

柔性1,5-二(2-甲基咪唑)戊烷配体构筑的 两种锌配合物的合成、结构及性质

张春华 王莹 唐海军 邓奕芳 陈满生*

(衡阳师范学院化学与材料科学学院, 功能金属有机化合物湖南省重点实验室,
功能金属有机材料湖南省普通高等学校重点实验室, 衡阳 421008)

摘要: 利用过渡金属锌盐与1,5-二(2-甲基咪唑)戊烷(BMIP)、5-羟基(或5-溴)间苯二甲酸(5-OHH₂IP或5-BrH₂IP)在水热条件下合成了配合物[Zn(5-OHIP)(BMIP)]_n (**1**)和[Zn(5-BrIP)(BMIP)]_n (**2**)(BMIP=1,5-二(2-甲基咪唑)戊烷,5-OHIP=5-羟基间苯二甲酸根,5-BrIP=5-溴间苯二甲酸根),对其进行了红外、元素分析表征并用单晶X射线衍射确定了其结构。晶体结构研究表明:配合物**1**属于单斜晶系,*P*2₁/*n*空间群, β 角为101.363(10)°。配合物**1**是由配体5-羟基间苯二甲酸连接锌离子形成一维链状结构,然后由1,5-二(2-甲基咪唑)戊烷将其连接成二维网络结构。配合物**2**是由配体5-溴间苯二甲酸和1,5-二(2-甲基咪唑)戊烷连接锌离子形成二维层状结构,由另一方向的1,5-二(2-甲基咪唑)戊烷连接成三维层柱状结构,最终形成三重贯穿网络结构。此外,研究了配合物**1**和**2**的荧光和光降解亚甲基蓝性能,结果表明配合物**1**和**2**对亚甲基蓝染料均有较好的降解作用。

关键词: 1,5-二(2-甲基咪唑)戊烷; 晶体结构; 荧光; 降解

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Syntheses, Crystal Structures and Properties of Two Zn(II) Complexes Constructed from Flexible 1,5-Bis(imidazol-2-methyl)pentane Ligand

ZHANG Chun-Hua WANG Ying TANG Hai-Jun DENG Yi-Fang CHEN Man-Sheng*

(Key Laboratory of Functional Metal-Organic Compounds of Hunan Province, Key Laboratory of Functional Organometallic Materials of Hengyang Normal University, College of Hunan Province, College of Chemistry and Materials Science, Hengyang Normal University, Hengyang, Hunan 421008, China)

Abstract: Hydrothermal assembly reactions of Zn(NO₃)₂·6H₂O, 1,5-bis-(2-methyl-imidazol)pentane (BMIP) and 5-hydroxyisophthalic acid (5-OHH₂IP) or 5-bromoisophthalic acid (5-BrH₂IP) ligands resulted in the formation of complexes [Zn(5-OHIP)(BMIP)]_n (**1**) and [Zn(5-BrIP)(BMIP)]_n (**2**), respectively. The resulting complexes were characterized by IR spectrum, elemental analysis and single-crystal X-ray diffraction. Crystal structure analysis shows that complex **1** crystallizes in the monoclinic system, space group *P*2₁/*n* with $\beta=101.363(10)^\circ$. Complex **1** displays a two-dimensional layer net constructed by 5-hydroxyisophthalic acid and 1,5-bis-(2-methyl-imidazol)pentane. For **2**, 5-bromoisophthalic acid and 1,5-bis-(2-methyl-imidazol)pentane link Zinc ion into a two-dimensional layers, which are pillared by the other BMIP ligands to result in the three-dimensional framework from another direction. Finally, it exhibits a fascinating three-fold interpenetrating net with *dmp* topology. Both complexes exhibit a strong photoluminescence in the solid state at room temperature. Moreover, two complexes present good photocatalytic activities in methylene blue (MB) degradation reactions. CCDC: 1502156, **1**; 1502157, **2**.

