ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 8, pp. 547–558. © Pleiades Publishing, Ltd., 2017.

Effect of Solvent on the Crystal Structures of Copper(II) Complexes Based on 4'-(4-Methoxyphenyl)-2,2':6',2"-Terpyridine and 4'-(3-Chlorophenyl)-2,2':6',2"-Terpyridine[1]

W. W. Fu*, Q. W. Cheng, H. Y. Wang, F. Z. R. He, Y. Liu, and F. X. Zhang

Key Laboratory of Functional Organometallic Materials of Hunan Province College, Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang, 421008 P.R. China

**e-mail: w.w.fu@hotmail.com*

Received May 14, 2016

Abstract—Four homoleptic copper(II) complexes, $[Cu(Meophtpy)_2](ClO_4)_2$ (Meophtpy = 4'-(4-methoxylphenyl)-2,2':6',2"-terpyridine) (**I**), $[Cu(Meophtpy)_2](ClO_4)_2 \cdot 2H_2O$ (**II**), $[Cu_2(m\text{-Clphtpy})_4](ClO_4)_4$ (*m*-ClPhtpy = 4'-(3-chlorophenyl)-2,2':6',2"-terpyridine) (**III**), and $[Cu_2(m\text{-ClPhtpy})_4](ClO_4)_4$ (**IV**) have been synthesized by hydrothermal methods and characterized by IR, elemental analysis and single crystal X-ray diffraction (CIF files CCDC nos. 963375 (**I**), 885457 (**II**), 963377 (**III**), and 963376 (**IV**)). Complex **II** is a polymorph of **I** and complex **IV** is a polymorph of **III**. All these complexes are obtained with 95% ethanol solution or 50% ethanol solution and the solvent control on the crystallization are obviously found. In all complexes, the face-to-face interactions between pyridyl rings or phenyl rings facilitate the construction of 3D network in the crystal in addition to hydrogen bonds. The fluorescence properties of these complexes have been investigated.

Keywords: copper(II) complexes, polymorphism, single crystal X-ray diffraction, fluorescence

DOI: 10.1134/S1070328417080024

INTRODUCTION

Polymorphism is a phenomenon which means same molecules have various crystal structures by adopting different packing modes [1] and it has been widely found in metal [2], organic molecules [3, 4], macromolecules [5] and coordination complexes [6, 7]. Coordination complexes with substituted 2,2':6',2"-terpyridines have been widely investigated for their diverse structures and various properties in luminescence [8], catalysis [9], magnetism [10], biology [11] and nonlinear optical properties [12] etc. In contrast to the massive investigations on structure and properties of 2,2':6',2"-terpyridine coordination complexes, a relatively few polymorphs of 2,2':6',2"-terpyridine coordination complexes have been studied, although they might be very useful to investigate structure property relationships. According to our incomplete statistics, there are only a few of examples about terpyridine and their complexes which could be divided into three catalogues. The first is polymorphs of terpyridine ligands, for example, 4'-(hex-5-ynyloxy)-2,2':6',2"-terpyridine and 4'-tolyl-2,2':6',2"-terpyridine [13–15]. The second is 2,2':6',2"-terpyridine Pt complexes which often show red and orange forms [16–19]. The third is 4'-substituted 2,2':6',2"-terpyridine 3*d* metal complexes like Mn [20, 21], Fe [22–24], Co [25–28], Ni [24, 29], Zn [30], Cd [31, 32] complexes in which solvent play an influential but enigmatic role.

In our ongoing research process, four Cu(II) complexes with 4'-(4-methoxylphenyl)-2,2':6',2"-terpyridine (Meophtpy) and 4'-(3-chlorophenyl)-2,2':6',2"-terpyridine (*m*-ClPhtpy) have been obtained all with solvothermal methods. Unexpectedly, two kinds of polymorphs of Cu(II) complexes with each ligand have been obtained which would be ascribed to solvents effect. The crystal structures and Stack mode influenced fluorescent properties will be reported here.

EXPERIMENTAL

Materials and methods. Meophtpy and *m*-ClPhtpy were synthesized by a literature method [33]. All the other reagents and solvents were commercially available and used as received. The infrared spectra of the complexes were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu FTIR-8700 spectrometer. Elemental analyses of C, H, and N were performed on an EA1110 CHNS-0 CE elemental analyzer. Photoluminescent analyses were performed on

---

[1] The article is published in the original.

an Edinburgh EI920 fluorescence spectrometer with 450 W xenon light.

Synthesis of [Cu(Meophtpy)$_2$](ClO$_4$)$_2$ (I). A mixture of $CuSO_4 \cdot 5H_2O$ (0.05 mmol, 0.0125 g), Meophtpy (0.1 mmol, 0.0340 g) and $NaClO_4$ (0.1 mmol, 0.0122 g) in 95% EtOH (10 mL) were sealed in a 15 mL Telfon-lined stainless steel container, which was heated to 160°C for 48 h. After cooling to room temperature at a rate of 5 K h^{-1}, the green block crystals were obtained in about 55% yield based on Cu.

For $C_{44}H_{34}N_6O_{10}Cl_2Cu$ (**I**)

anal. calcd., %:	C, 56.15;	H, 3.64;	N, 8.93.
Found, %:	C, 55.02;	H, 3.84;	N, 8.98.

IR (KBr; ν, cm^{-1}): 3566.38 m, 3068.75 m, 3014.74 m, 2935.66 m, 2839.22 m, 2015.61w, 1869.02 w, 1600.92 v.s, 1575.84 s, 1544.98 s, 1519.91 s, 1473.62 v.s, 1433.11 s, 1408.04 s, 1365.60 m, 1307.74 m, 1280.73 m, 1246.02 v.s, 1184.29 v.s, 1163.08 m, 1089.78 v.s, 1016.49 v.s, 831.47 m, 831.32 v.s, 792.74 v.s, 746.45 m, 731.02 m, 688.59 m, 657.73 m, 621.08 v.s, 582.50 s, 520.76 m, 472.56 m, 455.20 m, 433.98 m, 414.70 m.

Synthesis of [Cu(Meophtpy)$_2$](ClO$_4$)$_2$(H$_2$O)$_2$ (II). The preparation of **II** was similar to that of **I** except that EtOH–H$_2$O ($V : V = 1 : 1$, 10 mL) was used instead of 95% EtOH (10 mL). Green needle crystals of **II** were obtained in 74% yield based on Cu.

For $C_{44}H_{38}Cl_2N_6O_{12}Cu$ (**II**)

anal. calcd., %:	C, 54.08;	H, 3.92;	N, 8.60.
Found: %:	C, 50.51;	H, 3.82;	N, 8.20.

