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The Structure and Property of Two Different Metal-Organic Frameworks Based on N/O-Donor Mixed Ligands

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Abstract: Two different metal-organic frameworks (MOFs) [Cd₂(AZN)(HAZN)(btc)(Hbtc)·4H₂O]·2H₂O (**1**), and [Zn₃(AZN)₂(btc)₂·4H₂O] (**2**) were synthesized by the reactions of different metal salts with mixed ligands of 1-(4-(1H-imidazol-5-yl)phenyl)-1H-1,2,4-triazole (AZN) and trimesic acid (H₃btc). The different metal centers in the reaction condition have important impact on the resulting structures of MOFs **1** and **2**. Compound **1** is a one-dimensional (1D) chain structure, while **2** features a three-dimensional (3D) framework with 3-fold interpenetration topology of Point (Schläfli) symbol of (6·8²)₄(6²·8²·10²). Furthermore, the luminescent properties have been studied for MOFs **1** and **2**.

Keywords: coordination polymers; characterization; luminescent property



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1. Introduction

Metal-organic frameworks (MOFs) is a class of novel crystalline metal–organic hybrid materials, which has received considerable attention in recent decades, on one hand, because of their intriguing structures, and on the other hand, due to their potential applications in chemical probe, gas storage, luminescence, photovoltaic conversion, heterogeneous catalysis, and so on [1–5]. Generally speaking, the desired function of MOFs are mainly determined by their structure. For example, in order to obtain desirable functional materials for gas storage, it is a primary principle that porous MOFs with a stable structure and high surface area should be achieved. Moreover, the precise modification of organic linkers and metal ions can also effectively benefit the enhance the adsorption ability and selectivity of for diverse gas [6,7]. Luminescent MOFs have gradually emerged as effective candidates for fluorescence sensing materials due to their good optical absorption and electron transport properties [8,9]. Recently, some MOFs have been widely employed as luminescent sensors for heavy metal ions and organic pollutant detection, with high sensitivity and selectivity [10,11]. Commonly, the MOFs consist of organic ligands and metal ions, that is, the successful construction of MOFs involves an understanding of how organic ligands are designed. Generally, the multiple N/O-donor ligands are the most important candidates in this space as the N/O atoms possess a favorable coordinated ability with metal atoms. Therefore, the organic compounds possessing N or O-donor coordination sites are two types of the important ligands, which synthesize diverse MOFs due to their strong affinities with metal atoms [12–15]. For example, 1,2,4-triazole and its derivatives are effective organic compounds, and serve as N-donor ligands links with metal ions, thereby benefiting the construction for functionalized MOFs [16]. In addition to the N-donor ligands, carboxylic acids are extensively employed desired coordination polymers, due to their varied coordination modes for carboxylic group. However, other important

factors to the resulting structures of MOFs, including reaction temperature, solvent, coordination geometry of the metal, pH value, and counteranion, metal-to-ligand ratio [17–20]. Therefore, scientists face challenges in developing controllable synthesis of proposed compounds. It should be mentioned that the different coordination natures of N- or O-donor ligands can effectively meet the geometric configuration of metal centers. In this context, the mixed N/O-donor ligands strategy can be employed for the construction of desired MOFs. Recently, Chen group have designed the multi-N donor ligand 1-(4-(1H-imidazol-5-yl)phenyl)-1H-1,2,4-triazole, which potentially have diverse coordination modes due to the favorable multi-N coordination ability with metal atoms. Moreover, considering their good compatibility for the mixed multi-N and carboxylic acid ligands, the group have synthesized a series of various MOFs with good properties [21]. As an extension of this work, we use the N-donor 1-(4-(1H-imidazol-5-yl)phenyl)-1H-1,2,4-triazole (AZN) ligand together with trimesic acid (H₃btc) as mixed ligands to construct novel MOFs. We report the structures and property of two MOFs of [Cd₂(AZN)(HAZN)(btc)(Hbtc)·4H₂O]·2H₂O (**1**), and [Zn₃(AZN)₂(btc)₂·4H₂O] (**2**) by reactions of different metal salts based on N/O donor mixed system of AZN and H₃btc.

