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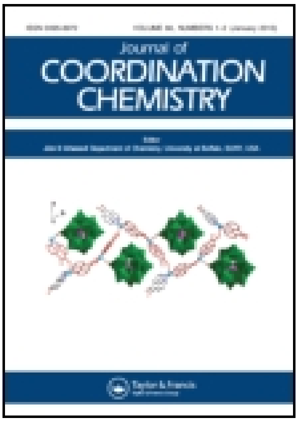

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# Synthesis, crystal structure, and blue photoluminescence of a 3D coordination polymer based on a $Ag_{10}$ cluster with the versatile 2-mercapto-5-benzimidazolesulfonic acid ligand

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The solvothermal reaction of 2-mercapto-5-benzimidazolesulfonic acid ($H_3MBZD$), which has imidazole, –SH, and $–SO_3H$ groups, with $Ag_2SO_4$ led to the 3D coordination polymer $\{Ag_5[(HMBZD)_2(H_2MBZD)(H_2O)]\}_n$ (**1**). X-ray single-crystal analysis showed that five independent Ag atoms are connected by the bridging mercapto group to generate asymmetric pentanuclear clusters, which are joined together to form a large $Ag_{10}$ ringed subunit. The $Ag_{10}$ subunits are linked together by the $–SO_3H$ groups to give the complex 3D framework. Strong blue photoluminescence of **1** can be assigned to the intraligand fluorescent emission.

*Keywords*: Coordination polymer; 2-Mercapto-5-benzimidazolesulfonic acid; $Ag_{10}$ Cluster; Blue luminescence

## 1. Introduction

In the broad domain of inorganic and organometallic research, the coordination chemistry of the sulfonate group is relatively less investigated due to the perception that it is a poor ligand [1], a perception perpetrated in part because the sulfonate group cannot readily displace water from the coordination sphere of a transition metal ion. However, when employed with suitably "soft" metal cations, sulfonate-containing ligands show potential for new functional materials [1–6]. In this regard, $Ag^+$ is a favorable selection as a "soft" metal because of the diversity and flexibility of its coordination chemistry as well as its tendency to coordinate sulfonate groups [1–4, 7–11]. Multifunctional ligands have proven to be effective in the synthesis of metal-organic framework materials, since such ligands combine coordination modes of two or even three different types of functional groups. For example, the pyridine-carboxylate ligands have been extensively investigated. However, to the best of our knowledge, multifunctional sulfonate ligands have been rarely reported.

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Hence, 2-mercapto-5-benzimidazolesulfonic acid ($H_3$MBZD), a multifunctional compound possessing imidazole, –SH, and –$SO_3$H groups, was selected to react with transition metal salts. We speculated that this new ligand could produce novel coordination complexes since the imidazole, –SH, and –$SO_3$H groups all have strong coordination ability with $Ag^+$. As a result, the solvothermal reaction of $H_3$MBZD with $Ag_2SO_4$ led to a novel coordination polymer, namely, $\{Ag_5[(HMBZD)_2(H_2MBZD)(H_2O)]\}_n$ (**1**), which exhibits a complex 3D framework based on large $Ag_{10}$ ringed subunits. Complex **1** has been characterized by X-ray single-crystal diffraction, FT-IR spectrum, powder X-ray diffraction (PXRD), thermal gravimetric analysis (TGA), and photoluminescence measurements.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All reagents were obtained commercially and used without purification. The Fourier-transform infrared spectra (KBr pellets) were recorded using a Nicolet Avatar 360 FT-IR Spectrometer from 4000 to 400 $cm^{-1}$. Thermal stability studies were carried out using a NETSCHZ STA−449C thermoanalyzer under a nitrogen atmosphere from 20 to 1000 °C at a heating rate of 10 °C/min. The fluorescence spectra were measured with a Cary Eclipse fluorescence spectrophotometer at room temperature using powdered crystal samples. The excitation slit and emission slit were both set at 5.0 nm. PXRD data were collected on a Bruker D8 Advance powder diffractometer with CuKα radiation (40 kV, 40 mA). The simulated powder pattern was calculated using single-crystal X-ray diffraction data and processed by the free Mercury 2.3 program provided by the Cambridge Crystallographic Data Center.

