

# Crystal Growth and Characterization Studies of a Zigzag 1D Sulfonated Coordination Polymer to Prepare Zinc Oxide Nanoparticles

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## Abstract

Single crystals of a new coordination polymer, {[Zn(2,2'-bipyridine)(H<sub>2</sub>O)<sub>2</sub>(1,5-NDS)].2H<sub>2</sub>O}, where 1,5-NDS is 1,5-naphthalenedisulfonate ion, have been successfully grown under hydrothermal conditions. The as-synthesised coordination polymer was characterised by X-ray Diffraction analysis which shows that the metal centres have been linked by 1,5-NDS linkers and then the structure has extended in a 1D chain. Moreover, the compound was studied using thermogravimetric analysis (TGA) to check its thermal stability and IR spectroscopy. The prepared compound was a good candidate as a precursor to prepare ZnO nanoparticles. ZnO nanoparticles which were achieved after calcinating the compound, were characterized by Scanning Electron Microscopy (SEM) and PXRD.

**Keywords:** Coordination polymer; Nanoparticles; Single crystal; Sulfonated.

## Introduction

Recently, Metal-Organic Frameworks (MOFs), which are known as crystalline porous materials and have been classified as a subset of coordination polymers, have fascinated a lot of attention due to their structure, topology, and also applications. Gas adsorption, drug delivery, magnetism, catalysis, separation, sensor technology, and luminescence can be listed as the most common applications of MOFs. These materials, which are characterized by their high specific surface areas and uniformly sized pores and channels, comprise metal ions or metal ion clusters that are bridged by organic linkers (1-14).

The sulfonate group with its three oxygen atoms provides variable coordination modes which leads to

various frameworks but their networks have been studied much less probably due to the weak coordination of sulfonate anions. However, sulfonate anions weak ligation accompanied with different modes of coordination are ideal for structural diversity and this is the main advantage of sulfonate solids. In complexation with sulfonates, soft metal ions have improved bonding patterns compared to hard metal ions which result in vastly hydrated and naturally zero- or one-dimensional assemblies. Softer metal ions are superior bonding collaborators. As a result, Rare-earth-based MOFs have been the most reported sulfonated MOFs (15, 16).

Among sulfonates, arenedisulfonate anions are flexible anions that have potential binding sites and can be used to make coordination polymers with a variety of

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topologies and multiple dimensions (17). As a good example of arenedisulfonates, 1,5-NDS with its firm construction and two dynamic assemblies in two locations can construct a material with the required structural and physico-chemical properties (18).

Herein, we are reporting a 1D structure consisting of 1,5-NDS and 2,2'-bipyridine as the organic linkers and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the inorganic precursor. Moreover, we refer to a simple process for the preparation of ZnO nanoparticles based on pyrolysis of the novel compound.

### Materials and Methods

All materials were industrially presented and applied as received. FTIR spectrum was obtained on EQUINOX 55 BRUKER Spectrometer. To assess the stability of the compound thermally, thermogravimetric analysis (TGA) was accomplished with TGA Q50 V6.3 analyser under flowing Argon. PXRD measurements were applied, to evaluate the purity of the prepared sample and characterize the nanoparticles, using a XPERT-PRO diffractometer with monochromatized  $\text{CuK}\alpha$  radiation. The morphology of ZnO Nanoparticles was characterized by KYKY EM-3200 Scanning Electron Microscope (SEM).

### Synthesis

The compound was gained hydrothermally by mixing  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol, 0.148 g) and 1,5-NDS (1 mmol, 0.360 g) in water (5ml). 2,2'-bipyridine was added to obtain the PH=3 while stirring the solution. Teflon vessel was used to put the mixture in and then the container was put in a steel autoclave which was sealed and then heated from 20 °C to 110 °C at the rate of 4 °C per hour for 19 hours. The needle-like colorless crystals were accumulated, rinsed with water, and dried at ambient temperature. The yield of this process is about 82 % based on zinc nitrate hexahydrate. Elem. Anal. Calc. (%): C, 41.41; H, 3.79; N, 4.83. Found (%): C, 41.19; H, 4.11; N, 4.67 for **1**

### Preparation of zinc oxide (ZnO) nanoparticles with direct calcination

Compound **1** was placed in crucible and heated at 600 °C for 6h and then cooled down to 30 °C. ZnO nanoparticles were obtained through the combustion of the organic moieties. The production of ZnO nanoparticles was confirmed by XRD patterns together with TGA.

