Supporting Information

Highly effective synthesis of Cobalt(II) metal-organic coordination polymer by using Continuous Flow Chemistry

Chunhua Gong, Junyong Zhang, Xianghua Zeng and Jingli Xie*

College of Biological, Chemical Science and Engineering, Jiaxing University, Jiaxing 314001, P. R. China E-mail: jlxie@mail.zjxu.edu.cn

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1. Reagents and general techniques

All chemicals were used as supplied from Aladdin-Reagent without further purification. The ligand HL was synthesized according to the literature. Elemental analyses of C, H and N were performed with a vario MICRO elemental analyzer. The IR spectrum (KBr pellet) was recorded by a VARIAN CARY5000 IR spectrometer. Thermal gravimetric analysis (TGA) was performed using a STA-409PC Synchronous thermal analyzer with a heating rate of 0.5 ^{o}C min^{-1}. The UV experiments were carried out on a Thermo EV 201CP. A CHI842B electrochemical workstation was used for electrochemical measurements. A conventional three-electrode system was used with Ag/AgCl as the reference electrode, a platinum wire as the counter electrode and the chemically bulk-modified carbon paste electrode (CPE) as the working electrode.

2. The method of preparing the bulk-modified CPEs (1-CPE).

The bulk-modified CPEs (1-CPE) of compound 1 was fabricated by mixing 0.10 g graphite powder and 0.010 g compound 1 in an agate mortar for approximately 30 minutes to achieve a uniform mixture; then two drops of methyl silicone oil were added and stirred with a glass rod. The homogenized mixture was packed into a 3 mm inner diameter glass tube. The electrical contact was established with the copper wire through the back of the electrode. The bare CPE was prepared by a similar process without compound 1.

3. X-ray crystallography

Suitable single crystals were selected and mounted on a glass fiber. The Crystallographic data of 1 was collected on a Xcalibur, Eos, Gemini diffractometer with Cu Kα (λ = 1.54184 Å) at 296 K. Using Olex2,[1] the structure was solved with the Superflip[2] structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss–Newton minimization. Crystallographic data and structure refinements for 1 are summarized in Table 1. Crystallographic data for 1 have been deposited in the Cambridge Crystallographic Data Center with CCDC

reference number 1449465.

Table 1 Crystal data and structure refinement for 1

Compound	$[Co_2L_4(H_2O)_2]\cdot CH_3CN\cdot H_2O$
Empirical formula	$C_{70}H_{53}Cl_4Co_2N_5O_7$
Formula weight	1335.83
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	15.7510(10)
b(Å)	22.3712(9)
c(Å)	19.2423(11)
α(deg)	90
β(deg)	109.938(6)
γ(deg)	90
V (Å^3)，Z	6374.0(6)，4
D_c (g·cm^{-3})	1.392
F(000)	2744
GOOF on F^2	1.022
μ（mm^{-1}）	6.092
Reflns	26792
R_1 , wR_2 (I>2σ(I))	0.0976，0.2661
$R_1 = \Sigma \| \| F_0 \| - \| F_c \| \| / \Sigma \| F_0 \|$.	$wR_2 = \{\Sigma[w(F_0^2-F_c)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

References

1 O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, **42**, 339.

2 (a) L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* 2007, **40**, 786;

(b) L. Palatinus, A. van der Lee, *J. Appl. Crystallogr.* 2008, **41**, 975;

(c) L. Palatinus, S.J. Prathapa, S. van Smaalen, *J. Appl. Crystallogr.* 2012, **45**, 575.

4. The photo of crystals

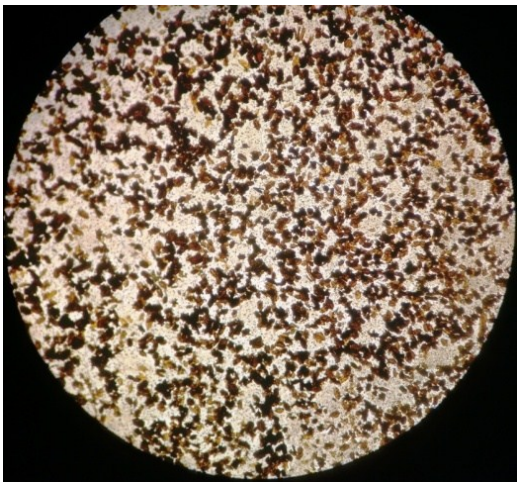

Fig. S1 The photo of crystals that were collected in the beaker (flow reaction).

5. IR spectra, PXRD pattern and UV analysis.

The IR spectrum of compound 1 is determined in the frequency range of 500–4000 cm^{-1}, as shown in Fig. S2.

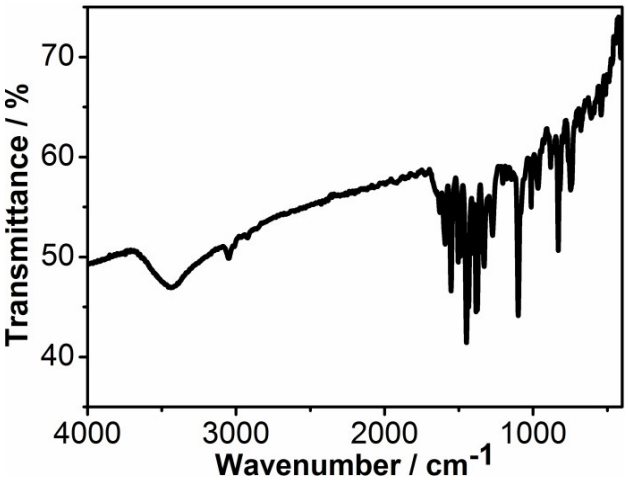

Fig. S2 The IR spectra of compound **1**.