### 2.2. *Synthesis of $\{Ag_5[(HMBZD)_2(H_2MBZD)(H_2O)]\}_n$*

A mixture containing $Ag_2SO_4$ (0.062 g, 0.2 mM), $H_3$MBZD (0.027 g, 0.1 mM), 2 mL $H_2O$, and 2 mL *n*-propyl alcohol was heated at 160 °C for four days under autogenous pressure. After 24 h of gradual cooling to room temperature, gray block-shaped crystals (0.14 g, 56% yield) were obtained and then filtered, washed with water and ethanol, and dried in air. Complex **1** is not soluble in water and usual organic solvents, such as alcohol, acetonitrile, benzene, acetone, THF, DMF, and DMSO. Anal. Calcd for $Ag_5C_{21}H_{15}N_6O_{10}S_6$: C, 20.29; H, 1.22; N, 6.76. Found: C, 20.43; H, 1.41; N, 6.82.

### 2.3. *Crystal structure determination*

A suitable single crystal of **1** was carefully selected under an optical microscope and glued to a thin glass fiber. Single crystal X-ray diffraction measurements were carried out at 293 K on an Oxford Gemini E CCD Diffractometer. Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71079$ Å) was used for data collection. Data collection and reduction along with absorption correction were performed using CrysAlis software package [12]. Absorption corrections were made using *SADABS* [13]. The structure was solved using direct methods and refined by full-matrix least-squares methods on $F^2$ using the *SHELXL*-97 program package [14]. All non-hydrogen atoms were refined anistropically. The hydrogens of the water molecule and the imidazole group were located from difference Fourier maps. Carbon-bound hydrogen atoms were placed on calculated positions with C–H distances of 0.93 Å and refined using a riding model with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$. The crystallographic data and refinement parameters are provided in table 1. Selected bond distances and angles are listed in table 2.

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

| | |
|---|---|
| Empirical formula | $C_{21}H_{15}Ag_5N_6O_{10}S_6$ |
| Formula weight | 1243.16 |
| Crystal system | Monoclinic |
| Space group | *P2(1)/c* |
| $a$ (Å) | 11.5012(2) |
| $b$ (Å) | 22.4604(4) |
| $c$ (Å) | 11.0577(2) |
| $\alpha$ (deg) | 90 |
| $\beta$ (deg) | 92.870(2) |
| $\gamma$ (deg) | 90 |
| $V$ (Å$^3$) | 2852.86(9) |
| $Z$ | 4 |
| $D_{\mathrm{Calcd}}$ (g cm$^{-3}$) | 2.756 |
| $\mu$ (mm$^{-1}$) | 3.846 |
| $F(000)$ | 2376 |
| $\theta$ for data collection (deg) | 3.08 to 25.10 |
| Reflections collected/unique | 11682/5077 |
| $R$(int) | 0.0265 |
| Parameters | 458 |
| GOF on $F^2$ | 1.049 |
| $R_1{}^{\mathrm{a}}$, $wR_2$ [$I > 2\delta(I)$] | 0.0399, 0.0885 |
| $R_1$, $wR_2$ (all data) | 0.0493, 0.0909 |
| $\rho_{\mathrm{fin}}$ (max/min) (e Å$^{-3}$) | 1.673 and −2.701 |

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{0.5}$.

