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# Synthesis, Crystal Structure, Theoretical Study, and Luminescence Property of a Copper(I) Complex with Dipyrido[3,2-f:2′,3′-h]-quinoxaline

AIHUA CHEN,[1,2] SUCI MENG,[2,4] JINFANG ZHANG,[2,3] AND CHI ZHANG[2,3,*]

[1]School of Chemical and Biological Engineering, Yancheng Institute of Technology, Yancheng 224051, P. R. China
[2]China-Australia Joint Research Center for Functional Molecular Materials, Scientific Research Academy, Jiangsu University, Zhenjiang 212013, P. R. China
[3]China-Australia Joint Research Center for Functional Molecular Materials, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China
[4]Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China

*The new copper(I) complex [CuCN(Dpq)($PPh_3$)] (**1**) (where Dpq = dipyrido[3,2-f:2′,3′-h]-quinoxaline, $PPh_3$ = triphenylphosphine) has been synthesized and characterized by elemental analysis, Infrared spectroscopy, X-ray single crystal analysis, thermogravimetric, and fluorescent analysis. Single crystal X-ray diffraction analysis reveals that complex **1** display a favorable pairwise π-π stacking. Density functional theory and time-dependent density functional theory calculations at the B3LYP/LanL2DZf+6-31G* level were performed on complex **1** to rationalize its experimental absorption spectra. Fluorescent analysis reveals that complex **1** exhibit intense luminescence in dimethylfomamide solution at room temperature.*

**Keywords** Copper(I) complex; crystal structure; DFT calculations; luminescence

## 1. Introduction

Recently, the construction and characterization of copper(I) complexes containing triphenylphosphine and heterocyclic nitrogen ligands have drawn much attention due to their appealing structures, catalytic, and luminescent properties [1–5]. The heterocyclic nitrogen ligands such as 2,2-bipyridyl (bpy), 1,10-phenanthroline (phen), and 2-(2-benzimidazoly)-6-methylpyridine (Hbmp) have been known as coligands to construct Cu(I)/$PPh_3$ complexes. Some examples for such complexes are [Cu($PPh_3$)($C_{16}H_6N_6$)Cl]·$H_2O$ ($C_{16}H_6N_6$ = [2,3-f]-pyrazino-[1,10] phenanthroline-2,3-dicarbonitrile) [6], [Cu(cbpy)($PPh_3$)$X$] ($X$ = I;

*Address correspondence to Dr. Chi Zhang, Director, China-Australia Joint Research Center for Functional Molecular Materials Scientific Research Academy, Jiangsu University, Zhenjiang 212013, People's Republic of China. Tel.: +86-511-88797128; Fax: +86-511-88797815. E-mail: chizhang@ujs.edu.cn, chizhang1985@yahoo.com

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Br; cbpy = 6-cyano-2,2-bipyridine) [7], [Cu(Hbmp)($PPh_3$)$X$] ($X$ = I; Br; Cl) [8]. The $\pi$-conjugated chelating ligands in the above complexes play a key role in improving the luminescence properties of these copper(I) complexes, while the auxiliary ligands such as phosphine and halide also have great effects on photophysical properties of the Cu(I) complexes [9–12]. Dipyrido[3,2-f:2,3-h]-quinoxaline (Dpq) as a derivative of 1,10-phenanthroline is an excellent chelating ligand and possesses an extensive $\pi$-conjugated system, and it is a good candidate for the construction of luminescent Cu(I)/$PPh_3$ complexes. In comparison with 2,2-bipyridine and 1,10-phenathroline, Dpq has larger aromatic-ring system and may provide potential supramolecular recognition sites for $\pi$-$\pi$ aromatic stacking interactions [13]. However, to the best of our knowledge, there is no report in the literature hitherto for Dpq being combined into luminescent Cu(I)/$PPh_3$ complex. In addition, cyanide group rather than halogen could be the better auxiliary ligand for synthesis such kind of luminescent copper(I) complexes. Cyanides are reducing quenching process because as strong field ligands they induce the d-d state, which has relatively inaccessible energies, and consequently suppresses nonradiative deactivation of the d-d state [14,15]. These properties made the cyanides have obvious advantages in the construction of functional fluorescent materials [16]. Herein, we report the synthesis and crystal structure of a copper(I) complex with chelating Dpq ligand and auxiliary cyanide group. The luminescence property and thermal behavior of this tetrahedron coordinated Cu(I) complex were investigated. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations have afforded further insight into the electronic transitions and spectral characterization of this luminous copper(I) complex.



