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2,9-二甲基菲咯啉 Cu(Ⅰ)和 Cu(Ⅱ)配合物的合成、晶体结构和性质

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摘要:以二水合氯化铜,2,9-二甲基菲咯啉(dmphen)和硫氰酸铵为原料,通过沉淀反应和 *N*,*N*-二甲基甲酰胺(DMF)重结晶得到了 2 个新型配合物[Cu(Ⅰ)(dmphen)(SCN)]$_n$ (**1**)和[Cu(Ⅱ)(dmphen)(DMF)(NCS)$_2$] (**2**),并采用元素分析、红外光谱、紫外可见光谱、X 射线单晶衍射、热重分析及荧光光谱对其进行了表征。结果表明:**1** 属单斜晶系,$P2_1/n$ 空间群,晶胞参数为 a=1.211 1 (4) nm,b=0.826 2(2) nm,c=1.367 5(4) nm,β=96.502(5)°,V=1.359 5(7) nm^3,Z=4;该配合物通过硫氰酸根的桥联作用形成了一维 Z 链结构。**2** 为三斜晶系,$P\bar{1}$ 空间群,晶胞参数 a=0.943 6(2) nm,b=1.010 9(2) nm,c=1.219 0(3) nm,α=95.628(4)°,β=103.114(4)°,γ=107.087(4)°,V=1.065 4(4) nm^3,Z=2;**2** 通过 C–H···S 氢键和 π-π 堆积构筑成一个超分子网络结构。热重和荧光分析表明:**1** 比 **2** 具有更高的热稳定性,且 **1** 在 603 nm 处有最强荧光发射强度。

关键词:2,9-二甲基菲咯啉;荧光;晶体结构;π-π 堆积
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Syntheses, Crystal Structures and Properties of Copper(Ⅰ) and Copper(Ⅱ) Complexes with 2,9-Dimethyl-1,10-phenanthroline

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Abstract: Two novel complexes, [Cu(Ⅰ)(dmphen)(SCN)]$_n$ (**1**) and [Cu(Ⅱ)(dmphen)(DMF)(NCS)$_2$] (**2**) (dmphen=2,9-dimethyl-1,10-phenanthroline, DMF=*N*,*N*-dimethylformamide), have been obtained by the precipitation reaction and DMF recrystallization with cupric chloride dihydrate, dmphen and ammonium thiocyanate as reactants, and characterized by elemental analysis, FTIR, UV-Vis and single crystal X-ray diffraction analysis. Their thermal stabilities and fluorescence properties have also been investigated. The results show that **1** belongs to monoclinic system, space group $P2_1/n$ with a=1.211 1(4) nm, b=0.826 2(2) nm, c=1.367 5(4) nm, β=96.502(5)°, V=1.359 5(7) nm^3, and Z=4. **1** features one-dimensional zigzag chains with Cu atoms bridged by thiocyanate groups. **2** crystallizes in the triclinic system, space group $P\bar{1}$ with a=0.943 6(2) nm, b=1.010 9(2) nm, c=1.219 0(3) nm, α=95.628(4)°, β=103.114(4)°, γ=107.087(4)°, V=1.065 4(4) nm^3, and Z=2; the three-dimensional supramolecular framework of **2** is constructed by C–H···S hydrogen bonds and π-π stacking interactions. TG and fluorescence analysis show the thermal stability of **1** is higher than of **2**, and **1** has the maximum emission band of the fluorescence at 603 nm. CCDC: 1063354, **1**; 1448398, **2**.

Keywords: 2,9-dimethyl-1,10-phenanthroline; fluorescence; crystal structure; π-π interactions

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0 Introduction

In recent years, transition-metal complexes constructed from inorganic metal salts and organic ligands have attracted considerable interest[1-2], due to their interesting topologies and potential applications in some fields, such as catalysts[3], electrochemistry[4], magnetism[5], nonlinear optical materials[6] and biological materials[7]. The topologies and properties can be controlled by rationally selected ligands, metal cations, anions and reaction conditions. *N*,*N*-donor ligands such as 2,2′-bipyridine and 1,10-phenanthroline are a kind of important ligands that coordinate to metal ions via the nitrogen atom, and have been studied extensively in coordination chemistry. Investigations in this direction have led to many materials of interesting structures[8]. The pseudo-halide SCN^- is known to coordinate to metals in terminal and bridging modes[9]. Two types of terminal coordination modes are observed: S-coordinated SCN^- termed as thiocyanate and N-coordinated NCS^- known as isothiocyanate[10]. The copper thiocyanate systems are of considerable interest owing to the broad structures and properties[11-12]. However, the vast majority of studies have focused on Cu(Ⅱ) isothiocyanate complexes[12].

