



Syntheses, crystal structures and properties of three compounds based on the dicarboxylate ligand with S-S flexible linkage

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Three new compounds, $[\text{MnL}(2,2'\text{-bipy})_2]_n \cdot 1.5\text{nH}_2\text{O}$ (**1**), $\text{Co}(4,4'\text{-bipy})(\text{H}_2\text{O})_4 \cdot 2\text{HL}$ (**2**) and $2\text{HL} \cdot (4,4'\text{-bipyH}) \cdot 2\text{H}_2\text{O}$ (**3**) ($\text{H}_2\text{L} = 2,2'\text{-dithiosalicylic acid}$, $2,2'\text{-bipy} = 2, 2'\text{-bipyridine}$, $4,4'\text{-bipy} = 4,4'\text{-bipyridine}$), have been synthesized by hydrothermal and evaporation methods. Structural determination reveals that compound **1** shows a one-dimensional chain structure with L^{2-} ligands adopting bridging coordination modes, compound **2** features a mononuclear structure with uncoordinated HL^- anions, balancing the charges, compound **3** is a new inclusion compound of HL^- anions and $4,4'\text{-bipyH}$ cation with $\pi\text{-}\pi$ stacking interactions. In compounds **1-3**, the flexible S-S linkages can make H_2L ligands present different conformations of dihedral angles between the terminal benzene rings. The S-O hypervalent bonds can stabilize the conformations. Thermogravimetric analyses and fluorescence measurements of compounds **1** and **2** have been performed. Compounds **1** and **2** exhibit broad blue fluorescent emission bands at 420 nm and 424 nm, respectively.

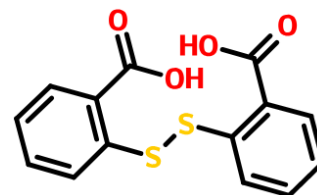
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Recently, the design and syntheses of metal-organic compounds have attracted wide attention of researchers, not only because of their intriguing topologies, but also due to their exploitable properties for potential applications such as catalysis, adsorption, luminescence, sensing and magnetism¹⁻⁵. However, the major challenge lies in the selection of the metallic nodes and the design of appropriate organic linkers for the desired topologies and fascinating properties⁶⁻¹⁰. The structure and functionality rely strongly on the nature of metallic nodes and type of organic linkers^{11,12}. In order to investigate the effect of organic ligands on the topologies, the flexible, rigid and semi-rigid ligands with different functional groups have been designed and synthesized^{13,14}. In principle, the ligands can adopt different conformations due to their flexibility, and thus provide a means to generate structural diversity during the synthesis process, such as supramolecular, one-dimensional and two-dimensional structures¹⁵⁻¹⁹. In fact, in contrast with rigid and semi-rigid ligands, it is more popular to construct metal-organic compounds with flexible ligands.

2,2'-dithiosalicylic acid (H_2L) is a widely used flexible carboxylate ligand, whose flexible and multifunction coordination sites provide the high possibility for building novel structures. The striking

feature is that the flexible S-S linkages between phenyl rings allow the ligands to present different conformations. The S-S linkages can remain uncoordinated and take part in weak interactions with adjacent carboxylic groups. In addition, the N-donor rigid molecules and their derivatives, acting as auxiliary ligands, such as phenanthroline and bipyridine, can influence the structural features of the metal-organic compounds and can form new products with reduced dimensionality²⁰.

Herein, we present three new compounds with H_2L and N-donor auxiliary ligands, $[\text{MnL}(2,2'\text{-bipy})_2]_n \cdot 1.5\text{nH}_2\text{O}$, $\text{Co}(4,4'\text{-bipy})(\text{H}_2\text{O})_4 \cdot 2\text{HL}$ and $2\text{HL} \cdot (4,4'\text{-bipyH}) \cdot 2\text{H}_2\text{O}$. H_2L is a dicarboxylate ligand with flexible S-S linkage, which is expected to present different conformations in the design of diverse compounds. The molecular structure of H_2L is shown in Scheme 1. Three compounds were synthesized and structurally characterized. Additionally, the thermal stability and fluorescence properties were investigated.



