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Auxiliary ligand-directed structural variation of the Zn(II)–1,4-bis(imidazol-1-yl)benzene net: synthesis, characterization, and luminescence

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In this article, two different anionic ligands, 3,4-oxybis(benzoate) (bopH₂) and sulfate, have been employed as co-ligands to perform a comparison on the structures of coordination polymers based on the Zn(II)–rigid 1,4-bis(imidazol-1-yl)benzene (bib) net. Two new coordination polymers, {Zn(bib)(bop)}_∞ (**1**) and {Zn(bib)(SO₄)}_∞ (**2**), were synthesized from hydrothermal reactions and characterized by elemental analyses, IR and single-crystal X-ray diffraction. Complex **1** contains two unique 2-D layers, which are further interpenetrated to form a two-fold 2-D → 2-D framework. However, **2** consists of a 3-D structure with pcu topology constructed by sulfates as pillars. The structural difference of **1** and **2** indicates that size of the ancillary ligands play important roles in formation of such coordination architectures. Thermal and fluorescence properties of **1** and **2** are also investigated in the solid state.

Keywords: Metal–organic framework; Rigid ligand; Ancillary ligand; Crystal structure; Fluorescence

1. Introduction

Coordination polymers, especially metal–organic frameworks (MOFs), have attracted attention for their intriguing topologies and potential applications in magnetism, adsorption, optical devices, and catalysis [1–8]. For self-assembly of MOFs, many synthetic strategies have been applied, with a mixed-ligand approach one of the most effective synthetic strategies [9–12]. To tune the mixed-ligand framework, the primary ligand must be judiciously selected [13]. As an important rigid N-donor, 1,4-bis(imidazol-1-yl)benzene (bib) with a long spacer between coordinated nitrogen atoms is an efficient building block to form MOFs [14]. Mixed-ligand architectures based on rigid imidazole ligands have been rarely studied [12, 15].

The role of organic carboxylate and inorganic anions can be illustrated in terms of differences in shape, size, and flexibility [16, 17]. Organic carboxylates and inorganic anions may be counteranions, however, the coordination behavior in determining

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assembly of MOFs are very different [18]. Therefore, we selected 3,4-oxybis(benzoate) (bopH₂) and sulfate as ancillary ligands to investigate the effect of the different anions on the formation of complexes with 1,4-bis(imidazol-1-yl)benzene ligand.

Coordination polymers containing metal ions with a d¹⁰ configuration are potential materials for optical applications [19]; organic ligands with hetero-aromatic rings are of interest in development of fluorescent materials [10]. Herein, we describe the syntheses and structures of two new Zn(II) complexes, {Zn(bib)(bop)}_∞ (**1**) and {Zn(bib)(SO₄)}_∞ (**2**). Thermal properties and the fluorescence of **1** and **2** are also investigated.

2. Experimental

2.1. Materials and general methods

All solvents and reagents for syntheses were commercially available and used without purification. The ligand 1,4-bis(imidazol-1-yl)benzene (bib) [20] was synthesized by literature method and characterized by FT-IR spectra and ¹H NMR. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric data were collected on a Pyris Diamond thermal analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

2.2. Syntheses

2.2.1. {Zn(bib)(bop)}_∞ (1**).** A mixture of Zn(NO₃)₂ · 6H₂O (0.5 mmol, 148 mg), NaOH (1 mmol, 40 mg), BOPH₂ (0.5 mmol, 128 mg), and 1,4-bis(imidazol-1-yl)-benzene (0.5 mmol, 108 mg) in 16 mL solvent (H₂O : CH₃OH = 2 : 1) was sealed in a Teflon-lined autoclave and heated to 160°C for 4 days. After the autoclave was cooled to room temperature at 10°C h⁻¹, pale yellow block crystals suitable for single crystal X-ray crystallographic analysis were obtained. The crystals were rinsed with ethanol (8 mL × 3) and dried in air. Yield: 31% based on Zn. Anal. Calcd for C₂₀H₁₃N₂O₅Zn: C, 56.29; H, 3.07; N, 6.56%. Found (%): C, 56.27; H, 3.09; N, 6.53. IR (KBr, cm⁻¹): 3140m, 2355w, 1602s, 1523s, 1358s, 1224s, 1069s, 956s, 874 m, 787s, 657s, 544w.