Keywords: 1,5-bis(2-methyl-imidazolyl)pentane; crystal structure; fluorescence; degradation

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*通信联系人。E-mail: cmsniu@163.com; 会员登记号: S06N7223M1009。

0 Introduction

The field of constructing coordination polymers (CPs) with controllable topology has now been studied extensively, and thus intriguing materials with potential applications such as gas sorption and storage, photocatalyst and luminescence, can be produced in different synthesized - methods^[1-6]. However, as we know, many multiple factors, such as temperature, solvent, central metal and co-ligands may affect the nature of CPs and the framework formation in the self-assembly process, which result in the complexity and uncertainty of them^[7]. Generally speaking, the fine tuning of CPs is difficult to realize, and even a subtle modulation of the synthesis conditions may lead to the formation of drastically different structures. As is well known, the combination of aromatic carboxylic acids and flexible N-donor coligands, especially bis(imidazole) ligands, usually have been used to construct CPs with interesting topologies. In such a system, the flexible bis(imidazole) ligands may bend and rotate freely when coordinating to the central metal atoms, which often result in structural diversities. At present, significant work has been carried out by using different metal ions assembly with flexible bis(imidazole) ligands and a series of outstanding examples have been documented in the literature^[8-11]. Furthermore, photoactive CPs have received much more attention as photocatalysts for dye effluent degradation due to large interfacial surface areas, short electron-hole diffusion lengths to internal interfaces, and multiple routes for band gap engineering through compositional and structural control^[12-15]. Recently, we synthesized 1,5-bis-(2-methyl-imidazol)pentane (BMIP) as a flexible N-donor ligand, which has attracted attention in the field of crystal engineering and has been not yet well developed^[16]. Taking inspiration from these views, herein, we report the syntheses and crystal structures of two Zn(II) metal-organic frameworks, namely $[\text{Zn}(\text{5-OHIP})(\text{BMIP})]_n$ (**1**) and $[\text{Zn}(\text{5-BrIP})(\text{BMIP})]_n$ (**2**) with BMIP and 5-hydroxyisophthalic acid (5-OHH₂IP) and 5-bromoisophthalic acid (5-BrH₂IP) ligands. Moreover, the luminescent and photocatalyst properties of these complexes were investigated in the solid state at

room temperature.

1 Experimental

1.1 Materials and instruments

The reagents were used as commercial sources without further purification. The IR spectra were recorded on Bruker Vector22 FT-IR spectrophotometer using KBr discs. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA) were performed on a TGA V5.1A Dupont 2100 instrument heating from room temperature to 900 K under N₂ with a heating rate of 20 K·min⁻¹. The Rigaku D/max-2500 X-ray powder diffractometer with graphite monochromated Cu K α radiation ($\lambda=0.154\ 18\ \text{nm}$) was applied to analyze the powder X-ray diffraction (PXRD) data at 296 K and using ω -2 θ scan mode within 5°~50° at 40 kV and 40 mA. Fluorescence measurements were performed using an F-7000 fluorescence spectrophotometer at room temperature in the solid state. The photocatalytic activity studies were carried out in a UV-visible spectrometer using a PerkinElmer Lambda 950 UV/Vis instrument.

1.2 Syntheses of complexes **1** and **2**

A mixture of 5-OHH₂IP (0.018 g, 0.1 mmol), Zn(NO₃)₂·6H₂O (0.028 g, 0.1 mmol), BMIP (0.013 g, 0.05 mmol), H₂O (10 mL) and NaOH (0.008 g, 0.2 mmol) was placed in a Teflon-lined stainless-steel vessel, heated to 413 K for 3 d, and then cooled to room temperature within 24 h. Colorless block-shaped crystals of **1** were obtained with a yield of 29%. Anal. Calcd. for C₄₂H₄₇ZnN₈O₁₀(%): C, 52.80; H, 4.92; N, 11.73. Found(%): C, 52.76; H, 4.95; N, 11.78. IR (KBr pellet, cm⁻¹): 3 116 (w), 2 968 (w), 1 628 (w), 1 605 (s), 1 519 (m), 1 464 (m), 1 376 (s), 1 364 (m), 1 156 (s), 789 (w), 772 (m), 730 (m), 668 (w). The synthesis of complex **2** was similar to that of **1** but 5-BrH₂IP was used (0.025 g, 0.1 mmol) instead of 5-OHH₂IP. Colorless block-shaped crystals were obtained (Yield: 25%). Anal. Calcd. for C₂₁H₂₃BrZnN₄O₄(%): C, 46.61; H, 4.25; N, 10.36. Found(%): C, 46.54; H, 4.32; N, 10.31. IR (KBr pellet, cm⁻¹): 3 120 (w), 2 960 (w), 1 626 (w), 1 608 (s), 1 521 (m), 1 468 (m), 1 379 (s), 1 366 (m), 1 150 (s), 793 (w), 775 (m), 732 (m), 670 (w).