## 2. Experimental Section

### *2.1. Materials and Physical Measurements*

All chemicals and solvents used for the syntheses were reagent grade without further purification. The Dpq ligand was prepared according to literature methods [17,18]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C system. Infrared spectra were recorded in the region 400–4000 $cm^{-1}$ on a Nicolet Nexus 470 spectrometer (Germany) with samples as KBr disks. The UV-Vis absorption spectra were obtained with a FLASH EA 1112 spectrophotometer. Thermogravimetric analysis (TGA) measurements were carried on a Perkin-Elmer Pyris 1 system under $N_2$ purge with a heating rate of 10°C/min. Steady-state fluorescence spectra were measured on a Fluoro-Max-P instrument; samples were dissolved in dry DMF solution, filtered, transferred to a long quartz cell, and then capped and deoxygenated by bubbling with $N_2$ before measurement.

### *2.2. Synthesis of [CuCN(Dpq)($PPh_3$)] (1)*

CuCN (0.009 g, 0.1 mmol) and $PPh_3$ (0.0262 g, 0.1 mmol) were added to 3 mL dimethylfomamide (DMF) and the resultant solution was stirred at room temperature for 0.5 hr. After filtration, 1 mL DMF as the buffer was carefully layered onto the colorless filtrate. 4 mL EtOH containing Dpq (0.0232 g, 0.1 mmol) was then very carefully layered on the top of the buffer solution. Red block crystals of **1** (0.0242 g) were obtained after several days (yield 41.4%). Analysis calculated for $C_{33}H_{23}CuN_5P$: C 67.86, H 3.97, N 11.99%; found: C 67.78, H 3.93, N 12.06%. IR for **1** (KBr pellets, $cm^{-1}$): 3051.3(w), 2245.5(w), 1576.7(m),

1474.3(m), 1431.3(s), 1390.2(s), 1093.6(m), 806.8(m), 736.7(s), 696.6(s), 520.2(s), and 496.8(s).

### *2.3. X-ray Crystallography*

Single crystal X-ray diffraction data for [CuCN(Dpq)($PPh_3$)] at 293 K were collected with the use of graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Rigaku Saturn $724^+$ CCD diffractometer. The SMART and SAINT program packages were used for data collection and integration, respectively. The collected data were also corrected for absorbance using equivalent reflections and SADABS based upon Laue symmetry. The structure was solved by direct methods and refined on $F^2$ by the full-matrix least-squares calculations with the use of SHELX-97 program package [19–21]. All the nonhydrogen atoms were refined with anisotropic thermal displacement coefficients. All the hydrogen atoms were placed at the calculated positions and refined following the riding model. Details of the crystal parameters, data collection and refinement of complex **1** are summarized in

**Table 1.** Crystal data and structure refinement for **1**

| | |
|---|---|
| Formula | $C_{33}H_{23}N_5CuP$ |
| Formula weight | 584.07 |
| Temperature/K | 293(2) |
| Wavelength/Å | 0.71073 |
| Crystal system | Triclinic |
| Space group | *P-1* |
| Description | Red block |
| Crystal size (mm) | 0.15 × 0.12 × 0.16 |
| *a*/Å | 8.1551(16) |
| *b*/Å | 9.2154(18) |
| *c*/Å | 19.874(4) |
| $\alpha$/° | 91.45(3) |
| $\beta$/° | 90.87(3) |
| $\gamma$/° | 116.19(3) |
| *V*/Å$^3$ | 1339.2(5) |
| *Z* | 2 |
| $\rho_{calcd.}$/g·cm$^{-3}$ | 1.448 |
| *F* (000) | 680 |
| *hkl* range | $-9 \le h \le 9 - 11 \le k \le 10 - 20 \le l \le 23$ |
| $\theta$ range (°) | 3.15–28.88 |
| Reflections collected | 9314 |
| Independent reflections ($R_{int}$) | 4612 (0.0267) |
| Data/restraint/parameters | 4758/0/361 |
| M (mm$^{-1}$) | 0.908 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final *R* indices *[I > 2σ(I)]* | $R_1 = 0.0393$, $wR_2 = 0.0868$ |
| *R* indices (all data) | $R_1 = 0.0482$, $wR_2 = 0.0917$ |
| Largest differences in peak and hole/e·Å$^{-3}$ | 0.422 and − 0.297 e·Å$^{-3}$ |

