三联吡啶羧基 Zn(Ⅱ),Cu(Ⅱ)和 Fe(Ⅱ)配合物研究

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摘要：本文通过溶剂热法合成了三个基于 4′-羧基-2,2′:6′,2″-三联吡啶(HL)的单核配合物,其分子式为[ML₂]·4H₂O(**1**,M=Zn(Ⅱ); **2**,M=Cu(Ⅱ);**3**,M=Fe(Ⅱ)),并分别对其进行了元素分析、波谱、单晶和粉末衍射表征。晶体结构测试结果表明 3 个配合物为异质同晶结构,都属于四方晶系的 $I\bar{4}2d$ 空间群。配合物 **1~3** 都是 1 个二价金属离子和 2 个羧基未配位且去质子化的三齿螯合配体 L 配位形成的单核结构,通过分子间 π-π 堆积和氢键作用拓展成三维超分子网络结构。由于二价 Zn 离子的全充满 d^{10} 电子构型,配合物 **1** 与其配体相比具有明显的室温固态蓝色荧光发射性质。

关键词：锌(Ⅱ)配合物;铜(Ⅱ)配合物;铁(Ⅱ)配合物;荧光性质;晶体结构

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Studies of Zinc(Ⅱ), Copper(Ⅱ) and Ferrous(Ⅱ) Complexes Having a Tridentate [2,2′:6′,2″-Terpyridine]-4′-carboxylate Ligand

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Abstract: Three mononuclear complexes, formulated as [ZnL₂]·4H₂O (**1**), [CuL₂]·4H₂O (**2**) and [FeL₂]·4H₂O (**3**) (LH=[2,2′:6′,2″-terpyridine]-4′-carboxylic acid),have been synthesized under the solvothermal conditions and characterized by elemental analysis, IR spectral, and single-crystal and powder X-ray diffraction methods. Complexes **1~3** are isomorphous structures and they crystallize in the tetragonal space group $I\bar{4}2d$. The ligand shows a tridentate chelating mode where the deprotonated carboxylate unit is free of coordinative bond. Three-dimensional supramolecular networks are observed in **1~3**, which are sustained by π-π stacking and hydrogen bonding interactions. In addition, the solid-state luminescence spectrum of zinc(Ⅱ) complex **1** reveals strong blue photoluminescence at room temperature. CCDC: 925947, **1**; 925948, **2**; 925949, **3**.

Key words: zinc(Ⅱ) complex; copper(Ⅱ) complex; ferrous(Ⅱ) complex; fluorescence property; crystal structure

0 Introduction

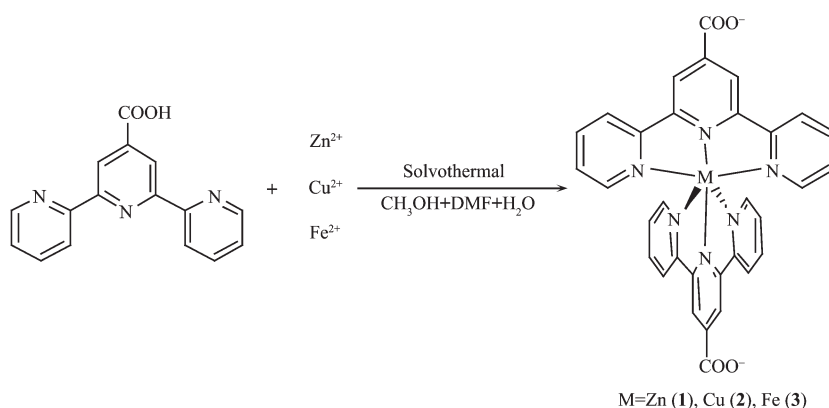Benefit to the strong binding affinity of 2,2′:6′,2′ -terpyridine (tpy) and their structural analogs containing three nitrogen atoms, they can coordinate with a variety of metal ions and they have attracted

M=Zn (**1**), Cu (**2**), Fe (**3**)

Scheme 1　Schematic illustration for the preparation of metal complexes 1, 2 and 3

much attention in the fields of supramolecular and coordination chemistry[1-4]. Furthermore, they have been widely used as multifunctional materials for photovoltaic applications[5-7], optoelectronic device[8-9], magnetic properties[10], nanomaterials[11], biomedical activities[12-15], catalysts[16] and so on.

