Five 3D Co(II)-MOFs constructed from 5-(2-methylimidazol-1-yl) isophthalic acid and different bis(imidazole) ligands and one of their derivatives as an efficient electrocatalystfor ORR

Ming-Xing Yang, Rong-Zhi Yan, Li-Juan Chen, and Shen Lin*

College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, People's Republic of China

E-mail: shenlin@fjnu.edu.cn

Contents

1. Structure analyses and table of crystallographic data.

The structure analysis was performed with direct methods and refined by full-matrix least-squares methods on F^2 by using the SHELX-2018/3 program package. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The hydrogen atoms of the coordinated water molecule and free water molecules and for compounds **1, 3** and **4** were located in difference Fourier map and their positions were refined. The highly disordered solvent molecules of compound **5** are removed using the *SQUEEZE* routine of the *PLATON*.[1] The final formulas of compound **5** were determined by crystal structure analysis combined with elemental analyses and TG.

1. A. L. Spek, *Acta Crystallogr., Sect. C*, 2015, 71, 9-18.

Table S1 Crystallographic data

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{12}H_{11}CoN_2O_{5.50}$	$C_{36}H_{26}Co_2N_8O_8$	$C_{42}H_{34}Co_2N_8O_{10}$	$C_{38}H_{33}Co_2N_8O_{9.5}$	$C_{42}H_{36}Co_2N_8O_{12}$
Formula weight	330.16	816.51	928.63	871.58	962.65
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1
a(Å)	9.9453(10)	10.064(2)	10.167(4)	10.1326(2)	10.1563(4)
b(Å)	18.0179(18)	14.736(3)	13.936(4)	12.8716(3)	13.5437(8)
c(Å)	7.1046(14)	15.222(3)	15.062(5)	14.3190(4)	15.3945(6)
α(°)	90	90	90	90	88.728(4)
β(°)	104.339(14)	129.134(10)	109.315(5)	91.030(2)	82.586(3)
γ(°)	90	90	90	90	87.645(4)
V(Å^3)	1233.4(3)	1751.1(6)	2014.0 (12)	1867.22(8)	2097.79(17)
Z	4	2	2	2	2
F(000)	672	832	952	894	988
D_{calcd}(g·cm^{-3})	1.778	1.549	1.531	1.550	1.524
μ(mm^{-1})	1.418	1.013	0.894	7.552	0.865
θ_{max}, θ_{min} (°)	25.997,3.168	27.487,2.953	27.554/3.218	74.960, 4.620	26.9920 3.9130
R_{int}	0.0377	0.0229	0.0307	0.0360	0.0398
No. of data collected	5510	13596	13927	9660	18432
No. of unique data	2424	3975	4542	3749	8322
No. of observed	1794	3555	3929	3263	5573
No. variables	207	245	324	269	550

Final R indicaes [I>2σ(I)]	R_1 = 0.0492 wR_2= 0.1063	R_1 =0.0334 wR_2=0.1009	R_1=0.0396, wR_2=0.0928	R_1=0.0376 wR_2=0.0933	R_1=0.0466 wR_2=0.0993
R indices(all data)	R_1 = 0.0734 wR_2 = 0.1197	R_1 = 0.0380 wR_2 =0.1046	R_1=0.0492, wR_2=0.0986	R_1=0.0458 wR_2=0.0984	R_1=0.0800 wR_2=0.1150
Goof	1.024	1.016	1.072	1.028	1.004
(Δ/σ)max,mean	0.002,0.000	-0.001,0.000	0.0002,0.0000	0.0000,0.0000	0.001,0.0000
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ (e/Å^3)	0.654/ -0.748	0.618/-0.420	0.248/-0.243	0.419/-0.426	0.400/-0.322

$^aR_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR = \{\sum[w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$

Table S2 Selected bond lengths (Å)and bond angles (º) of compound 1

Co1-O3#1	1.975(7)	Co1-O1	2.007(2)	Co1-N1#2	2.047(3)
Co1-O5	2.117(3)	Co1-O4B#1	2.212(17)	Co1-O3B#1	2.26(4)
Co1-O4#3	2.267(5)				

O3#1-Co1-O1	146.08(16)	O3#1-Co1-N1#2	99.67(17)
O1-Co1-N1#2	113.69(12)	O3#1-Co1-O5	89.5(4)
O1-Co1-O5	91.06(12)	N1#2-Co1-O5	99.11(13)
O3#1-Co1-O4B#1	53.8(4)	O1-Co1-O4B#1	92.6(3)
N1#2-Co1-O4B#1	148.3(5)	O5-Co1-O4B#1	97.8(6)
O3#1-Co1-O3B#1	5(2)	O1-Co1-O3B#1	148.6(5)
N1#2-Co1-O3B#1	97.6(5)	O5-Co1-O3B#1	85.2(19)
O3#1-Co1-O4#3	89.2(4)	O1-Co1-O4#3	85.73(12)
N1#2-Co1-O4#3	88.65(14)	O5-Co1-O4#3	172.24(14)