1.3 X-ray crystallography

The X-ray diffraction measurement for **1** and **2** was carried out on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The data were integrated by using SAINT program^[17], which also did the intensity corrections for Lorentz and polarization effect. An empirical absorption correction was applied using SADABS program^[18]. The structures were solved by

direct methods using program SHELXS-97 and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using SHELXL-97 crystallographic software package^[19-20]. Crystal data and structure refinement parameters are listed in Table 1. The selected bond lengths are given in Table 2.

CCDC: 1502156, **1**; 1502157, **2**.

Table 1 Crystal data and refinement parameters for complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{42}\text{H}_{47}\text{ZnN}_2\text{O}_{10}$	$\text{C}_{21}\text{H}_{23}\text{ZnBrN}_4\text{O}_4$
Formula weight	954.62	540.71
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
a / nm	0.951 88(6)	0.887 40(6)
b / nm	1.878 17(11)	1.518 59(10)
c / nm	1.201 20(7)	1.710 17(11)
$\beta / (^\circ)$	101.363(10)	
V / nm^3	2.105 4(2)	2.304 6(3)
Z	2	4
Crystal size / mm	0.26×0.22×0.20	0.20×0.14×0.10
μ / mm^{-1}	1.208	2.833
$F(000)$	990	1 096
No. of measured, independent, observed [$I > 2\sigma(I)$] reflections	11 405, 4 126, 3 208	11 998, 3 999, 3 634
Data, restraint, parameter	4 126, 0, 282	3 999, 0, 283
Final R indices [$I > 2\sigma(I)$], S	$R_1=0.057\ 1$, $wR_2=0.148\ 0$, 1.048	$R_1=0.025\ 3$, $wR_2=0.064\ 2$, 1.034
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	540, -543	316, -497

Table 2 Selected bond lengths (nm) for complexes **1** and **2**

1					
Zn1-N1	0.199 8(3)	Zn1-O1	0.196 7(3)	Zn1-N4A	0.201 6(3)
Zn1-O3B	0.195 0(3)				
2					
Zn1-N1	0.203 2(2)	Zn1-O5	0.195 6(2)	Zn1-N4A	0.202 1(2)
Zn1-O3B	0.192 5(2)				