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| Ag(1)-S(3) | 2.4914(18) | Ag(2)-N(5) | 2.184(4) |
| Ag(1)-O(7)#1 | 2.529(5) | Ag(2)-S(1) | 2.4416(16) |
| Ag(1)-O(5)#2 | 2.586(5) | Ag(2)-O(2)#3 | 2.583(4) |
| Ag(1)-S(1) | 2.5863(15) | Ag(4)-N(1) | 2.147(5) |
| Ag(3)-S(1) | 2.6520(16) | Ag(4)-S(5) | 2.3896(15) |
| Ag(3)-O(1 W) | 2.417(5) | Ag(5)-S(3)#4 | 2.4472(17) |
| Ag(2)···Ag(3) | 3.1413(8) | Ag(5)-S(5) | 2.4503(16) |
| Ag(1)···Ag(2) | 3.0405(10) | Ag(2)···Ag(3) | 3.1417(8) |
| Ag(2)···Ag(4) | 2.9581(8) | Ag(3)···S(5)#4 | 2.8482(15) |
| Ag(3)···S(1)#5 | 2.8571(14) | | |
| S(3)-Ag(1)-O(7)#1 | 99.85(11) | N(5)-Ag(2)-S(1) | 153.30(13) |
| S(3)-Ag(1)-O(5)#2 | 101.40(11) | N(5)-Ag(2)-O(2)#3 | 79.95(16) |
| O(7)#1-Ag(1)-O(5)#2 | 126.12(16) | S(1)-Ag(2)-O(2)#3 | 126.58(10) |
| S(3)-Ag(1)-S(1) | 135.81(6) | O(1 W)-Ag(3)-S(1) | 167.4(2) |
| O(7)#1-Ag(1)-S(1) | 104.40(12) | N(1)-Ag(4)-S(5) | 166.02(13) |
| O(5)#2-Ag(1)-S(1) | 93.30(14) | S(3)#6-Ag(5)-S(5) | 171.18(7) |

Symmetry transformations used to generate equivalent atoms: #1 $x$, $-y+1/2$, $z-1/2$; #2 $-x+1$, $y+1/2$, $-z+3/2$; #3 $-x$, $y-1/2$, $-z+3/2$; #4 $-x+1$, $-y+1$, $-z+2$; #5 $-x$, $-y+1$, $-z+1$.

## 3. Results and discussion

### 3.1. *Description of crystal structure*

X-ray single-crystal diffraction analysis showed that **1** crystallizes in the monoclinic *P2(1)/c* space group and features a complicated 3D framework. The asymmetric unit of **1** contains five crystallographically unique $Ag^+$ ions, three independent $H_3MBZD$ ligands, and one coordinated water. As shown in figure 1, Ag1 is coordinated to four ligands via two sulfonate oxygens (O5A and O7B) from two different ligands and two sulfhydryl sulfurs (S1 and S3) from two other, different ligands in a distorted tetrahedral coordination geometry. The bond angles around Ag1 are between 99.85(11) and 135.81(6)°, which are within the range of angles reported for other four-coordinate Ag complexes [7]. Ag2 is coordinated to one imidazole nitrogen, one sulfhydryl sulfur, and one sulfonate oxygen (N5, S1, O2C) in distorted T-shaped coordination geometry. The bond angles around Ag2 are 79.95(16), 126.58(10), and 153.30(13)°; while these deviate from the ideal angles of 90 and 180°, they are close to the range of angles (78.2(3) to 133.7(6)°) observed for a different three-coordinate Ag complex [7]. Ag3 is coordinated to one sulfhydryl sulfur and one coordinated water (S1, O1w), Ag4 to one sulfhydryl sulfur and one imidazole nitrogen (S5, N1), and Ag5 to two sulfhydryl sulfurs (S5, S3D). The bond angles of the two-coordinate Ag3, Ag4, and Ag5 atoms are near 170°. The $Ag-S_{sulfhydryl}$ (Ag1–S1, Ag1–S3, Ag2–S1, Ag3–S1, Ag4–S5, Ag5–S3D, and Ag5–S5) bond distances range from 2.3896 (15) to 2.6520(16) Å. The Ag(1)–S(1) (2.5863(15) and Ag(3)–S(1) (2.6520(16) Å) bonds are longer than the other $Ag–S_{sulfhydryl}$ bonds, which may indicate that they are dative Ag–S bonding interactions. The reported $Ag-S_{sulfhydryl}$ bonds in the Ag complexes with the ligands 2-mercaptobenzimidazole, 2-benzimidazolethiol, and 2-mercaptopyrimidine [15–17] range from 2.47 to 2.74 Å. Thus, the distances between Ag(3) and S(1) and S(5), 2.8571(14) and 2.8482(15) Å, respectively, suggest the existence of weaker Ag···S interactions. The $Ag-O_{sulfonate}$ (Ag1–O5A, Ag1–O7B, and Ag2–O2C) bond lengths