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

Table S3 Selected bond lengths (Å) and bond angles (º) of compound 2

Co1-O4#1	1.9797(13)	Co1-O2	1.9953(14)	Co1-N4	2.0124(16)
Co1-N2#2	2.0302(16)				

O4#1-Co1-O2	95.08(6)	O4#1-Co1-N4	116.59(7)
O2-Co1-N4	114.90(6)	O4#1-Co1-N2#2	107.03(7)
O2-Co1-N2#2	117.70(6)	N4-Co1-N2#2	105.56(6)

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

Table S4 Selected bond lengths (Å) and bond angles (º) of compound 3

Co1-O4	1.9856(16)	Co1-O1#1	2.0085(15)	Co1-N4	2.0121(19)
Co1-N2#2	2.0456(19)				

O4-Co1-O1#1	99.17(7)	O4-Co1-N4	106.16(7)
O1#1-Co1-N4	120.98(7)	O4-Co1-N2#2	108.19(7)
O1#1-Co1-N2#2	112.32(7)	N4-Co1-N2#2	108.77(7)

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

Table S5 Selected bond lengths (Å) and bond angles (º) of compound 4

Co1-O1	1.9849(15)	Co1-O4#1	2.0211(16)	Co1-N2#2	2.041(2)
Co1-N3	2.017(2)				

O1-Co1-N3	106.00(7)	O1-Co1-O4#1	98.25(7)
N3-Co1-O4#1	122.02(7)	O1-Co1-N2#2	110.34(7)
N3-Co1-N2#2	108.31(8)	O4#1-Co1-N2#2	111.05(8)

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

Table S6 Selected bond lengths (Å) and bond angles (º) of compound 5

Co1-O8	1.993(2)	Co1-O5#1	2.0088(19)	Co1-N8#2	2.030(3)
Co1-N2#3	2.037(3)	Co2-O1#1	1.986(2)	Co2-O4	2.002(2)
Co2-N5	2.008(3)	Co2-N3	2.027(3)		

O8-Co1-O5#1	97.73(9)	O8-Co1-N8#2	103.72(10)
O5#1-Co1-N8#2	111.25(9)	O8-Co1-N2#3	111.65(11)
O5#1-Co1-N2#3	109.58(10)	N8#2-Co1-N2#3	120.42(12)
O1#1-Co2-O4	97.45(8)	O1#1-Co2-N5	114.19(9)
O4-Co2-N5	111.52(10)	O1#1-Co2-N3	114.94(10)
O4-Co2-N3	108.31(10)	N5-Co2-N3	109.74(11)

Symmetry code: #1, *x*+1, *y*, *z*; #2, -*x*+2, -*y*+3, -*z*+1; #3, -*x*+2, -*y*+4, -*z*+2.

2. The coordination environments of Co(II) centres in compounds 3 and 4

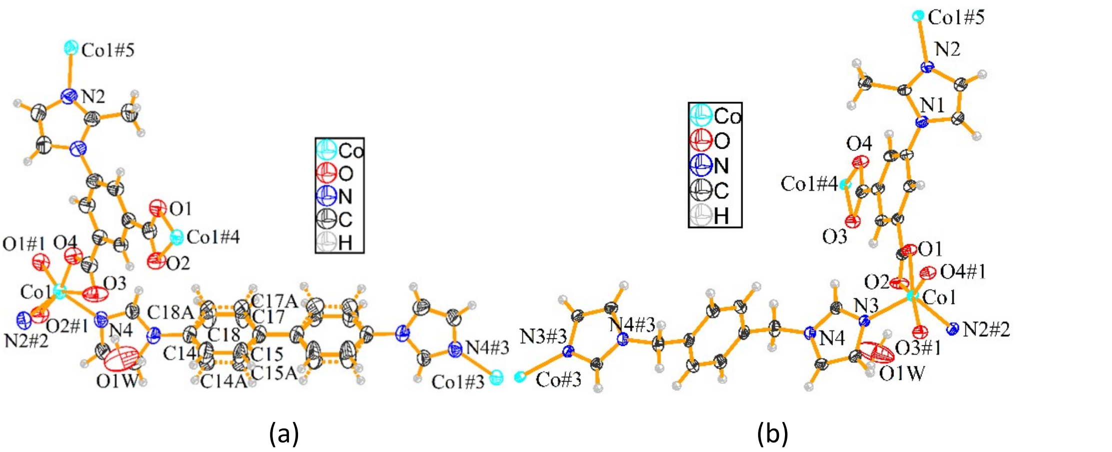


Fig. S1 The *ORTEP* drawing of the coordination environments of Co(II) centres in compounds **3** (a) and **4** (b) (50% probability level). Symmetry codes in compound **3**: #1, *x*-1, *y*, *z*; #2, -*x*+3/2, *y*-1/2, -*z*+3/2; #3, -*x*+1, -*y*+1, -*z*; #4 *x*+1, *y*, *z*; #5, -*x*+3/2, *y*+1/2, -*z*+3/2; symmetry codes in compound **4**: #1, *x*-1, *y*, *z*; #2, *x*-1/2, -*y*+3/2, *z*+1/2; #3, -*x*+1, -*y*, -*z*; #4, *x*+1, *y*, *z*; #5, *x*+1/2, -*y*+3/2, *z*-1/2.