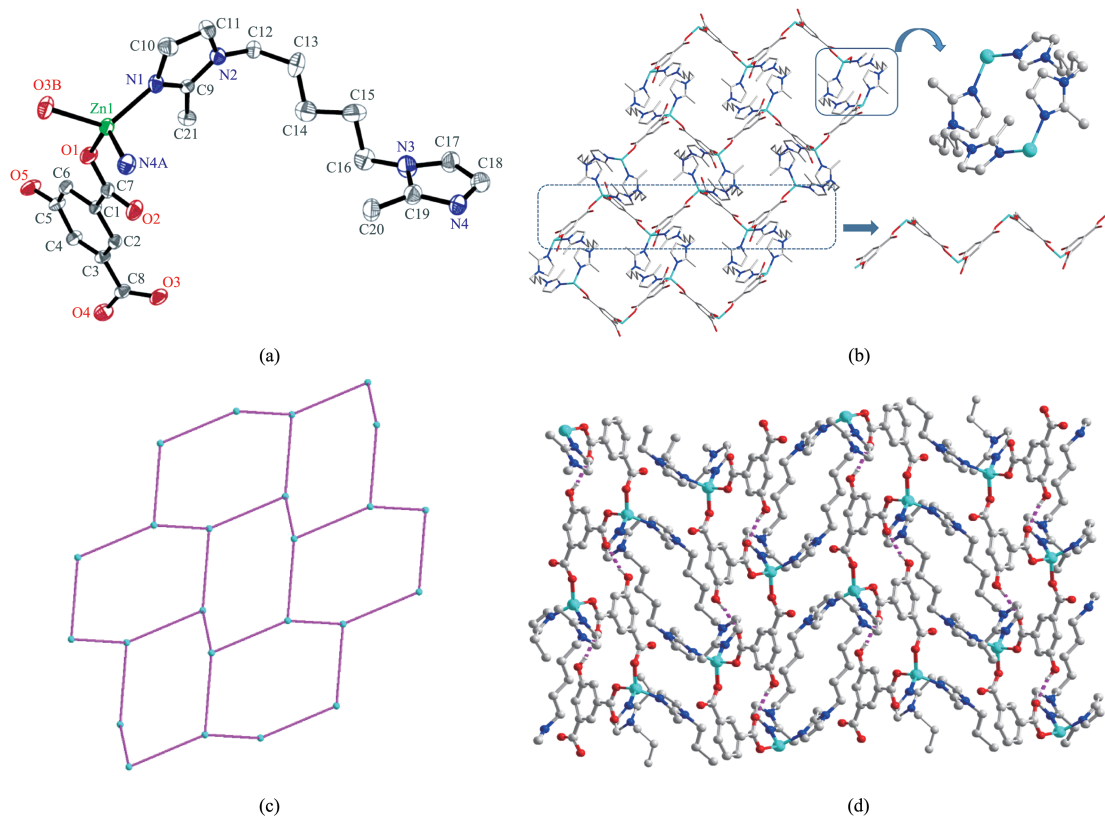
Symmetry codes: A: $-x, -y, 1-z$; B: $1+x, 3/2-y, 1/2+z$ for **1**; A: $5/2-x, -1/2+y, 1/2+z$; B: $1-x, 1-y, 1/2+z$ for **2**.

2 Results and discussion

2.1 Structure description

The crystallographic data shows that complex **1** crystallizes in the monoclinic system with $P2_1/n$ space group. There are one Zn(II), one 5-OHIP²⁻ ligand, one BMIP ligand in the asymmetric unit of **1**. Each Zn²⁺ ion

is four-coordinated in a distorted tetrahedral geometry by two nitrogen atoms from two BMIP ligands and two oxygen atoms from two 5-OHIP²⁻ ligands. The bond angles around the Zn²⁺ ion are in a range of $96.32(14)^\circ \sim 123.36(13)^\circ$. The bond lengths of Zn-O are $0.195\ 0(3) \sim 0.196\ 7(3)\ \text{nm}$ and Zn-N are $0.199\ 8(3), 0.201\ 6(3)\ \text{nm}$, respectively (Table 2). In **1**, each 5-OHIP²⁻ anion

