

一种 2-甲基-3-羟基喹啉-4-甲酸单核铜(II) 配合物的合成、晶体结构、理论计算与性质

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摘要: 以 2-甲基-3-羟基喹啉-4-甲酸和 1,10-菲咯啉为原料, 经溶剂热法合成了一种新颖的 Cu(II)配合物, $[\text{Cu}(\text{L})(\text{Phen})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{OH}$ (**1**, HL=2-甲基-3-羟基喹啉-4-甲酸, Phen=1,10-菲咯啉), 并通过红外光谱、元素分析、单晶衍射、固态漫反射、光致发光及理论计算对其结构和性质进行了研究。单晶结构分析表明配合物 **1** 的晶体属于单斜晶系, $P2_1/c$ 空间群, 是一种零维(0D)结构的单核体。固态光致发光表明其为蓝紫色光发射体。时间密度泛函理论 (TDDFT) 计算表明其发射归属于配体-配体电荷转移 (LLCT)。固态漫反射测量显示该化合物存在 1.91 eV 的窄带能隙。

关键词: 铜; 晶体结构; 光致发光; 半导体; 时间密度泛函理论; 配体-配体电荷转移

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Synthesis, Crystal Structure, Theoretical Calculation and Properties of Cu(II) Complex with 3-Hydroxy-2-methylquinoline-4-carboxylic Acid

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Abstract: A novel copper(II) complex $[\text{Cu}(\text{L})(\text{Phen})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{OH}$ (**1**) with the ligands of 3-hydroxy-2-methylquinoline-4-carboxylic acid (HL) and 1,10-phenanthroline (Phen) was synthesized by solvothermal synthesis. Its structure and properties were investigated with infrared spectrum, elemental analysis, single-crystal X-ray diffraction, solid-state diffuse reflectance spectrum, photoluminescent and theoretical calculations. Complex **1** crystallizes in $P2_1/c$ space group of the monoclinic system and has an isolated mononuclear (0D) structure. Solid-state photoluminescence spectrum reveals that it shows an emission in the blue violet region of the light spectrum. Time-dependent density functional theory (TDDFT) calculations reveal that this emission can be attributed to ligand-to-ligand charge transfer (LLCT). Solid-state diffuse reflectance data shows that the complex had a narrow optical band gap of 1.91 eV. CCDC: 1882929.

Keywords: copper; crystal structure; photoluminescence; semiconductor; TDDFT; LLCT

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0 Introduction

In the past decades, the design of coordination polymers were well developed, not only owing to their intriguing variety of architectures but also because of their potential applications in catalysis, biochemistry, photoluminescent materials, photoelectric materials, nonlinear optics materials, semiconductor, and so forth^[1-8]. The synthesis of coordination polymers with specific functions has gradually become a research focus in the field of material chemistry^[9]. From the perspective of crystal engineering, the most useful and facile way to construct coordination complexes is to adopt a suitable ligand to connect metal centers, to this end, the ligand is better to possess as much as donor atoms that enable it to bridge metal centers together to yield extended architectures. The important feature of metallo-organic coordination polymers is the extension of low dimensional building blocks to high dimensional networks through weak intermolecular interactions, including weak Van der Waals force, hydrogen bonding, π - π stacking, *etc*^[9-12].

Furthermore, N/O-donor ligands are effective cornerstones for the construction of inorganic-organic hybrid complexes, because of their ability to coordinate metal ions with nitrogen and oxygen atoms^[13-16]. It is well-known that, 1,10-phenanthroline^[17-18], as one of the N-donor ligands, is a good candidate in preparing light emitting materials. However, quinoline carboxylic acid^[19-20], as one of the O-donor ligands, is also a very interesting unit in the construction of inorganic-organic hybrid compounds with extended structure because of its carboxyl oxygen atoms and hydroxyl oxygen atoms, which can be bridged with metal ions. Up to now, there is few report on the complexes of quinoline carboxylic acid^[21-22].