### Crystallographic Data Collection and Refinement

STOE IPDS-II diffractometer was used for data

collection which is supplied with an image plate detector using  $\text{MoK}\alpha$  X-ray radiation. To integrate and index all the collected reflections, X-area package was applied. Concerning the absorption correction, X-SHAPE and X-RED packages were used (25). X-SHAPE were used to adjust crystal size and shape. SHELXS97 were applied to solve the structure through Direct methods and SHELXL97 was used to refine the structure through full matrix least squares on F2 (26). All the non-hydrogen atoms were anisotropically refined. Calculation on the position of aromatic hydrogen atoms and were done with isotropic displacement parameters of 1.2- and 1.5-times displacement parameters of the corresponding carbon atoms, respectively. Facts on investigational and crystallographic information, interatomic distances and chosen hydrogen bonds are displayed in Tables 1-3, correspondingly.

### Results and Discussion

Teflon-lined stainless-steel autoclaves was used for hydrothermal synthesis, as this method is one of the most powerful methods to prepare coordination polymers. Furthermore, as we have done in our previous investigation (19), we developed the solvothermal synthesis method by taking on the gradual temperature-programmed for the cooling method from 110 °C to ambient temperature through a rate of 4 °C/h.

The structure was satisfactorily described in the orthorhombic unit cell with space group of  $Pca2_1$ . The asymmetric unit comprises of a Zn(II) ion, one 2,2'-bipyridine, one NDS ligand, two coordinated and two free water molecules. The central metal ion is coordinated to two oxygen from two different NDS in trans configuration ( $\text{Zn}(1)-\text{O}(1)=2.196\text{Å}$ ,  $\text{Zn}(1)-\text{O}(4)=2.183\text{Å}$ ), two water oxygen atoms ( $\text{Zn}(1)-\text{O}(7)=2.044$ ,  $\text{Zn}(1)-\text{O}(8)=2.043$ ), and two nitrogen atoms from 2,2'-bipyridine ( $\text{Zn}(1)-\text{N}(1)=2.108$ ,  $\text{Zn}(1)-\text{N}(2)=2.104$ ) in a distorted octahedral fashion (Figure 1). Bond lengths range of Zn-N and Zn-O (Table 2) is consistent with the previously reported values (20). The bipyridine ligands display bidentate chelating mode. Each NDS connects two different Zn complexes entities in zigzag mode running along [100], founding 1-D coordination polymer (Figure 2).

In the preparation and design of supramolecular construction, intermolecular and intramolecular hydrogen bondings are playing important roles (21). Different hydrogen bondings between free and coordinated water molecules and oxygen of sulfonate ions stabilize the structure by linking the 1D chains of the compound (Table 3).

**Table 1.** Crystal data and structure refinement for the compound

Compound formula	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>10</sub> S <sub>2</sub> Zn
Molecular weight	579.93
Crystal system	Orthorhombic
Space group	Pca2 <sub>1</sub>
Temperature (K)	295(2)
Wavelength (Å)	0.71073
a (Å)	14.990 (3)
b (Å)	8.6570 (17)
c (Å)	17.689 (3)
Z	4
Cell volume (Å <sup>3</sup> )	2295.5 (8)
Density (g cm <sup>-3</sup> )	1.678
μ (mm <sup>-1</sup> )	1.312
F (000)	1192
Total reflections	10451
Unique reflections	4293
R <sub>int</sub>	0.0216
Data/restraints/parameters	4293 / 4/ 340
Goodness-of-fit on F <sup>2</sup>	1.028
R [I > 2σ(I)] (R <sub>1</sub> , wR <sub>2</sub> )	0.0264, 0.0499
R (all data) (R <sub>1</sub> , wR <sub>2</sub> )	0.0320, 0.0509
Completeness of data	0.977

**Table 2.** Selected bond distances (Å) and angles (°) in **1**

Bond lengths (Å)		Bond distances (°)	
Zn1-O1	2.196(2)	O1-Zn1-O7	82.47(8)
Zn1-O4	2.183(2)	O1-Zn1-O8	92.69(8)
Zn1-O7	2.044(2)	N1-Zn1-O4 <sup>a</sup>	94.94(8)
Zn1-O8	2.043(2)	N1-Zn1-O7	95.11(9)
Zn1-N1	2.107(2)	N2-Zn1-O4 <sup>a</sup>	95.60(8)
Zn1-N2	2.104(2)	N2-Zn1-O8	94.57(9)