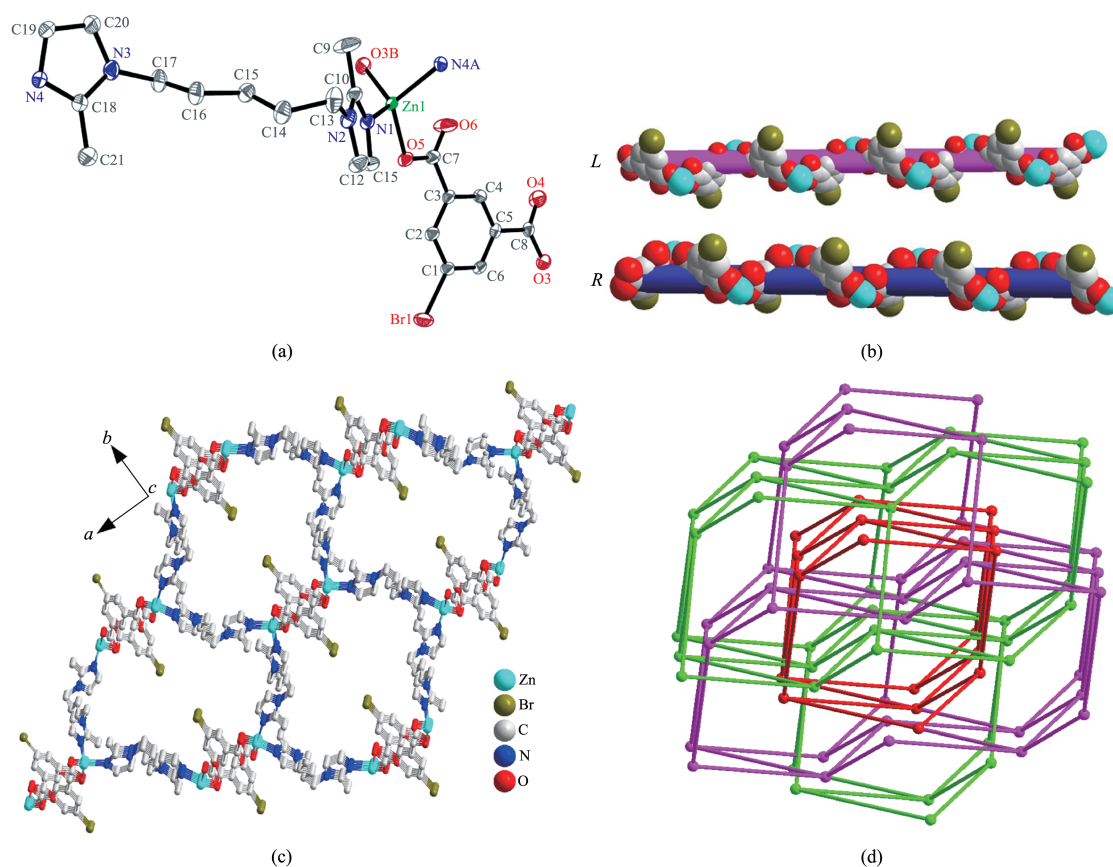


All H atoms are omitted for clarity; Symmetry codes: A: $-x, -y, 1-z$; B: $1+x, 3/2-y, 1/2+z$

Fig.1 (a) Coordination environment of Zn(II) in **1** showing 30% probability displacement ellipsoids; (b) 2D layer structure of **1**; (c) 3-connected 6³ topological network of **1**; (d) 3D molecular structure of complex **1**

serves as a μ_2 -bridge linking two adjacent Zn^{2+} ions in the bis-monodentate mode to give rise to a one-dimensional zigzag chain along c axis, while such one-dimensional chains are further double-bridged by BMIP ligands into a two-dimensional layer along the c axis (Fig.1b). Interestingly, each flexible BMIP is ligated to two Zn^{2+} ions with two terminal imidazole groups and a pair of oppositely arranged μ_2 -BMIP ligands bind two Zn^{2+} ions from adjacent chains to form a $[\text{Zn}_2(\text{BMIP})_2]$ 24-membered metallomacrocyclic ring, and the $\text{Zn} \cdots \text{Zn}$ separation across the BMIP ligands is 1.167 4 nm. From the viewpoint of network topology^[21], if the Zn^{2+} ions are considered as 3-connected nodes, 5-OHIP²⁻ ligand and $[\text{Zn}_2(\text{BMIP})_2]$ unit as linear connectors, the whole structure can be simplified to a 3-connected 6³ topological net (Fig. 1c). The 2D layers are further assembled by intermolecular hydrogen bonds with a $\text{H}(5\text{A}) \cdots \text{O}(2)$ distance of 0.170 nm and the angle of 160° ($\text{O}(5)-\text{H}(5\text{A}) \cdots \text{O}(2)$), leading to formation of a 3D supermolecule structure (Fig.1d).

With 5-BrH₂IP ligand instead of 5-OHH₂IP ligand, new complex **2** with a three-fold interpenetrating three-dimensional framework was obtained. X-ray structural analysis shows that **2** crystallizes in the orthorhombic system with $Pna2_1$ space group. Its asymmetric unit contains one Zn(II), one BMIP ligand, and one 5-BrIP²⁻ anion (Fig.2a). The coordination environment around Zn(II) is shown in Fig.2a. Each Zn(II) ion is in a distorted tetrahedron geometry defined by two nitrogen atoms (Zn1-N1 0.203 2(2) nm, Zn1-N4A 0.202 1(2) nm) of two BMIP ligands and two oxygen atoms (Zn1-O3B 0.192 5(2) nm, Zn1-O5 0.195 6(2) nm) from two separated 5-BrIP²⁻ anions. In complex **2**, Zn(II) ions are bridged by 5-BrIP²⁻ ligands to give rise to one-dimensional helical structures, which coexist as two kinds of helical chains: a left-handed and a right-handed. The BMIP ligand adopts an anti-anti coordinating fashion, while the completely deprotonated 5-BrIP²⁻ ligand adopts monodentately mode. The two carboxylic groups of 5-BrIP²⁻ take a uniform monodentate coordi-