Based on this, we are interested in the crystal

engineering of copper(II) ion with 3-hydroxy-2-methyl-quinoline-4-carboxylic acid and 1,10-phenanthroline as the ligands. In this article, we represented the solvothermal synthesis, X-ray crystal structure, photoluminescent and semiconductor properties, as well as time-dependent density functional theory (TDDFT) calculations for the novel copper(II) complex, $[\text{Cu}(\text{L})(\text{Phen})(\text{H}_2\text{O})] \cdot \text{CH}_3\text{OH}$ (**1**), (HL=3-hydroxy-2-methyl-quinoline-4-carboxylic acid; Phen=1,10-phenanthroline), which is an isolated mononuclear (0D) structure.

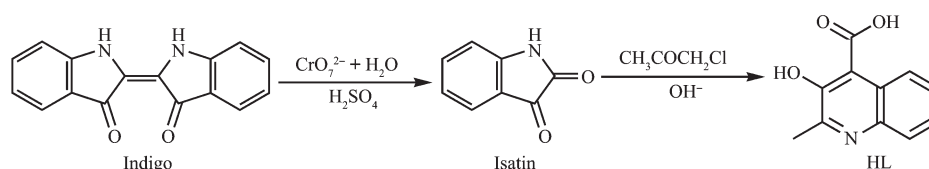
1 Experimental

1.1 Reagents and instruments

The reagents and chemicals for the synthesis of the title compound are analytical reagent grade, commercially available and applied without further purification. Mass spectrometry was determined with an Agilent Gas Chromatography-Mass Spectrometry 7890B GC/MSD. Elemental microanalyses of carbon, hydrogen and nitrogen were performed on an Elementar Vario EL elemental analyser. Infrared spectra were performed on a PE Spectrum-One FT-IR spectrometer using KBr discs. ^1H NMR was obtained with Bruker Avance 400 MHz based on deuterium DMSO as solvent. Solid-state UV-Vis reflectance spectroscopy was performed on a TU1901 UV/Vis spectrometer equipped with an integrating sphere. A BaSO_4 plate was acted as a 100% reflectance reference, on which the finely ground powder was coated. Photoluminescence measurement was carried out on a F97XP photoluminescence spectrometer. Time-dependent density functional theory (TDDFT) investigation was carried out by means of Gaussian09 suite of program packages.

1.2 Synthesis

The ligand HL was prepared according to the literature^[23-24] as shown in Scheme 1.



Scheme 1 Synthetic route of ligand HL

1.2.1 Synthesis of isatin

Indigo (1 mmol, 262 mg) and $\text{K}_2\text{Cr}_2\text{O}_7$ (0.5 mmol, 147 mg) were added into distilled water (500 mL) and stirred. After cooling, $\text{K}_2\text{Cr}_2\text{O}_7$ (0.5 mmol, 147 mg), distilled water (300 mL) and diluted H_2SO_4 (500 mL) were added and kept stirring at 45 °C for 2 hours. Then, the mixture was diluted with twice its volume of H_2O , filtered off, dissolved in a KOH solution, filtered again, acidified by HCl and refiltered. Yield: 230 mg ($\geq 90\%$); m.p. 210 °C; HRMS m/z (ESI) Calcd. for $\text{C}_8\text{H}_5\text{NO}_2$ ($[\text{M}+\text{H}^+]$): 147.032 0, Found: 147.082 6.