Scheme 1 — Molecular structure of H_2L

Materials and Methods

All chemicals and solvents used for the experiment were purchased from Sinopharm Chemical Reagent Co., Ltd, which were analytical reagents and used without further purification. After the heat treatment of the samples, elemental analyses of the samples were performed with an Elementar Vario EL analyzer. Thermogravimetric analyses were carried out on a TA Instrument Q600 thermal analyzer at the heating rate of 10 K·min⁻¹ under nitrogen atmosphere. Photoluminescence analyses of the solid samples were performed with an Edinburgh Instrument F920 fluorescence spectrometer.

Synthesis of compound 1

H₂L (0.011 g, 0.050 mmol) was added with constant stirring to a solution of 2,2'-bipy (0.014 g, 0.050 mmol) in ethanol (10 mL) and water (5 mL). Then MnSO₄ (0.033 g, 0.1 mmol) was added to the solution with stirring, and the pH value of the solution was adjusted to 7 with 0.1 mol L⁻¹ potassium hydroxide solution. Yellow blocked crystals were obtained from the solution after standing at room temperature for 5 days (Yield: 52% based on H₂L). FT-IR (cm⁻¹): 3417(ν_{OH}), 1596(ν_{asCOO^-}), 1553(ν_{asCOO^-}), 1490($\nu_{\text{C=C}}$), 1473($\nu_{\text{C=N}}$), 1439($\nu_{\text{C=C}}$), 1373(ν_{sCOO^-}), 1315(ν_{sCOO^-}), 1279($\nu_{\text{C-O}}$), 1246($\nu_{\text{C-O}}$), 1157($\nu_{\text{S-S}}$), 1054(ν_{OH}), 834($\nu_{\text{S-S}}$), 760($\delta_{\text{C-H}}$), 738($\delta_{\text{C-H}}$), 702($\delta_{\text{C-H}}$)²⁰.

Synthesis of compound 2

Co(NO₃)₂·6H₂O (0.242 g, 1 mmol), H₂L (0.268 g, 1 mmol) and 4,4'-bipy (0.156 g, 1 mmol) were

dissolved in the mixed solvent of water (10 mL) and DMF (10 mL). The solution was stirred for 1 h and transferred to a 25 mL Teflon-lined autoclave. After heating at 165 °C for 3 days, red blocked crystals were obtained (Yield: 59% based on H₂L). FT-IR (cm⁻¹): 3386(ν_{OH}), 1667(ν_{asCOO^-}), 1589(ν_{asCOO^-}), 1570($\delta_{\text{H-OH}}$), 1489($\nu_{\text{C=C}}$), 1461($\nu_{\text{C=N}}$), 1434($\nu_{\text{C=C}}$), 1410($\nu_{\text{C=C}}$), 1383(ν_{COO^-}), 1243($\nu_{\text{C-O}}$), 1147($\nu_{\text{S-S}}$), 1055(ν_{OH}), 808($\nu_{\text{S-S}}$), 746($\delta_{\text{C-H}}$), 693($\delta_{\text{C-H}}$), 546($\nu_{\text{S-S}}$)²⁰.

Synthesis of compound 3

MnSO₄ (0.033 g, 0.1 mmol) and H₂L (0.011 g, 0.050 mmol) in water (5 mL) was added to a solution of 2,2'-bipy (0.014 g, 0.050 mmol) in ethanol (10 mL). The mixed solution was allowed to stir for 1 h and was then filtered to remove the suspended particles. Light yellow blocked crystals suitable for single crystal X-ray diffraction were obtained after 7 days (Yield: 51% based on H₂L).