Hydrogen atoms are omitted for clarity; Symmetry codes: A: $5/2-x, -1/2+y, 1/2+z$; B: $1-x, 1-y, 1/2+z$

Fig.2 (a) ORTEP drawing of **2** with 30% thermal ellipsoids; (b) 1D helical-chain constructed by Zn(II) and 5-BrIP²⁻ ligands; (c) View of 3D framework of **2**; (d) Topological representation of 3-fold 3D *dmp* structure of **2**

nation mode. Zn (II) ions are connected by 5-BrIP²⁻ anions to form a one-dimensional chain with a Zn···Zn distance of 1.047 5 nm (Fig.2b top). Each BMIP ligand links two Zn(II) ions to form a one-dimensional wave-like chain with an adjacent Zn···Zn distance of 1.354 6 nm. Firstly, two kinds of helical chains and BMIP ligands form the two-dimensional layer (Fig. 2b, bottom). Then the combination of two-dimensional layers is pillared by the other BMIP ligands to result in the formation of ultimate three-dimensional framework (Fig.2c). Owing to the long distance of Zn···Zn, there is a large unoccupied void space existing in the single three-dimensional framework, which shows a possibility that **2** may display interpenetrating structural characteristics. The potential voids are filled via mutual interpenetration of two other independent equivalent frameworks, generating a three-fold interpenetrating 3D architecture. This feature can greatly enhance the sta-

bility of the whole structure. To further demonstrate the overall 3D structure of **2**, we consider each Zn(II) ion as a four-connecting node, which is linked by two 5-BrIP²⁻ anions and two BMIP ligands. Moreover, the BMIP and 5-BrIP²⁻ anions are simplified as a linear linker. With further topological analysis by the TOPOS program^[21], the whole structure of **2** can be simplified to a three-fold three-dimensional framework 4-c *dmp* topology with the point symbols (6⁵.8) (Fig.2d).

2.2 Thermal gravimetric analyses, PXRD and photoluminescence property

Both complexes are stable under ambient conditions and insoluble in common solvents. To identify the thermal stabilities of the complexes, TGA measurements were carried out in a range of 293~950 K. Since there are not any solvent molecules in the two complexes, they exhibit excellent thermal stability as no weight loss step occurred below 620 and 660 K for **1** and **2**, re-

spectively. When the temperature rose up, the whole framework began to collapse (Fig.3a). PXRD was used to check the purity of complexes **1** and **2**. The results show that all the peaks displayed in the measured patterns at room temperature closely match those in the simulated patterns generated from single-crystal diffraction data, indicating single phases of **1** and **2** were formed, as shown in Fig.3b. On the other hand, CPs with d^{10} metal centers have been investigated for their photoluminescent properties and potential applications in chemical sensors and photochemistry. The solid-state luminescent properties of **1**, **2** and BMIP were investigated at room temperature and the solid-state emission spectra are shown in Fig.4. BMIP exhibited

an emission band at 475 nm when excited at 360 nm. Upon exciting at 330 nm, the maximum emission peaks at about 465 and 460 nm were observed for complexes **1** and **2**, respectively. Compared with the emission peak of the free BMIP ligand, the luminescence emission peaks of complexes **1** and **2** are blue shifted. Because Zn(II) ions have fluorescent emissions that are tuned by the metal-ligand interactions and the deprotonated effect of the dicarboxylic ligands, the results suggest that complexes **1** and **2** may be good candidate of potential blue-fluorescent materials, since they are highly thermally stable and insoluble in common solvents.