It has been reported before, adding NH_4SCN to a light blue solution, which contains a pale green precipitate of [Cu(Ⅱ)(phen)Cl_2] (phen=1,10-phenanthroline) via the reaction of $CuCl_2\cdot 2H_2O$ and phen, produces a green solid [Cu(Ⅱ)(phen)$(NCS)_2$][13]. Interestingly, when phen was replaced with 2,9-dimethyl-1,10-phenanthroline (dmphen), which has a higher electron density because of the electron-donation effect of two methyl groups, we obtained two Cu complexes, [Cu(Ⅰ)(dmphen)(SCN)]$_n$ (**1**) and [Cu(Ⅱ)(dmphen)(DMF)$(NCS)_2$] (**2**), by recrystallization in *N*,*N*-dimethylformamide (DMF) solvent. Their crystal structures, thermal stabilities and fluorescence properties are reported, respectively.

1 Experimental

1.1 Materials and measurements

All reagents and solvents employed were commercially available and used without further purification. Elemental analysis (EA) was carried out on a Vario EL cube elemental analyzer. Diffraction intensity data were collected on a Bruker SMART APEX Ⅱ CCD diffractometer. FTIR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on an Impact 420 FT-IR spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer in the range of 200~800 nm. The fluorescence properties were recorded in a Hitachi F-4600 FL spectrophotometer under the excitation at 300 nm. TGA analysis was carried out on a TA Instruments Q50 thermogravimetric analysis under flowing N_2 atmosphere with a heating rate of 10 ℃·min^{-1} from 30 to 800 ℃.

1.2 Syntheses of the complexes

$CuCl_2\cdot 2H_2O$ (1 mmol, 0.170 g) was added to a stirred solution of dmphen (1 mmol, 0.208 g) in 30 mL absolute ethanol. After the solution was refluxed for 3 h, NH_4SCN (2 mmol, 0.152 g) was added, and the mixture were sequentially refluxed for 5 h, filtered, and washed with deionized water (20 mL×3) to obtain the brick-red powders. The powders were dissolved in DMF. The red block [Cu(dmphen)(NCS)]$_n$ (**1**) and green prismatic [Cu(dmphen)(DMF)$(SCN)_2$] (**2**) were grown by slow evaporation at room temperature for several weeks. Anal. Calcd. for $C_{15}H_{12}CuN_3S$(%): C, 54.56; N, 12.73; H, 3.64; S, 9.71. Found(%): C, 54.59; N, 12.71; H, 3.59; S, 9.73. FTIR (KBr, cm^{-1}): 3 443(m), 2 101(s), 1 617(m), 1 499(s), 1 422(w), 1 145(m), 854(s), 772(m), 429(w), Anal. Calcd. for $C_{19}H_{19}CuN_5OS_2$(%): C, 49.45; N, 15.18;H, 4.12; S, 13.88. Found(%): C, 49.47; N, 15.21; H, 4.02; S, 13.92. FTIR (KBr, cm^{-1}): 3 053(w), 2 079(s), 1 592(m), 1 502(s), 1 435(m), 1 152(w), 862(s), 434(w).

1.3 X-ray data collection and structure refinements

A suitable red bolck single-crystal for **1** with the dimension of 0.2 mm×0.2 mm×0.15 mm and green prismatic for complex **2** with the dimension of 0.2 mm×0.18 mm×0.14 mm were carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray

diffraction was carried out on a Bruker Smart Apex CCD area detector system with Mo $K\alpha$ (λ=0.071 073 nm) radiation at low temperature of 100 K for **1** and at 296 K for **2**. The structures of **1** and **2** were solved by the direct method and refined by full-matrix least squares method on F^2 with SHELXS97[14] and Olex2[15]. The hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and bond angles are listed in Table 2 for **1** and Table 3 for **2**. Crystal structure images were drawn using the DIAMOND software[16] and SHELXTL software package[17].

CCDC: 1063354, **1**; 1448398, **2**.