2. Materials and Methods

2.1. Materials and Techniques

All reagents were obtained from commercial sources, except for AZN ligand, which was obtained according to the literature [22]. Elemental analyses were carried out on an Elementar Vario EL III elemental analyzer. PXRD patterns were recorded on a Bruker D2 Phaser diffractometer with CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation. Luminescent tests were carried using HORIBA FluoroMax-4 fluorescence spectrophotometer.

2.2. Synthesis of [Cd₂(AZN)(HAZN)(btc)(Hbtc)·4H₂O]·2H₂O (**1**)

The mixed compounds of cadmium nitrate tetrahydrate (0.05 mmol, 0.015 g), 1-(4-(1H-imidazol-5-yl)phenyl)-1H-1,2,4-triazole (AZN, 0.05 mmol, 0.011 g), and Trimesic acid (0.1 mmol, 0.016 g) was placed in 25 mL Teflon-lined stainless steel vessel and stirred in 15 mL H₂O for 30 min. Then, the mixture reacted at 120 °C for 48 h. After being cooled, colorless crystals of **1** were obtained (Yield: 72%). Elemental analysis calcd (%) for C₄₀H₃₈N₁₀O₁₈Cd₂: C 41.01, H 3.27, N 11.96; found: C 40.95, H 3.35, N 12.08. IR (ν/cm^{-1}): 3448 (w), 3143 (m), 1720 (m), 1628 (s), 1529 (s), 1488 (m), 1376 (m), 1351 (s), 1268 (w), 1120 (w), 1072 (m), 948 (w), 837 (m), 821 (m), 790 (m), 649 (m), 611 (w), 520 (w), 492 (w), 421 (m).

2.3. Synthesis of [Zn₃(AZN)₂(btc)₂·4H₂O] (**2**)

MOF **2** was prepared using a similar procedure as MOF **1** by changing the cadmium nitrate tetrahydrate to zinc nitrate hexahydrate (0.1 mmol, 0.019 g) (Yield: 65%). Elemental analysis calcd (%) for C₄₀H₃₂N₁₀O₁₆Zn₃: C 43.48, H 2.92, N 12.68; found: C 43.55, H 3.05, N 12.72. IR (ν/cm^{-1}): 3461 (m), 3389(m), 3128 (m), 2859 (s), 1641 (s), 1580 (s), 1548 (s), 1488 (s), 1410 (m), 1359 (m), 1271 (m), 1180 (m), 1192 (w), 1129 (s), 1080 (m), 969 (m), 838 (m), 818 (m), 786 (w), 679 (m), 648 (w), 629 (m), 528 (w), 459 (m).

2.4. Crystallographic Data Collection and Refinements

The data collection for MOFs **1** and **2** were performed on a Rigaku Saturn 724 CCD diffractometer (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$). All structures were integrated and refined by using the SHELXS-97 [23–25]. The parameters are listed in Table 1. CCDC- 2,102,480 and 2,102,481 for MOFs **1** and **2**.

Table 1. Crystallographic data for MOFs 1 and 2.

	1	2
Formula	C ₄₀ H ₃₈ N ₁₀ O ₁₈ Cd ₂	C ₄₀ H ₃₂ N ₁₀ O ₁₆ Zn ₃
Formula weight	1171.60	1104.87
Temperature/K	296(2)	296(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	7.3281(9)	27.035(3)
<i>b</i> /Å	17.205(2)	12.1481(15)
<i>c</i> /Å	18.992(2)	14.9250(18)
α /°	64.7330(10)	90
β /°	88.3760(10)	116.9100(10)
γ /°	80.2420(10)	90
<i>V</i> (Å ³)	2131.5(4)	4371.0(9)
<i>Z</i> , <i>D</i> _{calc} /(Mg/m ³)	2, 1.826	4, 1.679
<i>F</i> (000)	1176	2240
θ range/°	2.13–27.49	1.69–27.50
Reflections collected	17,647	14,185
Independent reflections	9507	4924
Goodness-of-fit on <i>F</i> ²	1.003	1.029
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0248	0.0355
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.0617	0.1006

