Electronic Supplementary Information

Electrochemical sensing properties of cobalt-based coordination polymers for trace L-tryptophan in milk

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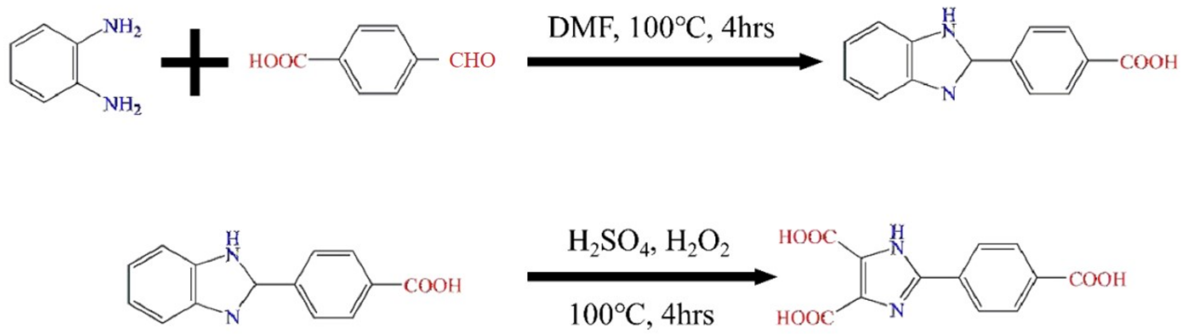
1. Synthesis of ligand H_3L



Scheme S1. Synthetic route of ligand H_3L.

Reaction 1 in Scheme S1. was synthesized according to the reported reaction conditions.[1] The 4-formylbenzoic acid (3.75 g, 25 mmol) was ultrasonic treated in ethanol (60 mL) solution for 1 h. The *o*-phenylenediamine (2.7g, 25 mmol) was dissolved in (50 mL) ethanol to form a suspension, which was added to the prepared solution and stirred at room temperature at a constant speed for about 1 h. Later, 5 mL of acetic acid aqueous solution (6 M) was added to the reaction mixture. The reaction mixture was continuously heated at 60°C for 12 h. After the reaction is stopped and cooled to room temperature, the resulting orange-yellow solid is filtered out and repeatedly rinsed with cold ethanol, deionized water and acetone. The product was heated in a vacuum drying oven at 100°C for 12 h, further recrystallized from the DMF/H_2O mixture and dried at 100°C for 24 hours to obtain the desired compound: 4-(1H-benzimidazole-2-yl) benzoic acid, a pale-yellow powder (4.5 g, 76% yield).

Reaction 2 was synthesized according to reported reaction conditions.[2] First, 4-(1H-benzimidazole-2-yl) benzoic acid (10 g, 41.2 mmol) was added to a 500 mL reactor. Then 120 mL concentrated sulfuric acid was added. Under constant agitation, 75 mL hydrogen peroxide is slowly added to the mixture and the solution temperature is maintained between 100 and 110°C. The solution is then heated to 140°C and reflow for 2 h. The hot solution was added to 600 mL of ice water and placed overnight in a refrigerator at 4°C and then filtered to give the final product 2-(4-carboxyl-phenyl) -1H-imidazole-4, 5-dicarboxylic acid (H_3L), a light yellow solid (6.1 g, yield 52.6%). IR (cm^{-1}, KBr): 3430(m), 3170(w), 2987(m), 2652(w), 1719(m), 1618(w), 1555(w), 1482(m), 1387(m), 1260(w), 1171(s), 1065(w), 1004(m), 878(s), 786(m), 712(s), 684(m), 574(s).

2. Crystal Data Collection and Refinement

2.1 Structure determination of the CPs

The rinsed crystals were dried and selected for regular, clean, crack-free crystals were tested for SC-XRD structure and the crystal data were collected using a Bruker Smart Apex CCD single crystal diffractometer. Crystal structure resolution was accomplished using the direct method on the SHELXS-97 procedure. All the non-hydrogen atomic coordinate data were synthesized by Fourier and refined with all the specific thermal parameters. The coordinates of hydrogen atoms are calculated by theory and refined in the same way. Detailed crystallographic data and structure refinement parameters for **1** can be found in Table S1**.** Selected bond distances [Å] and angles [deg] is presented in Table S2. The hydrogen bond data is shown in Table S3**.** The Cambridge Crystallographic Data Centre (CCDC) deposition numbers for **1** is 2385246, which include all supplementary crystallographic data for this compound.