3. PXRD and TGA of compounds 1-5

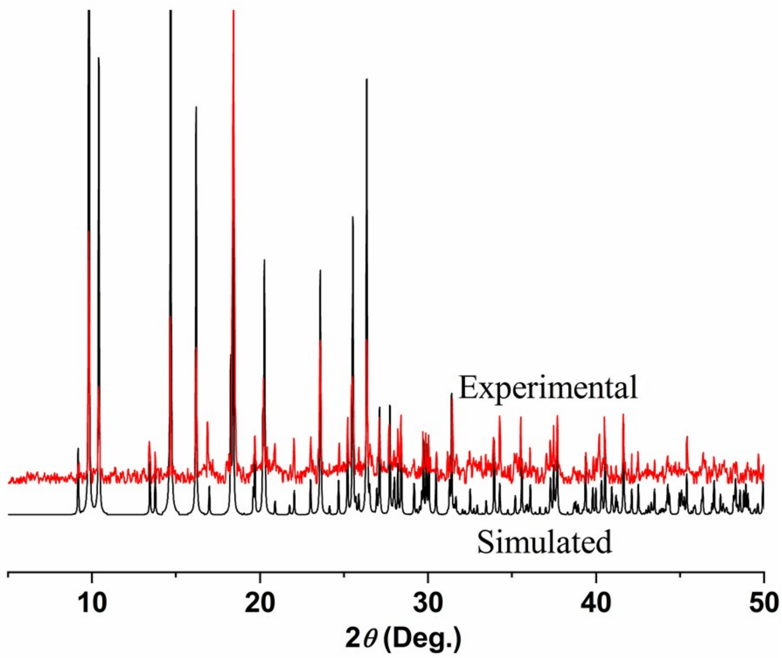


Fig. S2 Powder X-ray diffraction (PXRD) patterns for compound **1**.

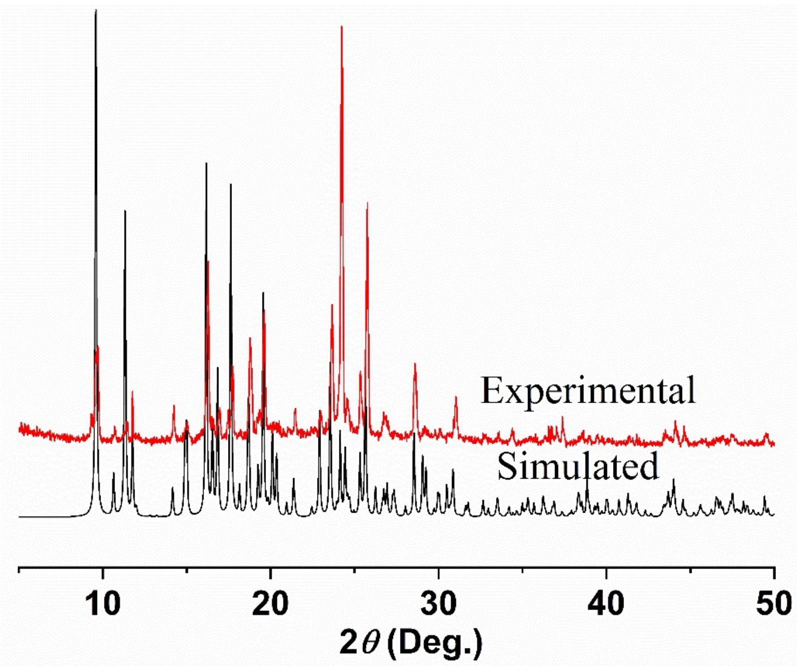


Fig. S3 Powder X-ray diffraction (PXRD) patterns for compound **2**.

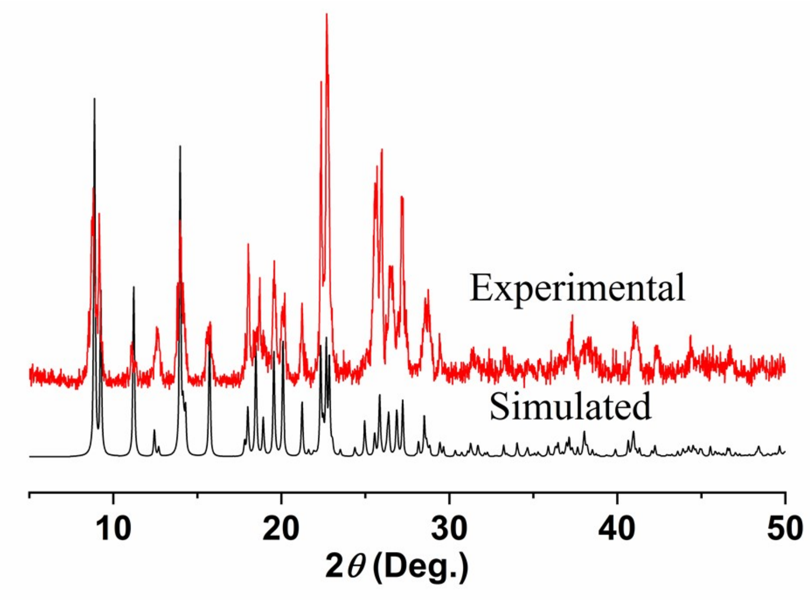


Fig. S4 Powder X-ray diffraction (PXRD) patterns for compound **3**.