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \sqrt{\sum w(|F_o|^2 - |F_c|^2)|^2} / \sum w(F_o)^2$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

3. Results

3.1. Structural Descriptions

3.1.1. Structure of [Cd₂(AZN)(HAZN)(btc)(Hbtc)·4H₂O]·2H₂O (1)

In this study, MOF 1 crystallized in the triclinic space group *P* -1. Figure 1 shows that the asymmetric unit includes two Cd(II) atoms, one neutral AZN molecule, one protonated HAZN⁺, one completely deprotonated btc³⁻, one partly deprotonated Hbtc²⁻, four coordinated H₂O molecules and two lattice H₂O molecules (Table 1). In the asymmetric unit, two distinct Cd(II) atoms and one protonated HAZN⁺ show a positive five nuclear charge number, while one completely deprotonated btc³⁻ together with one partly deprotonated Hbtc²⁻ show five negative charges. In this context, the complex is neutral molecules. The Cd1 ion is five-coordinated surrounding by one nitrogen atom from AZN molecule, two carboxylic oxygen atoms from one $\mu_1-\eta^1:\eta^0$ carboxyl group of two carboxyl groups and two oxygen atoms from two distinct coordinated H₂O molecules, forming a distorted trigonal bipyramidal configuration. The Cd2 atom lies in the distorted octahedral coordination environment with NO5 donor set. Cd2 atom coordinates with O3A atom and O11, O12 atoms of the carboxyl group from one distinct triacid ligand and N6 atom from AZN ligand in the equatorial plane, and two O atoms from two coordinated water molecules occupies the axial positions with O15–Cd2–O16 angle of 172.93(6)°. The Cd–O bonds range from 2.2232(14) to 2.5657(15) Å, while the bond angles vary from 52.85(5) to 172.93(6)° (Table S1). In this structure, triacid carboxylate ligands coordinate with Cd(II) atoms to generate one-dimensional (1D) chain structure, while the AZN ligand just as a terminal ligand to coordinated with Cd(II) metal centers (Figure 2). Interestingly, the molecules of btc³⁻ includes multi-O-donor atoms from the carboxyl groups and AZN ligands possess multi-N atoms, both of which can easily be employed as receptors of hydrogen bond. Therefore, the interaction arising from the hydrogen bonds extend to the adjacent 1D chain into three-dimensional (3D) supramolecular structure (Figure S1).

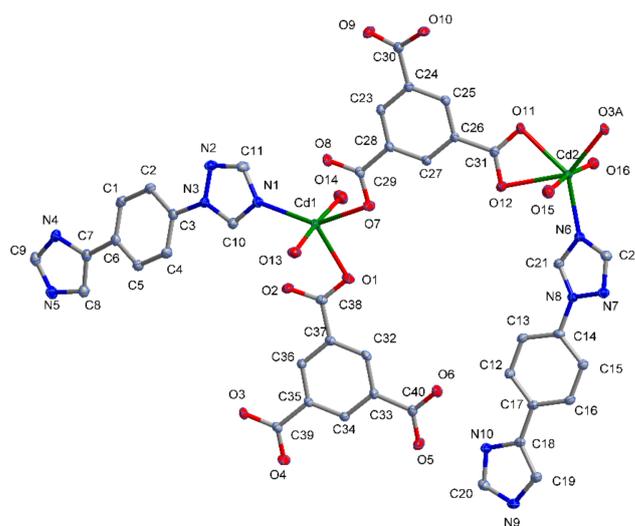


Figure 1. The Cd(II) atoms coordination environment in **1**.