IR (KBr; ν, cm^{-1}): 3566.38 m, 3502.73 m, 3107.32 w, 3078.39 w, 3010.88 w, 2941.44 w, 2835.36 w, 1602.85 v.s, 1570.06 m, 1541.12 m, 1519.91 s, 1508.33 m, 1473.62 s, 1435.04 m, 1409.96 m, 1363.67 m, 1338.60 w, 1307.74 m, 1282.66 m, 1246.02 s, 1188.15 s, 1103.28 v.s, 1089.78 v.s, 1081.41 s, 970.19 m, 896.90 m, 825.53 m, 794.67 s, 748.38 m, 657.73 m, 623.01 s, 590.22 m, 516.92 m, 472.56 w, 418.55 m.

Synthesis of [Cu$_2$(*m*-ClPhtpy)$_4$](ClO$_4$)$_4$ (III). The preparation of **III** was similar to that of **I** except that *m*-ClPhtpy was used instead of Meophtpy. Green needle crystals of **III** were obtained in 62% yield based on Cu.

For $C_{42}H_{28}N_6O_8Cl_4Cu$ (**III**)

anal. calcd., %:	C, 53.58;	H, 3.00;	N, 8.93.
Found, %:	C, 53.44;	H, 2.97;	N, 8.89.

IR (KBr; ν, cm^{-1}): 3078.39 m, 1614.42 v.s, 1595.13 s, 1571.99 s, 1544.98 v.s, 1473.62 v.s, 1435.04 s, 1398.39 s, 1361.74 m, 1300.02 m, 1264.02 s, 1165.00 m, 1085.92 v.s, 1014.56 s, 867.97 m, 783.10 v.s, 744.52 m, 723.31 s, 686.66 s, 657.73 m, 621.08 v.s, 516.92 w, 418.55 m.

Synthesis of [Cu$_2$(*m*-ClPhtpy)$_4$](ClO$_4$)$_4$ (IV). The preparation of **IV** was similar to that of **II** except that *m*-ClPhtpy was used instead of Meophtpy. Green needle crystals of **IV** were obtained in 58% yield based on Cu.

For $C_{42}H_{28}N_6O_8Cl_4Cu$ (**IV**)

anal. calcd., %:	C, 53.58;	H, 3.00;	N, 8.93.
Found, %:	C, 53.48;	H, 2.94;	N, 8.80.

IR (KBr; ν, cm^{-1}): 3061.03 w, 1795.73 w, 1614.42 v.s, 1571.99 m, 1544.98 v.s, 1471.69 v.s, 1435.04 m, 1398.39 s, 1361.74 w, 1340.53 w, 1300.02 w, 1246.02 s, 1165.00 m, 1083.99 v.s, 1012.63 s, 972.12 m, 867.97 m, 783.10 v.s, 744.52 w, 721.38 m, 686.66 m, 655.80 w, 621.08 v.s, 522.71 w, 491.85 w, 459.06 w, 439.71 w, 420.48 m.

X-ray crystallography. Crystals of **I**–**IV** were mounted on a Bruker SMART APEX II CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.071073$ nm) at 296 K for **I**, **II**, 293K for **III**, and 123 K for **IV**. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 via SHELXL-97 program [34]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically. Crystallographic data and structural refinement parameters for complexes **I**–**IV** are listed in Table 1. Selected bond lengths and angles are presented in Table 2.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 963375, 885457, 963377, and 963376; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The asymmetric unit of **I** contains one Cu^{2+} cation, two Meophtpy ligands and two perchlorate anions. The Cu^{2+} cation is coordinated by six N atoms from two Meophtpy ligands. The distances between Cu(II) and N from central pyridines (Cu–N(2) and Cu–N(5)) 1.950(5) and 1.997(5) Å) are slightly shorter than that between Cu and N from outer pyridines (Cu–N(3), Cu–N(1), Cu–N(6), and Cu–N(4) 2.107(5), 2.119(5), 2.235(5), and 2.245(6) Å, respectively). There are fifteen NCuN bond angles, which can be divided into two parts. Three are transoid angles with N(2)CuN(5), 177.73(19)°, N(3)CuN(1), 156.9(2)°, and N(6)CuN(4), 151.77(19)° and the other twelve are cisoid, ranged from 76.1(2)° to

Table 1. Crystallographic data and structure refinement parameters for **I**–**IV***

Parameter	Value			
	I	**II**	**III**	**IV**
Formula mass	941.21	977.24	950.04	950.04
Crystal system	Monoclinic	Tetragonal	Monoclinic,	Triclinic
Space group	$P2_1/c$	$I4_1/a$	$P2_1/c$	$P\bar{1}$
a, Å	18.235(4)	24.8820(13)	14.1737(7)	8.567(3)
b, Å	15.381(3)	24.8820(13)	24.2372(10)	15.417(6)
c, Å	15.998(3)	13.8711(9)	26.3460(11)	16.408(6)
α, deg	90	90	90	82.847(9)
β, deg	105.725(3)	90	120.982(3)	76.909(10)
γ, deg	90	90	90	75.505(9)
V, Å^3	4319.1(15)	8587.8(8)	7759.4(6)	2038.4(14)
Z	4	8	8	2
ρ_{calcd}, g/cm^3	1.447	1.512	1.627	1.548
μ, mm^{-1}	0.695	0.705	0.904	0.860
F(000)	1932	4024	3864	966
θ Range for data collection, deg	2.00–26.00	2.32–27.52	2.37–25.01	2.94–25.01
Reflections collected	23629	18518	50534	22039
Unique reflections (R_{int})	8463 (0.0343)	4893 (0.0612)	13638 (0.0566)	6906 (0.0905)
GOOF on F^2	1.083	1.033	1.072	1.026
Refinement parameters	568	294	1099	574
R_1, R_2 ($I > 2\sigma(I)$)	0.0790, 0.1752	0.0515, 0.1321	0.0710, 0.1708	0.0621, 0.1624
R_1, wR_2 (all data)	0.1196, 0.1976	0.0985, 0.1563	0.0825, 0.1801	0.0787, 0.1765
Largest diff. peak and hole, e/Å^3	1.296 and –0.624	0.502 and –0.388	2.690 and –1.741	0.884 and –0.558