2.2.2. {Zn(bib)(SO₄)}_∞ (2**).** A mixture of ZnSO₄ · 7H₂O (0.5 mmol, 143 mg) and 1,4-bis(imidazol-1-yl)-benzene (0.5 mmol, 108 mg) in 15 mL solvent (H₂O : CH₃OH = 2 : 1) was sealed in a Teflon-lined autoclave and heated to 165°C for 4 days. After the autoclave was cooled to room temperature at 10°C h⁻¹, colorless block crystals suitable for single crystal X-ray crystallographic analysis were obtained. The crystals were rinsed with ethanol (5 mL × 3) and dried in air. Yield: 41% based on Zn. Anal. Calcd for C₂₄H₂₀N₈O₄SZn (%): C, 49.53; H, 3.46; N, 19.25. Found (%): C, 49.55; H, 3.44; N, 19.26. IR (KBr, cm⁻¹): 2801w, 2711w, 2364s, 1579s, 1506s, 1359m, 1303m, 1255w, 1052s, 826s, 648 m.

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	1	2
Empirical formula	C ₂₀ H ₁₃ N ₂ O ₅ Zn	C ₂₄ H ₂₀ N ₈ O ₄ SZn
Formula weight	426.71	581.94
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> ₂ / <i>c</i>
Unit cell dimensions (Å, °)		
<i>a</i>	10.276(2)	19.756(4)
<i>b</i>	11.448(2)	9.754(2)
<i>c</i>	17.029(3)	11.908(2)
α	85.27(3)	90
β	86.55(3)	97.09(3)
γ	63.39(3)	90
Volume (Å ³), <i>Z</i>	1784.38, 4	2277.1(8), 4
Calculated density (g cm ⁻³)	1.588	1.697
Absorption coefficient (mm ⁻¹)	1.412	1.224
<i>F</i> (000)	868	1192
Reflections collected/unique	6274/4580	2603/2188
Goodness-of-fit on <i>F</i> ²	1.074	1.104
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a = 0.0547, <i>wR</i> ₂ ^b = 0.1033	<i>R</i> ₁ ^a = 0.0666, <i>wR</i> ₂ ^b = 0.1792

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; ^b wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}.$$

2.3. X-ray crystallography

All diffraction data were collected using a Rigaku MM-007/Saturn 70 with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). SAINT was used for integration of the diffraction profiles [21]. The structures were solved by direct methods with *SHELXS-97* and Fourier techniques and refined by full-matrix least-squares on *F*² with *SHELXL-97* [22, 23]. Metals in each complex were located from *E*-maps and other non-hydrogen atoms in successive difference Fourier syntheses and refined with anisotropic thermal parameters on *F*². Hydrogen atoms of ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. All crystal data and structure refinement details for the two complexes are given in table 1. Relevant bond distances and angles are listed in table 2.

3. Results and discussion

3.1. Description of crystal structures

3.1.1. Structural analysis of {Zn(bib)(bop)}_∞ (1). Single-crystal X-ray diffraction analysis reveals that **1** is a two-fold interpenetrating array. There are two crystallographically unique 2-D networks in **1**. The coordination environment of Zn(II), shown in figure 1, is four-coordinate, tetrahedral, supplied by one nitrogen from a bib with bond distances of 2.028(3) [Zn1–N1] and 2.004(3) Å [Zn2–N2] and three oxygen atoms belonging to three separated bop co-ligands [the bond lengths of Zn–O range from 1.929(3) to 1.987(3) Å].