Table 1　Crystallographic data for complexes 1 and 2

Complex	**1**	**2**
Expirical formula	$C_{15}H_{12}CuN_3S$	$C_{19}H_{19}CuN_5OS_2$
Formula weight	329.88	461.05
Crystal symmetry	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a / nm	1.211 1(4)	0.943 6(2)
b / nm	0.826 2(2)	1.010 9(2)
c / nm	1.367 5(4)	1.219 0(3)
α / (°)	90	95.628(4)
β / (°)	96.502(5)	103.114(4)
γ / (°)	90	107.087(4)
V / nm^3	1.359 5(7)	1.065 4(4)
Z	4	2
Measured, independent, observed [$I>2\sigma(I)$] reflections	12 549, 3 900, 2 725	8 143, 5 352, 3 345
R_{int}	0.071 2	0.028 7
R, wR, S	0.048 1, 0.148 3, 1.040	0.051 6, 0.132 9, 1.010
Parameters	184	257
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	581, −647	684, −431

Table 2　Selected bond lengths (nm) and bond angles (°) for 1

Cu(1)-N(3)	0.192 3(3)	N(1)-C(2)	0.133 1(5)	Cu(1)-N(2)	0.206 9(3)
N(1)-C(13)	0.135 8(4)	Cu(1)-N(1)	0.211 0(3)	N(2)-C(11)	0.133 5(4)
Cu(1)-S(1)#1	0.234 06(11)	N(2)-C(12)	0.135 7(4)	S(1)-Cu(1)#2	0.234 05(11)
N(3)-C(15)	0.117 8(5)				
N(3)-Cu(1)-N(2)	123.70(13)	N(3)-Cu(1)-N(1)	115.73(12)	N(2)-Cu(1)-N(1)	80.29(11)
N(3)-Cu(1)-S(1)#1	118.17(9)	N(2)-Cu(1)-S(1)#1	104.72(8)	N(1)-Cu(1)-S(1)#1	107.64(8)
C(15)-S(1)-Cu(1)#2	98.68(13)	N(3)-C(15)-S(1)	179.5(3)		

Symmetry codes: #1: $-x+3/2$, $y-1/2$, $-z+1/2$; #2: $-x+3/2$, $y+1/2$, $-z+1/2$

Table 3　Selected bond lengths (nm) and bond angles (°) for 2

C(18)-N(5)	0.143 6(5)	C(19)-N(5)	0.145 1(5)	Cu(1)-N(1)	0.197 3(4)
C(17)-N(5)	0.130 3(5)	Cu(1)-N(2)	0.195 7(3)	Cu(1)-N(3)	0.224 1(3)
Cu(1)-N(4)	0.201 1(3)	Cu(1)-O(1)	0.199 2(2)		
N(1)-Cu(1)-N(3)	104.97(12)	N(2)-Cu(1)-N(3)	104.03(12)	N(1)-Cu(1)-N(4)	90.44(12)
N(2)-Cu(1)-N(4)	90.16(12)	N(1)-Cu(1)-O(1)	89.35(13)	N(2)-Cu(1)-O(1)	88.95(12)

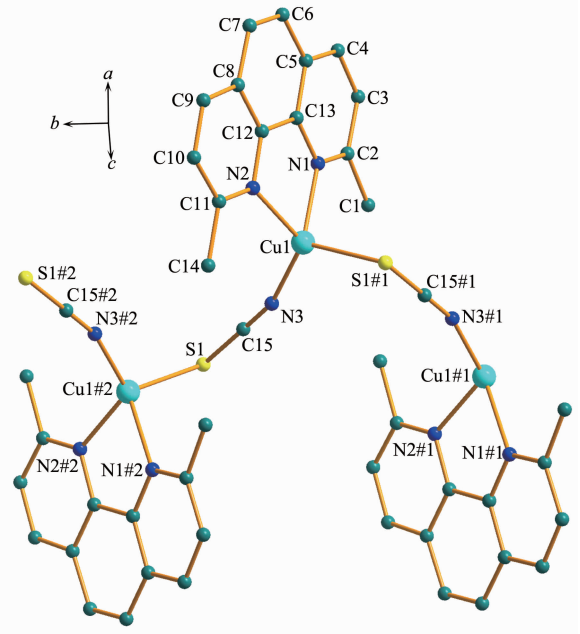
Continued Table 3

N(2)-Cu(1)-N(1)	150.58(15)	N(4)-Cu(1)-N(3)	79.22(10)	O(1)-Cu(1)-N(4)	177.82(10)
O(1)-Cu(1)-N(3)	102.93(10)				

2 Results and discussion

2.1 Structure description of 1

The structure of **1** shown in Fig.1 belongs to the monoclinic system, space group $P2_1/n$, and features a novel one-dimensional zigzag chain with copper(I) atoms bridged by thiocyanate groups.