1.2.2 Synthesis of 3-hydroxy-2-methylquinoline-4-carboxylic acid (HL)

Isatin (1 mmol, 147 mg) and KOH (1 mmol, 56 mg) were dissolved into a sufficient amount of distilled water and filtered. The filtrate and KOH (1 mmol, 56 mg) were added into chloroacetone (2 mmol, 95.5 mg), and hydrochloric acid was added dropwise to adjust pH value to 7, then filtered. Yield: 195 mg ($\geq 95\%$); m.p. 225 °C; HRMS m/z (ESI) Calcd. for $\text{C}_{11}\text{H}_9\text{NO}_3$ ($[\text{M}+\text{H}^+]$): 203.058 2, Found: 203.054 8; IR(KBr, cm^{-1}): 3 433(vs), 3 125(w), 3 043(w), 2 869(w), 2 499(m), 2 040(m), 1 668(m), 1 621(m), 1 553(s), 1 500(m), 1 462(m), 1 410(m), 1 242(vs), 1 160(m), 1 014(w), 906(m) and 686(s); ^1H NMR(400 MHz, DMSO): δ 9.15 (s, 1H), 7.93(d, $J=8.0$ Hz 1H), 7.64(t, $J=8.0$ Hz, 1H), 7.60~7.52(m, 2H), 2.70(s, 3H).

1.2.3 Synthesis of $[\text{Cu}(\text{L})(\text{Phen})(\text{H}_2\text{O})]\cdot\text{CH}_3\text{OH}$ (**1**)

The title complex was synthesized by mixing HL (1 mmol, 203 mg), Phen (1 mmol, 180 mg), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (1 mmol, 170.5 mg), 9.5 mL CH_3OH and 0.5 mL distilled water (using NaOH to adjust pH value to 8) into a 25 mL Teflon-lined stainless steel autoclave.

The autoclave was heated to 105 °C in an oven and kept there for five days. When the autoclave was cooled down to room temperature, brown block crystals were obtained. The yield was 70% based on $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$. IR (KBr, cm^{-1}): 3 443 (vs), 2 925(w), 2 851(w), 2 361(w), 2 334(w), 1 660(m), 1 595(vs), 1 522(m), 1 443(vs), 1 362(m), 1 319(w), 1 229(w), 849(m), 722(m), 650(w) and 520(w); Anal. Calcd. for $\text{C}_{24}\text{H}_{21}\text{CuN}_3\text{O}_5$ (%): C, 58.24; H, 4.28; N, 8.49. Found (%): C, 58.31; H, 4.21; N, 8.53.

1.3 X-ray crystallographic determination

The X-ray diffraction data was collected on a SuperNova CCD X-ray diffractometer with a carefully selected single crystal (the dimension of 0.37 mm×0.19 mm×0.13 mm). The X-ray source was graphite monochromatic Mo $K\alpha$ radiation with the λ being of 0.071 073 nm. The reduction and empirical absorption correction of the diffraction data were carried out with the CrystalClear software. The crystal structure was solved by means of the direct method and the Siemens SHELXTL V5 software and refined with a full-matrix least-squares refinement on F^2 ^[25]. All non-hydrogen atoms were located on the difference Fourier maps and applied anisotropic refinement. The hydrogen atoms, except for water and methanol, were theoretically attached to their parent atoms and included in the structural factor calculations with assigned isotropic thermal parameters. The summary of the crystallographic data for the complex is provided in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 1882929.

Table 1 Crystal data and structure parameters for complex 1

Empirical formula	$\text{C}_{24}\text{H}_{21}\text{CuN}_3\text{O}_5$	Z	4
Formula weight	494.98	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.514
Crystal system	Monoclinic	Absorption coefficient / mm^{-1}	1.048
Space group	$P2_1/c$	$F(000)$	1 020
a / nm	1.274 58(8)	Final R indices $[I>2\sigma(I)]$	$R_1=0.059 2$, $wR_2=0.164 0$
b / nm	0.836 43(4)	R indices (all)	$R_1=0.074 8$, $wR_2=0.177 4$
c / nm	2.091 53(10)	S	1.035
$\beta / (^\circ)$	103.064(6)	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e}\cdot\text{nm}^{-3})$	1 535, -519
V / nm^3	2.172 1(2)		

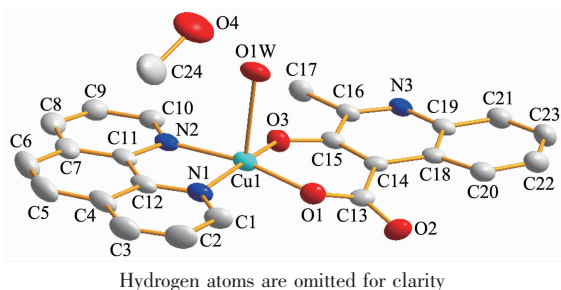
Table 2 Selected bond lengths (nm) and bond angles (°) for complex **1**