<sup>a</sup>-0.5+x, -y, z**Table 3.** Distances (Å) and angles (°) of the selected hydrogen bond

D-H...A	d(D-H)	d(H...A)	d(D...A)	D-H...A
O7-H1...O10	0.76(3)	1.91(3)	2.654(3)	167(3)
O7-H2...O5	0.66(3)	2.20(3)	2.829(3)	160(4)
O9-H1...O5	0.79(5)	2.51(5)	3.191(4)	145(4)
O9-H2...O3	0.85(4)	1.99(4)	2.829(3)	169(3)
O10-H1...O3	0.73(3)	2.11(3)	2.822(3)	165(5)

The structure can be simplified by considering the tetrahedral Zn atoms and the centroid of NDS ligands as nodes, which construct one-dimensional zig-zag chains. This simplification can be seen in Figure 3 as pink and blue balls representing the tetrahedral Zn atoms and NDS ligands, respectively. Also, the interstitial water molecules are removed for clarity. This type of explanation can give a better understanding of the wave-like coordination polymer.

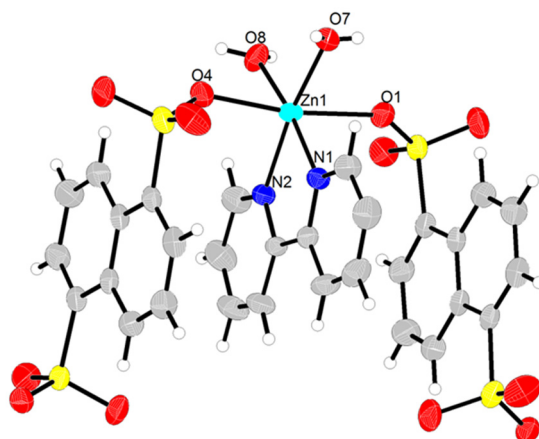
#### X-ray powder diffraction

With the intention of approving the pureness of the bulk sample, the X-ray powder diffraction patterns are measured as presented in Figure 4. It is evident that there is satisfactory similarity between the peak

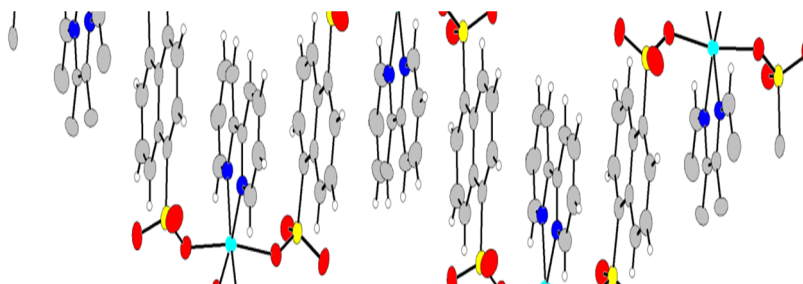
positions of the simulated XRD pattern based on single crystal X-ray data and experimental PXRD pattern, which indicates the purity of the bulk sample. The chosen alignment of the powder samples in the course of collection of the experimental XRD data could be responsible for the insignificant variations in the intensity of reflections (22).

#### IR spectrum

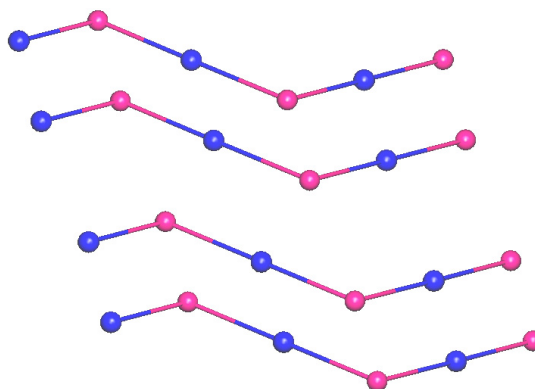
In the IR spectrum of **1** a wide-ranging band at 3100-3500 cm<sup>-1</sup> corresponds to the coordinated water molecules. In the 600-800 cm<sup>-1</sup> and 1500-1600 cm<sup>-1</sup> regions the frequencies of the naphthalene rings can be seen. (23, 24) The spectrum indicates both ν<sub>as</sub> and ν<sub>s</sub> of the S=O bonds which are found at about 1030 cm<sup>-1</sup> (ν<sub>s</sub>)