　　Among them, the tpy derivatives having one or more carboxylate groups, such as [2,2′:6′,2″-terpyridine]-4′-carboxylic acid, 4-([2,2′:6′,2″-terpyridin]-4′-yl)benzoic acid and [2,2′:6′,2″-terpyridine]-3,3″,4′-tricarboxylic acid, are excellent multidentate ligands to form novel metal complexes with high thermal and chemical stabilities and intriguing architectures and functions. In addition, their ruthenium(II) complexes can be used in the investigations of dye sensitized solar cells by anchoring their carboxylate groups on TiO_2[5,7,17-18]. With regard to ligand [2,2′:6′,2″-terpyridine]-4′-carboxylic acid (HL) in this work[19-20], their structural reports are mainly involved in the Ru(II) photosensitizers[17,21-22] but less related to other transition-metal ions[23]. Our purpose is to use this rigid multidentate chelating ligand as a building block to react with transition-metal ions forming self-assembled coordination complexes with interesting fluorescence properties. In our previous work, we have successfully constructed a family of Ru(II), Cu(II), Zn(II), Cd(II), Ni(II), and Fe(II) transition-metal complexes based on a tpyCl ligand with different counterions[24-26]. As related studies in this field, we report herein the syntheses, characterizations and luminescence properties of three mononuclear complexes (Scheme 1) formulated as

$[ML_2] \cdot 4H_2O$ (**1**, M=Zn(II); **2**, M=Cu(II); **3**, M=Fe(II)).

1　Experimental

1.1　Materials and instruments

　　All reagents and solvents were of analytical grade and used without any further purification. The anhydrous solvents were drawn into syringes under a flow of dry N_2 gas and directly transferred into the reaction flask to avoid contamination. HL was prepared via a previously reported approach[19].

　　Elemental analyses (EA) for carbon, hydrogen, and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Fourier transform infrared (FT-IR) spectra (4 000~400 cm^{-1}) were recorded using a Nicolet FT-IR 170X spectrophotometer on KBr disks. Powder X-ray diffraction (PXRD) measurements were performed on a Philips X′pert MPD Pro X-ray diffractometer using Cu $K\alpha$ radiation (λ=0.154 18 nm), in which the X-ray tube was operated at 40 kV and 40 mA at room temperature. Luminescence spectra were recorded on a Hitachi 850 fluorescent spectrophotometer at room temperature (25 ℃).

1.2　Synthesis of the compounds

　　Preparation of complex **1**: $[ZnL_2] \cdot 4H_2O$ (**1**):

　　A mixture of HL (0.028 g, 0.1 mmol), Zn(OAc)$_2$· 2H$_2$O (0.022 g, 0.1 mmol), deionized water (1.0 mL), methanol (10.0 mL) and DMF (1.0 mL) was adjusted to pH=8.0 with triethylamine. The mixture was frozen and sealed under a vacuum in a thick-walled Pyrex tube, then placed inside an oven at 150 ℃ for 96 h. The yellow block crystals were obtained in a yield of

0.019 g (55.1%) on the basis of HL. Main FT-IR absorptions (KBr pellets, ν / cm^{-1}): 3 059 (m), 1 646 (s), 1 623 (s), 1 599 (m), 1 576 (m), 1 554 (m), 1 463 (w), 1 410 (m), 1 369 (m), 1 322 (s), 1 245 (w), 1 161 (w), 1 013 (m), 805 (w), 781 (m), 745 (m), 731 (w), 684 (w), 654 (w), 637 (w). Elemental Anal. Calcd. for $C_{32}H_{28}ZnN_6O_8$ (%): C 55.70; N 12.18; H 4.09. Found (%): C 55.43; N 12.37; H 4.42.

[CuL$_2$]·4H$_2$O (**2**): The preparation of **2** is similar to that of **1** except that Cu(OAc)$_2$·H$_2$O (0.020 g, 0.1 mmol) was used instead of Zn(OAc)$_2$·2H$_2$O. Green block single crystals of **2** suitable for X-ray crystallographic analysis were obtained after one week. Yield: 16.8 mg (48.8% based on HL). Main FT-IR absorptions (KBr pellets, ν / cm^{-1}): 3 392 (b), 3 050 (w), 1 604 (m), 1 587(s), 1 560(s), 1 477(w), 1 413 (m), 1 394(s), 1 367(m), 1 341(w), 1 325(m), 1 305(w), 1 253(w), 1 161(w), 1 052(w), 1 022(w), 784(m), 745(w), 728(w), 687 (m), and 654 (w). Elemental Anal. Calcd. for $C_{32}H_{28}CuN_6O_8$ (%): C 55.85; N 12.21; H 4.10. Found (%): C 55.57; N 12.45; H 3.92.