Cu(1)-O(3)	0.187 72(16)	Cu(1)-N(1)	0.201 0(2)	Cu(1)-O(1W)	0.240 7(2)
Cu(1)-O(1)	0.189 22(19)	Cu(1)-N(2)	0.203 0(2)		
O(1)-Cu(1)-N(1)	91.16(9)	O(1)-Cu(1)-O(1W)	95.12(8)	N(1)-Cu(1)-O(1W)	90.12(8)
O(3)-Cu(1)-N(1)	169.52(9)	O(3)-Cu(1)-O(1)	93.83(7)	N(2)-Cu(1)-O(1W)	93.51(8)
O(1)-Cu(1)-N(2)	169.08(8)	O(3)-Cu(1)-O(1W)	98.59(7)		
O(3)-Cu(1)-N(2)	91.50(8)	N(1)-Cu(1)-N(2)	82.12(9)		

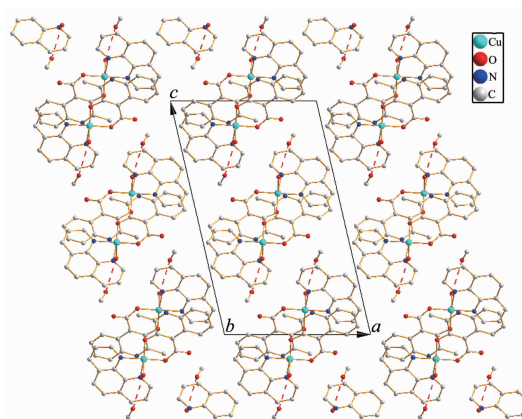
2 Results and discussion

2.1 Crystal structure of [Cu(L)(Phen)(H₂O)]·CH₃OH (**1**)

X-ray single-crystal diffraction analysis reveals that complex **1** is composed of an isolated electronically neutral [Cu(L)(Phen)(H₂O)] and an isolated solvent methanol molecule, as shown in Fig.1. Complex **1** crystallizes in *P*2₁/*c* space group of monoclinic system. The Cu(II) ion is coordinated with three oxygen atoms and two nitrogen atoms. Among them, two of the three oxygen atoms are derived from hydroxyl and carboxyl group on the same HL ligand, one from the solvent water, and the two nitrogen atoms come from the same 1,10-phenanthroline ligand, yielding a slightly distorted rectangular pyramid geometry. The bottom plane of pyramid is composed of O(1), O(3), N(1), N(2) atoms, and the top point of pyramid is occupied by the oxygen atom O(W) of the coordinated water. The bond lengths of Cu(1)-O(1)(0.189 22(19) nm) and Cu(1)-O(3)(0.187 72(16) nm) are normal and comparable with those reported in the literature^[26-27], the bond length of Cu(1)-O(1W) is 0.240 7(2) nm. The bond lengths of Cu(1)-N(1) (0.201 0(2) nm) and Cu(1)-N(2)(0.203 0(2) nm) are normal and comparable with those reported in the literature^[28-29]. The bond angles of top oxygen atom and bottom planes are in a range of 90.12(8)°~

Fig.1 ORTEP view of **1** with 25% thermal ellipsoids

98.59(7)°. Supramolecular layers via $\pi \cdots \pi$ stacking interactions and Van der Waals attraction form a crystal packing structure, as presented in Fig.2.