Crystal structure determination

X-ray single crystal data collection for compounds **1-3** was performed on a Rigaku Saturn 70 CCD diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K, 123 K or 193 K. After absorption correction, the structures were solved by direct methods and refined by full-matrix least squares methods on F^2 using SHELXT 2014 and SHELXL 2014 programs^{21,22}. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. In compound **1**, the occupancy of the free water molecule (O2W) is

Table 1— Crystal data and structure refinement for compounds **1-3**

	1	2	3
Chemical formula	C ₆₈ H ₅₄ Mn ₂ N ₈ O ₁₁ S ₄	C ₂₄ H ₂₁ Co _{0.5} N ₂ O ₆ S ₂	C ₁₉ H ₁₆ NO ₅ S ₂
M_r	1397.31	527.01	402.45
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P-1$	Triclinic, $P-1$
Temperature (K)	296	123	193
a, b, c (Å)	12.835 (10), 17.963 (14), 14.83 (1)	7.6374 (3), 10.9183 (5), 14.0454 (7)	7.8193 (5), 11.1280 (7), 11.4087 (7)
β (°)	105.93 (2)	71.418 (4), 88.871 (4), 81.344 (4)	64.748 (3), 82.867 (3), 77.674 (3)
V (Å ³)	3288 (4)	1097.01 (9)	876.53 (10)
Z	2	2	2
Crystal size (mm)	0.22 × 0.22 × 0.20	0.2 × 0.18 × 0.16	0.18 × 0.15 × 0.11
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27133, 3995, 2626	11614, 4497, 4100	9958, 3115, 2405
R_{int}	0.171	0.024	0.066
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.527	0.625	0.595
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.098, 0.251, 1.07	0.032, 0.084, 1.07	0.049, 0.133, 1.01
No. of reflections	3995	4497	3115
No. of parameters	414	320	246
No. of restraints	0	2	2
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e·Å ⁻³)	1.16, -0.39	0.65, -0.75	0.36, -0.42

0.5. The crystallographic data are summarized in Table 1, while selected bond lengths and angles are given in Table 2. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC 2022010, 2022008, 2022009). The 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).

Results and Discussion

Crystal structure of compounds 1-3

Compound **1** crystallizes in the monoclinic system with the space group $P2_1/n$ (Table 1). In the asymmetric unit, there are one crystallographically independent Mn ion, one L^2 ligand, two 2,2'-bipy

Table 2 — Selected bond lengths (Å) and bond angles (°) for compounds 1-3

1		2		3	
Mn1—O1	2.095(7)	Co1—O1 ⁱ	2.1131(13)	C1—O1	1.259(4)
Mn1—O3	2.112(8)	Co1—O1	2.1131(13)	C1—O2	1.261(4)
Mn1—N1	2.266(8)	Co1—O2	2.0729(13)	C7—S1	1.791(3)
Mn1—N2	2.290(9)	Co1—O2 ⁱ	2.0730(13)	S1—S2	2.0579(11)
Mn1—N4	2.311(8)	Co1—N1 ⁱ	2.1461(15)	C19—N1	1.323(4)
Mn1—N3	2.423(8)	Co1—N1	2.1460(15)	C8—S2	1.792(3)
O1—Mn1—O3	102.5(3)	O1 ⁱ —Co1—O1	180.00	O1—C1—O2	124.1(3)
O1—Mn1—N1	115.7(3)	O1—Co1—N1 ⁱ	88.72(6)	O1—C1—C2	119.6(3)
O3—Mn1—N1	93.0(3)	O1 ⁱ —Co1—N1 ⁱ	91.28(6)	O2—C1—C2	116.3(3)
O1—Mn1—N2	89.8(3)	O1 ⁱ —Co1—N1	88.72(6)	C6—C7—S1	121.0(2)
O3—Mn1—N2	163.9(3)	O1—Co1—N1	91.28(6)	C2—C7—S1	119.9(2)
N1—Mn1—N2	72.1(3)	O2 ⁱ —Co1—O1	88.34(5)	C9—C8—S2	120.7(2)
O1—Mn1—N4	87.4(3)	O2—Co1—O1 ⁱ	88.34(5)	C13—C8—S2	120.7(2)
O3—Mn1—N4	92.6(3)	O2 ⁱ —Co1—O1 ⁱ	91.66(6)	O4—C14—O3	123.2(3)
N1—Mn1—N4	154.3(3)	O2—Co1—O1	91.66(6)	O4—C14—C13	122.1(3)
N2—Mn1—N4	98.5(3)	O2—Co1—O2 ⁱ	180.00	O3—C14—C13	114.7(3)
O1—Mn1—N3	155.5(3)	O2—Co1—N1 ⁱ	88.76(5)	N1—C19—C18	121.2(3)
O3—Mn1—N3	84.7(3)	O2 ⁱ —Co1—N1	88.76(6)	C19—N1—C15	120.7(3)
N1—Mn1—N3	86.8(3)	O2—Co1—N1	91.24(6)	C7—S1—S2	106.46(10)
N2—Mn1—N3	88.3(3)	O2 ⁱ —Co1—N1 ⁱ	91.24(6)	C8—S2—S1	104.83(10)
N4—Mn1—N3	68.7(3)	N1—Co1—N1 ⁱ	180.00(8)		