In **1**, all bop ligands are bridging: bridging mono-monodentate and bridging bi-monodentate. Therefore, bop ligands with the different coordination modes bridge Zn₂ units to form an infinite 1-D band chain (figure 2a). A 25-member circuit exists

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

1			
Zn(1)–N(1)	2.028(3)	Zn(2)–O(5)	1.954(3)
Zn(2)#1–O(6)	1.929(3)	Zn(2)–N(2)	2.004(3)
Zn(1)#2–O(2)	1.987(3)	Zn(1)–O(3)	1.929(3)
Zn(1)#3–O(1)	1.965(3)	Zn(2)#4–O(4)	1.984(3)
Zn(1)–O(1)#1	1.965(3)	O(3)–Zn(1)–N(1)	122.83(12)
O(3)–Zn(1)–O(1)#1	115.75(12)	O(1)#1–Zn(1)–N(1)	97.68(12)
O(3)–Zn(1)–O(2)#2	108.19(11)	O(2)#2–Zn(1)–N(1)	100.35(12)
O(1)#1–Zn(1)–O(2)#2	110.71(12)	O(6)#3–Zn(2)–N(2)	118.04(14)
O(6)#3–Zn(2)–O(5)	110.96(12)	O(5)–Zn(2)–N(2)	109.36(13)
O(6)#3–Zn(2)–O(4)#4	110.10(12)	O(4)#4–Zn(2)–N(2)	91.41(12)
O(5)–Zn(2)–O(4)#4	115.93(12)		
2			
Zn(1)–O(1)	2.092(3)	Zn(1)–N(1)	2.230(4)
Zn(1)–N(2)	2.236(4)	O(1)–Zn(1)–N(1)#2	88.95(17)
O(1)–Zn(1)–N(2)#2	93.09(16)	O(1)–Zn(1)–N(1)	91.05(17)
O(1)#1–Zn(1)–N(2)#2	86.91(16)	N(1)#1–Zn(1)–N(2)#2	83.18(14)
N(1)–Zn(1)–N(2)#2	96.82(14)	S(1)–O(1)–Zn(1)	163.8(3)

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

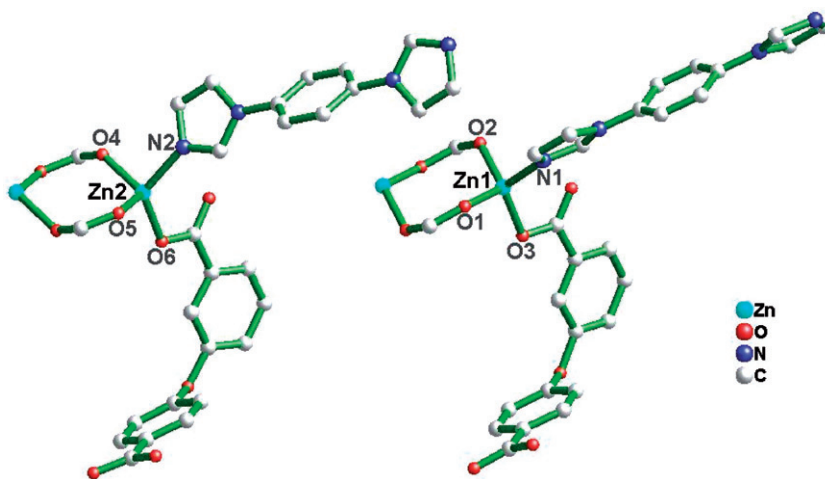


Figure 1. Coordination environment of Zn(II) in **1**. H atoms have been omitted for clarity.

connecting in a Zn/bop/Zn fashion. Each bib is a bridging ligand coordinating to two Zn(II) ions further linking adjacent 1-D chains to a 2-D network with (4,4) topology (figure 2b). Since the single 2-D layer contains large meshes, $8.20 \times 10.09 \text{ \AA}$ (atom-to-atom distance), in order to stabilize the framework, two unique 2-D layers are further extended into a two-fold 2-D \rightarrow 2-D parallel interpenetrating layer (figure 2c).