**Table 2.** Selected bond lengths (Å) and bond angles (°) of **1**

| | | | |
|---|---|---|---|
| Cu(1)–C(33) | 1.940(3) | Cu(1)–N(1) | 2.108(2) |
| Cu(1)–N(2) | 2.112(2) | Cu(1)–P(1) | 2.2338(9) |
| N(1)–C(1) | 1.332(3) | N(1)–C(5) | 1.356(3) |
| N(2)–C(7) | 1.335(3) | N(2)–C(6) | 1.357(3) |
| N(3)–C(14) | 1.326(4) | N(3)–C(12) | 1.358(3) |
| N(4)–C(13) | 1.321(4) | N(4)–C(11) | 1.351(3) |
| C(33)–N(5) | 1.123(4) | C(33)–Cu(1)–N(1) | 118.61(11) |
| C(33)–Cu(1)–N(2) | 112.91(12) | N(1)–Cu(1)–N(2) | 79.00(8) |
| C(33)–Cu(1)–P(1) | 119.67(8) | N(1)–Cu(1)–P(1) | 107.23(6) |
| N(2)–Cu(1)–P(1) | 112.50(7) | C(15)–P(1)–Cu(1) | 115.32(8) |
| C(27)–P(1)–Cu(1) | 114.99(8) | C(21)–P(1)–Cu(1) | 115.44(9) |
| C(1)–N(1)–C(5) | 117.5(2) | C(1)–N(1)–Cu(1) | 129.05(19) |
| C(5)–N(1)–Cu(1) | 113.48(15) | C(7)–N(2)–C(6) | 117.1(2) |
| C(7)–N(2)–Cu(1) | 129.12(18) | C(6)–N(2)–Cu(1) | 113.68(16) |
| C(14)–N(3)–C(12) | 115.5(3) | C(13)–N(4)–C(11) | 115.7(3) |
| N(5)–C(33)–Cu(1) | 171.8(4) | | |

Table 1. The selected bond lengths and angles for complex **1** are listed in Table 2. CCDC-952972 contains the supplementary crystallographic data for the complex **1**. These data can be obtained free of charge via http://www.ccdc. cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

### *2.4. Density Functional Theory Study*

DFT and TD-DFT calculations were performed to characterize the experimental absorption spectra by using the Gaussian 09 program [22]. The model compound of **1** was selected from experimental X-ray single-crystal structure. The restricted singlet wave function in DMF (dielectric constant $\varepsilon = 36.71$) solution was test to be stable with the framework of the polarized continuum model (PCM) using B3LYP functional [23]. Herein, the basis set 6-31G*+LanL2DZ* (using 6-31G* basis set for C, N, P, and H atoms, adding the *f*-type polarization functions to Cu atoms at the basis set LanL2DZ) was employed in view of the influence of *d* and *f* functions on the absorption spectra. The exponent (3.525) of f orbital for Cu atoms was selected as those in previous work [24]. The vertical electronic excitation energies of **1** in DMF solution were then obtained through TD-DFT/PCM calculation at the same level.

## 3. Results and Discussion

### *3.1. Description of Crystal Structure*

The new copper(I) complex [CuCN(Dpq)($PPh_3$)] (**1**) crystallizes in the triclinic crystal system with *P-1* space group, its crystal data and structure refinement information are summarized in Table 1 and the selected bond lengths and angles of **1** are listed in Table 2. The crystal structure of complex **1** is depicted in Fig. 1. In this copper(I) complex, the copper atom is surrounded by two N atoms from chelating Dpq ligand, one P atom from

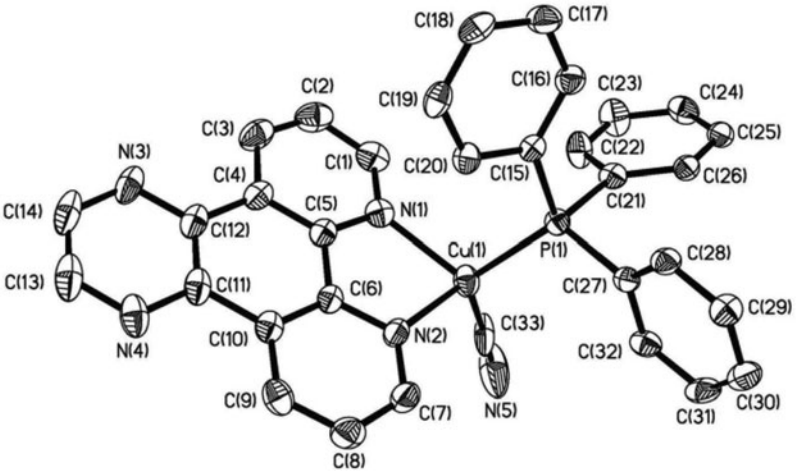


**Figure 1.** A view of the title complex, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and all H atoms have been omitted for clarity.

$PPh_3$ and one carbon atom from the CN group. The angles around Cu atom are in the range 79.00(8)–119.67(8)°, which indicates that the geometry around the CuN2CP core is approximately tetrahedral. The distorted tetrahedral geometry from ideal angles can be due to the restricted bite angle of Dpq and the need to accommodate the bulky triphenylphosphine ligand. The bond distance of Cu–P of **1** (2.2338(9) Å) is obviously longer than those in [CuI($PPh_3$)(phen)] (2.1977(9) Å) [25] and [CuI($PPh_3$)(DPPZ)]·DMF (2.2146(16) Å) [26], possibly attributed to the strong electron acceptor cyanide group with Cu–C bond length being 1.940(3) Å.