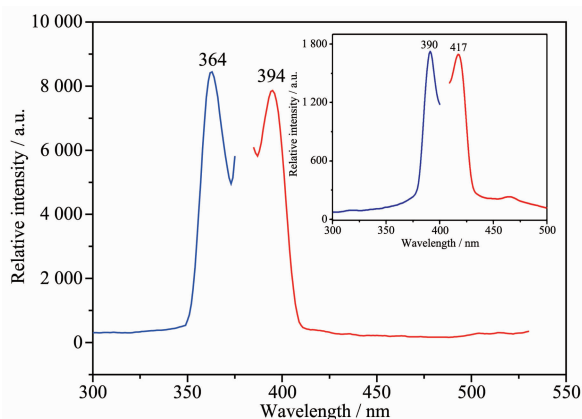
O1W \cdots O4 0.3069(7) nm, \angle O1W-H1WA \cdots O4 178(2)°

Fig.2 Packing diagram of **1** with the dashed lines representing hydrogen bonds O1W-H1WA \cdots O4

2.2 Solid-state photoluminescence spectra

In order to reveal the potential photoluminescent properties of complex **1**, the photoluminescence spectra was determined for solid state samples of **1** at room temperature and the results is presented in Fig.3 and 4. It is obvious that the photoluminescent spectrum of complex **1** displayed an effective energy absorption in a wavelength range of 350~375 nm. Upon the emission of 394 nm, the excitation spectrum showed a band at 364 nm. Upon excitation at 364 nm, the emission spectrum was characterized by a sharp band at 394 nm in the blue violet region. The emission band of complex **1** located in the blue violet light region with the CIE1931 chromaticity coordinate (0.136 6, 0.161 6) (Fig.4). The quantum yield of the title complex was 0.2%. In order to reveal the nature of the photoluminescence properties of **1**, the solid-

state photoluminescence spectrum of the ligand was measured, as shown in the inset of Fig.3. Upon excitation at 390 nm, the emission spectrum of the ligand was characterized by a sharp band at 417 nm. The photoluminescence spectra for complex **1** and the ligand are very similar. So, the photoluminescence of **1** is obviously originated from the ligands.



Blue curve: excitation; Red curve: emission; Inset: solid-state photoluminescence spectrum of HL

Fig.3 Solid-state photoluminescence spectrum of **1** measured at room temperature

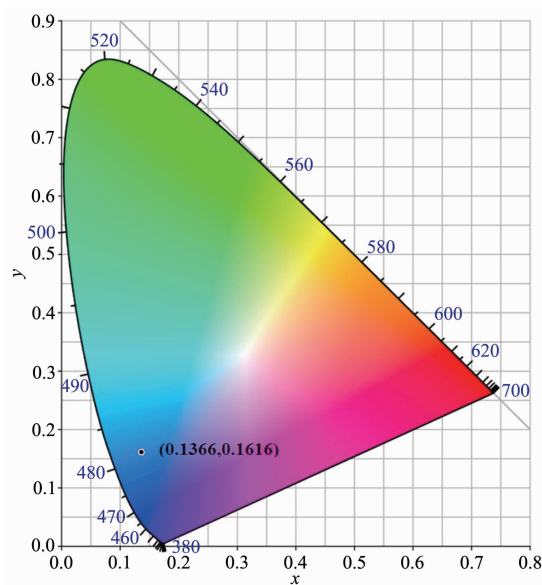


Fig.4 CIE chromaticity diagram and chromaticity coordinates of the emission spectrum of **1**

2.3 TDDFT calculations

In order to reveal the nature of the photoluminescence emission of complex **1**, we truncated ground state geometry from its single-crystal X-ray diffraction data set (without optimization) and carried out its

theoretical calculation in light of the time-dependent density functional theory (TDDFT) based on this ground state geometry. The TDDFT calculations were performed using the B3LYP function^[30-31] and carried out by means of the Gaussian09 suite of program package^[32], with basis set of 6-31G for C, H, N and of LANL2DZ for Cu considering the relativistic effects. The characteristics of HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) of complex **1** is shown in Fig.5. It is easy to find out that the electron-density distribution of HOMO was totally resided at the coordinating π -orbital of carboxylic acid ligand HL with an energy of $-0.164\ 555$ Hartree; however, the electron-density population of LUMO locates at π -orbital of ligand Phen and the energy of LUMO was calculated to be $-0.106\ 175$ Hartree. The energy difference between LUMO and HOMO is $0.058\ 38$ Hartree, and this is small enough to allow the charge transfer from HOMO to LUMO. In light of this observation, it is proposed that the essence of the photoluminescence of complex **1** could be assigned to the ligand-to-ligand charge transfer (LLCT; from the HOMO of the π -orbital of ligand HL to the LUMO of the π -orbital of ligand Phen). This calculation result is in good agreement with the experimental observations.