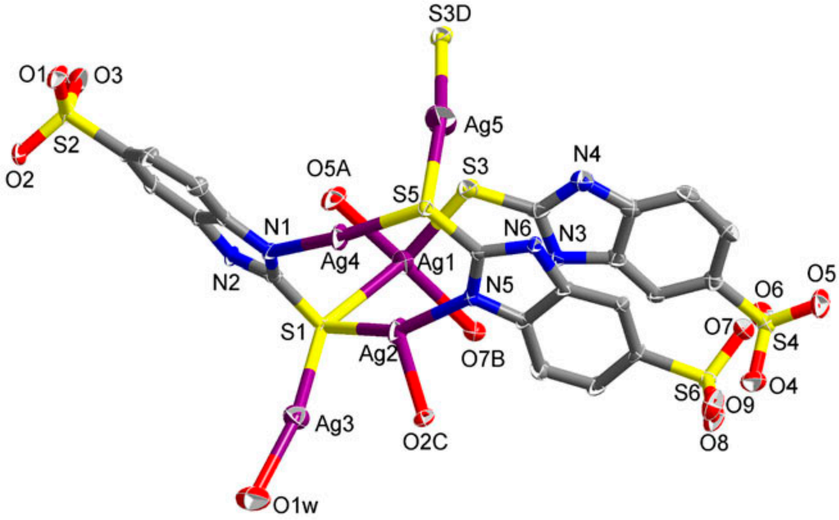
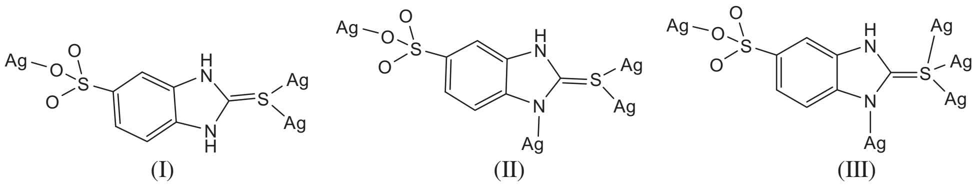


Figure 1. ORTEP diagram of **1** showing the local coordination environments of five independent $Ag^+$ centers, with 30% thermal ellipsoids. All hydrogens are omitted for clarity. [Symmetry codes: A 1−*x*, 0.5+*x*, 1.5−*z*; B *x*, 0.5−*y*, −0.5+*z*; C −*x*, −0.5+*y*, 1.5−*z*; D 1−*x*, 1−*y*, 2−*z*].

are 2.586(5), 2.529(5), and 2.583(4) Å, respectively, consistent with other reported Ag−sulfonate complexes [4, 7, 8, 10]. Moreover, the Ag−O$_{water}$ (Ag−O1w, 2.417(5)) and Ag–N$_{imidazole}$ (Ag2−N5, 2.184(4) and Ag4−N1, 2.147(5) Å) bond distances are also comparable with data from literature compounds [4, 15, 16]. The Ag···Ag separations are in the range 2.9581(8) – 3.1413(8) Å, which is shorter than the sum of the van der Waals radii (3.44 Å), suggesting the existence of strong metal–metal interactions. Reports on Ag···Ag interactions in other Ag clusters give distances from 2.89 to 3.15 Å [15–18].