[FeL$_2$]·4H$_2$O (**3**): complex **3** was prepared in the same method as that of **1** except that Fe(ClO$_4$)$_2$·6H$_2$O (0.018 g, 0.05 mmol) was used instead of Zn (OAc)$_2$·2H$_2$O. Purple block single crystals of **3** suitable for X-ray crystallographic analysis were obtained after one week. Yield: 12.8 mg (37.6% based on HL). Main FT-IR absorptions (KBr pellets, ν / cm^{-1}): 3 052(w), 1 660 (w), 1 647(w), 1 602(w), 1 546(w), 1 536(m), 1 429 (m), 1 374(w), 1 337(w), 1 113(w), 831(m), 558(m), 529 (w), 477 (w). Elemental Anal. Calcd. for $C_{32}H_{28}FeN_6O_8$ (%): C 56.48; N 12.35; H 4.15. Found (%): C 56.72; N 12.61; H 4.02.

Caution! Perchlorate salt of Fe(Ⅱ) used in this study is potentially explosive and should be prepared in small quantities. No such problems were encountered in any of the syntheses reported, but great care must always be exercised. In addition, the sealed tubes should be placed inside a protective case for protection against explosion when heating and the temperature should be less than 160 ℃.

1.3 X-ray data collection and solution

Single-crystal samples of **1~3** were glue-covered and mounted on glass fibers and then used for data collection at 291(2) K. The diffraction data were collected on a Bruker SMART 1K CCD diffractometer using graphite mono-chromated Mo $K\alpha$ radiation (λ = 0.071 073 nm). The crystal systems were determined by Laue symmetry and the space groups were assigned on the basis of systematic absences using XPREP. Absorption corrections were performed to all data and the structures were solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 by using the SHELXTL-PC software package[27-29]. All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complexes **1~3** is listed in Table 1, while selected bond distances and bond angles related to the central Zn(Ⅱ), Cu(Ⅱ) and Fe(Ⅱ) ions are given in Table 2. Hydrogen bonding interactions in complexes **1~3** are shown in Table 3.

CCDC: 925947, **1**; 925948, **2**; 925949, **3**.

Table 1　Crystal data and structure refinement parameters for complexes 1~3

Complex	1	2	3
Empirical formula	$ZnC_{32}H_{28}N_6O_8$	$CuC_{32}H_{28}N_6O_8$	$FeC_{32}H_{28}N_6O_8$
Formula weight	689.97	688.14	680.45
T / K	291(2)	291(2)	273(2)
Wavelength / nm	0.071 073	0.071 073	0.071 073
Crystal size / mm	0.12×0.12×0.10	0.12×0.10×0.10	0.14×0.14× 0.10
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$
a / nm	0.868 42(5)	0.870 83(12)	0.868 17(4)

Continued Table 1

b / nm	0.868 42(5)	0.870 83(12)	0.868 17(4)
c / nm	0.404 84(5)	0.403 14(8)	0.402 20(4)
V / nm³	0.305 31(5)	0.305 72(9)	0.303 15(4)
Z	4	4	4
D_c / (g·cm⁻³)	1.501	1.495	1.491
$F(000)$	1424	1420	1408
μ(Mo $K\alpha$) / mm⁻¹	0.868	0.778	0.561
Abs corr	Multi−scan	Multi−scan	Multi−scan
Max. / min. transmission	0.918 2 / 0.903 0	0.926 3 / 0.912 5	0.946 0 / 0.925 6
refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Limiting indices	$-10 \leqslant h \leqslant 10$,	$-10 \leqslant h \leqslant 10$	$-10 \leqslant h \leqslant 8$
	$-8 \leqslant k \leqslant 10$	$-10 \leqslant k \leqslant 10$	$-10 \leqslant k \leqslant 7$
	$-35 \leqslant l \leqslant 18$	$-10 \leqslant l \leqslant 10$	$-47 \leqslant l \leqslant 47$
Parameters	108	108	108
final R indices ($I>2\sigma(I)$)ᵃ	R_1=0.038 4, wR_2=0.091 4	R_1=0.047 7, wR_2=0.130 0	R_1=0.035 8, wR_2=0.081 3
R indices (all data)	R_1=0.044 3, wR_2=0.095 5	R_1=0.054 5, wR_2=0.134 3	R_1=0.040 7, wR_2=0.084 5
Goodness of fit on F^2	1.097	1.118	1.080
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / (e·nm⁻³)	191, −158	383, −451	210, −311