* $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **I**–**IV**

Bond	*d*, Å	Bond	*d*, Å
I			
Cu(1)–N(2)	1.950(5)	Cu(1)–N(5)	1.997(5)
Cu(1)–N(3)	2.107(5)	Cu(1)–N(1)	2.119(5)
Cu(1)–N(6)	2.235(5)	Cu(1)–N(4)	2.245(6)
II			
Cu(1)–N(2)	1.959(3)	Cu(1)–N(1)	2.171(3)
Cu(1)–N(3)	2.181(3)		
III			
Cu(2)–N(2)	1.948(3)	Cu(2)–N(5)	2.028(4)
Cu(2)–N(1)	2.066(4)	Cu(2)–N(3)	2.074(4)
Cu(2)–N(6)	2.268(4)	Cu(2)–N(4)	2.285(4)
Cu(1)–N(11)	1.948(3)	Cu(1)–N(8)	2.025(3)
Cu(1)–N(12)	2.080(4)	Cu(1)–N(10)	2.081(4)
Cu(1)–N(9)	2.277(4)	Cu(1)–N(7)	2.278(4)
IV			
Cu(1)–N(1)	1.947(3)	Cu(1)–N(4)	2.008(3)
Cu(1)–N(2)	2.107(3)	Cu(1)–N(3)	2.122(3)
Cu(1)–N(6)	2.225(4)	Cu(1)–N(5)	2.269(4)
Angle	ω, deg	Angle	ω, deg
I			
N(2)Cu(1)N(5)	177.73(19)	N(2)Cu(1)N(3)	78.42(19)
N(5)Cu(1)N(3)	103.62(19)	N(2)Cu(1)N(1)	78.47(19)
N(5)Cu(1)N(1)	99.51(19)	N(3)Cu(1)N(1)	156.9(2)
N(2)Cu(1)N(6)	104.96(19)	N(5)Cu(1)N(6)	76.12(19)
N(3)Cu(1)N(6)	91.03(18)	N(1)Cu(1)N(6)	93.87(18)
N(2)Cu(1)N(4)	103.0(2)	N(5)Cu(1)N(4)	76.1(2)
N(3)Cu(1)N(4)	90.8(2)	N(1)Cu(1)N(4)	95.4(2)
N(6)Cu(1)N(4)	151.77(19)		
II			
N(2)Cu(1)N(2)$^{\#1}$	175.65(14)	N(2)Cu(1)N(1)	77.79(10)
N(2)Cu(1)N(1)$^{\#1}$	105.17(10)	N(2)Cu(1)N(3)$^{\#1}$	99.30(10)
N(2)Cu(1)N(3)	77.87(10)	N(1)Cu(1)N(1)$^{\#1}$	97.30(15)
N(1)Cu(1)N(3)$^{\#1}$	86.17(11)	N(1)Cu(1)N(3)	155.47(10)
N(3)$^{\#1}$Cu(1)N(3)	100.71(16)		
III			
N(2)Cu(2)N(5)	176.15(15)	N(2)Cu(2)N(1)	79.30(14)
N(5)Cu(2)N(1)	100.74(14)	N(2)Cu(2)N(3)	79.05(14)
N(5)Cu(2)N(3)	100.90(14)	N(1)Cu(2)N(3)	158.34(14)
N(2)Cu(2)N(6)	108.26(14)	N(5)Cu(2)N(6)	75.57(14)
N(1)Cu(2)N(6)	89.13(14)	N(3)Cu(2)N(6)	97.10(14)
N(2)Cu(2)N(4)	100.20(14)	N(5)Cu(2)N(4)	75.97(14)
N(6)Cu(2)N(4)	151.54(13)	N(11)Cu(1)N(8)	176.61(15)
N(11)Cu(1)N(12)	79.36(14)	N(8)Cu(1)N(12)	99.59(14)
N(11)Cu(1)N(10)	78.94(14)	N(8)Cu(1)N(10)	101.99(14)

Table 2. (Contd.)

Angle	ω, deg	Angle	ω, deg
N(12)Cu(1)N(10)	158.24(14)	N(11)Cu(1)N(9)	100.57(14)
N(8)Cu(1)N(9)	76.27(14)	N(12)Cu(1)N(9)	95.21(14)
N(10)Cu(1)N(9)	87.25(14)	N(11)Cu(1)N(7)	107.80(14)
N(8)Cu(1)N(7)	75.34(14)	N(12)Cu(1)N(7)	88.73(14)
N(10)Cu(1)N(7)	99.36(15)	N(9)Cu(1)N(7)	151.60(13)
IV			
N(1)Cu(1)N(4)	176.28(14)	N(1)Cu(1)N(2)	78.71(13)
N(4)Cu(1)N(2)	101.38(13)	N(1)Cu(1)N(3)	78.28(13)
N(4)Cu(1)N(3)	101.62(13)	N(2)Cu(1)N(3)	156.98(14)
N(1)Cu(1)N(6)	99.50(14)	N(4)Cu(1)N(6)	76.79(13)
N(2)Cu(1)N(6)	95.10(13)	N(3)Cu(1)N(6)	89.37(13)
N(1)Cu(1)N(5)	107.61(14)	N(4)Cu(1)N(5)	76.11(13)
N(2)Cu(1)N(5)	90.85(13)	N(3)Cu(1)N(5)	95.41(12)
N(6)Cu(1)N(5)	152.88(13)		

* Symmetry code: $^{\#1}$ $-x$, $-y + 1/2$, z (**II**).

104.96(19)°. Both the differences of bond lengths and bond angles show a distorted octahedral geometry in **I** which are common for terpyridine coordinated complexes. The angles between phenyl ring and terpyridine ring are 20.6° and 38.7° showing non-coplanar relationship. The angle between two terpyridine rings is 87.4°. Four hydrogen bonds all with C–H···O type and link the individual components in **I** into three-dimensional network (Fig. 1b, Table 3). Two O atoms on perchlorate anions are acceptors with hydrogen on C as donors. The O(3) atom is a double acceptor linked with hydrogens H(13*A*), H(37*A*) which are attached to C(13) and C(37). The O(9) atom is also a double acceptor with hydrogen H(26*A*), and H(43*A*) which are attached to C(26) and C(43), respectively. All these hydrogen bonds are weak ranging from 2.55 to 2.59 Å. In addition, two kinds of moderate offset face-to-face interactions, one between centroids of outer pyridine rings (N(1), C(1)–C(5)) and (N(3), C(11)–C(15)) and the other between centroids of pyridine ring (N(1), C(1)–C(5)) and benzene ring (C(16)–C(21)) which are 3.917 and 3.830 Å also facilitated the formation of 3D network.

The asymmetric unit of **II** contains one half of Cu^{2+} cation, two Meophtpy ligands, two perchlorate anions and two water molecules. The Cu^{2+} cation is coordinated by six N atoms from two Meophtpy ligands. The distances between Cu and N from central pyridines ((Cu–N(2) 1.959(3) Å) are slightly shorter than that between Cu and N from outer pyridines (Cu–N(1) and Cu–N(3) 2.171(3) and 2.181(3) Å). Among fifteen NCuN bond angles, three transoid angles, N(2)Cu(2)$^{\#1}$, N(1)CuN(3), and N(1)$^{\#1}$CuN(3)$^{\#1}$ are 175.65(14)°, 155.47(10)°, and 155.47(10)°, respectively, and other twelve cisoid angles are ranging from 77.79(10)° to 105.17(10)°. All these fifteen bond angles are similar with that in **I**. Both the differences of bond lengths and bond angles show a distorted octahedral geometry in **II** like **I** and other terpyridine coordinated complexes. The angles between phenyl ring and terpyridine ring planes are 35.9° showing non-coplanar relationship. The angle between two terpyridine rings is 76.4°. Seven hydrogen bonds, two with O–H···O type and others with C–H···O type, link the individual components in **II** into three-dimensional network (Fig. 2b, Table 3). The O(6) atom is a double acceptor linked with hydrogen H(4) and H(7) which are attached with C(4) and C(7). The most shortest hydrogen bonds H···O are 2.09 Å for O(6)–H(6*A*)···O(1)$^{\#1}$ and 2.18 Å for O(6)–H(6*B*)···O(5)$^{\#2}$. The other moderate hydrogen bonds H···O are 2.37 Å for C(7)–H(7)···O(6)$^{\#4}$, 2.43 Å for C(12)–H(12)···O(2) (symmetry codes are shown in Table 3). All the other hydrogen bond lengths are longer than 2.51 Å and they are weak hydrogen bonds. There exists only one kind of offset face-to-face interaction between benzene rings with a distance of 3.880 Å, which facilitated the formation of 3D network.

