



Co-containing metal organic framework with a linear bis-imidazole and dicarboxylate: Electrochemical and electrocatalytic properties



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ABSTRACT

A new Co-containing metal-organic framework (Co-MOF), [Co(BDC)(bib)]_n (bib = 1,4-bis-imidazolebenzene; H₂BDC = 1,4-benzenedicarboxylic), has been synthesized under hydrothermal conditions. Its structural characterization was carried out by means of elemental analysis, infrared spectroscopy, thermogravimetric analysis, UV–Vis and single X-ray diffraction. The Co-MOF exhibits 2-fold interpenetrated sql topology, which is further stacked through hydrogen-bond interactions leading to the formation of a 3D supramolecular architecture. The CV results of [Co(BDC)(bib)]_n modified electrode show a pair of redox peaks at ca. 0.13 V in 0.5 M NaOH solution and also display good electrocatalytic activity for oxidation of hydrogen peroxide in alkaline medium.

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1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid. They are attracting considerable attention because of unique structural properties such as high surface areas, tunable pore sizes and open metal sites, and finding a variety of potential applications in gas storage, catalysis, sensors and optics [1–15]. MOFs are composed of repeated metal complex units that may be electrochemically active depending on the type of metal ions and ligands. Thus, it's a potentially interesting strategy for modulating the redox properties of MOF-based materials with good electrochemical properties and electrocatalytic activities. Pioneering work on the electrochemistry and electrocatalytic studies of solid-state MOFs has been reported [16–19]. However, apart from these studies there is only very little information about MOF systems for electrocatalytic oxidation of hydrogen peroxide (H₂O₂) [4]. H₂O₂ is very important in pharmaceutical, environmental, and biological applications [20,21]. Various H₂O₂ detection techniques have been widely studied, among which the electrochemistry method is of great significance. However, the direct reduction or

oxidation of H₂O₂ at the unmodified electrode is not suited for analytical application due to high overpotential and slow electrode kinetics. For this reason, developing new redox mediators for modification of electrode surface to decrease the overpotential and increase the kinetics of electron transfer has been the fundamental principal of electrochemistry studies.

In this context, great efforts have been made to synthesize new metal-organic frameworks with diversified structural features and encouraging electrochemical properties. The constitution of MOFs using mixed O- and N-donor organic ligands to bridge metal ions has been demonstrated to be a successful paradigm [22–25]. For the O-donor ligands, the carboxylate-containing ligands play an important role in construction of multidimensional limitless geometry. Most of the work reported concentrates on the benzene dicarboxylates [24,26–29]. Among the N-donor ligands, bis(imidazole) ligands have attracted great interest in process of ligand design [30–33]. According to the reports, mixed-ligand coordination polymers with aromatic carboxylate and bib are rarely presented up to now.

This paper presents the synthesis of a new Co-MOF ([Co(BDC)(bib)]_n) for the first time. Electrochemical studies indicate that the glass carbon electrode (GCE) modified with as-synthesized Co-MOF exhibits good redox activity. Its electrocatalytic activity toward H₂O₂ oxidation in alkaline is then studied. Results show that Co-MOF possesses excellent electrocatalytic activity toward H₂O₂ oxidation.

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2. Experimental

2.1. Materials and methods

All the chemicals and solvents used in the experiments are of analytical grade without further purification. Bib was prepared by literature methods [4].

Elemental analyses were carried out on a Perkin–Elmer 2400 elemental analyzer. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer in the 4000–400 cm^{-1} region. Thermogravimetric analyses were performed on a NETZSCH STA 449F3 differential thermal analyzer under N_2 atmosphere with a heating rate of 10 $^\circ\text{C}/\text{min}$ from 30 $^\circ\text{C}$ to 900 $^\circ\text{C}$. The powder XRD data were collected on an X Pert Pro diffractometer with monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) with 2θ going from 5 $^\circ$ to 40 $^\circ$ in 1 $^\circ$ steps. The solid-state diffuse-reflectance UV–Vis spectra for powder samples were recorded on a Thermo Evolution 220 equipped with an integrating sphere by using BaSO_4 as a white standard.

Electrochemical measurements were performed on a CHI660c electrochemical workstation at room temperature with a three-electrode system, which consisted of a working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The glassy carbon electrode (GCE, area 0.38 cm^2) was hand polished directly to a mirror-like with 1.0, 0.3 and 0.05 μm alumina slurry. The working electrode was prepared by casting the GCE with 6 μL aqueous suspension of the solid sample (2 mg/mL) and drying under ambient condition.

2.2. Synthesis of $[\text{Co}(\text{BDC})(\text{bib})]_n$

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 48 mg), H_2BDC (0.2 mmol, 33 mg) and bib (0.2 mmol, 42 mg) was dissolved in 10 mL distilled water and the pH value was adjusted to 8.0 with 0.5 M NaOH solution. The resulting mixture was sealed in a 25 mL Teflon-lined stainless steel vessel, heated at 160 $^\circ\text{C}$ for 3 days and then slowly cooled to room temperature. Crimson blockshaped crystals were obtained in 51% yield (based on Co). Elemental Anal. (%): calcd. for $[\text{Co}(\text{BDC})(\text{bib})]_n$: C, 55.44; H, 3.26; N, 12.93. Found: C, 58.75; H, 3.56; N, 13.31.

