Metal-Organic Framework Derived Hybrid Materials
Effect of Charge on the Structures of Zn(II) Coordination Polymers with Triazole-carboxylate Ligands: Syntheses, Structures, and Luminescent Properties

Shaobin Miao, Xiaojuan Sun, Kexin Wang, Chunying Xu, Zhaohao Li and Zhiqiang Wang *

College of Chemistry and Chemical Engineering, and Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China; miaoshaobin@126.com (S.M.); xiaojuansunhao@163.com (X.S.); 17737465896@163.com (K.W.); xuchunying8@163.com (C.X.); lylizh@126.com (Z.L.)

* Correspondence: wzq197811@163.com; Tel.: +86-379-6861-8321

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Abstract: Three new Zn(II) coordination polymers, \([\text{Zn(L1)}_2(\text{H}_2\text{O})_2]\cdot4\text{H}_2\text{O}\) \(\text{n}\) (1), \([\text{Zn(L2)}(\text{H}_2\text{O})_2]\cdot0.5\text{H}_2\text{O}\) \(\text{n}\) (2), and \([\text{Zn}_1.5(\text{L1})(\text{o-bdc})(\text{H}_2\text{O})]\cdot0.5\text{H}_2\text{O}\) \(\text{n}\) (3) (HL1 = 3,5-di(1,2,4-triazol-1-yl)benzoic acid, H\(_2\)L2 = 5-(triazol-1-yl)isophthalic acid, o-H\(_2\)bdc = 1,2-benzenedicarboxylic acid), were successfully synthesized and characterized. Compound 1 exhibits 1D chain structure containing \([\text{Zn(L1)}_2]\) unit. Compound 2 shows a 2D plane with the ratio of Zn:L2 was 1:1 since L2 can match the positive charge of Zn(II). When L1 and o-bdc\(^{2-}\) were presented together, Zn(II) centers are linked by L1 to form 2D double layers, then o-bdc\(^{2-}\) further connected the adjacent layers to generate final 3D framework of 3. The ligand charges may play key roles in tuning the frameworks of compounds 1–3. The solid state luminescence of compounds 1–3 and all ligands have been investigated here.

Keywords: coordination polymer; bifunctional ligand; synthesis; crystal structure; luminescence

1. Introduction

As a kind of promising hybrid materials, coordination polymers (CPs) have recently attracted a great amount of research interest on account of their fascinating variety of structural patterns and unique properties, such as gas adsorption, luminescence, electrochemistry, catalysis, magnetism, and so on [1–7]. The construction of the CPs is mainly formed by two basic components, metal ions or clusters and organic linkers. Through varying metal centers and organic linkers, CPs with specific characteristics can be obtained [8–13]. But in fact, the rational design and tuned synthesis of CPs still remains a major challenge since assembly is influenced by many factors such as the coordination requirements of the metal ions and the properties of the ligands, including shape, coordination mode, and flexibility, metal-to-ligand ratio, temperature, pH, solvent, and so on [14–21]. In addition, the assembly rule must concern the charges of metal ions and organic linkers since the final CPs are electrically neutral. Unfortunately, the architectural effects induced by the variations of charges on the structures of CPs are rarely reported [22–25]. In this sense, it is still necessary to continue to explore the effect of charges on the assembly of CPs.

With these considerations in mind, we would like to herein report the syntheses and structures of three new Zn(II) CPs, \([\text{Zn(L1)}_2(\text{H}_2\text{O})_2]\cdot4\text{H}_2\text{O}\) \(\text{n}\) (1), \([\text{Zn(L2)}(\text{H}_2\text{O})_2]\cdot0.5\text{H}_2\text{O}\) \(\text{n}\) (2), and \([\text{Zn}_1.5(\text{L1})(\text{o-bdc})(\text{H}_2\text{O})]\cdot0.5\text{H}_2\text{O}\) \(\text{n}\) (3) (HL1 = 3,5-di(1,2,4-triazol-1-yl)benzoic acid, H\(_2\)L2 = 5-(triazol-1-yl)isophthalic acid, o-H\(_2\)bdc = 1,2-benzenedicarboxylic acid). Zinc(II) coordination polymers with benzoic or triazole ligands have been extensively studied [26–29]. In which the Zn(II)
centers and organic ligands are bonded together by versatile coordination interactions to give various frameworks from 1D to 3D with superior properties. Benzoic and triazole present together in the bifunctional ligands HL1 and H2L2. So the two ligands have similar shapes and coordination groups except that deprotonation of L1– and L22– exhibit different charges. The influences of ligand charges on structures of compounds 1–3 have been discussed. The fluorescent properties of compounds 1–3 and ligands have also been investigated.