Symmetry codes: #1: $-x+3/2$, $y-1/2$, $-z+1/2$; #2: $-x+3/2$, $y+1/2$, $-z+1/2$

Fig.1 Molecular structure of **1**

The asymmetric unit of **1** contains one thiocyanato anion, one dmphen ligand, and a central Cu(I) cation. The coordination geometry of the Cu(I) cation, which is defined by one N and one S from SCN^- anions, respectively, and two nitrogen atoms from a bidentate chelating dmphen ligand, can be described as a tetrahedron. Bond angles being related to the Cu(I) atoms are a rather wide range from 80.29(11)° to 123.70(13)°, which indicates that there is a highly distorted tetrahedral geometry. The Cu-N bond lengths vary from 0.192 3(3) to 0.211 0(3) nm, which are comparable to other analogous Cu(I) complexes[18-19]. The Cu-S bond length is also comparable to the values in the end-to-end thiocyanato bridged copper(I) complxes[20]. The bridging thiocyanato groups in the complex show bent coordination modes with the copper atoms (Cu(1)-N(3)-C(15)-C(15) 162.5(3)°). The distance of 0.552 6(9) nm between Cu1 and Cu1#2 (Symmetry codes: #2: $-x+3/2$, $y+1/2$, $-z+1/2$) is much longer than twice the sum of the van der Waals radii of Cu atoms of 0.280 nm, indicating that there are no Cu(I)···Cu(I) interactions[21].

Obviously, as shown in Fig.2, there are diverse π-π interactions[22] during six membered rings of dmphen. The centroid-centroid distances ($d_{c\text{-}c}$) vary from 0.358 9(5) nm to 0.392 4(2) nm, the parameters of which are listed in Table 4 in detail.

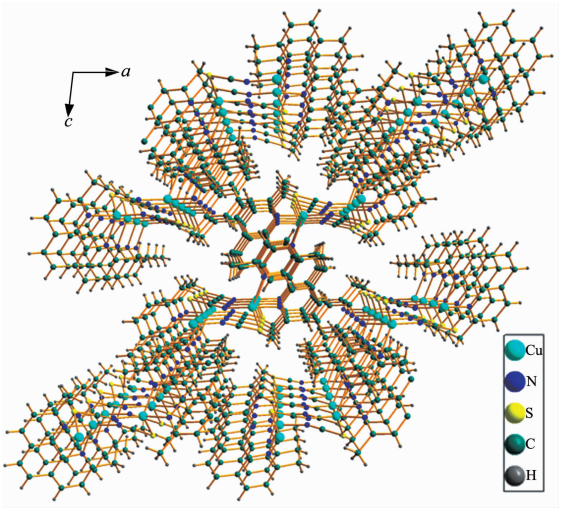


Fig.2 Packing diagram for **1** along *b* axis

2.2 Structural description of 2

The structure of **2** is shown in Fig.3. The asymmetric unit of **2** contains two isothiocyanato anions, one DMF solvent molecule, one dmphen and a central copper(Ⅱ) cation. The copper(Ⅱ) cation displays a distorted trigonal bipyramid geometry, which is coordinated by four N atoms from one dmphen ligand and two isothiocyanato anions, respectively, and one O atom from the DMF solvent molecule. The perpendicular distance between Cu and the plane of N(3)N(4)O(1) is 0.000 6(3) nm, which indicates that the four atoms obtain an ideal plane. Two axial sites are occupied by N(1) and N(2) from two isothiocyanato

Table 4　Parameters for π-π interactions between selected rings*

Complex	Cg(*i*)→Cg(*j*)	$d_{\pi-\pi}$ / nm	d_{c-c} / nm	θ / (°)	ϕ / (°)	η / (°)
1	Cg(2)→Cg(2)#1	0.332 08	0.375 27	0	27.76	27.76
	Cg(2)→Cg(3)#2	0.339 18	0.359 61	3.02	22.27	19.41
	Cg(2)→Cg(4)#2	0.338 93	0.358 95	2.183	17.28	19.23
	Cg(4)→Cg(4)#2	0.342 21	0.407 19	0	32.82	32.82
2	Cg(4)→Cg(2)#3	0.367 77	0.370 71	1.494	7.61	7.23