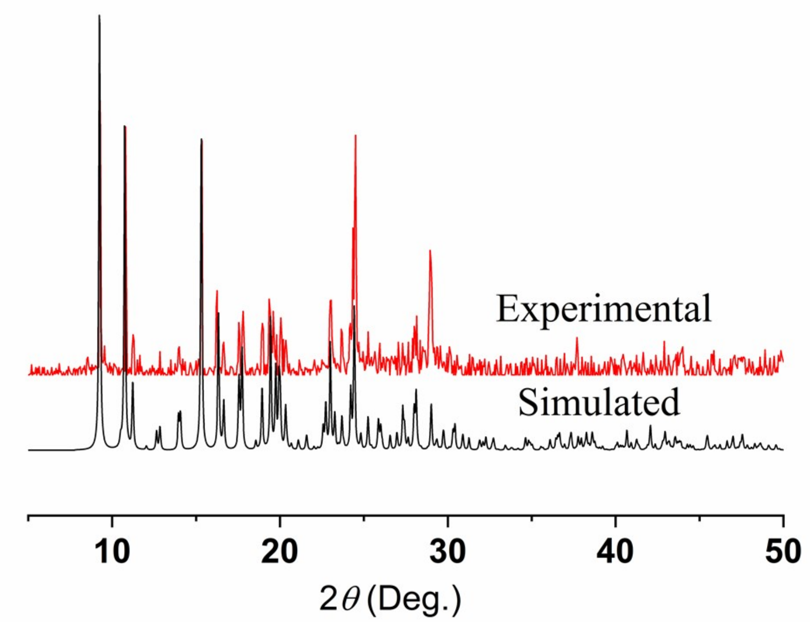


Fig. S5 Powder X-ray diffraction (PXRD) patterns for compound **4**.

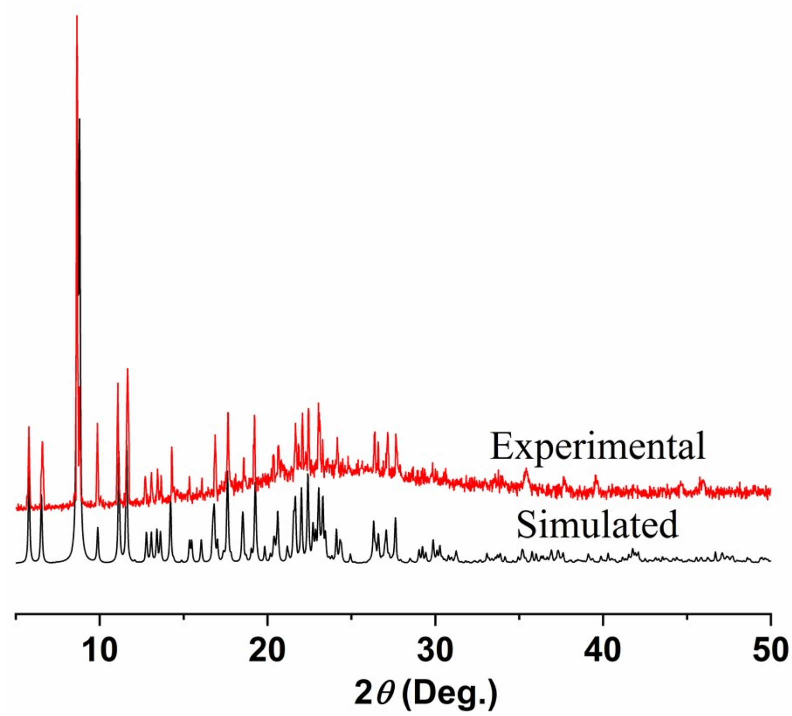


Fig. S6 Powder X-ray diffraction (PXRD) patterns for compound **5**.