2. Materials and Methods

2.1. Reagents and Instruments

All chemicals and solvents used in the syntheses were purchased commercially, and used directly without any purification process. The infrared spectra were obtained with a Nicolet Avatar-360 spectrometer using KBr pellets in the range of 4000–600 cm⁻¹. Powder X-ray diffraction (PXRD) patterns of the compounds were carried out on a Bruker AXS D8-Advanced diffractometer with Cu–Kα (λ = 1.5406 Å) radiation. The luminescent analysis was measured with a FL-4500 fluorescent spectrometer using solid samples.

2.2. Single-Crystal X-ray Diffraction

The single-crystal diffraction data for 1–3 were collected by using a Oxford Diffraction Gemini with MoKα radiation (λ = 0.71073 Å) at 290 K. The Olex 2 program was used as an interface, together with the SHELXT and SHELXL programs to solve the structures [30,31]. Atomic positions of all non-hydrogen atoms were refined with anisotropic parameters in the refinement. Positions of hydrogen atoms were located geometrically and refined using a riding model. The detailed crystallographic data for crystals 1–3 are listed in Table 1. Selected bond lengths and bond angles are provided in Table S1 (Supporting information). CCDC 1842442, 1842811, and 1842911 contain the supplementary crystallographic data for crystals in this paper. These data can be obtained free of charge via 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. Details on XRD patterns and selected bond lengths and bond angles for 1, 2, and 3 are list in supplementary content.

### Table 1. Crystallographic parameters for compounds 1–3.

<table>
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<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td><strong>Formula</strong></td>
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<td>C10H10N3O6.5Zn</td>
<td>C38H36N12O14Zn3</td>
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<td>341.58</td>
<td>1070.82</td>
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<tr>
<td><strong>Space group</strong></td>
<td>Pccn</td>
<td>I2/a</td>
<td>C2/c</td>
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<tr>
<td><strong>a (Å)</strong></td>
<td>13.3477(4)</td>
<td>13.5074(5)</td>
<td>20.5014(12)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>15.2594(6)</td>
<td>10.7712(4)</td>
<td>7.0380(7)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>13.5167(6)</td>
<td>16.3959(5)</td>
<td>26.7095(15)</td>
</tr>
<tr>
<td><strong>α (°)</strong></td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>β (°)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td><strong>γ (°)</strong></td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td><strong>V (Å³)</strong></td>
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<td>2357.45(14)</td>
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<td>4</td>
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<td><strong>µ (mm⁻¹)</strong></td>
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<td>2.121</td>
<td>1.969</td>
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<tr>
<td><strong>F(000)</strong></td>
<td>1408</td>
<td>1384</td>
<td>2160</td>
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<tr>
<td><strong>R₁, wR₂ (I &gt; 2σ(I))</strong></td>
<td>0.0368, 0.0863</td>
<td>0.0501, 0.1123</td>
<td>0.0556, 0.1334</td>
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<td><strong>R₁, wR₂ (all data)</strong></td>
<td>0.0480, 0.0905</td>
<td>0.0535, 0.1135</td>
<td>0.0617, 0.1366</td>
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<tr>
<td><strong>Goodness-of-fit (GOF) on F²</strong></td>
<td>1.074</td>
<td>1.184</td>
<td>1.186</td>
</tr>
</tbody>
</table>
2.3. Preparation of Compounds 1–3

2.3.1. Synthesis of \([\text{Zn}(\text{L}1)_2(\text{H}_2\text{O})_2]4\text{H}_2\text{O}]\) (1)

A mixture of Zn(CH₃COO)$_2$·2H₂O (44 mg, 0.2 mmol), HL1 (0.1 mmol, 25.6 mg), H₂O (10 mL), and acetonitrile (5 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for 4 days. Then the reaction mixture was naturally cooled down to room temperature, and the colorless block crystals were obtained. Yield (based on Zn): 44%. IR (KBr, cm$^{-1}$): 3109(w), 1618(m), 1534(s), 1241(w), 1048(m), 815(m), 761(s), 675(m).

2.3.2. Synthesis of \([\text{Zn}(\text{L}2)(\text{H}_2\text{O})_2]0.5\text{H}_2\text{O}]\) (2)

Compound 2 was obtained using similar method as described above, except that H₂L2 was used instead of HL1. Colorless crystals were collected with a yield of 62% based on Zn. IR (KBr, cm$^{-1}$): 3143(w), 3012(m), 1616(w), 1555(s), 1241(w), 1039(m), 852(m), 761(m), 632(s).