The asymmetric unit of **III** contains two independent Cu^{2+} cations, four *m*-ClPhtpy ligands and four perchlorate anions. The Cu^{2+} cations are coordinated by six N atoms from four *m*-ClPhtpy ligands. The distance between Cu(1) and N from central pyridines (Cu(1)–N(11) and Cu(1)–N(8) 1.948(3) and 2.025(3) Å) are slightly shorter than that between Cu(1) and N from outer pyridines (Cu(1)–N(12), Cu(1)–N(10), Cu(1)–N(9), and Cu(1)–N(7)) 2.080(4), 2.081(4), 2.277(4), and 2.278(4) Å, respectively). There are fifteen NCu(1)N bond angles, which

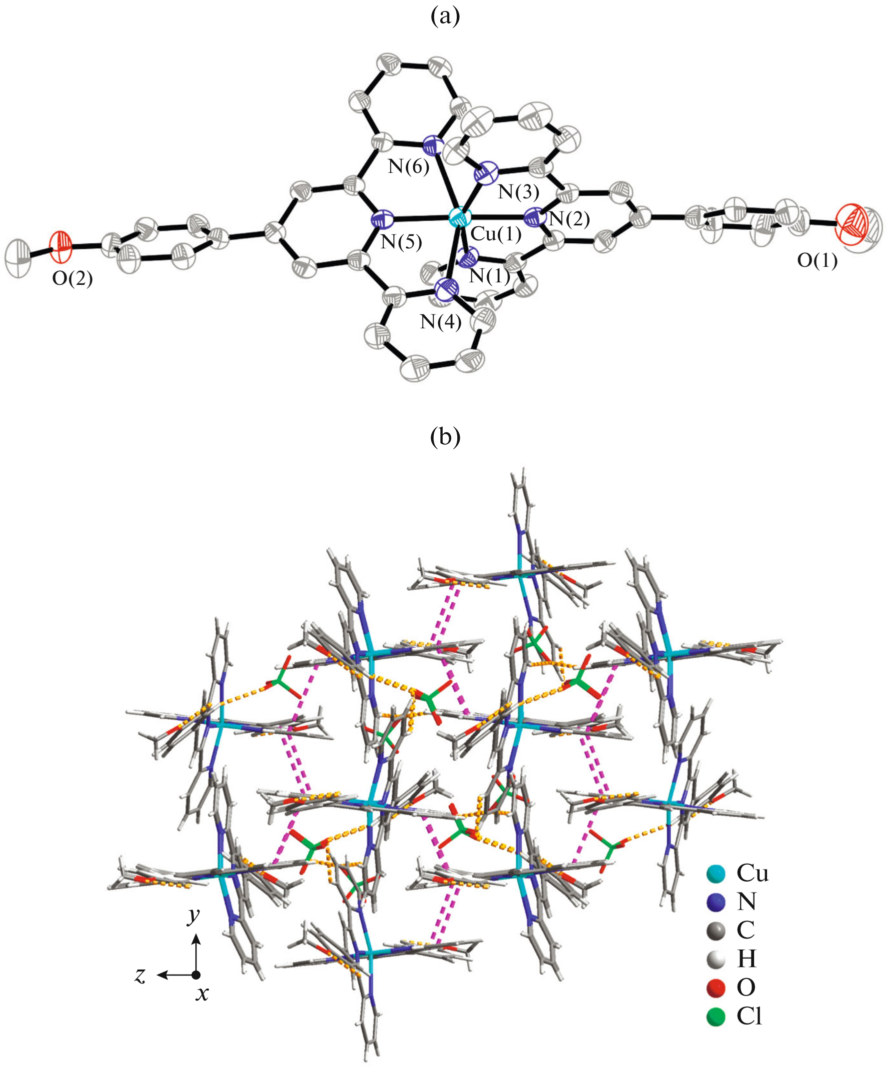

Fig. 1. The ORTEP view of $[Cu(Meophtpy)_2]^{2+}$ in **I** with thermal ellipsoids at 30% probalitity level (a); the 3D supramolecular network of **I** formed through hydrogen bonds and the face-to-face π–π interactions (shown in dashed lines with different colors in electric print) (b).

can be divided into two parts. Three are transoid angles with N(11)Cu(1)N(8), 176.61(15)°, N(12)Cu(1)N(10), 158.24(14)°, and N(9)Cu(1)N(7), 151.60(13)° and the other twelve are cisoid, ranged from 75.34(14)° to 107.80(14)°. Both the differences of bond lengths and bond angles show a distorted octahedral geometry in **III** like **I** and **II**. The angle between phenyl ring and terpyridine ring is 35.8° and 34.3°. The angle between two terpyridine rings is 77.9° which are slightly deviated from right angle. All the bond lengths and bond angles about Cu(2) are similar with Cu(1) and omitted for clarity. Fifteen kinds of hydrogen bonds, fourteen with C–H···O type and one with C–H···Cl type, link the individual components in **III** into three-dimensional network (Fig. 3b, Table 3). The O(11) atom is a triple acceptor linked to hydrogens H(34), H(58), and H(61) which are attached to C(34), C(58), and C(61), respectively. The O(4) atom is a double acceptor linked to H(48) and H(81) with C(48) and C(81) as donors. The O(16) atom is also a double acceptor linked to H(39) and H(83) with C(39) and C(83) as donors. The shortest hydrogen bonds H···O are 2.31 Å for C(36)–H(36)···O(8)$^{\#3}$ and 2.32 Å for C(42)–H(42)···O(12)$^{\#1}$ showing strong interactions. The other moderate hydrogen bonds H···O are 2.45 Å for C(81)–H(81)···O(4) and C(83)–H(83)···O(16), 2.47 Å for C(79)–H(79)···O(1)$^{\#6}$ and C(39)–H(39)···O(16)$^{\#4}$, and 2.48 Å for C(27)–H(27)···O(5). Other C–H···O type hydrogen bonds are weak ranging from 2.54 Å to 2.58 Å (symmetry codes are shown in Table 3). There exist two kinds of offset face-to-face interactions all between benzene rings. The distances between centroids of two adjacent benzene rings (C(43)–C(48)) are 3.590 Å shows mod-