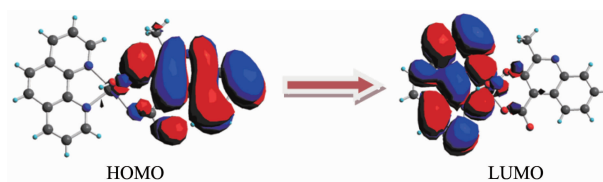


Fig.5 HOMO and LUMO of complex **1** with isosurface of 0.003 a.u.

2.4 Solid-state diffuse reflectance spectrum

To investigate the semiconductive properties of complex **1**, the solid-state UV-Vis diffuse reflectance spectra of powder sample of complex **1** was measured at room temperature, using barium sulfate as the reference for 100% reflectivity. After measuring the solid-state diffuse reflectance spectra, the data was treated with the Kubelka-Munk function that is known as $\alpha/S = (1-R)^2/(2R)$. With regard to this function, the parameter α means the absorption coefficient, S

means the scattering coefficient, and R means the reflectance, which is actually wavelength independent when the size of the particle is larger than 5 μm . From the α/S vs energy gap diagram, we can obtain the value the optical band gap, which can be extrapolated from the linear portion of the absorption edges. The solid-state UV-Vis diffuse reflectance spectrum reveals that complex **1** has a narrow optical energy band gap of 1.91 eV, as shown in Fig.6. As a result, complex **1** is a possible candidate for narrow band gap semiconductors. The slow slop of the optical absorption edge of complex **1** indicates that it must be an indirect transition. The energy band gap of 1.91 eV of complex **1** is obviously larger than those of GaAs (1.4 eV), CdTe (1.5 eV)^[33-34] and CuInS₂ (1.55 eV), which are well known as highly efficient band gap photovoltaic materials.

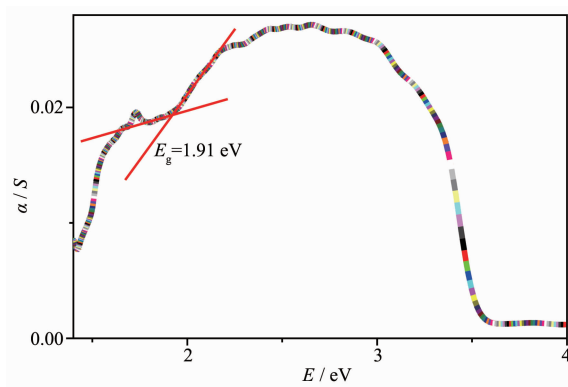


Fig.6 Solid-state UV-Vis diffuse reflectance spectrum of **1**

3 Conclusions

In conclusion, a novel copper complex containing 3-hydroxy-2-methylquinoline-4-carboxylic acid and 1,10-phenanthroline ligands has been synthesized and characterized by single-crystal X-ray diffraction. It exhibits a OD structure, and solid-state photoluminescent characterization reveals that it displays an emission in the blue violet region. TDDFT calculation reveals that the nature of the photoluminescence is originated from the ligand-to-ligand charge transfer (LLCT; from the HOMO of the HL to the LUMO of the Phen). A narrow optical band gap of 1.91 eV is determined by the solid-state UV-Vis diffuse reflectance spectrum.

3-Hydroxy-2-methylquinoline-4-carboxylic acid is an important intermediate for the synthesis of dye disperse yellow 54#. It is coordinated with copper to give complex **1**, with its blue-violet light-emitting properties and the semiconductive properties, which makes it be a potential fluorescent probe and a possible candidate for narrow band gap semiconductors. The subsequent research is still in progress.

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