2.3.3. Synthesis of \([\text{Zn}_{1.5}(\text{L}1)(\text{o-bdc})(\text{H}_2\text{O})]0.5\text{H}_2\text{O}]\) (3)

A mixture of Zn(CH₃COO)$_2$·2H₂O (44 mg, 0.2 mmol), HL1 (0.1 mmol, 25.6 mg), o-H₂bdc (16.6 mg, 0.1 mmol), H₂O (10 mL), and acetonitrile (5 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 4 days. Then the reaction mixture was naturally cooled down to room temperature, and the colorless block crystals were obtained. Yield (based on Zn): 44%. IR (KBr, cm$^{-1}$): 3122(w), 1605(m), 1568(s), 1276(s), 1043(m), 845(m), 774(m), 688(s).

3. Results and Discussion

3.1. Structural Description

3.1.1. Crystal Structure of 1

Compound 1 crystallizes in orthorhombic space group Pccn. Figure 1a shows the asymmetric unit of 1, which consists of one Zn(II) atom, two L1 ligands, two coordinated water molecules, and four crystallized water molecules. Each zinc atom is surrounded by four nitrogen atoms from four different L1 ligands and two water oxygen atoms to give ZnN$_4$O$_2$ octahedron geometry. The Zn–O distance is 2.1400(18) Å, and the Zn–N distances are 2.159(2) and 2.148(2) Å, respectively. In the structure of 1, adjacent Zn(II) centers are bridged by η$^2$–κN–κN′–κL1 to obtain a 1D infinite chain (Figure 1b). The –COO$^-$ group is not involved in the coordination but is responsible for neutralizing the charge. Due to the existence of the coordinated water and lattice water molecules, there are a large number of intermolecular O–H⋯O hydrogen bonds between water molecules or between water molecules and L1 ligands in the structure of 1. By which, the 1D chains are connected into a 2D network.

![Figure 1](image-url)
3.1.2. Crystal Structure of 2

Compound 2 shows a 2D planar layer structure presenting an asymmetric unit formed by one Zn(II) atom, one L2 ligand, two coordinated water molecules, and one half lattice water (Figure 2a). The Zn(II) atom exhibits a distorted octahedron geometry with a ZnNO$_5$ coordination sphere, formed by three η$^3$-κN–κO,O$'$–κO$''$–L2 ligands and two coordinated water molecules. The equatorial positions are occupied by three oxygen atoms from two carboxyl groups and a triazole nitrogen atom, and two water oxygen atoms occupy the axial positions. The Zn–N distance is 2.117(4) Å, and the Zn–O distances are in the range of 1.975(3)–2.304(4) Å. Each L2 ligand links three Zn(II) atoms to generate a 2D layer (Figure 2b). In each layer, all L2 ligands and Zn(II) atoms are in a plane, showing the rigidity of L2. There are also exist intermolecular O–H···O hydrogen bonds in the crystal structure of compound 2, a 3D framework is constructed by which.

![Figure 2. (a) Coordination environment of Zn(II) ion in 2. (b) The 2D layer of 2.](image)

3.1.3. Crystal Structure of 3

When o-H$_2$bdc was introduced in compound 3 as a coligand with L1, an interesting 3D framework was constructed. Single crystal X-ray structural analysis reveals that the asymmetric unit of compound 3 consists of one and a half Zn(II) atoms, one L1 ligand, one o-bdc$^{2-}$ anions, one half coordinated water molecule, and one half lattice water molecule (Figure 3a). The Zn1 atom is coordinated by two oxygen atoms from two o-bdc$^{2-}$ ligands, two nitrogen atoms from two L1 ligands, and one water molecule. The coordination geometry of Zn1 can be described as a slightly distorted tetragonal pyramidal. Zn2 presents four-coordinated distorted tetrahedron geometry. The coordination positions are occupied by three oxygen atoms from two o-bdc$^{2-}$ ligands and one L1 ligand, and one nitrogen atom from the other L1 ligand. The Zn–O lengths are in the range of 1.942(4)–2.137(3) Å, while the Zn–N ones vary from 2.064(4) to 2.069(4) Å. In compound 3, adjacent Zn2 atoms are connected by L1 utilize Zn2–O1 and Zn2–N3 bonds. So novel 1D [Zn2L1]$_n$ chain formed in two directions on the ab plane (Figure 3b). Then such chains are linked into a 2D double layer network via Zn1–N6 coordination bonds (Figure 3c). In addition, neighboring 2D layers are connected by the o-bdc$^{2-}$ ligands through the Zn1–O6, Zn2–O3, and Zn2–O5 bonds to give a 3D framework (Figure 3d). There are also exist intermolecular O–H···O hydrogen bonds in 3, which stabilizes the framework.
patterns in key positions, indicating the good purity of these compounds. The use of L1 – induces a [Zn(L1)2] building unit in compound 1, the carboxyl group of L1 was not involved in the coordination because of the low metal content effected by the charge, resulting only a 1D chain. L2 carries –2 charge so satisfies the charge requirement of Zn(II), thus a 2D plane with [ZnL2] units was constructed. When L1 and o-bdc2– present together, compound 3 exhibits a 3D framework including 2D [Zn1Zn2L1]2+ layers, then the o-bdc2– extended the structure and match the charge.