$R_1=\sum ||F_o|-|F_c|| \sum |F_o|$, $wR_2=[\sum [w(F_o^2-F_c^2)^2] \sum w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond distances (nm) and angles (°) for complexes 1~3

1					
Zn1-N2ⁱ	0.206 7(3)	Zn1-N1ⁱ	0.217 4(3)	Zn1-N2ⁱⁱ	0.217 4(3)
Zn1-N2	0.206 7(3)	Zn1-N1	0.217 4(3)	Zn1-N2ⁱⁱⁱ	0.217 4(3)
N2ⁱ-Zn1-N2	180.0	N1ⁱ-Zn1-N1	93.5(1)	N2ⁱ-Zn1-N1ⁱⁱⁱ	104.2(1)
N2ⁱ-Zn1-N1ⁱ	75.8(1)	N2ⁱ-Zn1-N1ⁱⁱ	75.8(1)	N2-Zn1-N1ⁱⁱⁱ	75.8(1)
N2-Zn1-N1ⁱ	104.2(1)	N2-Zn1-N1ⁱⁱ	104.2(1)	N1ⁱ-Zn1-N1ⁱⁱⁱ	93.5(1)
N2ⁱ-Zn1-N1	104.2(1)	N1ⁱ-Zn1-N1ⁱⁱ	151.6(1)	N1-Zn1-N1ⁱⁱⁱ	151.6(1)
N2-Zn1-N1	75.8(1)	N1-Zn1-N1ⁱⁱ	93.5(1)	N1ⁱⁱ-Zn1-N1ⁱⁱⁱ	93.5(1)
2					
Cu1-N2ⁱ	0.197 1(4)	Cu1-N1ⁱⁱ	0.216 9(4)	Cu1-N1	0.216 9(4)
Cu1-N2	0.197 1(4)	Cu1-N1ⁱⁱⁱ	0.216 9(4)	Cu1-N1ⁱ	0.216 9(4)
N2-Cu1-N2ⁱ	180.0	N1ⁱⁱ-Cu1-N1ⁱⁱⁱ	92.6(1)	N2-Cu1-N1ⁱ	102.3(1)
N2-Cu1-N1ⁱⁱ	77.7(1)	N2-Cu1-N1	77.7(1)	N2ⁱ-Cu1-N1ⁱ	77.7(1)
N2ⁱ-Cu1-N1ⁱⁱ	102.3(1)	N2ⁱ-Cu1-N1	102.3(1)	N1ⁱⁱ-Cu1-N1ⁱ	92.6(1)
N2-Cu1-N1ⁱⁱⁱ	102.3(1)	N1ⁱⁱ-Cu1-N1	155.4(2)	N1ⁱⁱⁱ-Cu1-N1ⁱ	155.4(2)
N2ⁱ-Cu1-N1ⁱⁱⁱ	77.7(1)	N1ⁱⁱⁱ-Cu1-N1	92.6(1)	N1-Cu1-N1ⁱ	92.6(1)
3					
Fe1-N2ⁱ	0.188 5(2)	Fe1-N1ⁱ	0.198 9(2)	Fe1-N1ⁱⁱⁱ	0.198 9(2)
Fe1-N2	0.188 5(2)	Fe1-N1ⁱⁱ	0.198 9(2)	Fe1-N1	0.198 9(2)
N2ⁱ-Fe1-N2	180.0	N1ⁱ-Fe1-N1ⁱⁱ	161.1(1)	N2ⁱ-Fe1-N1	99.4(1)
N2ⁱ-Fe1-N1ⁱ	80.6(1)	N2ⁱ-Fe1-N1ⁱⁱⁱ	99.4(1)	N2-Fe1-N1	80.6(1)
N2-Fe1-N1ⁱ	99.4(1)	N2-Fe1-N1ⁱⁱⁱ	80.6(1)	N1ⁱ-Fe1-N1	91.5(2)

Continued Table 2

N2^i-Fe1-N1^{ii}	80.6(1)	N1^i-Fe1-N1^{iii}	91.5(1)	N1^{ii}-Fe1-N1	91.5(2)
N2-Fe1-N1^{ii}	99.4(1)	N1ii-Fe1-N1^{iii}	91.5(2)	N1^{iii}-Fe1-N1	161.1(1)