The multifunctional $H_3MBZD$ ligand may undergo varying degrees of deprotonation, which can provide a range of multidentate bindings with variable coordination modes. As depicted in scheme 1, the $H_{3-n}HMZD^{n-}$ ligand adopts three different types of linking modes ($\mu_3$-I, $\mu_4$-II, and $\mu_5$-III). The sulfonate group is monodentate in each of these three modes. The imidazole group is uncoordinated in type I and monodentate in II and III. The sulfhydryl–S group behaves as a $\mu_2$-linker in I and II, but as a $\mu_3$-linker in III. It can be seen that the different coordination modes of the ligand can mainly be attributed to the multifunctional 2-mercaptobenzimidazole group. The reported coordination behavior of the sulfhydryl sulfur atom is as a formally non-covalent thione, as a formally deprotonated anionic thiol, or as a resonance structure between the two. Detailed analysis of the bond lengths in **1** as compared to corresponding bond lengths in the literature [15, 18–20], suggests that the best description for the sulfhydryl sulfur atoms in **1** is as a thione group (scheme 1). In **1**, five independent Ag atoms are connected by one type-II ligand and one type-III ligand to form an asymmetric [$Ag_5L_2$] cluster. The two [$Ag_5L_2$] clusters are linked by two type-I ligands to give an unprecedented [$Ag_{10}L_6$] cluster (figure 2(a)). An 8-membered ring is generated by two silvers (Ag2 and Ag4), two sulfhydryl sulfurs (S5 and S1), two imidazole nitrogens (N1 and N5), and two imidazole carbons (C1 and C15). The 8-membered ring (S1−C1−N1−Ag4−S5−C15−N5−Ag2) is likewise also extended through two sulfhydryl sulfur atoms and four Ag atoms into two 16-membered rings $(S1-C1-N1-Ag4-S5-Ag5-S3-Ag1)_2$ and $(S1-Ag2-N5\text{-}C15-S5-Ag5-S3-Ag1)_2$, as shown in figure 2(a). Naturally, the two 16-membered rings share the two S$_{thiolate}$ and four Ag atoms which extend the two 8-membered rings to the two 16-membered rings. Finally, the large [$Ag_{10}$]-ringed motifs are linked to each other via the monodentate –$SO_3$ groups to generate the complicated three-dimensional framework (figure 2(b)). This 3D structure exhibits alternant layers, one is a benzimidazole organic layer, and the other is a [$Ag_{10}$] cluster inorganic layer (figure 2(b)). When the $Ag_{10}$ clusters are linked, the ligands above and below the cluster all rotate to minimize the steric hindrance so, the nearest benzimidazole groups are separated by a distance of 3.67 Å. Calculations using the program PLATON suggest that the unit cell contains no residual solvent accessible voids and shows a dense structure.

There are no classical π···π interactions in the structure despite the presence of aromatic phenyl and imidazole rings in the ligand, which may be due to steric hindrance and the



Scheme 1. The different bridging modes for the three independent $H_3MBZD$ ligands (I, II, and III).