2.2 Crystallographic structural parameters of 1

Table S1. Crystal data and structure refinement parameters of **1**

Compound	**1**
Empirical formula	$C_{24}H_{38}Co_3N_4O_{26}$
Formula weight	975.37
Temperature/K	293(2)
Crystal system	monoclinic

Space group	$P2_1/c$
a/Å	7.3877(2)
b/Å	16.7147(4)
c/Å	14.2730(4)
α/°	90
β/°	96.2301(10)
γ/°	90
Volume/Å^3	1752.07(7)
Z	2
ρ_{calc}g/cm^3	1.849
μ/mmol^{-1}	1.513
F(000)	998.0
Crystal size/mmol^3	0.12 × 0.11 × 0.1
Radiation	MoK\a (λ = 0.71073)
2θ range for data collection/°	5.548 to 56.734
Index ranges	$-9 \leq h \leq 9$, $-22 \leq k \leq 22$, $-2 \leq l \leq 19$
Reflections collected	38955
Independent reflections	4363 [R_{int} = 0.0675, R_{sigma} = 0.0414]
Data/restraints/parameters	4363/1/260
Goodness-of-fit on F^2	1.140
Final R indexes	R_1 = 0.0635,
[I>=2σ (I)]	wR_2 = 0.1699
Final R indexes [all data]	R_1 = 0.0934 wR_2 = 0.1855
Largest diff. peak/hole / e Å^{-3}	1.24/-0.54

$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

$wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$,$w=[\sigma^2(F_o^2)+(0.0784P)^2+1.3233P]^{-1}$,where $P=(F_o^2+2F_c^2)/3$.

GOF$=[\Sigma w(F_o^2-F_c^2)^2/n_{obs}-n_{param})]^{1/2}$

2.2 Selected distances and angles (deg) for 1

Table S2. Bond length (Å) and bond angle (°) of **1.**

1

	Bond	Length/Å	Bond	Length/Å	
	Co1-O2	2.024(4)	Co2-O3W	2.037(5)	
	Co1-O2#1	2.024(4)	Co2-O1	2.038(4)	
	Co1-O3#1	2.040(4)	Co2-O2W	2.070(4)	
	Co1-O3	2.040(4)	Co2-O4W	2.119(5)	
	Co1-O1W	2.114(5)	Co2-O4#2	2.166(4)	
	Co1-O1W#1	2.114(5)	Co2-N1	2.202(4)	
Bond	Angle/°	Bond	Angle/°	Bond	Angle/°
O2-Co1-O2#1	180.0	O3#1-Co1-O3	180.0	O2-Co1-O1W#1	93.0(2)
O2-Co1-O3#1	86.87(15)	O2-Co1-O1W	87.0(2)	O2#1-Co1-O1W#1	87.0(2)
O2#1-Co1-O3#1	93.13(15)	O2#1-Co1-O1W	93.0	O3#1-Co1-O1W#1	83.78(19)
O2-Co1-O3	93.13(15)	O3#1-Co1-O1W	96.22(19)	O3-Co1-O1W#1	96.22(19)
O2#1-Co1-O3	86.87(15)	O3-Co1-O1W	83.78(19)	O1W-Co1-O1W#1	180.00(5)
O3W-Co2-O1	93.7(2)	O2W-Co2-O4W	88.1(2)	O3W-Co2-N1	87.18(18)
O3W-Co2-O2W	91.8(2)	O3W-Co2-O4#2	92.11(19)	O1-Co2-N1	77.72(15)
O1-Co2-O2W	173.68(19)	O1-Co2-O4#2	85.17(15)	O2W-Co2-N1	105.72(16)
O3W-Co2-O4W	179.6(2)	O2W-Co2-O4#2	91.48(15)	O4W-Co2-N1	93.27(19)
O1-Co2-O4W	86.4(2)	O4W-Co2-O4#2	87.46(19)	O4#2-Co2-N1	162.79(15)

Symmetry operation ：#1:1-X,1-Y,1-Z; #2:1-X,-1/2+Y,1/2-Z; #3:1-X,1/2+Y,1/2-Z

Table S3. Hydrogen bonds in **1**

1

Donor-H···Acceptor	D-H(Å)	H···A(Å)	D···A(Å)	∠DHA/(°)
N2-H2···O5W	0.88	1.99	2.861(7)	168
O1W-H11···O5	0.84	1.92	2.707(7)	155
O1-H12···O5	0.84	2.38	3.123(7)	148
O2W-H22···O5W	0.84	2.10	2.934(7)	172