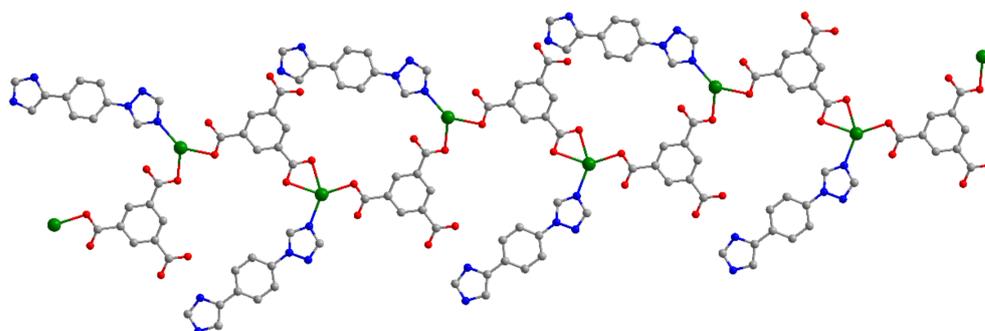


Figure 2. 1D chain structure of **1**.

3.1.2. Structure of $[\text{Zn}_3(\text{AZN})_2(\text{btc})_2 \cdot 4\text{H}_2\text{O}]$ (**2**)

A new MOF **2** was obtained when the different metal salt of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ replaced the $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in the reaction of **1**. X-ray crystallographic analysis showed that MOF **2** is monoclinic space group $C2/c$ (Table 1). From the coordination environment in **2**, the asymmetric unit has two different Zn(II) atoms (Figure 3). Zn1 is four-coordinated by two N atoms (N1 and N1A) from two AZN ligands, and two O atoms (O1 and O1A) from two distinct btc^{3-} ligands, forming the distorted tetrahedral coordination environment. The Zn1-N and Zn1-O distances are 2.003(2) and 1.9074(19) Å. Zn2 with a NO_5 donor set is coordinated by three oxygen atoms (O6, O3C and O4C) from two different btc^{3-} ligands, two O atoms (O7 and O8) from two water molecules, and one N atom (N3B) from AZN to complete a distorted octahedral geometry. The Zn2-O distances are in range of 1.9940(17)–2.198(3) Å and the Zn2-N distances is 2.057(2) Å, respectively, while coordinated bond angles around Zn2 range from 60.56(8) to 174.31(9)° (Table S1). In MOF **2**, the H_3btc ligands are completely deprotonated to be btc^{3-} , and act as 3-connected nodes to coordinate with three Zn(II) ions through its each carboxylate group in a $\mu_1\text{-}\eta^1\text{:}\eta^0$ -monodentate or $\mu_1\text{-}\eta^1\text{:}\eta^1$ -chelating coordination modes, producing a 1D chain (Figure 4). As a return, the Zn(II) ions are linked by AZN and btc^{3-} , which give rise to the complicated 3D framework, where 1D square channels with a pore diameter approximately 5.8 Å exist in the single 3D framework (Figure 5). Topological method can be used to analysis the framework. Each btc^{3-} ligand links three Zn(II) atoms, and Zn1 atom links two btc^{3-} ligands and two Zn(II) atoms by two linear AZN ligands, while each Zn2 connects two btc^{3-} ligands and one Zn(II) atom by one linear AZN ligand. In this context, the Zn1, Zn2, btc^{3-} , and AZN are considered as 4-, 3-, 3-, and 2-connected nodes, respectively, therefore, the resulting framework can be simplified as a trinodal (3, 4)-connected nor-3,4-C2/m net with its Point (Schläfli) symbol of $(6\cdot 8^2)_4(6^2\cdot 8^2\cdot 10^2)$ (Figure 6) [26]. As the single 3D framework has 1D square channels with