Symmetry code for compound 2: (i) $-x+1, -y+2, -z+1$

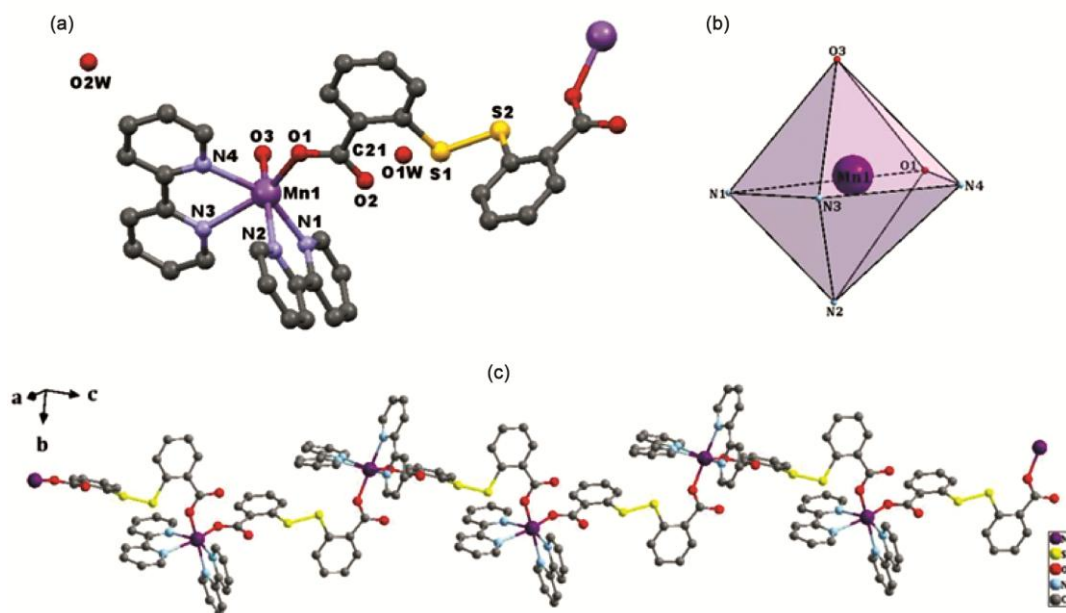


Fig. 1 — (a) Molecular structure of compound **1** (the asymmetric structure unit of compound **1** with atomic labeling scheme, all hydrogen atoms are omitted for clarity), (b) coordination configuration of Mn ion, and (c) one-dimensional chain structure of compound **1**