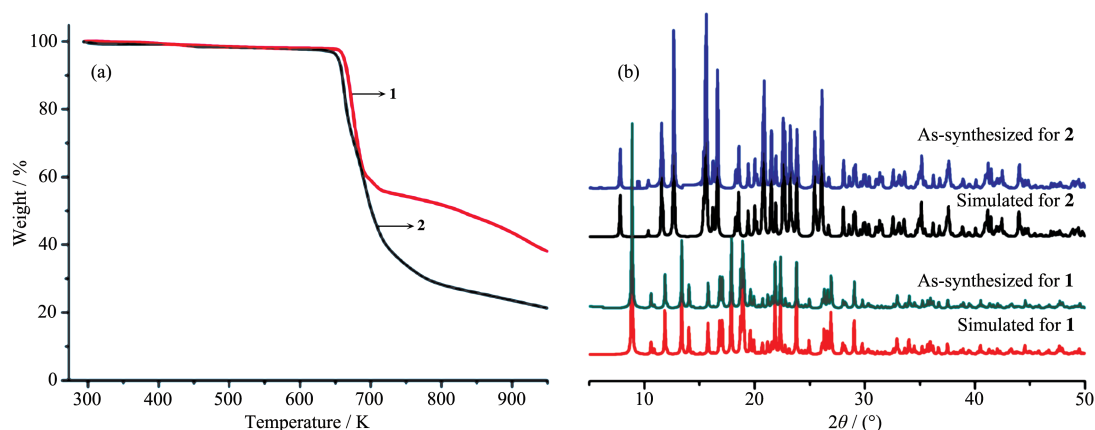


Fig.3 (a) TG curves of complexes **1** and **2**; (b) PXRD patterns of complexes **1** and **2**

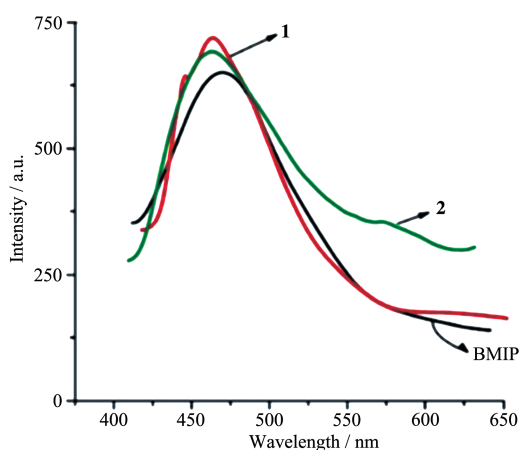


Fig.4 Emission spectra of **1**, **2** and ligand BMIP in the solid state at room temperature

2.3 Photocatalytic activity

As we know, organic dyes such as methyl orange, methylene blue (MB) and rhodamine B are extensively

used in the textile industry, which are resistant to biodegradation commonly. In recent years, much effort has been devoted to develop new photocatalytic materials based on CPs to reduce the environment pollution of such dye molecules^[22-23]. Hence, in this work, the photocatalytic activities of complexes **1** and **2** were evaluated by the degradation of MB under irradiation at room temperature. Typically, 15 mg of powder of the complexes and 0.5 mL of 30% H_2O_2 were dispersed in a 50 mL MB aqueous solution, then magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium of the working solution. The solution was then exposed to the irradiation from a 500 W high pressure mercury vapor lamp and kept under continuous stirring. And 5 mL samples were taken out and then analyzed by UV-Vis spectrometer. By contrast, the control photocatalysis experiment

was also performed under the same conditions with only H_2O_2 or H_2O_2 and ZnSO_4 without any catalysts. The photocatalytic properties of the crystalline products are illustrated in Fig. 5a~5c. Obviously, the irradiation caused a significant decrease of the absorption with increasing reaction time in the presence of two complexes. The major absorption of MB at about 665 nm was selected to supervise the photocatalytic degradation process. Additionally, the ratios of concentration of MB (c/c_0) vs reaction time (t) for two complexes were plotted. It can be seen that approximately 15% of MB had

been decomposed after reacting for 120 min with only H_2O_2 without any catalyst in the solution, while 26% of MB had been decomposed in the same condition with H_2O_2 and ZnSO_4 . In comparison with that, the systems with photocatalysts have shown much better photocatalytic activities during the degradation processes (Degradation rate: 88% for **1** and 77% for **2**, respectively). These results indicate that the two complexes are good candidates for photocatalytic degradation of MB, and may have potential photocatalytic application in the reduction of some other organic dyes.