**Figure 1.** ORTEP plot of Zn surrounding with 50% probability ellipsoids. Free water molecules are omitted



**Figure 2.** 1D chain of the prepared coordination polymer



**Figure 3.** Simplified net by considering the centroid of the NDS ligands as blue circle and Zn atoms as pink circles

and  $1200\text{ cm}^{-1}$  ( $\nu_s$ ) (Figure 5).

#### **Thermal analysis**

Thermogravimetric study of **1** was performed under argon atmosphere in the temperature range between 25 to 600 °C. The heating rate for this experiment was set to 10 °C/min. TGA of the compound shows quite high stability of the solid. Despite the loss of four water molecules (theoretical weight loss 12.41%, observed

12%), the compound remains stable up to 400 °C. The organic moiety vanished at 460 °C and the structure start to decompose. As a final point, the residual is possibly zinc oxide (found 35.03%, calcd. 38.4%), which is in agreement with PXRD pattern (Figure 6).

#### **Characterization of ZnO nanoparticles**

The nanoparticles of ZnO, which were obtained by calcinating the coordination polymer, were

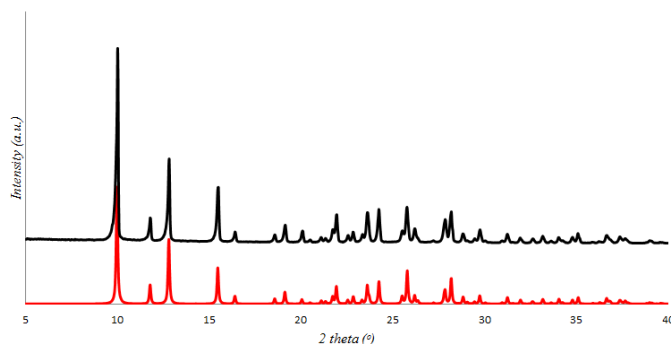


Figure 4. PXRD pattern (black) and simulated pattern from single XRD (red) for the compound

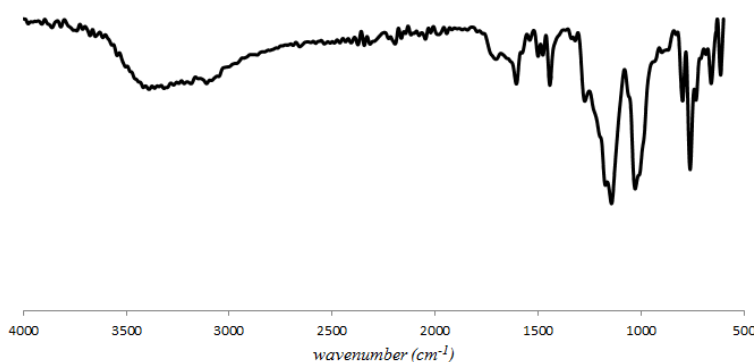


Figure 5. IR spectrum of the compound

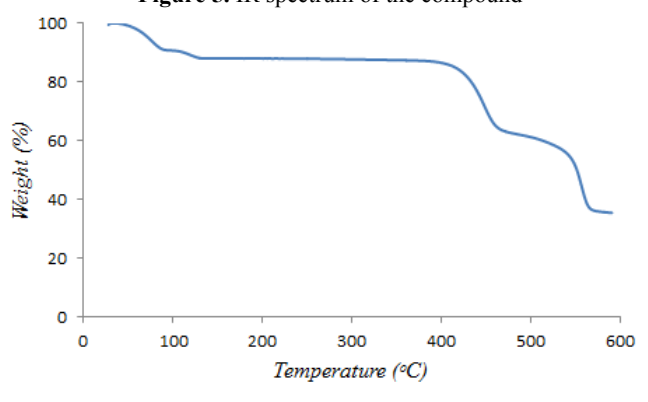


Figure 6. TGA profiles of the as-synthesized compound 1 with a heating rate of 10 °C/min

characterized by PXRD and the pattern matches the standard PXRD pattern of ZnO (hexagonal phase, space group  $P6_3mc$ , with lattice constants  $a=3.24982 \text{ \AA}$ ,  $c=1.6021 \text{ \AA}$ ,  $Z=2$ , JCPDS No. 36-1451) (Figure 7). The line broadening in PXRD together with the SEM image (Figure 8) specifies that the particles of the prepared compound are on the nanometer scale. The crystalline dimension ( $D$ ) of the sub-micrometer crystallites has been considered by the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where  $\lambda$  is the X-ray wavelength ( $1.5406 \text{ \AA}$  for Cu