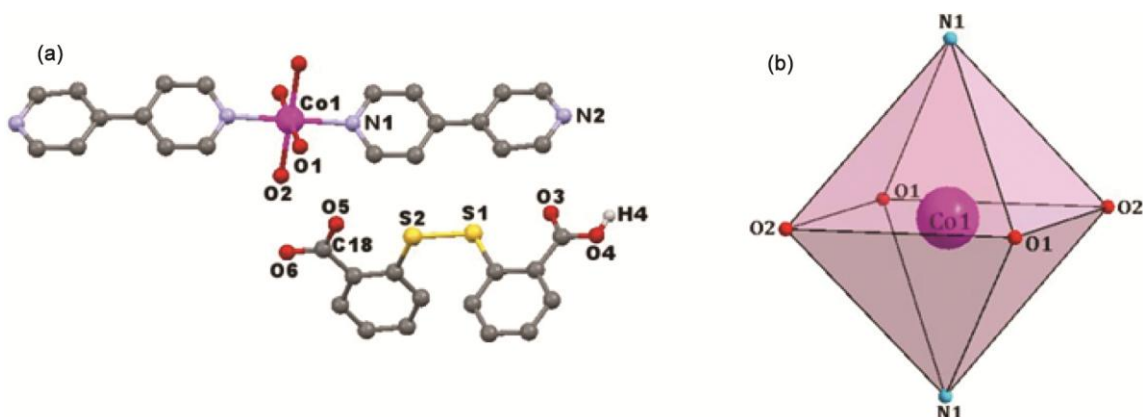


Fig. 2 — (a) Molecular structure of compound **2** (the asymmetric structure unit of compound **2** with atomic labeling scheme, all hydrogen atoms, but H4, are omitted for clarity) and (b) coordination configuration of Co ion

molecules and one free water molecule (Fig. 1a). Each Mn is six-coordinated by four nitrogen atoms (N1, N2, N3 and N4) from two 2,2'-bipy ligands and two carboxylate oxygen atoms (O1 and O3) from two different L^{2-} ligands, exhibiting a distorted octahedral coordination geometry (Fig. 1b). The Mn-O distances are 2.427(6) Å and 2.947(6) Å, and the Mn-N distances are between 2.266(8) Å and 2.423(8) Å (Table 2), which are close to those of reported Mn complexes²³⁻²⁵. Each L^{2-} ligand coordinates with two Mn atoms through the coordination of two carboxylate groups in the monodentate fashion, respectively, leading to the formation of one-dimensional chain structure (Fig. 1c).

Single crystal X-ray diffraction indicates that compound **2** is crystallized in triclinic system with the space group $P-1$ (Table 1). The asymmetric unit of compound **2** consists of half Co ion, one 4,4'-bipy molecule, two coordinated water molecules and one free HL^- anion (Fig. 2a). Each Co1 atom is six-coordinated by two nitrogen atoms from two different 4,4'-bipy molecules and two coordinated water molecules in a distorted octahedral geometry (Fig. 2b). The Co-O distances are 2.0729(13) Å and 2.1131(13) Å, and the Co-N distances are 2.1461(15) Å (Table 2). The Co ion, 4,4'-bipy and water molecules can form a mononuclear cobalt unit $[Co(4,4'-bipy)(H_2O)_4]^{2+}$, leaving two uncoordinated HL^- anions to balance charges.

Single crystal X-ray diffraction indicates that compound **3** is crystallized in triclinic system with the space group $P-1$ (Table 1). There are one HL^- anion, half protonated 4,4'-bipy molecule and one water molecule in the asymmetric unit for compound **3** (Fig. 3). The C-O bond lengths are 1.259(4) Å and

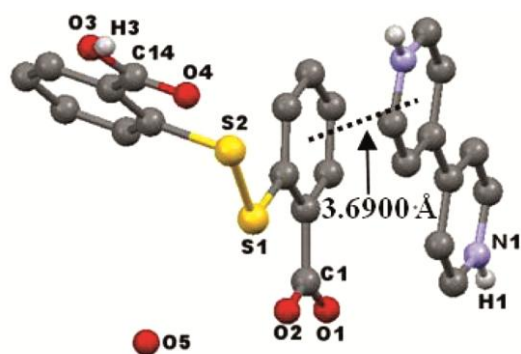


Fig. 3 — Molecular structure of compound **3** (the asymmetric structure unit of compound **3** with atomic labeling scheme, all hydrogen atoms, but H1 and H3, are omitted for clarity)