*Stacking parameters for the analysis of π-π interactions between two rings: θ=dihedral angle between planes *i* and *j*; ϕ and η= slipping angles defined by centroid-centroid distance (d_{c-c}) and the normal to the plane *i* or *j*, respectively; $d_{\pi-\pi}$=stacking distance defined as the centroid-normal to the plane averaged distance, $\phi=\eta$ when $\theta=0°$. Definition of rings for **1**: Cg(2) N(1)-C(2)-C(3)-C(4)-C(5)-C(13), Cg(3) N(2)-C(11)-C(10)-C(9)-C(8)-C(12), Cg(4) C(5)-C(6)-C(7)-C(8)-C(12)-C(13); for **2**: Cg(2) N(3)-C(3)-C(4)-C(5)-C(6)-C(7), Cg(4) C(6)-C(7)-C(8)-C(9)-C(14)-C(13). Symmetry codes: #1: −*x*, −*y*, −*z*; #2: −*x*, 1−*y*, −*z*; #3: 1−*x*, 2−*y*, 1−*z*.

ligands, respectively. Thus, the geometry is very different from that observed in **1**. The bond lengths and bond angles in **2** are comparable to other similar compounds[19-20]. The torsion angles of N(5)-C(17)-O(1)-Cu(1) (177.0(3)°), O(1)-C(17)-N(5)-C(18) (178.0(4)°) and O(1)-C(17)-N(5)-C(19) (178.5(4)°) indicate that all non-hydrogen atoms of DMF and the copper(Ⅱ) atom lie in an approximate plane.

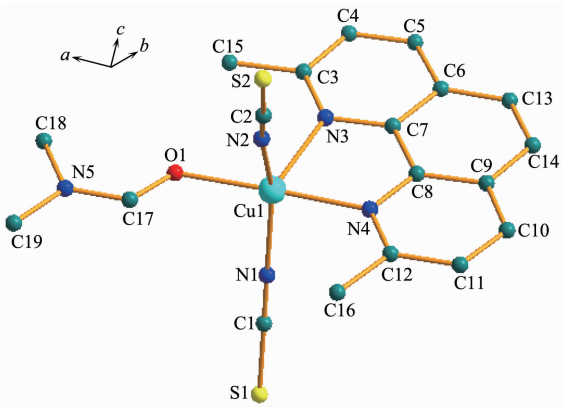


Fig.3　View of the molecular structure of **2**

From the structure shown in Fig.4, the most remarkable feature is that a three-dimensional supramolecular structure of **2** is constructed through strong C−H···S hydrogen bonds[23] ($d_{C\text{-}S}$=0.376 4(2) nm, $d_{H\cdots S}$= 0.287 nm, ∠CHS=162°) and inter-layer π-π stacking interactions [22] between six-membered rings of dmphen. The centroid-centroid distance (d_{c-c}) is 0.370 7(1) nm (Table 4).

2.3　Thermal stability

The thermal analysis curves of **1** and **2** are shown in Fig.5. Before 278 ℃, **1** is stable and then begins to lose weight above 278 ℃. Continuous

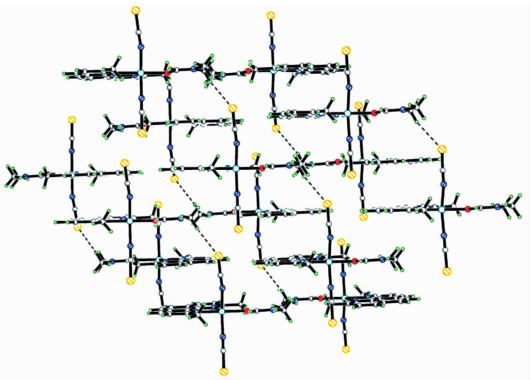


Fig.4　View of three-dimensional packing structure via C−H···S hydrogen bonds and inter-layer π-π stacking interactions

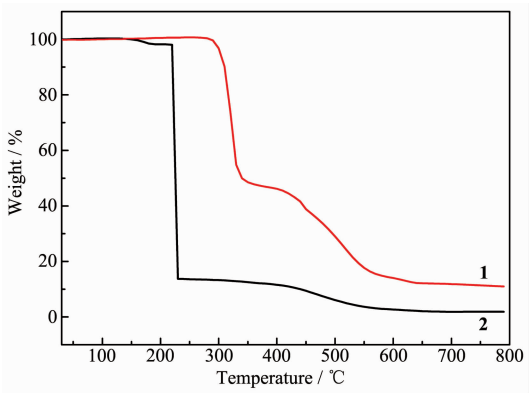


Fig.5　TGA curves of **1** and **2**

decomposition, which is ascribed to the release of dmphen ligand and thiocyanato ligand, is observed in the temperature range of 278~621 ℃. After 621 ℃ has been reached, the total weight loss of 88.3% indicates that the final residue of 11.7% might be the pure copper, which is close to the mass fraction of pure copper in **1** (19.3%).