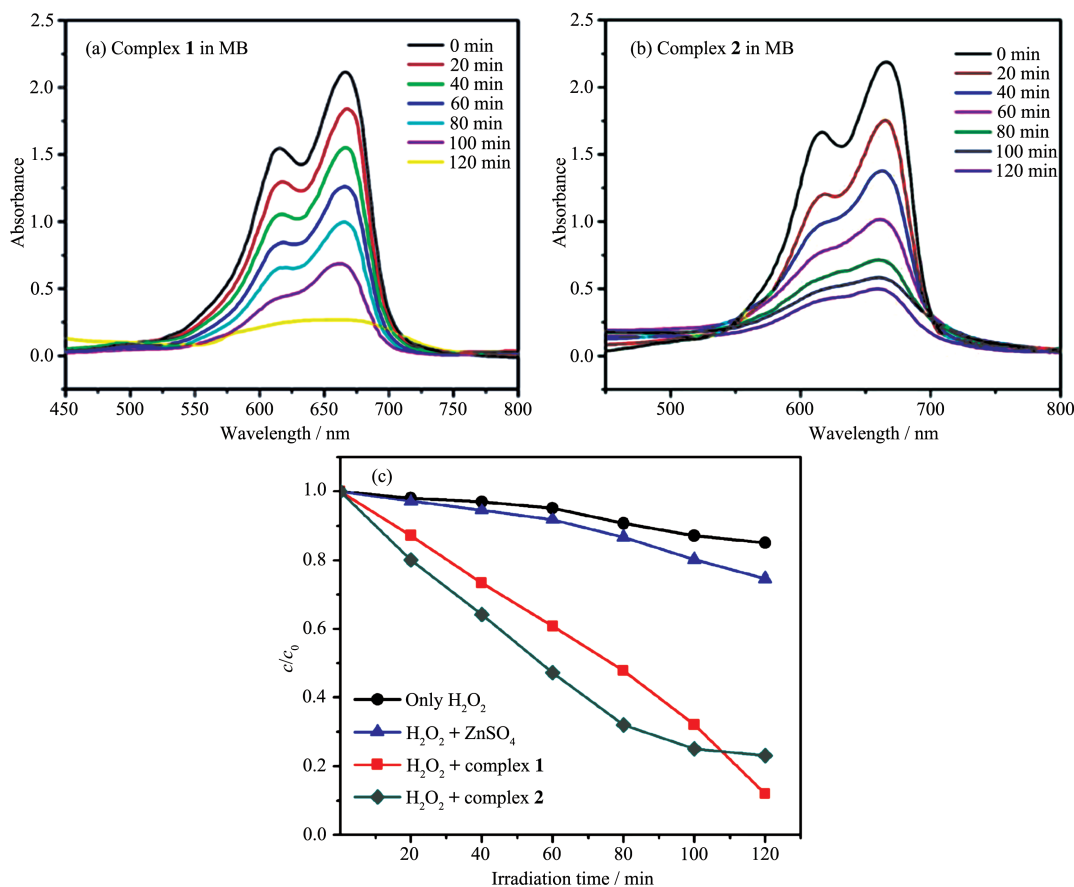


Fig.5 View of time-dependent absorption of MB solution in the presence of complex **1** (a) and complex **2** (b) during the decomposition reaction under UV light irradiation; (c) Photocatalytic performances of complexes **1** and **2**

3 Conclusions

In summary, two new CPs with different framework structures have been successfully constructed based on the connectivity co-effect between the flexible BMIP ligand and 5-substitued carboxylates together with zinc salts under hydrothermal conditions. The results exhibit that the structural diversification of CPs

may result from different 5-substitued carboxylates. Furthermore, complexes **1** and **2** both show photoluminescence property, which appear to be potential hybrid inorganic - organic photoactive materials. And both of the complexes exhibit photocatalytic activity for the degradation of MB solution under ultraviolet light irradiation.

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