2.3. Crystallographic data collection and refinement

Suitable single crystal of the title compound was selected and mounted in air onto thin glass fiber. X-ray intensity data were measured at 293 K on a Bruker Smart 1000 diffractometer with a graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data reductions and absorption corrections were performed with SAINT and SADABS software package. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program [34].

The crystallographic data and structure refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2.

3. Results and discussion

3.1. Description of the structures of $[\text{Co}(\text{BDC})(\text{bib})]_n$

Single-crystal X-ray diffraction study reveals that $[\text{Co}(\text{BDC})(\text{bib})]_n$ crystallises in the triclinic, space group $P\bar{1}$. In the asymmetric unit of Co-MOF, there exist one crystallographically independent Co^{II} center, one BDC^{2-} anion and one bib ligand. The Co^{II} center is in a distorted six-coordinated octahedral geometry (CoO_4N_2) by coordinating to four carboxylate oxygen atoms (O1, O2, O3

Table 1
Crystallographic data and structure refinement parameters for Co-MOF.

Chemical formula	$\text{C}_{20}\text{H}_{14}\text{CoN}_4\text{O}_4$	Formula weight	433.28
λ (\AA)	0.71073	Crystal system, space group	triclinic, $P\bar{1}$
a (\AA)	7.8440(8)	α ($^\circ$)	69.5700(10)
b (\AA)	10.8659(12)	β ($^\circ$)	75.768(2)
c (\AA)	11.8711(15)	γ ($^\circ$)	70.8630(10)
V (\AA^3)	885.84(17)	Z	1
D_{calc} (Mg/m^3)	6.307	$F(000)$	1617
R_{int}	0.0276	Reflections collected/unique	3085/2463
Goodness-of-fit (GOF) on F^2	1.106	Data/restraints/parameters	3085/0/262
R indices (all data)	$R_1 = 0.0923$ $wR_2 = 0.2361$	Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0766$ $wR_2 = 0.2239$

Table 2
Selected bond distances (\AA) and angles ($^\circ$) for Co-MOF.

Co(1)–O(1)	2.047(5)	Co(1)–O(2)	2.312(5)
Co(1)–O(3)	2.020(5)	Co(1)–O(4)	2.434(5)
Co(1)–N(2)	2.090(6)	Co(1)–N(4) ^{#1}	2.091(6)
O(3)–Co(1)–O(1)	152.0(2)	O(1)–Co(1)–N(2)	100.5(2)
N(2)–Co(1)–N(4) ^{#1}	104.3(2)	O(3)–Co(1)–N(2)	96.5(2)
N(2)–Co(1)–O(2)	159.5(2)	N(4) ^{#1} –Co(1)–O(2)	86.3(2)
O(3)–Co(1)–O(2)	99.2(2)	O(1)–Co(1)–O(2)	60.06(19)

Symmetry codes: #1: $x, y - 1, z + 1$.

and O4) from BDC^{2-} unit and two nitrogen atoms from bib ligand (N2 and N4), as shown in Fig. 1a. The Co–O distances fall in the range 2.020(5)–2.434(5) \AA , and the Co–N2 and Co–N4 distances are 2.090(6) \AA and 2.091(6) \AA , respectively.

The bib ligands, in a bidentate fashion, bridge Co^{II} centers to propagate the chains in a linear manner with the angle 180 $^\circ$, which are further connected through BDC^{2-} ligands at 137 $^\circ$ angle to generate 2D (4,4) network, as illustrated in Fig. 1b. In this 2D network, the lengths of the edges are not equivalent. The intermetallic separations by BDC^{2-} and bib are 10.694 \AA and 12.998 \AA , respectively. An infinite 2D layer structure (Fig. 1c) is formed with interpenetration of two adjacent 2D layers. Then, the interpenetrating 2D layers are further stacked in ---ABAB--- fashion through strong hydrogen-bonds interactions, leading to the formation of a 3D supramolecular architecture, as shown in Fig. S1. Topological analysis shows that it is a uninodal 4-connected sql net with point symbol ($4^4 \cdot 6^2$) (Fig. 1d).

The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD). The PXRD patterns of as-synthesized Co-MOF closely match the simulated ones from single-crystal data, indicating that the product is in a pure phase (Fig. S2).

3.2. Spectroscopic characterization and thermal study

In the IR spectra of the title compound (Fig. S3), the expected absorption band at around 1680 cm^{-1} for the protonated carboxylic groups is absent, the characteristic bands of the carboxylate group at 1555 cm^{-1} (antisymmetric stretching vibration) and 1308 cm^{-1} (symmetric vibration stretching) indicate the complete deprotonation of H_2BDC ligand. The absorption bands at 1533 cm^{-1} , 1399 cm^{-1} and 1247 cm^{-1} are attributed to the stretching vibrations of the C=N and C=C in the imidazole ring. Therefore, the IR analysis of the title compound is well consistent with crystal composition.

Fig. 2 reveals the UV–Vis diffuse-reflectance absorption spectra of the $[\text{Co}(\text{BDC})(\text{bib})]_n$, showing the absorption components in the UV and Vis regions. The intense absorption peak at 264 nm for the

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