1.261(4) Å in the deprotonated carboxylate group, and 1.212(4) Å and 1.311(4) Å in the protonated carboxylate group, which indicates that the C-O distances tend to be similar after deprotonation. To balance the negative charge of the HL^- anion, half 4,4'-bipy molecule accepts one H atom to become a cation. The aromatic π - π stacking interactions are observed between HL^- anion and 4,4'-bipyH cation with the centroid-to-centroid distance of 3.6900 Å.

H_2L molecule displays L-shape structure along the flexible S-S axis. In addition, the flexible S-S axis allows two terminal benzene rings to rotate freely to generate various dihedral angles (Fig. 4a). In compounds **1-3**, the dihedral angles between the planes of two benzene rings are 87.045°, 71.190° and 76.786°, respectively. Interestingly, the S-O hypervalent bonds with the distances of 2.5612 Å–2.6963 Å (Fig. 4b), between the S atoms of the rotation axis and the carboxylate oxygen atoms, can effectively make the L-shaped configuration of H_2L stable. H_2L , acting as a potential host molecule, can

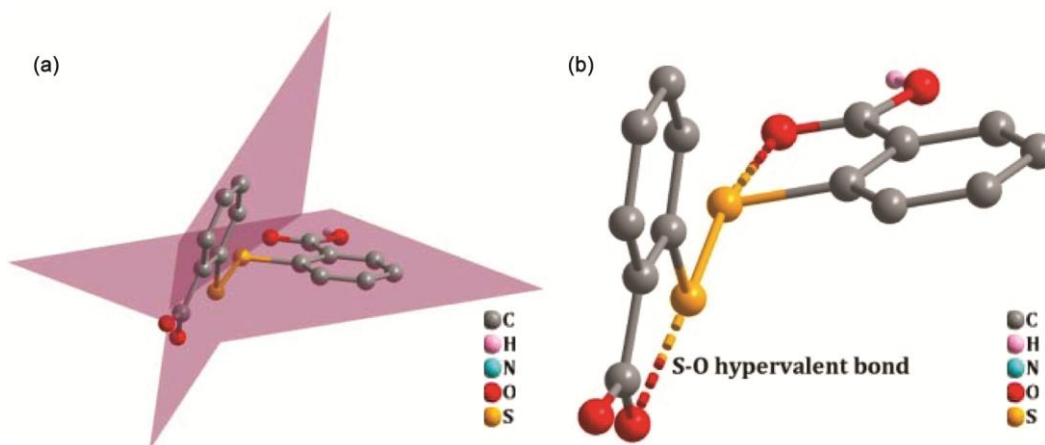


Fig. 4 — (a) The dihedral angle between terminal benzene rings in HL^- Ligand and (b) the S-O hypervalent bond

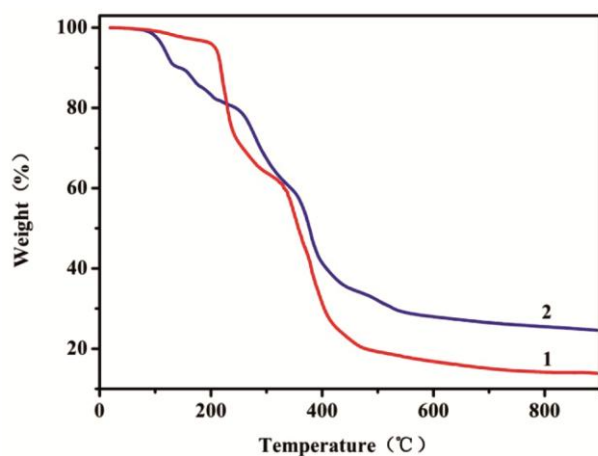


Fig. 5 — TG curves of compounds **1** and **2**

generate new coordination complex or inclusion compound with suitable host ion or molecule²⁰.