To check the phase purity of compound 1, powder X-ray diffraction (PXRD) experiment has been carried out (Fig. S3). The as-synthesized pattern match with the corresponding simulated one, indicating the phase purity of the sample. The observed differences in intensity may due to preferred orientation of the powder sample.

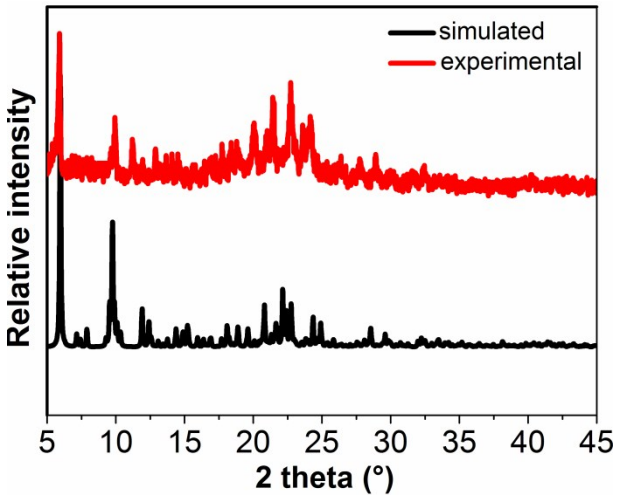

Fig. S3 PXRD patterns of compound 1: (black line) simulated from crystal structure; (red line) experimental.

As depicted in Fig. S4, the absorption band of HL in DMF is 305 nm. The band of 1 is 328 nm and it has an obvious red shift.

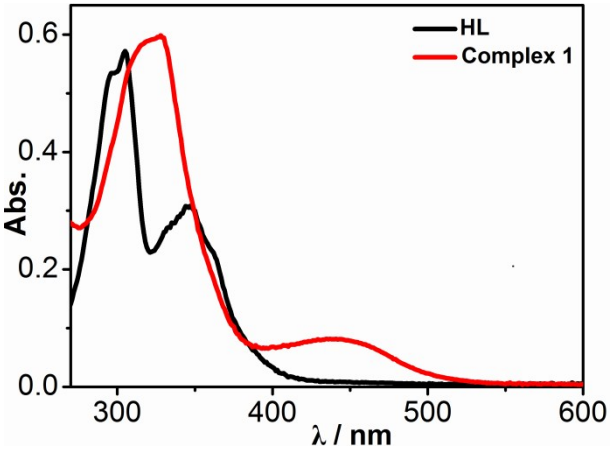

Fig. S4 The UV spectra of HL (black line) and compound **1** (red line) in DMF.

6. Themogravimetric analysis (TGA)

To estimate the thermal stability of 1, thermogravimetric (TG) analysis is performed under N_2 atmosphere from 17 to 1000 ℃ with a heating rate of 0.5 $^oC\ min^{-1}$ (Fig. S5). TGA curve indicates that compound 1 exhibits two main weight loss steps, and it starts to lose its weight (~ 7.09%) for the first step due to the loss of one interstitial water molecule, one CH_3CN molecule and two coordinated water molecules (calcd. 7.11%). Then it does not decompose until 406 ^oC which indicates that the framework begin to collapse. As for the free ligand HL, it starts to decompose at the temperature of 205 ^oC. This suggests that the thermal stability of 1 was significantly higher than the ligand L due to the coordination of metal Co(II) and the ligand HL.

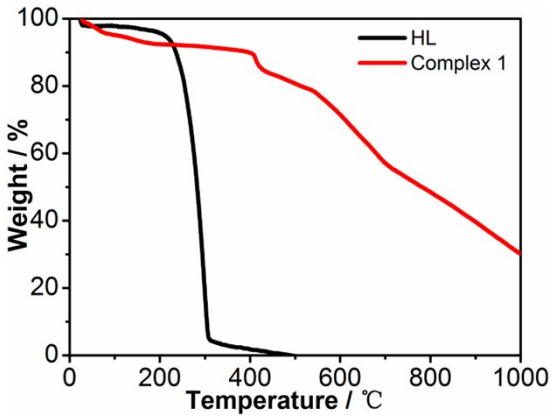

Fig. S5 The TGA curves of HL (black line) and compound 1 (red line).

7. Table S2 The comparison of yield of crystalline product by using different synthetic methods (with increasing the amount of starting materials).

The amount of reaction reagents (N)	Flow chemistry (Chip Reactor)	Diffusion	Heating reflux	Solvothermal
N	95%	No crystallization product	No crystallization product	~20%
3×N	92%	No crystallization product	No crystallization product	~25%
5×N	90%	No crystallization product	No crystallization product	No crystallization product
10×N	85%	No crystallization product	No crystallization product	No crystallization product