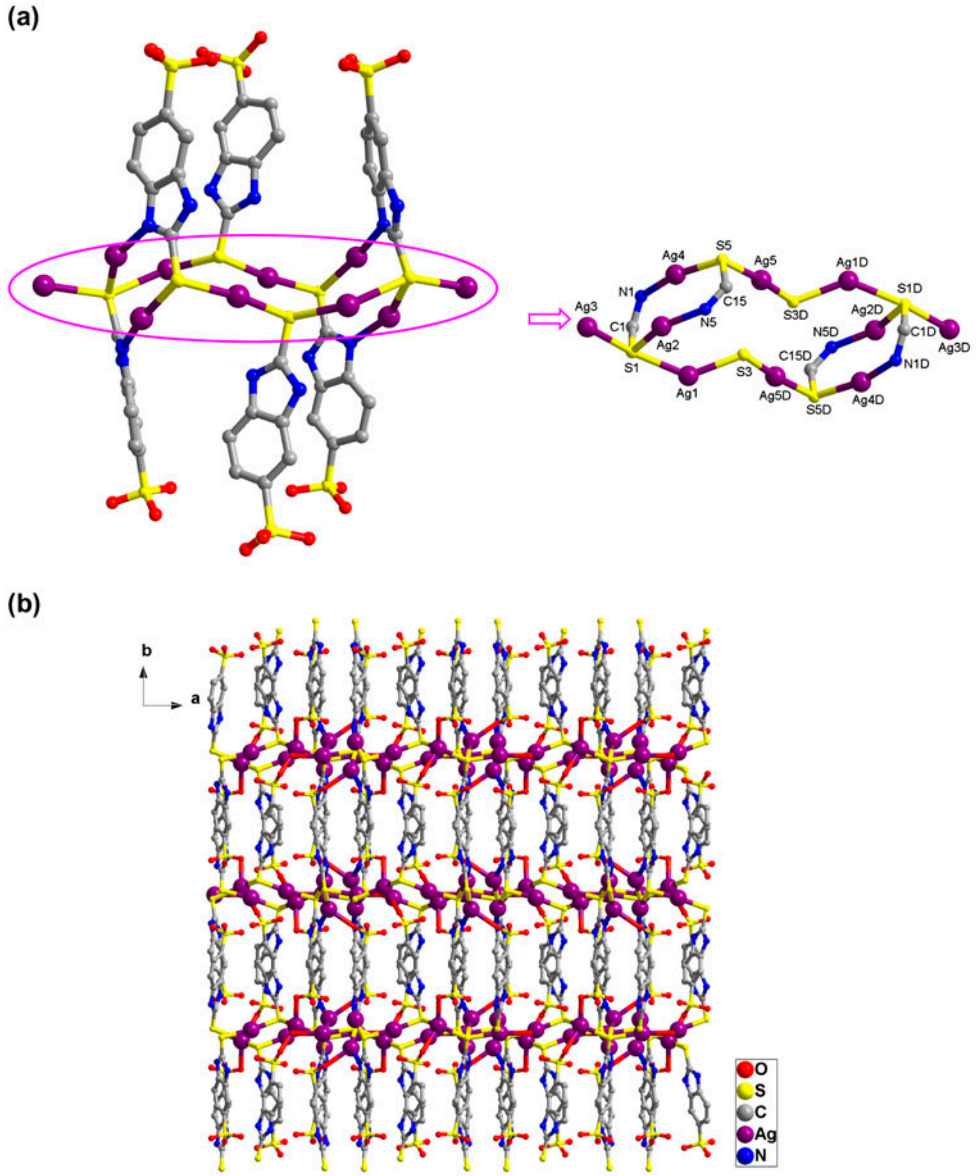


Figure 2. (a) The large $[Ag_{10}]$ ringed cluster in **1**. (b) The complex 3D framework of **1** viewed from the *c*-axis direction.

arrangement of the large $Ag_{10}$ cluster. The only potential $\pi \cdots \pi$ interaction is that between the 5-membered rings Ag2–Ag4–S5–C15–N5 (part of the 8-membered ring) from different asymmetric units, with a distance of 3.6222 Å between any two rings. There are also hydrogen bonds in the structure and these may help stabilize it. The abundant O atoms of the sulfonate group can act as potential acceptors to facilitate the formation of hydrogen bonds in the structure. The $O_{water}-H\ldots O_{sulfonate}$ and $N_{imidazole}-H\cdots O_{sulfonate}$ hydrogen bonds have distances from 2.7 to 3.0 Å (table S2).

Although many silver sulfonate compounds have been reported to date, such an organic–inorganic hybrid structure as **1**, based on high nuclear silver clusters, is rare. For example, $Ag_4(L)(Pyr)_4(H_2O)_2$ (L = 1,3,6,8-pyrenetetrasulfonate, Pyr = pyrazine) was observed in a Ag–sulfonate complex [21]. A $Ag_6$ cluster was found in a complex using 2-hydroxyl-5-carboxylbenzenesulfonic acid as ligand [22]. The highnuclear $Ag_{10}$ cluster was obtained by combining $AgCF_3SO_3$ with the betaine ligand [23]. In our opinion, the selection of the multifunctional $H_3MBZD$ ligand is a key factor for the formation of this novel 3D framework.