K $\alpha$ ),  $\beta$  is FWHM (line broadening at half the maximum intensity) and  $\theta$  is the position of maximum diffraction peak. The crystalline dimension of the particles has been discovered to be about 45 nm which is in accordance with the SEM image that shows the particles in the nanometer range.

ZnO nanoparticles with an average diameter in the nanometer range are shown through SEM image in Figure 8.

### Conclusions

In the present study, we have synthesized and

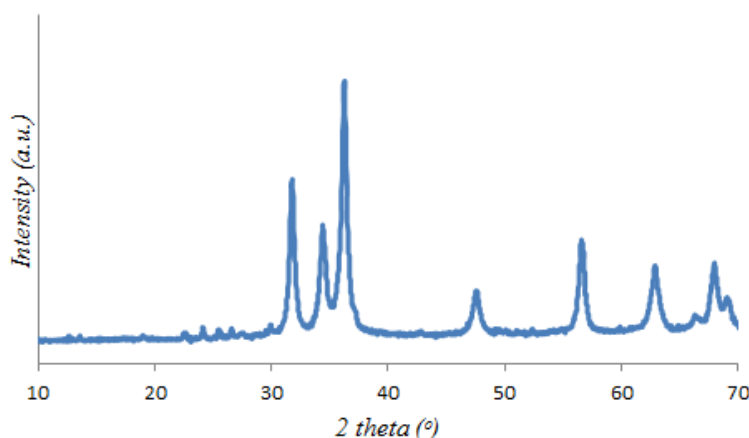


Figure 7. PXRD pattern of ZnO nanoparticles, after calcinating the coordination polymer

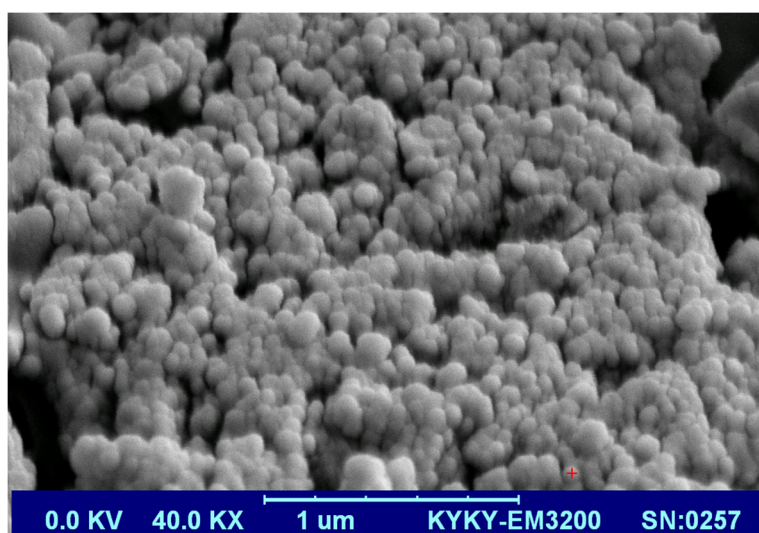


Figure 8. SEM image of ZnO nanoparticles with an average diameter in nanometer range

characterized a novel 1D coordination polymer,  $\{[\text{Zn}(2,2'\text{-bipyridine})(\text{H}_2\text{O})_2(1,5\text{-NDS})].2\text{H}_2\text{O}\}$ , which was obtained using  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the inorganic precursor and 1,5-NDS as the organic linkers. The TGA of the compound shows its thermal stability up to 400 °C. After calcinating the coordination polymer, ZnO was obtained and then characterized using PXRD and SEM.

#### Acknowledgments

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#### Supplementary Material

CCDC 914936 covers the additional crystallographic records for the prepared structure. The information may

be acquired for free through <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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