A thermal analysis curve of **2** exhibits that the

decomposition of the complex starts at 172 ℃. Compared with **1**, the steric hindrance of **2** from isothiocyanato anions, DMF and dmphen is more conducive to decomposition. There is a rapid decomposition in the temperature range of 172~229 ℃, especially, the weight loss is up to 86.0% in the range of 220~229 ℃. Then there is a very flat line on the TGA curve in range of 229~334 ℃, namely, no weight loss is observed during the temperature range. In the temperature range of 334 ~621 ℃ , the weight loss is ascribed to the decomposition of the residue. Last but not least, like structure **1**, when the temperature exceeds 621 ℃, the final residue is stable, which may be the pure copper, too.

2.4 UV-Vis spectra

The UV-Vis spectra of **1**, **2** and dmphen in DMF (c=5.0×10^{-5} mol·L^{-1}) are shown in Fig.S6 (Supporting Information). Absorption peaks of **1** and **2** are obviously different from that of dmphen. The dmphen exhibits the absorption peak at 270 nm, which is attributed to the spin-allowed π-π* ligand centered (LC) transition of dmphen. Compared with the absorption peak of dmphen, the corresponding peaks have red-shift to 281 nm for **1** and 276 nm for **2**. An additional weak peak at 455 nm for both **1** and **2** that is not observed in the spectrum of dmphen is assigned to spin-allowed d-π* transition involving mainly the 3d orbitals of Cu(I) and the π* orbitals of the dmphen.

2.5 Fluorescence properties

The fluorescence properties of **1**, **2** and dmphen were studied in dilute DMF solution (c=5.0×10^{-5} mol·L^{-1}) at room temperature, as depicted in Fig.6. The ligand exhibits the strongest fluorescence emission intensity at 390 nm upon excitation at 300 nm, which should be attributed to the intra-ligand π-π* transition. Compared with the free ligand, a weak fluorescence emission band at 603 nm for **1** is observed. The significant red shift of the emission band is ascribed to the influence of the introduction of the Cu(I) ion. However, **2** shows no fluorescence, which is comparable to the similar Cu(Ⅱ) compounds[24].

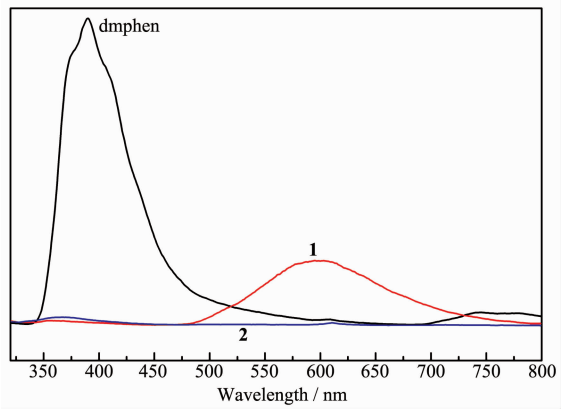


Fig.6 Emission spectra of dmphen, **1** and **2** in dilute DMF solution at room temperature

3 Conclusions

In summary, two copper complexs **1** and **2** have been synthesized simultaneously by ethanol refluxing and DMF recrystallization. X-ray crystallography data reveal that the structure of **1** is a one-dimensional zigzag chain, while the stacking mode of **2** is a three-dimensional supramolecular structure by C –H ⋯ S hydrogen bonds and π-π stacking interactions. **2** exhibits a lower stability because of steric hindrance from isothiocyanato anions, DMF and dmphen, while **1** is stable below 278 ℃. Comparison with dmphen, the fluorescence emission band for **1** shifts from 390 to 603 nm. Further we will explore this reaction mechanism for the rational formation of title compounds.

Supporting information is available at http://www.wjhxxb.cn

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