a pore diameter approximately 5.8 Å, it allows other two similar framework to interpenetrate in the channels, and as a result, the 3D networks of **2** interlock each other, forming a 3-fold interpenetration networks (Figure 7). It should be mentioned that both of the MOF **2** and the reported structure of $[\text{Co}_3(\text{L})_2(\text{BTC})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ crystallize in the same monoclinic $C2/c$ space group with similar cell parameters (Table 1), they are isomorphous and isostructural as confirmed by X-ray crystallographic analysis [21]. The reported compound of $[\text{Co}_3(\text{L})_2(\text{BTC})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ has the same composition constructed by the mixed N/O-donor ligands, but with different metal centers. However, the different Zn(II)/Co(II) metal centers have the same coordination configuration, and both of them act as 3, 4-nodes, which are further extended by the mixed ligands to form (3,4)-connected nor-3,4-C2/m net with its Point (Schläfli) symbol of $(6 \cdot 8^2)_4(6^2 \cdot 8^2 \cdot 10^2)$. But for the compound **1** built from the same N/O mixed ligands in this study, the metal Cd(II) centers show different coordination configurations, which result in different structures. Certainly, the different composition can affect the resulting structures. The reported MOF of $[\text{Co}_3(\text{L})_2(\text{OBTC})_2(\text{H}_2\text{O})_2]$ built from AZN and the isomer H_3OBTC of H_3btc [21], the quite different coordination modes of OBTC^{3-} make distinct structures for these two Co-based compounds.

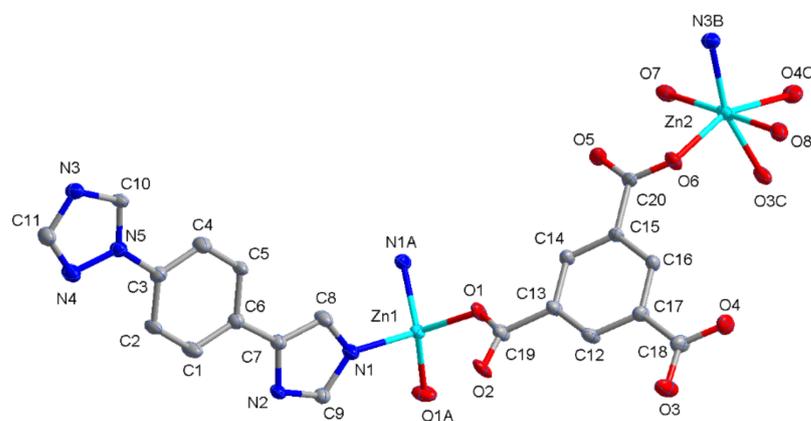


Figure 3. The Zn(II) atom coordination environment in **2**.

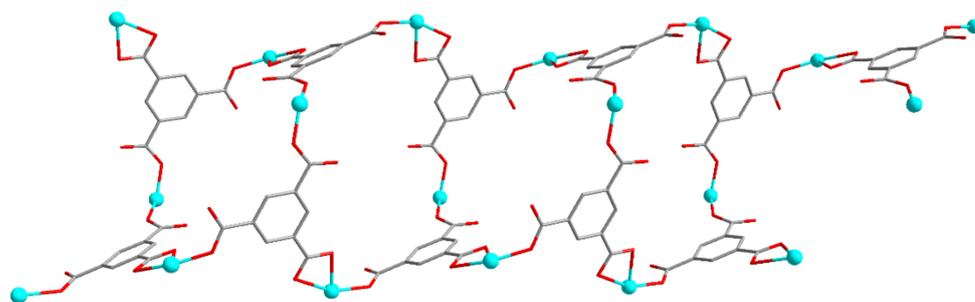


Figure 4. 1D chain structure built from the Zn-carboxylate chain in **2**.