3.1.2. Structural analysis of $\{\text{Zn}(\text{bib})(\text{SO}_4)\}_\infty$ (2**).** To investigate the influence of the size of ancillary ligand on the structure of complex, sulfate instead of bopH₂ was used and a new complex, **2**, was obtained. Single-crystal X-ray diffraction analysis reveals

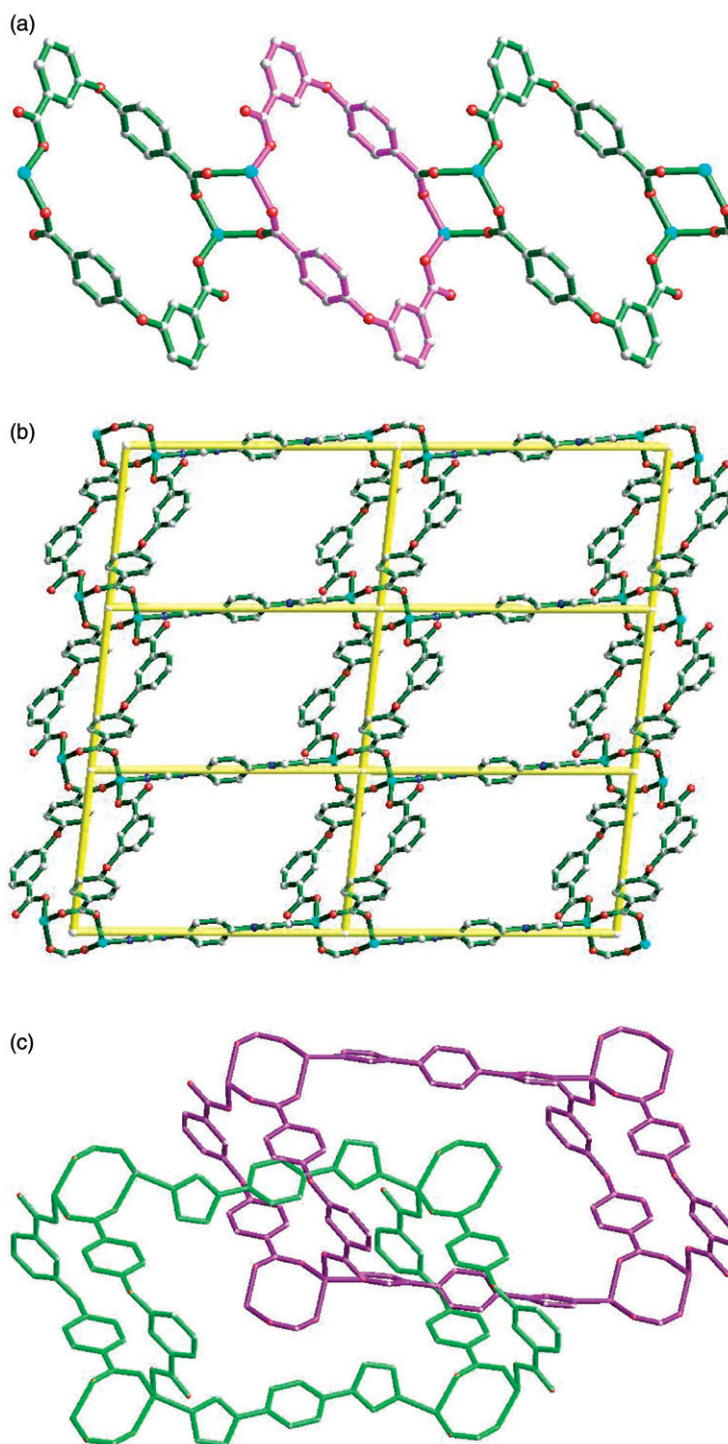


Figure 2. View of (a) the 1-D band structure with a 25-member ring, (b) the 2-D network with (4,4)-connected topology, and (c) the catenation of two unique layers in **1**.

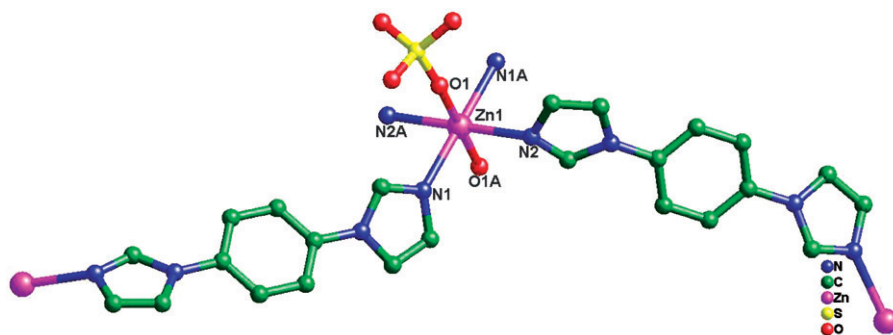


Figure 3. Coordination environment for Zn(II) in **2**. H atoms were omitted for clarity. Symmetry code A: $-x+2, -y, -z$.