Table 3. Geometric parameters of hydrogen bonds of **I**–**IV**

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
C(13)–H(13*A*)···O(3)$^{\#1}$	0.93	2.59	3.500(14)	165
C(26)–H(26*A*)···O(9)$^{\#2}$	0.93	2.56	3.253(16)	132
C(37)–H(37*A*)···O(3)	0.93	2.55	3.461(12)	167
C(43)–H(43*A*)···O(9)$^{\#3}$	0.93	2.59	3.496(15)	164
Symmetry codes: $^{\#1}$ $x, -y + 1/2, z - 1/2$; $^{\#2}$ $-x, y + 3/2, -z + 3/2$; $^{\#3}$ $x, -y + 1/2, z + 1/2$.				
II				
O(6)–H(6*A*)···O(1)$^{\#1}$	0.85	2.09	2.910(4)	164
O(6)–H(6*B*)···O(5)$^{\#2}$	0.85	2.18	2.993(7)	160
C(1)–H(1)···O(4)$^{\#3}$	0.93	2.55	3.153(5)	123
C(4)–H(4)···O(6)$^{\#4}$	0.93	2.57	3.434(5)	155
C(7)–H(7)···O(6)$^{\#4}$	0.93	2.37	3.244(5)	157
C(12)–H(12)···O(2)	0.93	2.43	3.260(6)	149
C(17)–H(17)···O(3)$^{\#2}$	0.93	2.56	3.349(5)	143
Symmetry codes: $^{\#1}$ $-y - 3/4, x - 7/4, -z + 1/4$; $^{\#2}$ $y + 3/4, -x + 3/4, z + 3/4$; $^{\#3}$ $x - 1/2, y, -z + 1/2$; $^{\#4}$ $x + 1, y + 3/2, -z + 2$.				
III				
C(3)–H(3) ···O(10)$^{\#1}$	0.93	2.58	3.434(7)	153
C(21)–H(21)···O(7)	0.93	2.56	3.095(7)	117
C(27)–H(27)···O(5)	0.93	2.48	3.401(6)	169
C(34)–H(34)···O(11)$^{\#2}$	0.93	2.55	3.241(7)	131
C(36)–H(36)···O(8)$^{\#3}$	0.93	2.31	3.185(7)	156
C(37)–H(37)···O(6)$^{\#3}$	0.93	2.58	3.299(7)	135
C(39)–H(39)···O(16)$^{\#4}$	0.93	2.47	3.288(6)	147
C(42)–H(42)···O(12)$^{\#1}$	0.93	2.32	3.221(6)	163
C(48)–H(48)···O(4)$^{\#4}$	0.93	2.57	3.473(6)	164
C(58)–H(58)···O(11)	0.93	2.55	3.187(6)	126
C(61)–H(61)···Cl(1)$^{\#5}$	0.93	2.77	3.522(5)	139
C(61)–H(61)···O(11)$^{\#1}$	0.93	2.54	3.335(7)	143
C(79)–H(79)···O(1)$^{\#6}$	0.93	2.47	3.353(6)	159
C(81)–H(81)···O(4)	0.93	2.45	3.220(6)	140
C(83)–H(83)···O(16)	0.93	2.45	3.285(6)	150
Symmetry codes: $^{\#1}$ $x + 1, -y + 1/2, z + 1/2$; $^{\#2}$ $x + 1, y, z$; $^{\#3}$ $-x, -y - 1, -z - 1$; $^{\#4}$ $-x - 1, -y, -z - 1$; $^{\#5}$ $-x, y + 1/2, -z + 1/2$; $^{\#6}$ $x, -y + 1/2, z + 1/2$.				
IV				
C(8)–H(8)···O(10)$^{\#1}$	0.95	2.59	3.21(2)	124
C(8)–H(8)···O(11)$^{\#1}$	0.95	2.58	3.355(16)	139
C(9)–H(9)···O(4)$^{\#1}$	0.95	2.56	3.163(7)	122
C(16)–H(16)···O(14)$^{\#2}$	0.95	2.44	3.359(17)	162
C(35)–H(35)···O(14)$^{\#3}$	0.95	2.53	3.233(17)	131
Symmetry codes: $^{\#1}$ $x - 1, y, z$; $^{\#2}$ $-x + 1, -y, -z + 1$; $^{\#3}$ $-x, -y, z - 1$.				

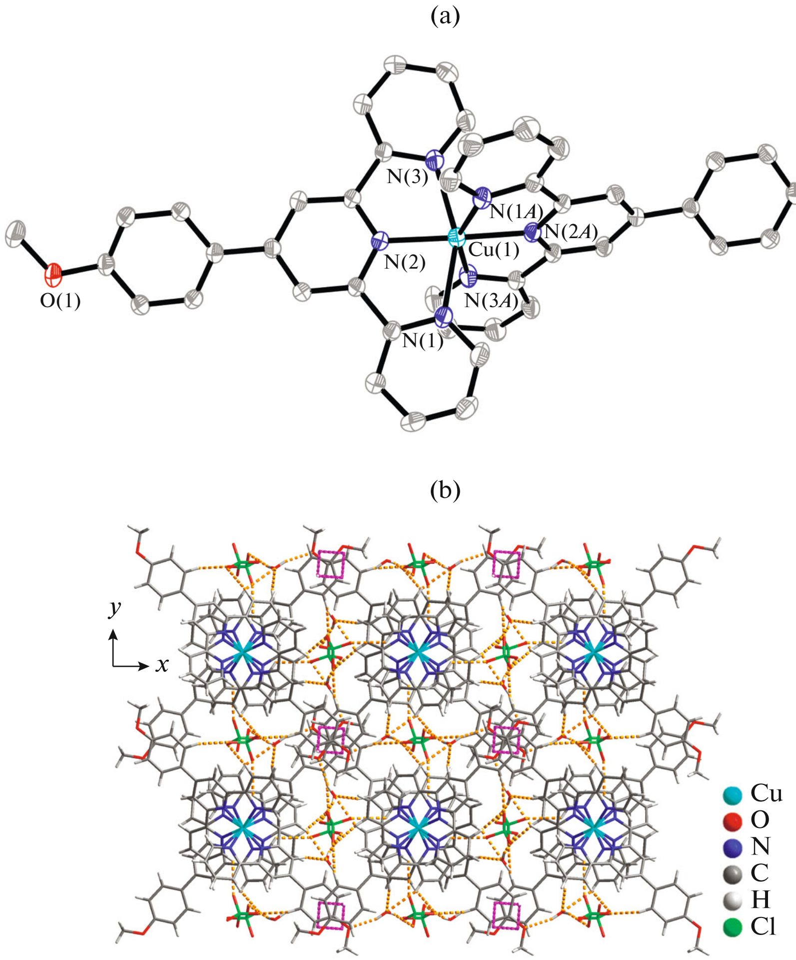

Fig. 2. The ORTEP view of $[Cu(Meophtpy)_2]^{2+}$ in **II** with thermal ellipsoids at 30% probalitity level (a); the 3D supramolecular network of **II** formed through hydrogen bonds and the face-to-face π–π interactions (shown in dashed lines with different colors in electric print) (b).

erate interaction. The distances between centroids of benzene ring (C(43)–C(48)) and (C(64)–C(69)) are 3.752 Å shows weak interaction.