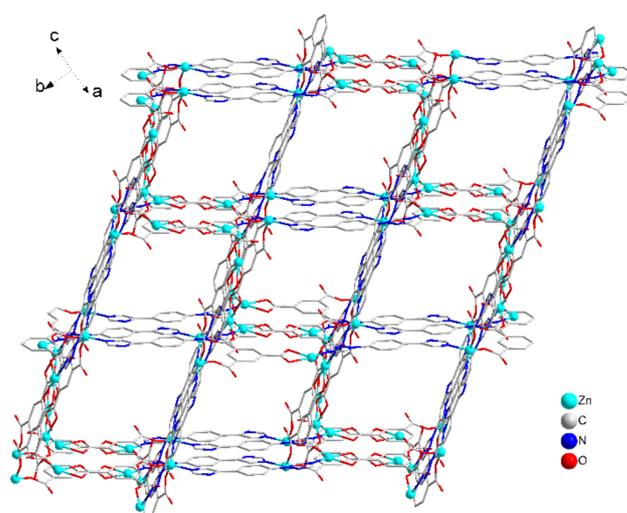


Figure 5. 3D structure with 1D void channels.

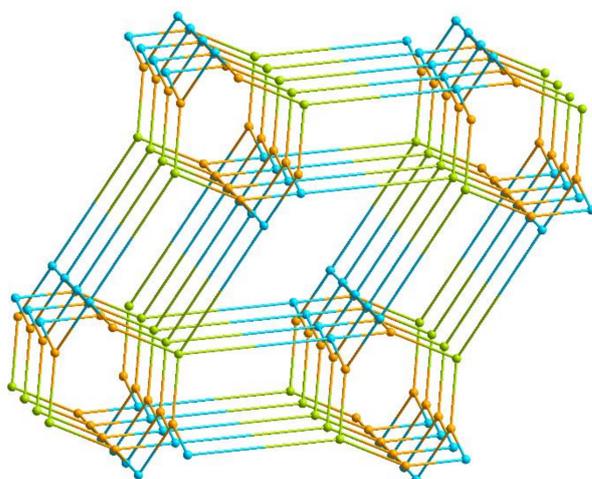


Figure 6. Three-dimensional topological structure with its Point (Schläfli) symbol of $(6-8^2)_4(6^2-8^2-10^2)$.

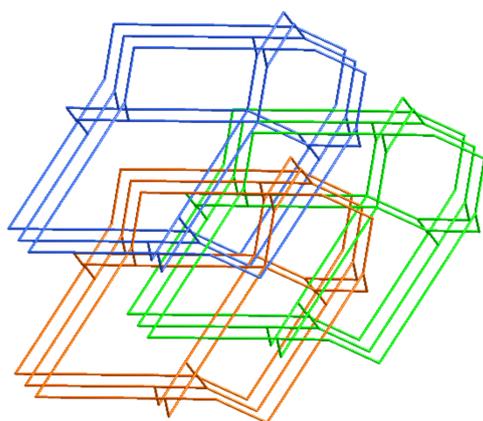


Figure 7. Three-fold interpenetrating net of 2.

3.2. Thermal Analyses and X-ray Powder Diffraction Analyses

The thermal stabilities of MOFs **1** and **2** were evaluated by thermal gravimetric analyses (Figure S2). The compound **1** indicates a weight loss of 6.60%, ranging from 80 to 120 °C, based on the loss of the coordinated and lattice H₂O molecules (calc. 6.52%) and the framework collapse at approximately 320 °C. A loss of 9.48% (calc. 9.22%) was found for **2**, ranging from 120 to 190 °C, and followed by the continual collapse at 350 °C. The

pure phases for MOFs 1 and 2 were confirmed, as their patterns from the powder XRD fit within the simulated pattern (Figures S3 and S4).