that **1** crystallizes in the monoclinic space group C_2/c . Each Zn(II) coordinates four nitrogen atoms of two imidazolyl rings of different bib ligands and two oxygen atoms of two sulfates in a distorted octahedral geometry. The coordination environment of Zn(II) in **2** is clearly different from **1**, probably as a result of size from the anionic ligands. The length of Zn–O/N bonds are 2.092(3)–2.236(4) Å (figure 3).

In **2**, bib takes a μ_2 -bidentate coordination bridging Zn(II) to form an infinite 2-D 4(4) network (figure 4a). However, sulfates are bridging bidentate linking adjacent Zn(II) [Zn...Zn = 5.954 Å] to form a unique 1-D zigzag chain (figure 4b). Finally, sulfates act as pillars to extend the 2-D nets to the 3-D structure. In order to better understand the final architecture, the framework of **2** can be considered a uni-nodal six-connected network topology. As illustrated in figure 4(c), Zn(II) can be viewed as a six-connected node connecting four bib ligands and two sulfates, resulting in the formation of a cubic framework with pcu topology (figure 4c and d). The short Schläfli symbol is $4^{12}.6^3$.

Among previous studies, organic ligands with imidazole groups have been widely studied [24, 25]. However, the research on mixed-ligand architectures based on rigid 1,4-bis(imidazol-1-yl)benzene ligand is relatively rare. Compared with previously reported related complex [Zn(μ -Me₂biim)Cl₂]_n (Me₂biim = *N,N'*-dimethyl-2,2'-biimidazole) [24], in which a 1-D zigzag chain was obtained, **1** and **2** are quite different. In contrast to the Me₂biim, 1,4-bis(imidazol-1-yl)benzene is a good candidate for bridging ligand with the larger spacer length and structural rigidity. Thus, 1,4-bis(imidazol-1-yl)benzene has more probability to form high-dimensional architectures among coordination polymers.

3.2. Thermogravimetric analysis

To examine the thermal stability of **1** and **2**, thermal behavior was studied by thermal gravimetric analyses (TGA). TGA of **1** and **2** were performed under N₂ with a heating rate of 10 K min⁻¹ (Supplementary material). Complex **1** is stable to ca 210°C. The TGA curve of **1** shows that the first weight loss takes place at 220–360°C for loss of bib (obsd: 30.3% and Calcd 30.5%). Then, almost no weight loss is observed until 380°C at which temperature it starts to lose bop²⁻ (obsd: 34.61% and Calcd 34.72%) and the final residue is ZnO (found: 35.09% and Calcd 34.82%). **2** is stable to ca 310°C and