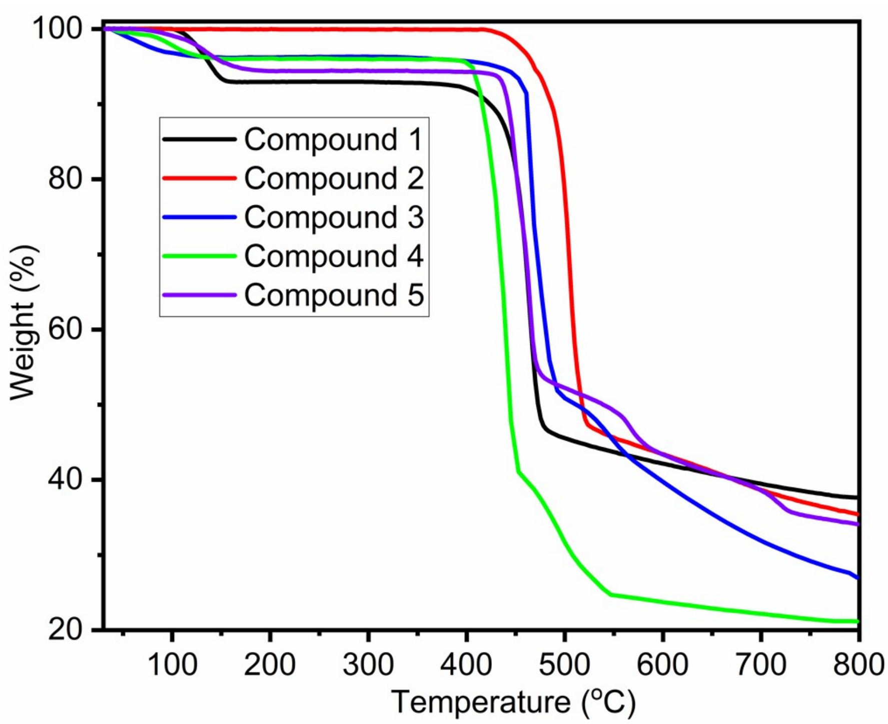


Fig. S7 The TG curves of compounds **1-5** under N_2atmosphere at a heating rate of 10 K·min^{-1}.

4. PXRD, N_2 adsorption and desorption isotherms and corresponding pore size distribution plots for CoNC-5.

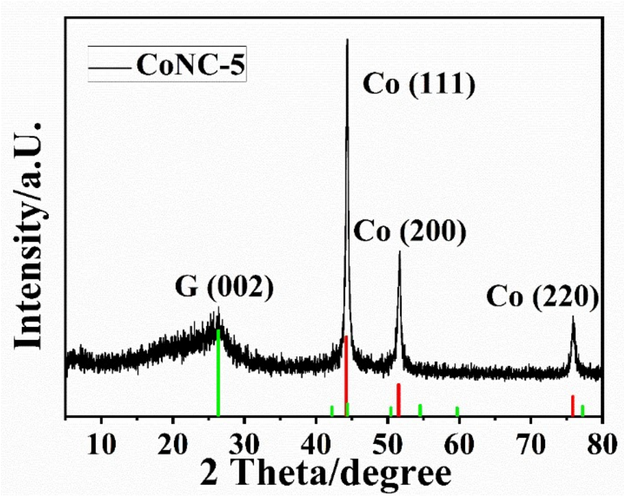


Fig. S8 Powder X-ray diffraction (PXRD) patterns for CoNC-5.

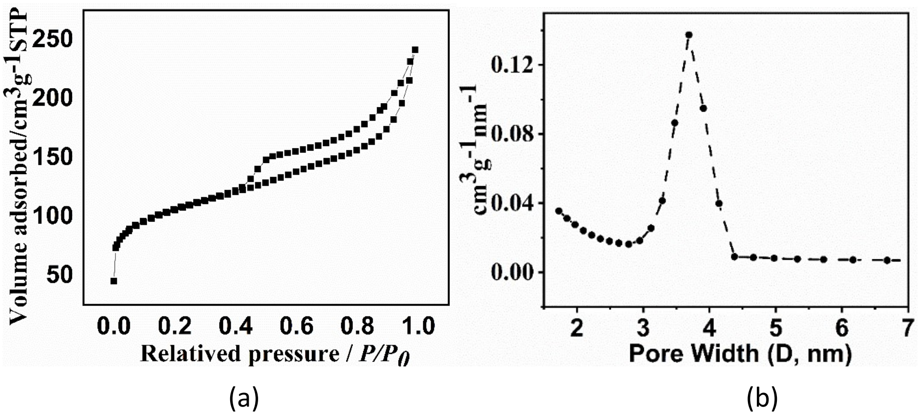


Fig. S9 (a) N_2 adsorption and desorption isotherms for CoNC-5. (b) Corresponding pore size distribution plots.

5. Calculating the electron transfer number (n).

The electron transfer numbers (n) were calculated by the Koutecky-Levich equation:

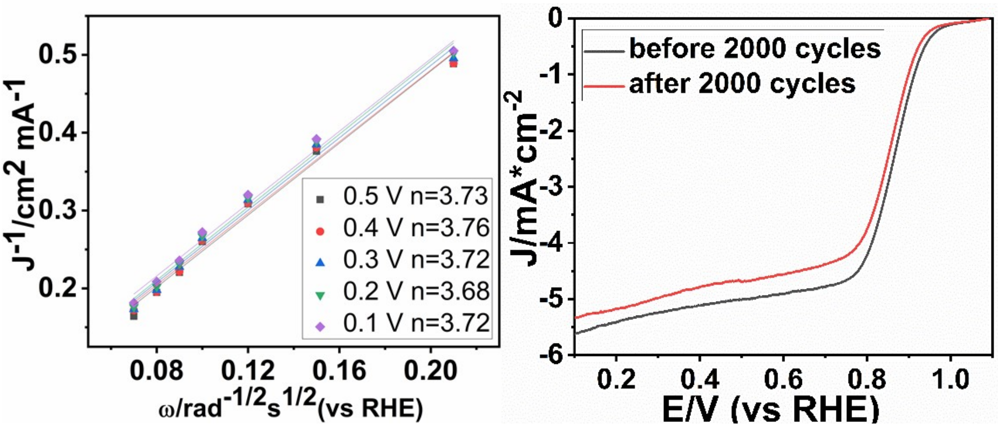
$$\frac{1}{J}=\frac{1}{J_L}+\frac{1}{J_K}=\frac{1}{B\omega^{\frac{1}{2}}}+\frac{1}{J_K}$$

