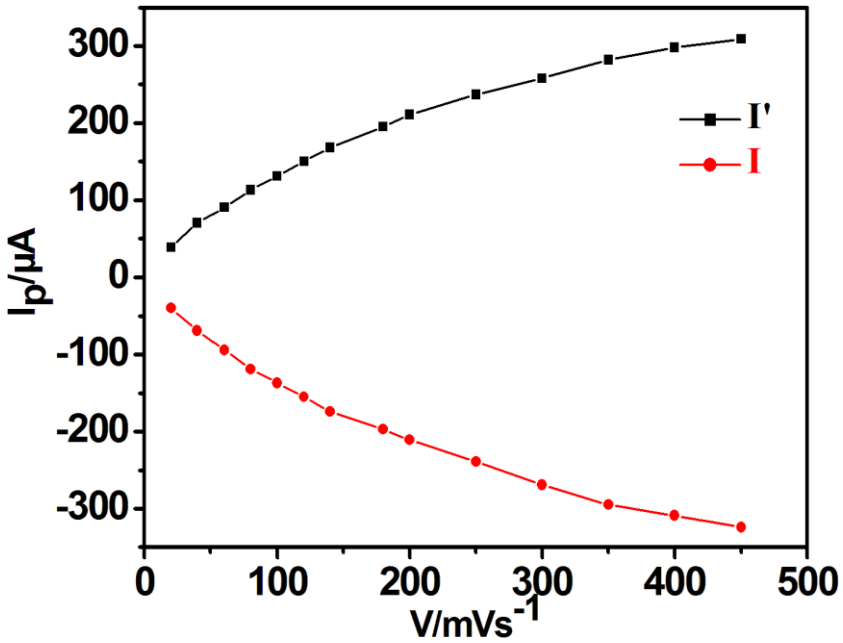

Fig. S9 The plots of the anodic and cathodic peak currents against scan rates for the **1**-CPE.

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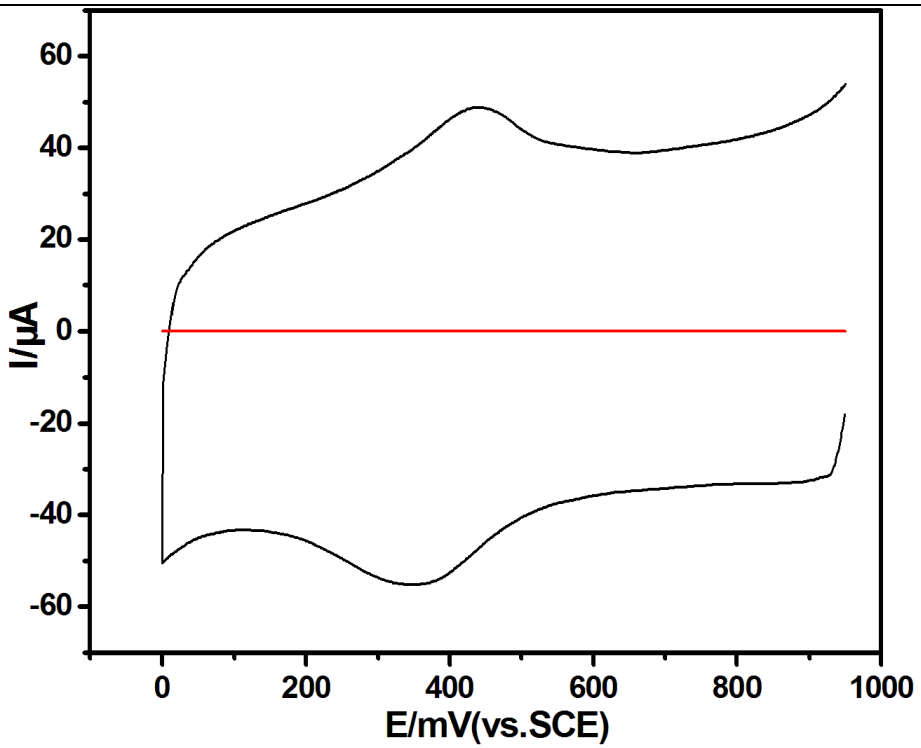

Fig. S10 Cyclic voltammograms of the bare CPE and **2**-CPE in 0.5 M Na_2SO_4 aqueous solution (pH = 3 adjusted by H_2SO_4) in the potential range of 950 – 0 mV. Scan rate: 80 mVs^{-1}.