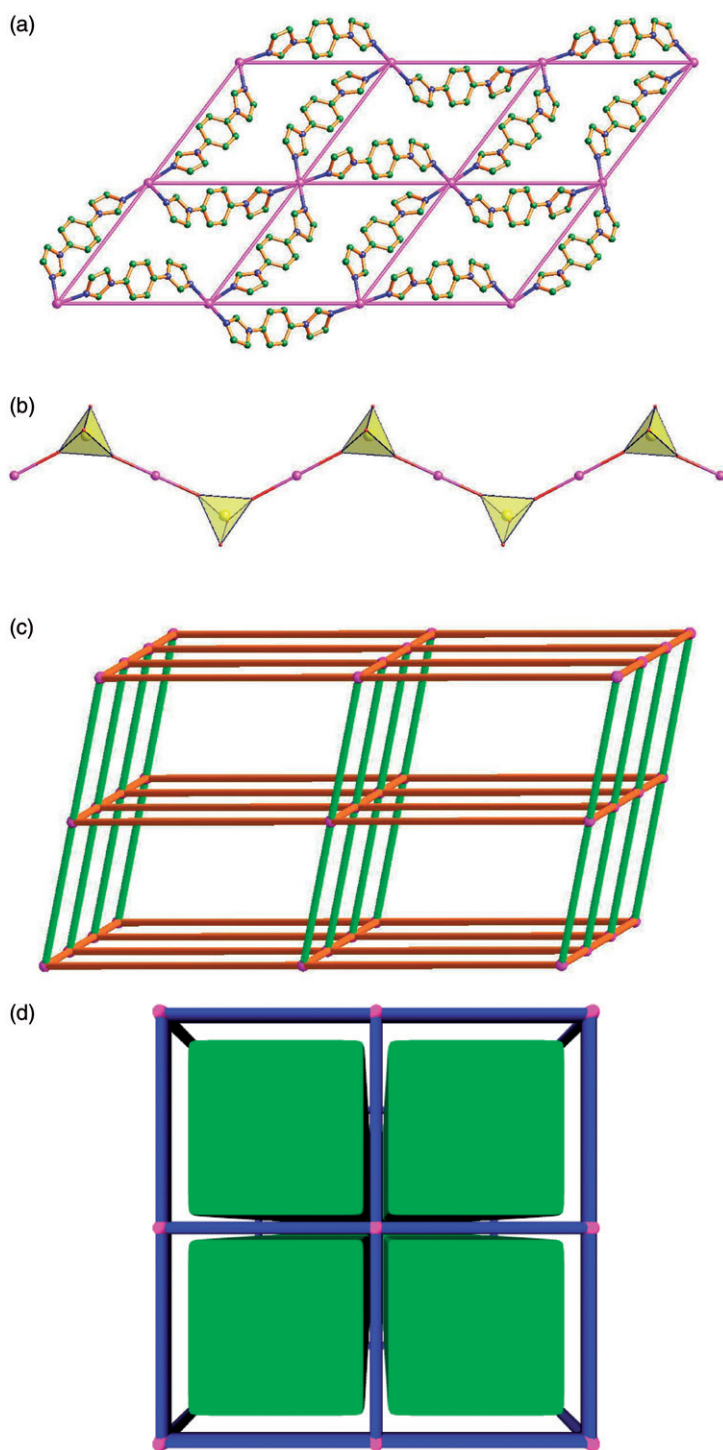


Figure 4. View of (a) the 2-D network formed by Zn(II) and bib ligand, (b) the 1-D zigzag chain linked by SO_4^{2-} , (c) the six-connected 3-D network with pcu topology, and (d) the tiling of the framework in **2**.

weight loss at 420°C is due to the decomposition of the overall framework (Supplementary material) as the sheet starts to decompose along with loss of bib (obsd: 69.25% and Calcd 69.27%), and the final residue is ZnSO₄ (found: 27.72% and Calcd 27.66%).

3.3. Fluorescence of **1** and **2**

Metal-organic coordination complexes constructed from d¹⁰ metals and conjugated organic ligands are promising candidates for hybrid photoactive materials with potential applications such as light-emitting diodes [26]. The solid-state luminescent emission spectra of **1**, **2**, and bib were studied at room temperature. As shown in Supplementary material, the emission of bib shows a peak at 293 upon 288 nm excitation, which is ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. Compared with luminescence of bib, the emissions of **1** ($\lambda_{em} = 390$ nm, $\lambda_{ex} = 320$ nm) and **2** ($\lambda_{em} = 397$ nm, $\lambda_{ex} = 320$ nm) are neither metal-to-ligand charge transfer nor ligand-to-metal transfer since Zn(II) is difficult to oxidize or reduce [27]. Thus, they may be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) emissions. Emission spectra for **1** and **2** exhibit no red-shift with respect to free bib, ascribed to deprotonation of bib and coordination of bib to Zn(II) [28].

4. Conclusions

Two new coordination polymers, {Zn(bib)(bop)}_∞ (**1**) and {Zn(bib)(SO₄²⁻)}_∞ (**2**), have been isolated with different auxiliary ligands. Complex **1** is a two-fold 2-D → 2-D framework. Complex **2** consists of a 3-D structure with pcu topology. The results reveal that the size of anionic ligands can affect formation of complexes. The fluorescence properties of **1** and **2** indicate their potential application in photoactive materials.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 861947 and 861948 for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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