Thermogravimetric analyses

Thermogravimetric analyses of compounds **1** and **2** were measured to study the thermal stability (Fig. 5). Both the compounds were heated from 25 °C to 900 °C under nitrogen atmosphere. In compound **1**, the first step started at 25 °C and completed at 199 °C, which corresponds to the release of the free water molecules. The observed weight loss of 3.94% is close to the calculated value (3.86%). The second and the third steps are overlapping and started at 199 °C and completed at 797 °C, which corresponds to the combustion of 2,2'-bipy and L^{2-} ligands. The total observed weight loss at 900 °C is 86.04%, the final residue is MnO. In compound **2**, the first step started at 25 °C and completed at 125 °C, which corresponds to the release of the coordinated water molecules. The observed weight loss of 7.89% is close to the calculated value (6.83%). The second step started at

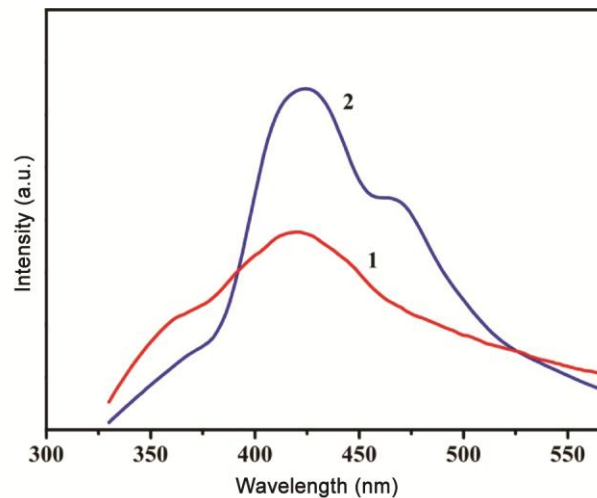


Fig. 6 — Solid-state emission spectra of compounds **1** and **2**

125 °C and completed at 259 °C, which corresponds to the combustion of the 4,4'-bipy ligands. The observed weight loss of 14.14% is close to the calculated value (14.82%). On further heating, HL^- anions are decomposed in the temperature range of 259–900 °C. The total observed weight loss at 900 °C is 75.42% with a final residue of CoO ²⁶.

Luminescence property

The solid-state luminescent properties of compounds **1** and **2** were investigated at room temperature (Fig. 6). The free H_2L ligand exhibits only a fluorescent emission band at 435 nm upon excitation at 310 nm²⁷. The 2, 2'-bipy and 4, 4'-bipy ligands display the fluorescent emission bands at 362 nm and 423 nm, respectively²⁸. Excitation of compound **1** leads to the generation of the blue-shifted fluorescent emission with the maximum emission centered at 420 nm, which may be attributed

to π - π^* or n- n^* intraligand fluorescence, indicating that 2,2'-bipy auxiliary ligand has no influence on the emission mechanism²⁸. So, the blue shift for compound **1** is likely caused by the coordination of the ligands perturbed by Mn ions. A blue-shifted emission with the maximum emission peak at 424 nm was observed in compound **2**, which indicates that the 4, 4'-bipy auxiliary ligand has a great influence on the positions and fluorescent emission. Such a blue shift may likely be caused by the coordination of 4, 4'-bipy ligands with Co ions^{29,30}.

Conclusions

In summary, we have successfully synthesized three novel compounds based H₂L molecules, including one-dimensional chain coordination polymer, mononuclear complex with uncoordinated HL⁻ cation, and inclusion compound by introducing N-donor auxiliary ligands. The H₂L molecules in compounds **1-3** adopt various L-shaped conformations, which are subjected to the changes of molecular structures, resulting in the different dihedral angles between two terminal benzene rings. The main interactions for stabilizing L-type conformations are the S-O hypervalent bonds. Compounds **1** and **2** exhibit broad blue fluorescent emission bands at 420 nm and 424 nm, respectively, which may be attributed to coordination interactions of the ligands with metal ions.

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