3.3. Photoluminescent Property

Metal-organic frameworks built from d^{10} , such as Zn(II) and Cd(II) metal centers and aromatic organic molecules with π -conjugated system may have potential photoluminescent properties [27–29]. In this regard, we carried out the study on their fluorescence properties of MOFs 1 and 2, together with AZN ligand (Figure 8). As shown in Figure 8, MOFs 1 shows an emission maxima at 392 nm upon excitation at 342 nm, while MOF 2 exhibits emission maxima at 430 nm upon excitation at 350 nm. MOFs 1 and 2 show 18 nm blue-shift and 20 nm red-shift in comparison with the emission peak at 410 nm from AZN ligand. The emission nature of MOFs 1 and 2 may originate in intraligand charge transfer [30]. Under the same condition, MOF 2 has a stronger fluorescent emission in contrast with MOF 1. Enhanced luminescence of the MOF 1 compared with 2, under the same conditions, may enhance its conformational rigidity and decrease the nonradiative energy loss due to the coordination interactions between the metal Zn(II) atom and the ligand.

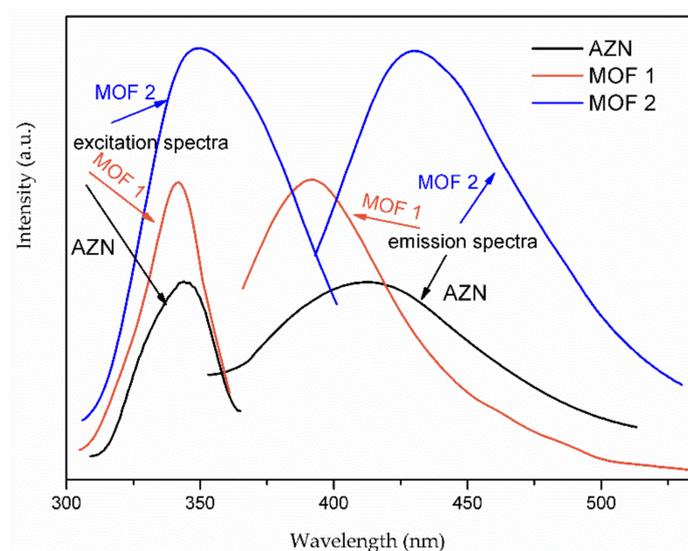


Figure 8. Luminescent excitation and emission spectra of AZN and MOFs 1–2.

Furthermore, the quantum yield (QY) and decay lifetimes are areas that need to be investigated further (Figure 9). The exponential function as $I(t) = A \exp(-t/\tau)$ can be used to determine the luminescence lifetimes and the results are 36.23, and 62.54 ns for 1 and 2 [31]. Apparently, the luminescence lifetime of 2 is much longer than MOF 1, however, both MOFs 1 and 2 have shorter luminescence lifetimes, which are attributable to the characteristic of a singlet state, rather than a triplet state ($>10^{-3}$ s) [32]. Moreover, the corresponding QY values of MOFs 1 and 2 are 4.35%, and 5.68%.