The asymmetric unit of **IV** contains one Cu^{2+} cation, two *m*-ClPhtpy ligands and two perchlorate anions. The Cu^{2+} cation is coordinated by six N atoms from two *m*-ClPhtpy ligands. The distances between Cu(II) and N from central pyridines (Cu–N(1) and Cu–N(4)) 1.947(3) and 2.008(3) Å) are slightly shorter than that between Cu and N from outer pyridines (Cu–N(2), Cu–N(3), Cu–N(6), and Cu–N(5) 2.107(3), 2.122(3), 2.225(4), and 2.269(4) Å, respectively). There are fifteen NCuN bond angles, which can be divided into two parts. Three are transoid angles with N(1)CuN(4), 176.28(14)°, N(2)CuN(3), 156.98(14)°, and N(6)CuN(5), 152.88(13)° and the other twelve are cisoid, ranged from 76.11(13)° to 107.61(14)°. Both the differences of bond lengths and bond angles show a distorted octahedral geometry in **IV** which are common for terpyridine coordinated complexes. The angles between phenyl ring and terpyridine ring are 27.3° and 35.1°. The angle between two terpyridine rings is 86.9° which are deviated from right angle. Five kinds of hydrogen bonds all with C–H···O type, link the individual components in **IV** into three-dimensional network (Fig. 4b, Table 3). The O(14) atom is a double acceptor linked to hydrogens H(16) and H(35) which are attached to C(16) and C(35), respectively. The shortest hydrogen bond H···O is 2.44 Å for C(16)–H(16)···O(14)$^{\#2}$ showing moderate interactions. Others are weak hydrogen bonds ranging from 2.53 to 2.59 Å (symmetry codes are shown in Table 3). In addition, two kinds of moderate offset face-to-face interactions, one between centroids of outer pyridine rings (N(2), C(6)–C(10)) and (N(3), C(11)–C(15)) and the other between centroids of phenyl rings (C(16)–C(21)) and (C(37)–C(42)) which

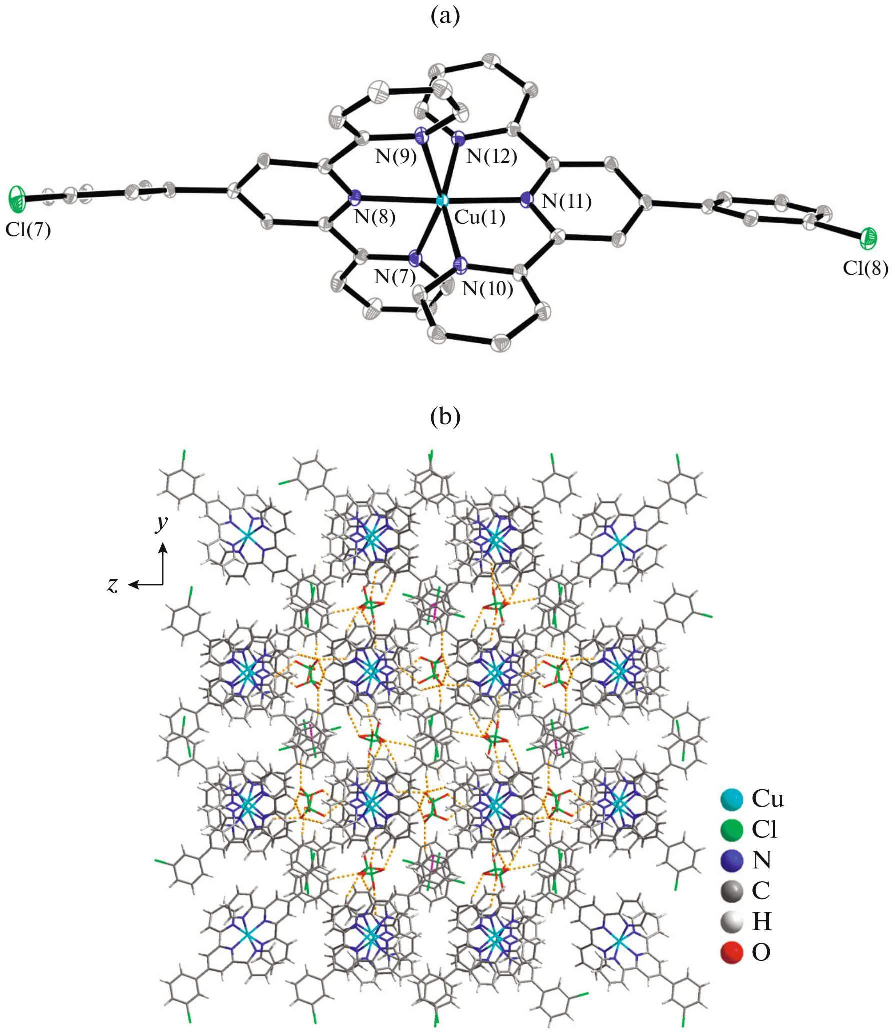

Fig. 3. The ORTEP view of [Cu(Meophtpy)$_2$]$^{2+}$ in **III** with thermal ellipsoids at 30% probalitity level (a); the 3D supramolecular network of **III** formed through hydrogen bonds and the face-to-face π–π interactions (shown in dashed lines with different colors in electric print) (b).

are 3.627 and 3.660 Å also promoted the formation of 3D network.

It is easily found that **II** is polymorph of **I** and **IV** is polymorph of **III**. The difference of crystal structures would be attributed to the solvent effect which was not uncommon in terpyridine complexes. In complexes **I**–**IV**, except for the slight differences of bond lengths and bond angles, the most significant features are the interactions between pyridine (Py) or phenyl (Ph) rings on adjacent terpyridiens [24, 35]. In complex **I**, offset face-to-face interaction with a distance of 3.830 Å between outer Py and pendant Ph rings were found forming a dimer and it was connected by the other kind of interaction between outer Py and Py rings with a distance of 3.917 Å (Fig. 5). In contrast to **I**, there is only one kind of offset face-to-face interaction in **II** with a distance of 3.880 Å between Ph rings. In complex **II**, all the terpyridine cations are also overlapped upon each other like that in **II**, however, there are two kinds of interactions between Ph rings with distances of 3.590 and 3.792 Å and there are some weak interactions with distances longer than 4.0 Å between some adjacent Ph rings. In contrast to **III**, two kinds of interactions in **IV**, one with Py–Py interaction with a distance of 3.626 Å and the other with Ph–Ph with a distance of 3.659 Å were found.