Symmetry codes: ^{i} y, $-x$, $-z$; ^{ii} $-y$, x, $-z$; ^{iii} $-x$, $-y$, z for **1**; ^{i} $1+y$, $1-x$, $-z$; ^{ii} $2-x$, $-y$, z; ^{iii} $1-y$, $-1+x$, $-z$ for **2**; ^{i} y, $1-x$, $-z$; ^{ii} $1-y$, x, $-z$; ^{iii} $1-x$, $1-y$, z for **3**.

Table 3　Hydrogen bonding interactions in complexes 1~3

D–H⋯A	d(D–H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
1				
C1–H1⋯O1^i	0.093	0.253	0.323 5(6)	133.0
2				
O2–H2B⋯O1^{ii}	0.085	0.204	0.273 5(10)	138.0
C1–H1⋯O1^{iii}	0.093	0.252	0.322 4(8)	132.0
3				
C2–H2⋯O1^i	0.093	0.257	0.318 9(4)	125.0

Symmetry codes: ^{i} $1/2+y$, x, $-1/4+z$ for **1** and **3**; ^{ii} $1-x$, $1/2+y$, $1/4-z$; ^{iii} $1/2-y$, $1-x$, $-1/4+z$ for **2**.

2　Results and discussion

2.1　Synthesis and spectral characterizations

Three complexes **1~3** were prepared by a simple solvothermal method in a thick-walled Pyrex tube with stoichiometric zinc(Ⅱ) acetate　(copper(Ⅱ) acetate or ferrous(Ⅱ) perchlorate) and HL for 4 d, as shown in scheme 1. The formation of stable, neutral and divalent metal complexes was verified by their elemental and FT-IR spectral analyses. To better understand the nature of the luminescence properties, fluorescence emission of complex **1** in the solid state is illustrated in Fig.1. The ligand shows one intense emission peak at 400 nm　(λ_{ex} =347 nm), which is assigned to the π-π* electronic transitions. Compared with the photoluminescence spectrum of free ligand, the intraligand π-π* transition between the heterocy-

Fig.1　Solid-state fluorescence emission spectra of HL and complex **1** at room temperature

clic aromatic rings in complex **1** shows an obvious bathochromic shift and enhancement from 400 to 494 nm (λ_{ex}=397 nm), because the ligand coordinated with the Zn^{2+} ion increases electron delocalization on the complex backbone. In contrast, no emission peaks can be detected in the photoluminescence spectra of complexes of **2** and **3**　(data are not shown here). The fluorescence deactivation can be attributed to an increase of energy gap required for electron transfer between the central Cu^{2+} and Fe^{2+} ion and the fluorophore ligand　(HL) after coordination. In addition, the pure phase of mononuclear complexes **1~3** are also confirmed by PXRD patterns as shown in Fig.SI1-3.