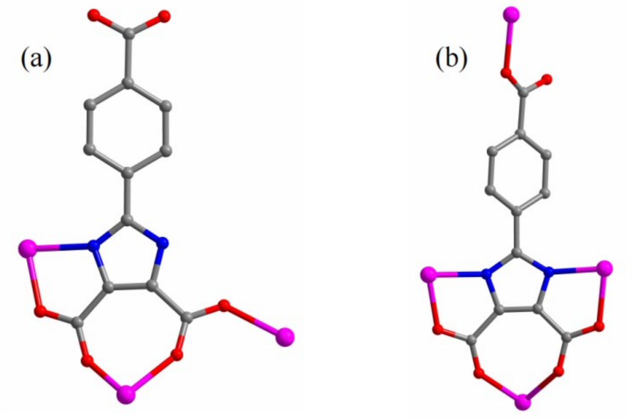
O3W-H32···O7W	0.84	2.02	2.709(7）	138
O4W-H41···O7W	0.84	2.06	2.891(8)	169
O4W-H42···O6W	0.84	2.40	3.080(8)	138
O4W-H42···O6	0.84	2.57	3.287(7)	144
O5W-H51···O1	0.84	2.08	2.759(6)	137
O5W-H52···O6W	0.84	2.37	2.846(8)	117
O6W-H61···O2	0.84	2.03	2.866(8)	176
O6W-H62···O6	0.84	1.93	2.766(7)	176
O7W-H71···O5	0.84	1.87	2.714(7)	177
O7W-H72···O6W	0.84	2.15	2.945(8)	157

Table S4. Key information for **1** and **2**

Main ligand	CP	Coligand	Structural dimensions	hydrogen bond
H_3L	**1**	/	2D	14
H_3L	**2**	4,4'-bipy	3D	0

3. Characterization

Elemental analysis (C, H, N) was characterized by elemental analyzer of VxRio EL instrument (Vario), data detection of powder X-ray diffraction (PXRD) was performed on D/max-2400 diffractor instrument, infrared spectroscopy by KBr infrared spectrometer in range 4000-400 cm^{-1} and thermalgravimetric weight analysis was increased at room temperature from 10℃ to 800℃ to obtain sample weight loss rate.



Scheme S2. Coordination pattern of ligand H_3L in (a) **1** and (b) **2**.

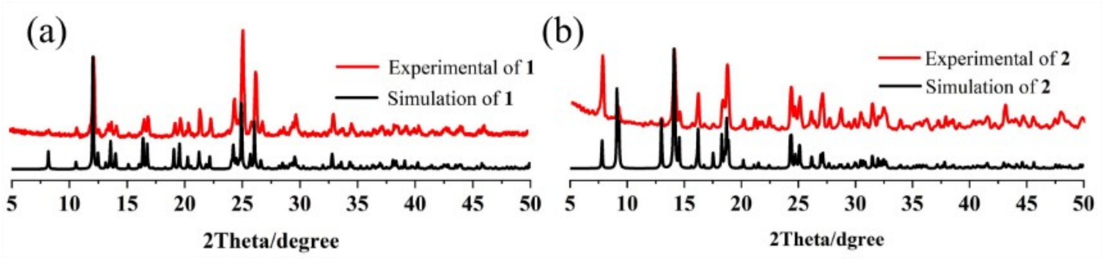


Fig. S1 PXRD diagram of (a) **1**, (b) **2**.

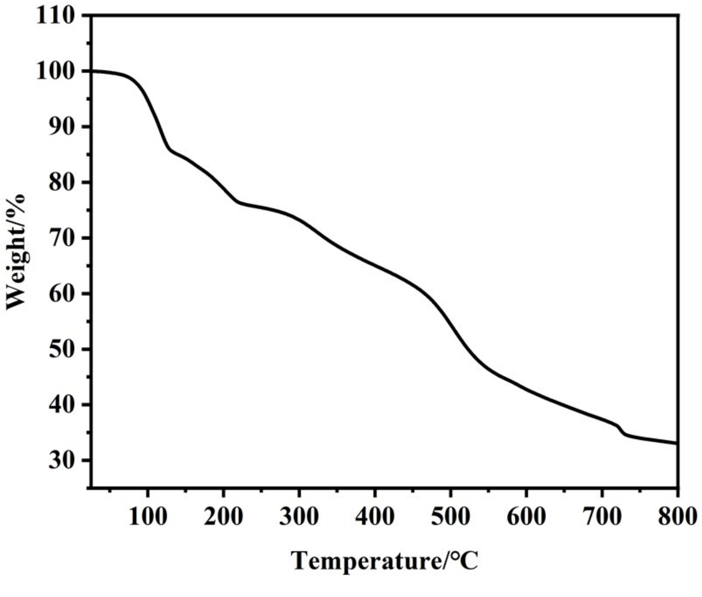


Fig. S2 TGA of **1.**

References

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(2) Li, J.; Luo, X.; Zhou, Y.; Zhang, L. Two Metal–Organic Frameworks with Structural Varieties Derived from cis–trans Isomerism Nodes and Effective Detection of Nitroaromatic Explosives. *Cryst. Growth Des.* **2018,** 18, 1857.