### 3.2. *PXRD, FT-IR spectrum, TGA, and photoluminescence properties*

As shown in figure S1, **1** was characterized by PXRD at room temperature. The PXRD pattern measured for the as-synthesized sample was consistent with the PXRD pattern simulated from the respective single-crystal X-ray data using the Mercury 2.3 program, indicating that the title compound was a single phase. The FT-IR spectrum showed the characteristic absorption peaks of the main functional groups for the title compound (figure S2). The absorption band at 3444 $cm^{-1}$ can be assigned to the O–H stretching vibrations of the coordinated water molecule. The stretching vibration absorption bands of the sulfonate group appeared at 1030, 666, and 628 $cm^{-1}$. The bands at 1631 and 721 $cm^{-1}$ are attributed to the imidazole ring stretching vibrations, which show a slight shift from the value for uncoordinated imidazole (1544 and 758 $cm^{-1}$), due to coordination of Ag to the imidazole ring. The TGA for **1** is shown in figure S3. It can be seen that **1** was stable from room-temperature to about 200 °C then the first weight loss took place from 200 to 340 °C, corresponding to the release of the coordinated water molecules (obsd 1.40%, Calcd 1.45%). A sharp weight loss was then observed due to decomposition of the ligand. During this process, there was a break in the TG curve at about 490 °C, which we tentatively regard as the loss of the ligand with the $\mu_3$-I coordination mode (obsd 18.05%,

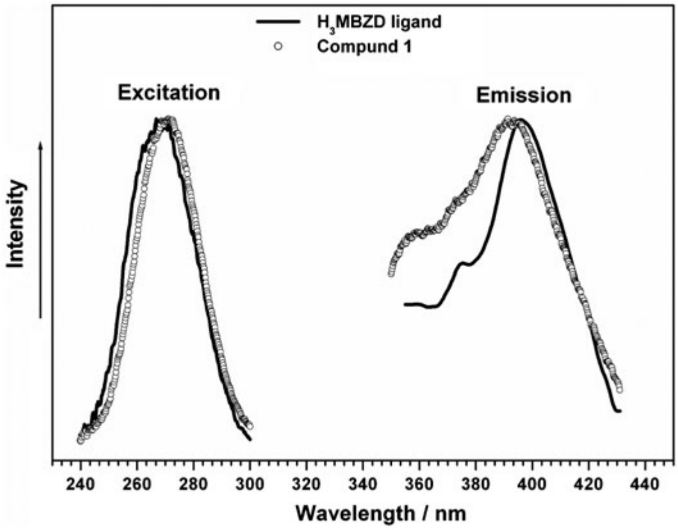


Figure 3. Solid state emission spectra of $H_3MBZD$ and **1** at ambient temperature.

Calcd 18.50%). The other two ligands then decomposed completely with increasing temperature. The final residue was likely $Ag_2O$ (obsd 50.80%, Calcd 49.88%).

The solid-state luminescence property of **1** was also investigated at room temperature. As shown in figure 3, upon excitation of the solid sample at $\lambda = 271$ nm, an intense band in the emission spectra was observed at 391 nm. To understand more thoroughly the nature of this band, the luminescence of $H_3$MBZD was also investigated. For $H_3$MBZD, the emission maximum was at 395 nm, similar to the emission of **1**. Therefore, the luminescence of **1** is tentatively assigned to an intraligand fluorescent transition. Compared with the organic ligand, the weak blue-shift for **1** is probably due to the coordination of $H_3$MBZD to the Ag center, increasing the ligand conformational rigidity, and thereby reducing the non-radiative decay of the intraligand ($\pi$-$\pi^*$) excited state [24, 25].

## 4. Conclusion

2-Mercapto-5-benzimidazolesulfonic acid was utilized as ligand to produce a 3D organic–inorganic hybrid framework with large [$Ag_{10}$]-ringed subunits. Based on this work, in-depth research to produce more coordination polymers with this interesting ligand is ongoing in our lab.

## Supplementary material

X-ray crystallographic files in CIF format, additional plots of the structure, FT-IR, PXRD, and TGA for **1**.

## Acknowledgments

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