

# Synthesis, crystal structure and optical property of two zinc metal organic frameworks constructed from isonicotinic acid



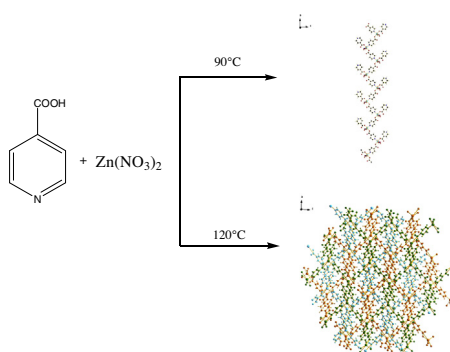
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## HIGHLIGHTS

- Two novel metal organic frameworks have been synthesized by  $\text{Zn}(\text{NO}_3)_2$  and isonicotinic acid.
- Compound 1 and reported compound 1' are framework isomers.
- Two isomers have different optical properties and specific area due to the structure.
- There was a crystal phase transformation for 2 when it activated at 100 °C.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Two new zinc Metal Organic Frameworks(MOFs),  $\text{Zn}(\text{IN})_2$  (1) and  $\text{Zn}(\text{IN})_2(\text{NO}_3)(\text{H}_2\text{O})$  (2)(HIN = isonicotinic acid), have been synthesized and characterized by PXRD,IR, BET surface area test, uv–vis spectra, thermogravimetric analysis, fluorescent Spectra and single crystal X-ray diffraction. 1 is a 3D 3-fold interpenetrating framework. While 2 reveals a 1D chain structure. Different structures resulted in different optical properties. And there was a crystal phase transformation for 2 when it activated at 100 °C.

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## Introduction

Frameworks isomerism is the term used to describe the occurrence of MOFs which possess the same formula while the structure is different [1]. Even though researchers use the same metal and ligand, combine different synthetic conditions such as reaction time, pH and temperature in multiple ways to produce different structures [2–4].

Isonicotinic acid (HIN) is widely used in synthesizing metal organic frameworks as asymmetrical rigid ligand. Research area includes transition metal [5–12], lanthanide metal [13–16] and Multi metal [17–23] compounds. And many researchers used HIN as an auxiliary ligand.

As for Zn MOFs with isonicotinic acid, Wu et al. [24] synthesized a microporous 3-D chiral  $\text{Zn}(\text{IN})_2 \cdot 2\text{H}_2\text{O}$  (1'). Shen Liang [25] synthesized a zinc complex  $[\text{Zn}(\text{IN})_2(\text{H}_2\text{O})_4](\text{IN} = \text{C}_6\text{H}_4\text{NO}_2^-)$ . In which the zinc atom coordinates to two nitrogens of two IN ligands and four  $\text{H}_2\text{O}$ . Hong [26] Prepared a three-dimensional supramolecular compound  $[\text{Zn}(\text{INO})_2(\text{DMF})]$  DMF(INO = isonicotinic acid N-oxide). James et al. [27] studied discrete aquo complexes  $[\text{Zn}(\text{INA})_2(\text{OH}_2)_4]$

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interconverted to their corresponding extended network structures  $[\text{M}(\text{INA})_2]$ . Zhang et al. [28] used MOFs,  $\text{Zn}(\text{ISN})_2 \cdot 2\text{H}_2\text{O}$  as chiral stationary phase for high-resolution gas chromatography.

In this paper, we reported the synthesis and characterization of two MOFs  $\text{Zn}(\text{IN})_2(1)$  and  $\text{Zn}(\text{IN})_2(\text{HNO}_3)(\text{H}_2\text{O})(2)$ . Compound 1 is a framework isomer of the reported compound  $\text{Zn}(\text{IN})_2 \cdot 2\text{H}_2\text{O}$  (1') [24] with 3-fold interpenetrating networks. They have the same coordination environment, but different interpenetrating networks, as result there are many different properties between them, like color, space group and especially optical properties. 2 is a 1D chain MOFs with a similar structure as reported [26]. And there was process of crystal phase transformation for 2.

## Experimental

### Materials and measurements

All of the solvents and reagents for synthesis were commercially available. FT-IR spectra were recorded from KBr pellets in the range 4000–400  $\text{cm}^{-1}$  on a Bruker EQUINOX-55 spectrometer. Fluorescence spectra were performed on Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses (TGA) were performed under nitrogen with a heating rate of 50  $^\circ\text{C}/\text{min}$  using a Q600 SDT thermogravimetric analyzer. Variable-temperature powder X-ray diffraction (PXRD) was carried out on a Shimadzu XRD-7000 analyzer. BET surface area test was carried out on 3H-2000PS1/2 Specific surface & pore size analysis instrument. The mesopore size distribution and total mesopore volumes were determined using the modified BJH method from the adsorption isotherm data

### Synthesis

#### Preparation of $\text{Zn}(\text{IN})_2(1)$

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.03 g), HIN (0.1 mmol, 0.022 g), in EtOH (4 mL) was heated in a 23 mL Teflon-lined autoclave at 120  $^\circ\text{C}$  for 1 day. After being cooled to room temperature, yellow crystals of 1 were collected by filtration, washed with water, and dried in air (54% yield based on  $\text{H}_2\text{IN}$ ). Anal. Calc. for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{Zn}$  (%): C, 46.76; H, 2.60; N, 9.00. Found: C, 46.57; H, 2.41; N, 8.78. IR (KBr,  $\text{cm}^{-1}$ ): 3424, 1962, 1634, 1557, 1234, 1213, 1101, 1058, 1034, 774, 701.