3.3. Powder X-ray Diffraction (PXRD) and Luminescent Properties

Comparing the structures of compounds 1–3, it is clear that the variation of ligand charges produces profound structural changes in the networks. The use of L1– induces a [Zn(L1)2] building unit in compound 1, the carboxyl group of L1 was not involved in the coordination because of the low metal content effected by the charge, resulting only a 1D chain. L2 carries –2 charge so satisfies the charge requirement of Zn(II), thus a 2D plane with [ZnL2] units was constructed. When L1 and o-bdc2– present together, compound 3 exhibits a 3D framework including 2D [Zn1Zn2L1]2+ layers, then the o-bdc2– extended the structure and match the charge.

3.2. Effects of Ligand Charge on the Structures of the Title Compounds

Comparing the structures of compounds 1–3, it is clear that the variation of ligand charges produces profound structural changes in the networks. The use of L1– induces a [Zn(L1)2] building unit in compound 1, the carboxyl group of L1 was not involved in the coordination because of the low metal content effected by the charge, resulting only a 1D chain. L2 carries –2 charge so satisfies the charge requirement of Zn(II), thus a 2D plane with [ZnL2] units was constructed. When L1 and o-bdc2– present together, compound 3 exhibits a 3D framework including 2D [Zn1Zn2L1]2+ layers, then the o-bdc2– extended the structure and match the charge.

In order to verify the purity, the PXRD experiments were carried out at room temperature (Figures S1–S3). The simulated PXRD patterns of compounds 1–3 are consistent with their experimental PXRD patterns in key positions, indicating the good purity of these compounds.

The solid state luminescence of CPs 1–3 and the free ligands were investigated at ambient temperature. As shown in Figure 4, compounds 1, 2, and 3 reveal the emission bands centered at 445 (λex = 383 nm), 422 (λex = 341 nm), and 431 nm (λex = 373 nm), respectively. All these bands can be assigned to intraligand (π* → π or π* → n) emission [32–34]. In comparison with the emission maximum values of the free HL1 at 414 nm (λex = 356 nm), H2L2 at 398 nm (λex = 336 nm), and o-H2bdc at 407 nm (λex = 341 nm), obvious red-shifts were observed for all CPs. The red-shifts may be caused by the coordination of ligands to the center Zn(II) atoms, which can increase the conjugate degree of ligands [35].
Acknowledgments:
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Author Contributions:
1
1
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Figure 4. (a) Solid-state luminescent spectra of compound 1, 3, HL1, and o-H2bdc; (b) Solid-state luminescent spectra of compound 2 and H2L2.

4. Conclusions
In summary, three Zn(II) coordination polymers based on two similar triazole-carboxyl
bifunctional ligands have been successfully constructed. Compounds 1–3 exhibit different 1D, 2D,
and 3D structures, which may be induced by different ligand charges of L1 and L2. The luminescent
properties of the three compounds also have been studied. The results show compounds 1–3 exhibit
strong ligand-based fluorescence. This systematic investigation reveals the influences of ligand charges
on the construction and the final structures of coordination polymers. Further studies in this field are
underway in our lab.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/8/8/312/s1.
Table S1: Selected bond lengths (Å) and bond angles (°) for

Author Contributions: X.S. and K.W. synthesized the three compounds. S.M. and C.X. performed the X-ray
structure determination and analyzed the results. Z.L. and Z.W. wrote the paper.

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Conflicts of Interest: The authors declare no conflicts of interest.

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[CrossRef]


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