The solid-state luminescence of the ligand Meophtpy (L^1), *m*-ClPhtpy (L^2) and complexes **I**–**IV** were measured at room temperature. In comparison to the emission of Meophtpy (406 nm, excited at 332 nm), **I** and **II** (Fig. 6) show different fluorescent peaks at 437 nm (excited at 335 nm) and 448 nm (excited at 332 nm) with a red-shift of 31 and 42 nm, respectively, accompanied by a low intensity for **I** and

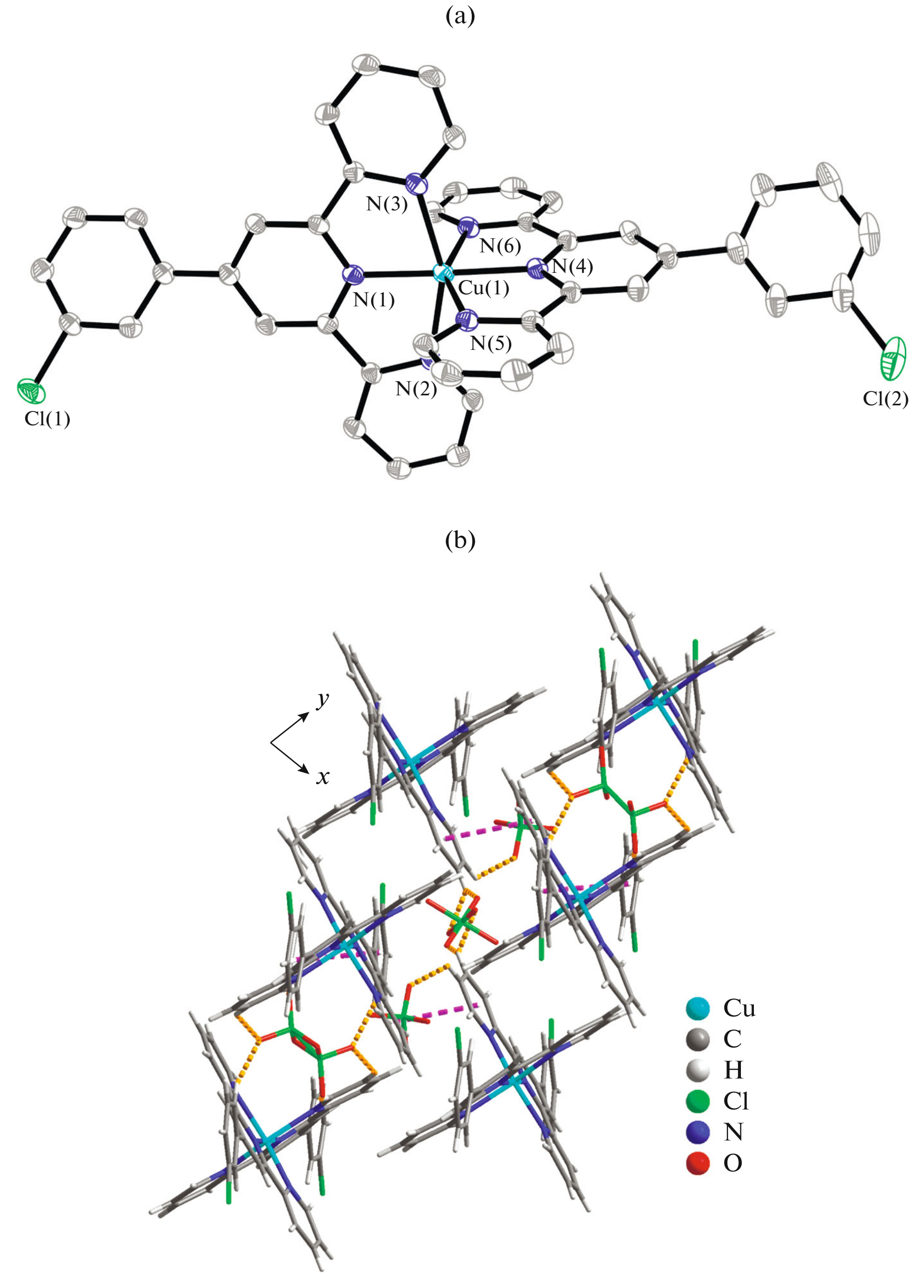

Fig. 4. The ORTEP view of $[Cu(Meophtpy)_2]^{2+}$ in **IV** with thermal ellipsoids at 30% probalitity level (a); the 3D supramolecular network of **IV** formed through hydrogen bonds and the face-to-face π–π interactions (shown in dashed lines with different colors in electric print) (b).

high intensity for **II** which would be attributed to Cu(II) influenced intramolecular charge-transfer (ICT). In comparison to the emission of *m*-ClPhtpy (444 nm, excited at 330 nm), **III** and **IV** show almost same peaks at 444 nm (excited at 325 nm) and 440 nm (excited at 330 nm), respectively, and the intensities were also similar with L^2 which would be attributed to LLCT, too. The ligand L^1 may be used as violet luminescence materials and L^2, **I**–**IV** may be used as purple-blue luminescence materials.

ACKNOWLEDGMENTS

Financial support by the Key Discipline Project of Hunan Province, Key Laboratory of Functional Organometallic Materials of Hunan Province College and Aid program for Science and Technology Innova-

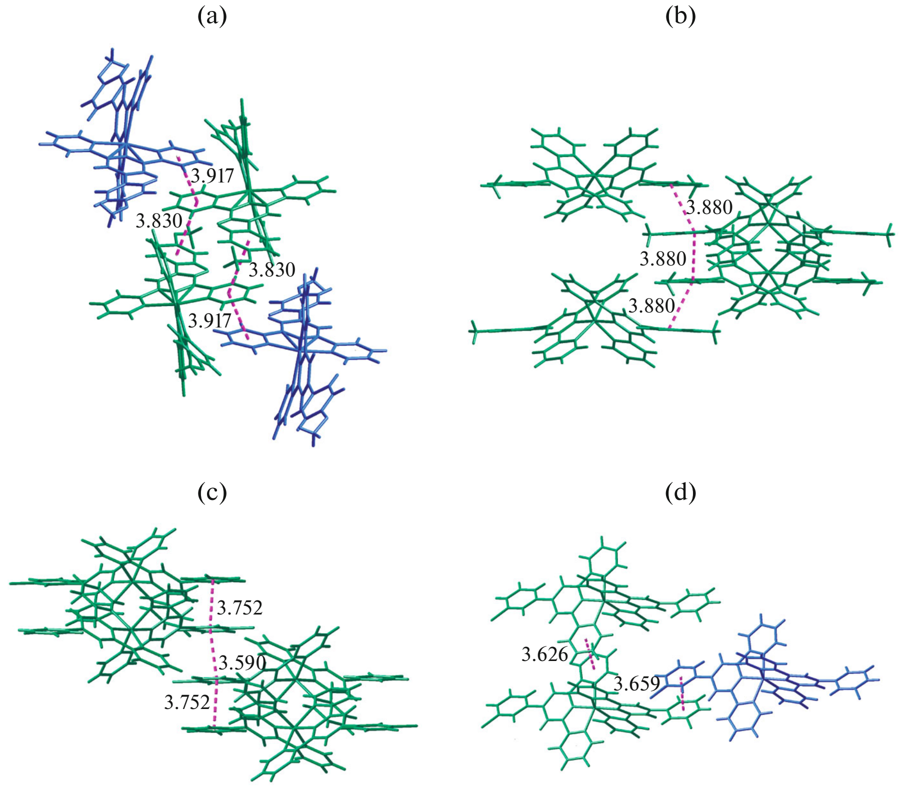

Fig. 5. Crystal packing interaction modes for complexes: **I** (a); **II** (b); **III** (c); **IV** (d).