$$B=0.62\mathrm{n}FC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

Where J is the measured current density, J_K and J_L are the kinetic and limiting current densities, ω is the angular velocity of the disk, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant (96485 $C \cdot mol^{-1}$), C_0 is the bulk concentration of O_2 (1.2 × 10^{-6} $mol \cdot cm^{-3}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH (1.9 × 10^{-5} $cm^2 \cdot s^{-1}$), and V is the kinematic viscosity of the electrolyte (0.01 $cm^2 \cdot s^{-1}$), and k is the electron transfer rate constant.

The electron transfer number (n) were calculated by the results of the rotating ring-disk electrode (RRDE) test with the following equations:

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}}$$



(a) (b)

Fig. S10 (a) The K-L plots at the potentials of 0.10 to 0.50 V. (b) LSV curves (5 mV/s) of CoNC-5 before and after 2000 potential cycles in O_2-saturated 0.1 M KOH solution at a RRDE rotation rate of 1600 rpm.

6. The equation about the measured potentials converted to the reversible hydrogen electrode (RHE):

All the potentials in this work were converted into reference potential of reversible hydrogen electrode (RHE) by the conversion formula as follows:

$$RHE = E_{Ag/AgCl} + 0.059 pH + 0.2224 V - 0.059 \lg a(Cl^-)$$

Where $E_{Ag/AgCl}$ represents potential which is measured by silver chloride electrode as reference electrode. 0.2224V is the standard electrode potential of silver chloride electrode at 25ºC. The $a(Cl^-)$ is the concentration of Cl^- in saturated silver chloride electrode (3.4M).

7. IR spectra of compounds 1-5

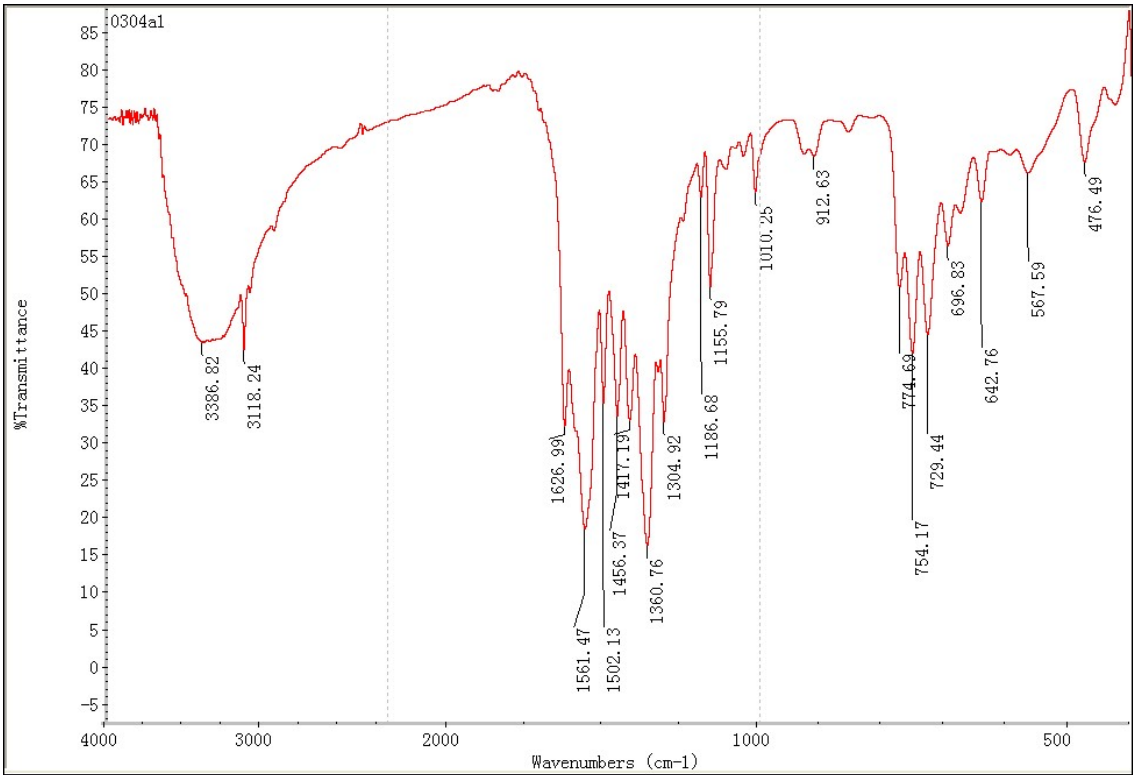


Fig.S11 IR spectrum of **1**.