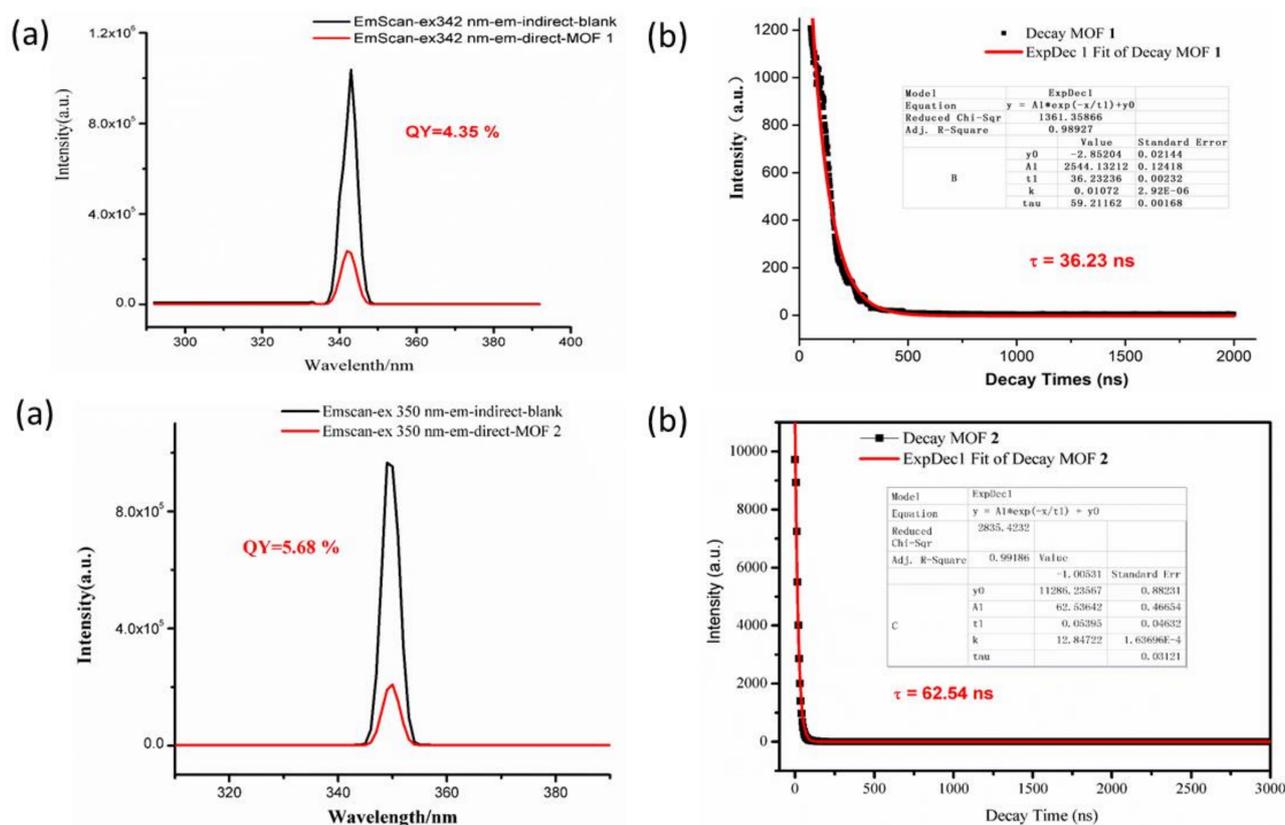


Figure 9. The quantum yield; and (a) decay curves; (b) for MOF 1 and MOF 2.

4. Conclusions

Two new metal-organic MOFs based on N-donor AZN and O-donor H₃btc mixed ligands have been obtained by reactions with different metal salts under hydrothermal reaction. MOF 1 is a 1D chain structure, while 2 is a 3D networks with a three-fold interpenetration topology with its Point (Schläfli) symbol of $(6 \cdot 8^2)_4(6^2 \cdot 8^2 \cdot 10^2)$. The study has further demonstrated that the on N/O-donor mixed ligands can effectively be employed to construct metal-organic coordination polymers. Apparently, many factors have a significant effect on the resulting structures, including the nature of different metal centers and ligands. Moreover, the luminescent properties of MOFs 1 and 2 have been studied.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/cryst11091129/s1>, Figure S1. The 3D supramolecular structure of 1. Figure S2. TG curves of MOFs 1 and 2. Figure S3. PXRD of MOF 1: a, simulated; b, experimental. Figure S4. PXRD of MOF 2: a, simulated; b, experimental. Table S1. Bond lengths [\AA] and bond angles [$^\circ$] for MOFs 1 and 2.

Author Contributions: Z.L. charged the project, carried out the experiments and organized this paper. Y.L., Y.R., S.Y., C.H., M.Z., R.J. performed the experiments. Y.L. and H.Y. dealt with the data. All authors have read and agreed to the published version of the manuscript.

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

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