2.2　Single-crystal structures of mononuclear Zn(Ⅱ), Cu(Ⅱ) and Fe(Ⅱ) complexes 1~3

As shown in Fig.2~4, X-ray single-crystal structural determination of complexes **1~3** reveals that they are all crystallize in the tetragonal $I\bar{4}2d$ space group in which the crystallographically imposed center of symmetry is observed. The asymmetric unit of **1~3** is composed of one central metal ion　(Zn(Ⅱ) for **1**, Cu(Ⅱ) for **2** and Fe(Ⅱ) for **3**), two ligands, and four lattice water molecules. The central metal ions are six-coordinated by six nitrogen atoms from two tridentate L ligands to form a compressed octahedral coordination environment leaving the two protonated carboxylate groups free of coordinative bond. In the molecular structures of **1~3**, the ZnN bond lengths are
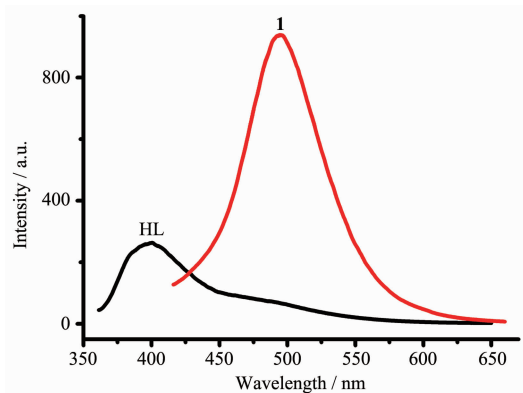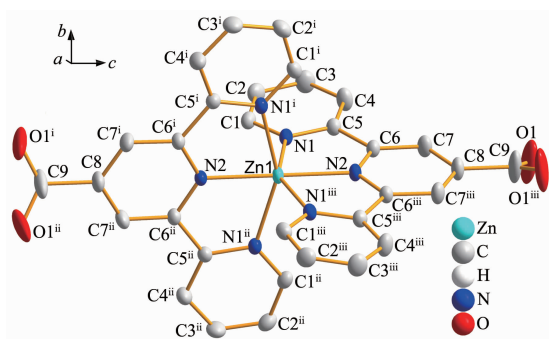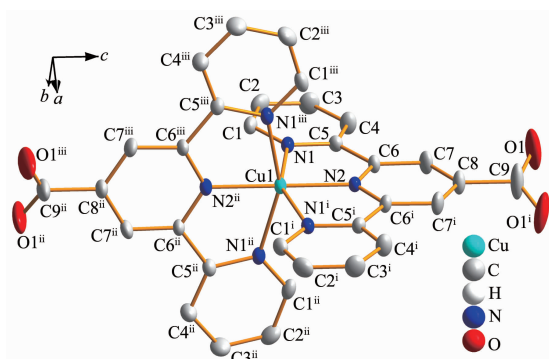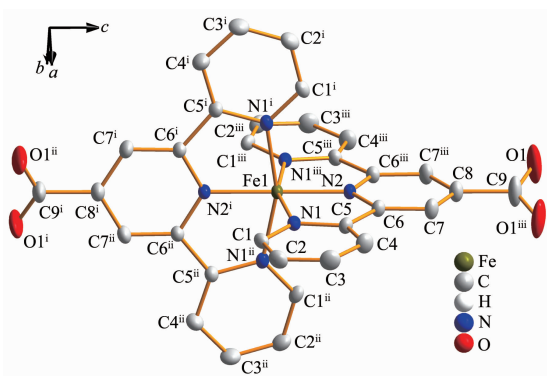
Hydrogen atoms and solvent molecules are omitted for clarity and the displacement ellipsoids are drawn at the 30% probability level; Symmetry codes: ^{i} y, $-x$, $-z$; ^{ii} $-y$, x, $-z$; ^{iii} $-x$, $-y$, z

Fig.2　ORTEP diagram of the molecular structure of complex **1**

Hydrogen atoms and solvent molecules are omitted for clarity and the displacement ellipsoids are drawn at the 30% probability level; Symmetry codes: ^{i} $1+y$, $1-x$, $-z$; ^{ii} $2-x$, $-y$, z; ^{iii} $1-y$, $-1+x$, $-z$

Fig.3　ORTEP diagram of the molecular structure of complex **2**

Hydrogen atoms and solvent molecules are omitted for clarity and the displacement ellipsoids are drawn at the 30% probability level; Symmetry codes: ^{i} y, $1-x$, $-z$; ^{ii} $1-y$, x, $-z$; ^{iii} $1-x$, $1-y$, z

Fig.4　ORTEP diagram of the molecular structure of complex **3**

0.206 7(3) and 0.217 4(3) nm and the Cu-N distances are 0.197 1(4) and 0. 216 9(4) nm, while the Fe-N

distances are shorter at 0.188 5(2) and 0.198 9(2) nm, respectively (Table 2). These measured MN bond lengths are in good agreement with those reported in literature[30-31]. The carboxylic groups are not completely coplanar with the central terpyridine ring with dihedral angles of 25.6(3)°, 23.1(4)° and 18.6(2)° in **1~3**. The related two CO bond lengths are the same as 0.122 4(4), 0.122 2(6) and 0.122 2(3) nm in **1~3**, indicative of the delocalized and deprotonated forms of carboxylic groups.