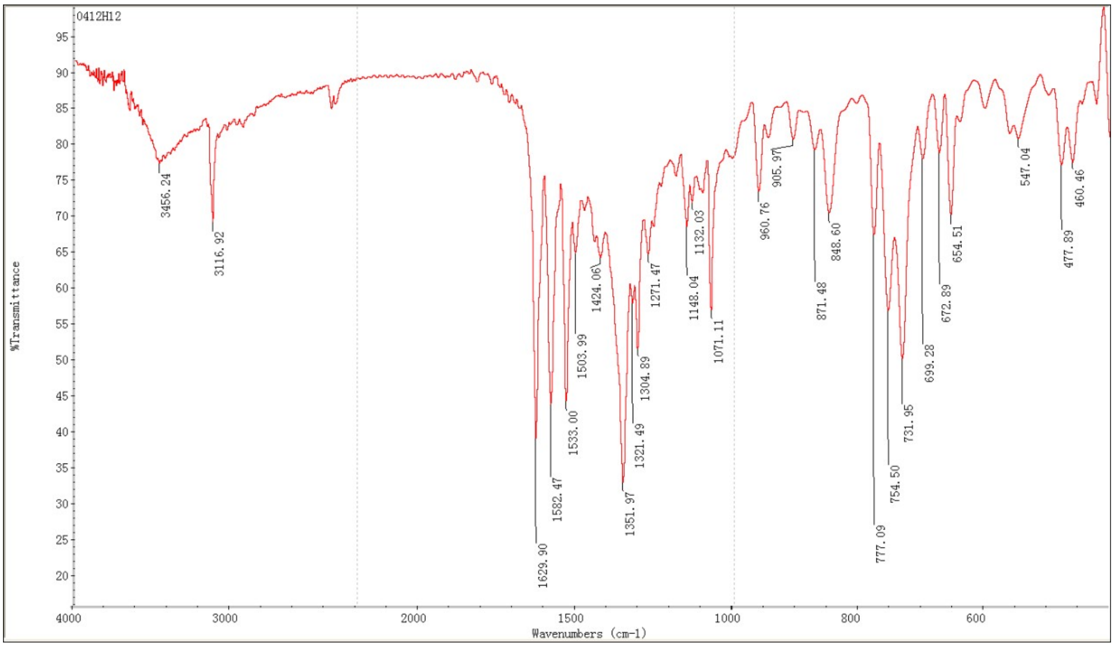


Fig.S12 IR spectrum of **2**

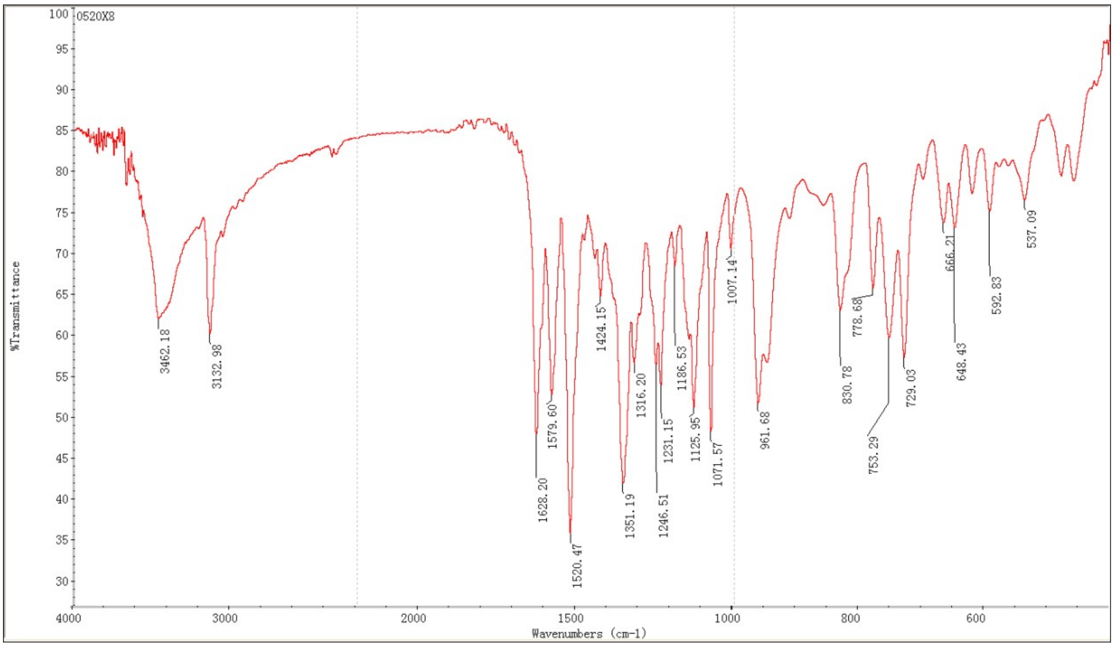


Fig.S13 IR spectrum of **3**