#### Preparation of $\text{Zn}(\text{IN})_2(\text{HNO}_3)(\text{H}_2\text{O})(2)$

A similar reaction of a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1 mmol, 0.03 g), HIN (0.1 mmol, 0.022 g), in EtOH (4 mL) was heated in a 23 mL Teflon-lined autoclave at 90  $^\circ\text{C}$  for 1 day. Colorless blocks of crystals of 2 were isolated in yield 37%. Anal. Calc. for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_8\text{Zn}$  (%): C, 37.02; H, 2.83; N, 10.80. Found: C, 36.90; H, 3.06; N, 10.47. IR (KBr,  $\text{cm}^{-1}$ ): 3413, 2311, 1649, 1551, 1385, 1231, 1025, 775, 694, 620.

#### Preparation of $\text{Zn}(\text{IN})_2(1')$

$\text{Zn}(\text{IN})_2 \cdot 2\text{H}_2\text{O}$  (1') was synthesized according to the method reported previously [24]. A dimethylsulfoxide (DMSO) solution (50 mL) of isonicotinic anhydride (1 mmol, 0.228 g) was placed at the bottom of a straight glass tube, over which a solution of  $\text{Zn}(\text{OAC})_2 \cdot 2\text{H}_2\text{O}$  (2 mmol, 0.439 g) in methanol (50 mL) was carefully layered. The tube was sealed under vacuum and put into a refrigerator. Over 2 weeks, large colorless needle-like single crystals were obtained (63% yield based on  $\text{H}_2\text{IN}$ ). Anal. Calc. for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{Zn}$  (%): C, 41.7; H, 3.5; N, 8.6. Found: C, 41.5; H, 3.6; N, 8.8.

### X-ray crystallography

Crystals of 1 and 2 were selected for lattice parameter determination and collection of intensity data at 296 K on a Bruker Smart APEX II CCD diffractometer with monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a  $\varphi - \omega$  scan mode. The structures were solved by direct methods and refined on F2 by full matrix least-squares using SHELXTL. All non-hydrogen atoms were refined anisotropically. The contribution of these hydrogens was included in the structure factor calculations. Crystallographic data are summarized in Table 1. Selected bond lengths and angles for 1 and 2 are listed in Table 2.

### Metal ion exchange

The crystals of 1 and 1' were first immersed in a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$  for 30 days. Then the solid samples were suspended in  $\text{H}_2\text{O}$  for two weeks in order to remove quest molecule. The exchanged samples were decomposed with concentrated  $\text{HNO}_3$ , and the ratio of Zn/Ni and Zn ions output (ppm) was determined by atomic absorption spectrophotometer.

## Results and discussion

### Crystal structure

#### $\text{Zn}(\text{IN})_2(1)$

Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the orthorhombic space group  $P2_12_12_1$ . Each Zn(II)

**Table 1**  
Crystal data and refinement parameters of 1 and 2.

Empirical formula	$\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_6\text{Zn}$	$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_8\text{Zn}$
Formula weight	309.57	390.61
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pbca$
<i>a</i>	8.1614(5)	14.0883(13)
<i>b</i>	11.9032(9)	13.8063(11)
<i>c</i>	12.8351(9)	14.5821(15)
<i>V</i> ( $\text{Å}^3$ )	1246.89(15)	2836.3(5)
<i>Z</i>	4	8
D <sub>calc</sub> ( $\text{g}/\text{cm}^3$ )	1.649	1.829
<i>F</i> (000)	624	1584
Theta range	2.96–25.02	2.89–25.02
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.008	1.093
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $I \geq 2\sigma(I)$ ]	0.0465, 0.0661	0.0369, 0.0785
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0756, 0.0768	0.0693, 0.1003

**Table 2**  
Selected bond lengths ( $\text{Å}$ ) and angles (deg) for 1 and 2.

1			
Zn1–O1	1.935(5)	Zn1–N1	2.020(6)
Zn1–O3	1.920(4)	Zn1–N2	2.040(5)
O1–Zn1–O3	115.1(2)	O1–Zn1–N1	106.14(18)
O1–Zn1–N2	99.5(2)	O3–Zn1–N2	104.02(17)
O3–Zn1–N1	106.14(18)	N1–Zn1–N2	107.7(3)
2			
Zn1–O1	2.013(3)	Zn1–N1	2.112(3)
Zn1–O3	2.035(3)	Zn1–O5	2.218(4)
Zn1–O8	2.058(3)	Zn1–O6	2.496(4)
O1–Zn1–O3	173.26(11)	O1–Zn1–O8	90.92(12)
O3–Zn1–O8	89.87(11)	O1–Zn1–N1	94.54(12)
O3–Zn1–N1	91.82(12)	O8–Zn1–N1	102.50(13)
O1–Zn1–O5	90.88(11)	O3–Zn1–O5	86.68(11)
O8–Zn1–O5	165.33(12)	N1–Zn1–O5	91.86(13)
O1–Zn1–O6	86.12(12)	O3–Zn1–O6	87.38(11)
O8–Zn1–O6	112.37(12)	N1–Zn1–O6	145.11(13)
O5–Zn1–O6	53.26(11)		

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