In the crystal packing of **1~3**, hydrogen bonding interactions are found between the carboxylic oxygen atoms and the protons of one of the terpyridine ring
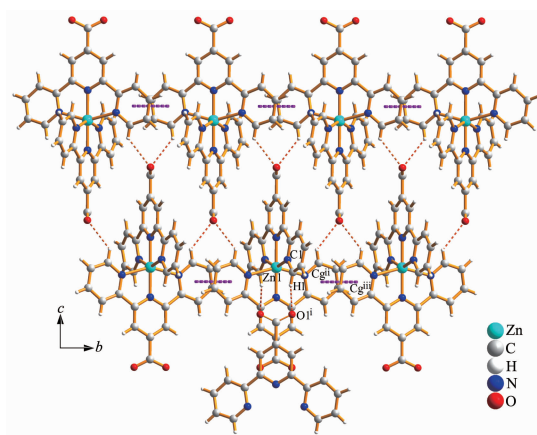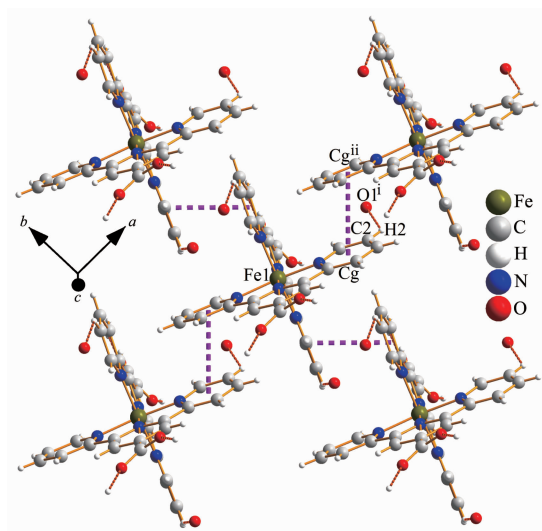

Symmetry codes: ^{i} $1/2+y$, x, $-1/4+z$; ^{ii} $-y$, x, $-z$; ^{iii} y, $1-x$, $-z$

Fig.5　Perspective view of the π-π stacking interactions in the crystal packing of complex **1**
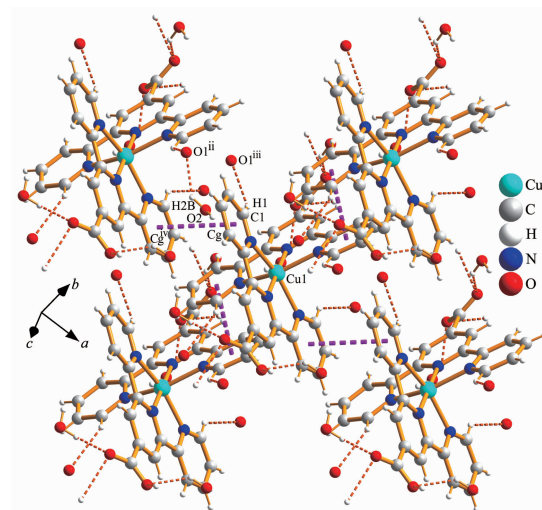
Symmetry codes: ^{ii} $1-x$, $1/2+y$, $1/4-z$; ^{iii} $1/2-y$, $1-x$, $-1/4+z$; ^{iv} $1-x$, $-y$, z

Fig.6　Perspective view of the π-π stacking interactions in the crystal packing of complex **2**

Symmetry codes: ^{i} 1/2+y, x, −1/4+z, ^{ii} 2−x, 1−y, z

Fig.7　Perspective view of the π-π stacking interactions in the crystal packing of complex **3**

(Table 3). It is also noteworthy that π-π stacking interactions are observed between adjacent aromatic rings and the centroid-to-centroid separations between neighboring pyridine rings are 0.366 4(6) nm for complex 1, 0.367 3(6) nm for complex **2** and 0.371 7(4) nm for complex **3**. As can be seen in Fig.5~7, complex **1~3** are extended into three-dimensional supramolecular networks by virtue of these π-π stacking and hydrogen bonding interactions, which will significantly stabilize the overall solid-state structures.

3　Conclusions

In conclusion, a [2,2′:6′,2″-terpyridine]-4′-carboxylic acid ligand is used to prepare three new mononuclear zinc(Ⅱ), copper(Ⅱ) and ferrous(Ⅱ) complexes **1~3** under solvothermal synthetic conditions. Ligand L shows a tridentate chelating fashion where the deprotonated carboxylate unit is free of coordinative bond. The solid-state luminescence spectrum of complex **1** indicates the blue photoluminescence. Further work is being undertaken in our lab on the preparation and properties of heterometal coordination polymers based upon these mononuclear metal complexes where the uncoordinated and deprotonated carboxylate groups in **1~3** are used to coordinate with other metal ions with or without the presence of certain auxiliary ligands.

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