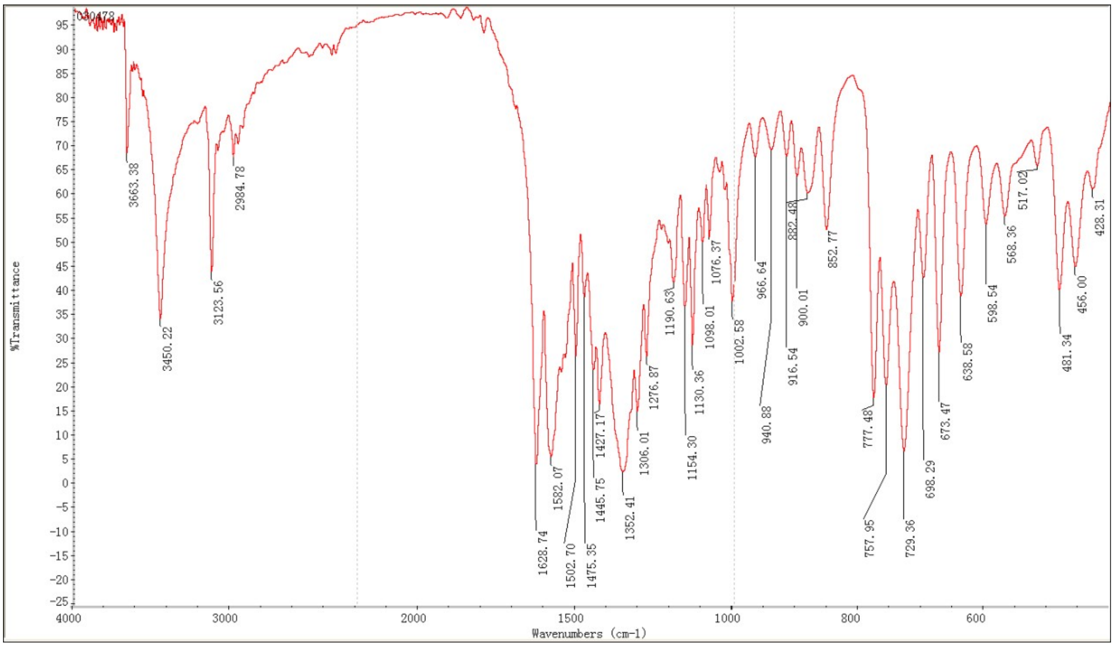


Fig.S14 IR spectrum of **4**

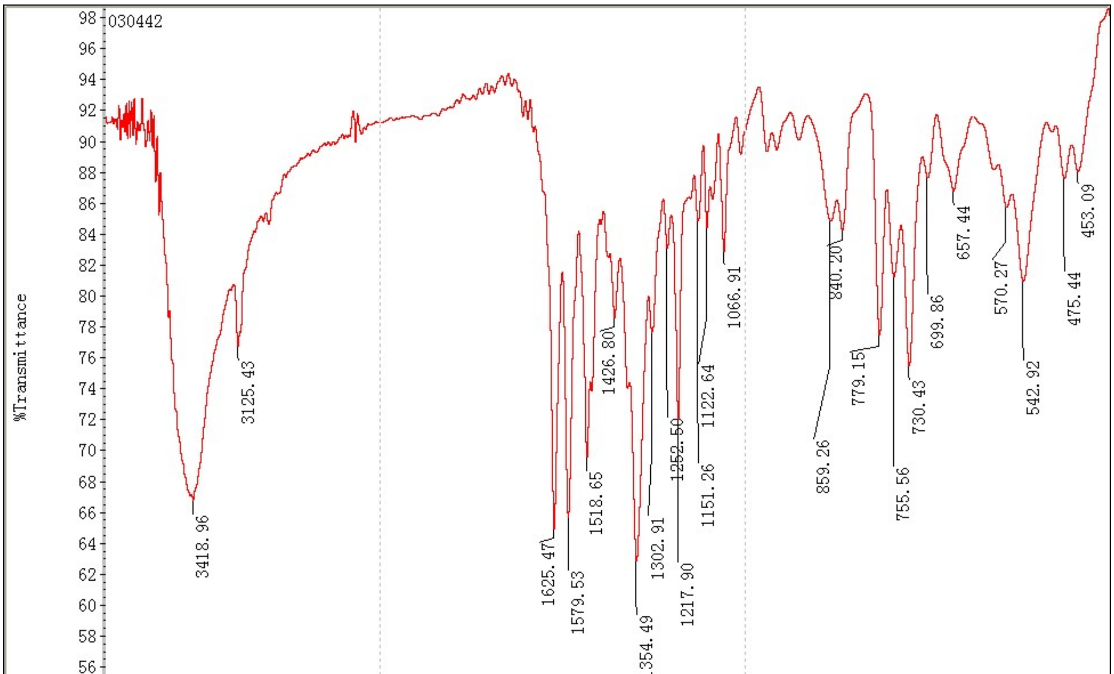


Fig.S15 IR spectrum of **5**