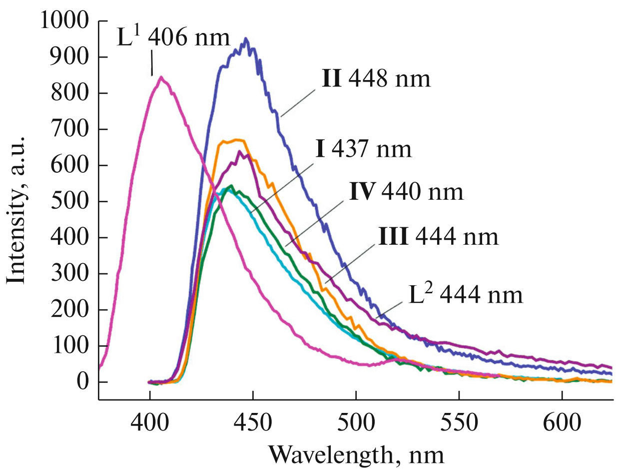

Fig. 6. Emission spectra of the complexes **I–IV** and free ligands Meophtpy (L^1) and *m*-ClPhtpy (L^2).

tive Research Team in Higher Educational Institutions of Hunan Province are gratefully acknowledged.

REFERENCES

1. Brog, J.-P., Chanez, C.-L., Crochet, A., et al., *RSC Advances*, 2013, vol. 3, p. 16905.
2. Yang, Z., Yang, J., Bergstrom, J., et al., *Phys. Chem. Chem. Phys.*, 2014, vol. 16, p. 9791.
3. Nicolini, T., Famulari, A., Gatti, T., et al., *J. Phys. Chem. Lett.*, 2014, vol. 5, p. 2171.
4. Okuno, T. and Umezono, S., *J. Mol. Struct.*, 2014, vol. 1064, p. 88.
5. Milani, A. and Galimberti, D., *Macromolecules*, 2014, vol. 47, p. 1046.
6. Krisyuk, V.V., Baidina, I.A., Korolkov, I.V., et al., *Polyhedron*, 2013, vol. 49, p. 1.
7. Shi, F.-N., Ananias, D., Yang, T.-H., et al., *J. Solid State Chem.*, 2013, vol. 204, p. 321.
8. Lee, Y.H., Kubota, E., Fuyuhiro, A., et al., *Dalton Trans.*, 2012, vol. 41, p. 10825.
9. Liu, P., Wong, E.L.-M., Yuen, A.W.-H., et al., *Org. Lett.*, 2008, vol. 10, p. 3275.
10. Misra, P., Liao, C.-Y., Wei, H.-H., et al., *Polyhedron*, 2008, vol. 27, p. 1185.
11. Zhou, W., Wang, X., Hu, M., et al., *J. Inorg. Biochem.*, 2013, vol. 121, p. 114.
12. Senechal, K., Toupet, L., Ledoux, I., et al., *Chem. Commun.*, 2004, p. 2180.
13. Bowes, K.F., Clark, I.P., Cole, J.M., et al., *CrystEngComm*, 2005, vol. 7, p. 269.
14. Beves, J.E., Chwalisz, P., Constable, E.C., et al., *Inorg. Chem. Commun.*, 2008, vol. 11, p. 1009.
15. Constable, E.C., Housecroft, C.E., Neuburger, M., et al., *CrystEngComm*, 2005, vol. 7, p. 599.

16. Zhang, R., Liang, Z., Han, A., et al., *CrystEngComm*, 2014, vol. 16, p. 5531.
17. Janzen, D.E. and Mann, K.R., *J. Chem. Crystallogr.*, 2013, vol. 43, p. 292.
18. Field, J.S., Ledwaba, L.P., Munro, O.Q., et al., *CrystEngComm*, 2008, vol. 10, p. 740.
19. Angle, C.S., DiPasquale, A.G., Rheingold, A.L., et al., *Acta. Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2006, vol. 62. , p. m 340.
20. Romain, S., Duboc, C., Neese, F., et al., *Chem. Eur. J.*, 2009, vol. 15, p. 980.
21. Sjödin, M., Gätjens, J., Tabares, L.C., et al., *Inorg. Chem.*, 2008, vol. 47, p. 2897.
22. Padhi, S.K., Sahu, R., Saha, D., et al., *Inorg. Chim. Acta*, 2011, vol. 372, p. 383.
23. Davidson, R.J., Ainscough, E.W., Brodie, A.M., et al., *Inorg. Chem.*, 2012, vol. 51, p. 8307.
24. McMurtrie, J. and Dance, I., *CrystEngComm*, 2009, vol. 11, p. 1141.
25. Hayami, S., Nakaya, M., Ohmagari, H., et al., *Dalton Trans.*, 2015, vol. 44, p. 9345.
26. Komatsu, Y., Kato, K., Yamamoto, Y., et al., *Eur. J. Inorg. Chem.*, 2012, vol. 2012, p. 2769.
27. Constable, E.C., Harris, K., Housecroft, C.E., et al., *CrystEngComm*, 2010, vol. 12, p. 2949.
28. Hayami, S., Urakami, D., Kojima, Y., et al., *Inorg. Chem.*, 2010, vol. 49, p. 1428.
29. McMurtrie, J. and Dance, I., *CrystEngComm*, 2005, vol. 7, p. 216.
30. Constable, E.C., Housecroft, C.E., Murray, N.S., et al., *Polyhedron*, 2013, vol. 54, p. 110.
31. Ma, Z., Liu, B., Yang, H., et al., *J. Coord. Chem.*, 2009, vol. 62, p. 3314.
32. Chen, G.-J., Wang, Z.-G., Kou, Y.-Y., et al., *J. Inorg. Biochem.*, 2013, vol. 122, p. 49.
33. Wang, J. and Hanan, G.S., *Synlett*, 2005, vol. 2005, p. 1251.
34. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
35. McMurtrie, J. and Dance, I., *CrystEngComm*, 2010, vol. 12, p. 3207.