The Cu–N distances between Cu(I) and chelating Dpq ligand are 2.108(2) Å for Cu(1)–N(1) and 2.112(2) Å for Cu(1)–N(2), respectively, which are comparable to those of the reported copper(I) complexes with $PPh_3$ ligand [26,27]. The bond angle of the two coordinating nitrogen atoms of the Dpq ligand N(1)–Cu(1)–N(2) is 79.00(8)°, which is 0.93° smaller than that in [CuI($PPh_3$)(phen)] [25] and almost the same as that in [CuI($PPh_3$)(DPPZ)]·DMF (79.00(17)° [26]. The Cu(1)–C(33)–N(5) angle is 171.8(4)° and the C(33)–Cu(1)–P(1) angle is 119.67(8)°. The N1–C5–C6–N2 torsion angle is 2.02°, and the dihedral angle formed by the N3/C14/C13/N4/C11/C12 and Cu1/N1/C5/C6/N2 planes is 4.26°. The Dpq ligand coordinated with Cu(I) atom in complex **1** is essentially in planar configuration, similar to that in [$Pb_2(Dpq)_2(adip)(NO_3)_2$] [28]. It is worth noting that the Dpq ligands of two adjacent enantiomeric molecules in complex **1** are essentially parallel and display a favorable pairwise $\pi$-$\pi$ stacking (Fig. 2), such that the pairs of Dpq ligands overlay one another. The moieties of this pair are related to one another through an inversion center located between the Dpq rings. The interplanar separation is approximately 3.30 Å, which indicates the presence of $\pi$-$\pi$ stacking interactions between two neighboring Dpq ligands.

### *3.2. Infrared Spectroscopy*

In complex **1**, the $\nu$(C–H) vibration of aromatic ring is observed at about 3051 $cm^{-1}$. The peaks at 1577, 1474, 1431, and 1390 $cm^{-1}$ may be attributed to the vibrations of the

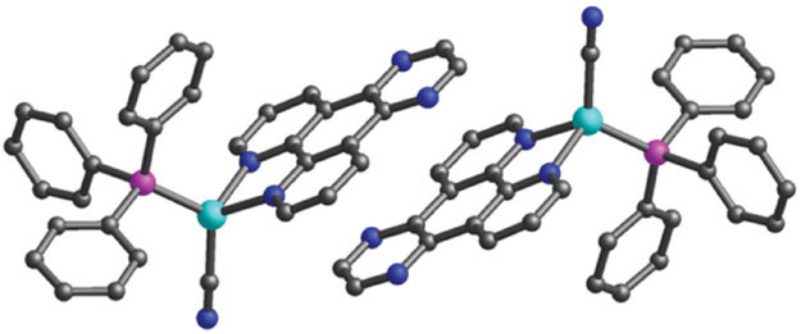

**Figure 2.** Pairwise stacking view of **1**, all H atoms have been omitted for clarity. (Cu, light green; P, red; N, blue; C, grey).



C=C/C=N bonds in **1**. The band at 2245 $cm^{-1}$ can be assigned to the $\nu$(C≡N) vibration. The presence of the $PPh_3$ groups is confirmed by the appearance of IR bands near 1094 $cm^{-1}$, which may be due to $\nu$(P-$C_{ph}$) vibrations [29]. The IR bands near 807, 737, and 697 $cm^{-1}$ belong to $\nu$(C–H) vibrations of the coordinated $PPh_3$ and Dpq [30]. The observed several bands in the 520–497 $cm^{-1}$ region can be assigned to $\nu$(Cu-P) stretches [31].

### *3.3. Experimental and Theoretical Absorption Spectra*

To gain deeper insight into the electronic transitions and spectral characterization of this copper(I) complex, the TD-DFT/PCM calculations were performed for **1**. The experimental absorption spectra of **1** were measured in a 2.45 × $10^{-5}$ mol $dm^{-3}$ DMF solution. Fig. 3 shows a comparison between the scaled absorption spectra of complex **1** with the Lorentzian function [32] and the experimental results, displaying a qualitative agreement in the shape of the absorption spectra. The lowest dipole-allowed absorption bands (Peak 1) are mainly assigned to be $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. As schematically illustrated in Fig. 4, the $\sigma$ molecular orbital of complex **1** is mainly contributed form the *p* orbital of P atom and *d* orbital of Cu atom. The $\pi$ and $\pi^*$ orbitals are dominated by the *p* orbitals of C and N atoms. The relatively stronger absorption bands (Peak 2) are mainly ascribed to the transitions from $\pi$ to $\pi^*$ orbitals. The $\pi$ orbital is dominated by the *p* orbitals of C atom in ligands and $\pi^*$ orbital is mainly contributed from *p* orbitals of P and Cu atoms.

### *3.4. Thermogravimetric Analysis*

To examine the thermal stability of complex **1**, TGA was carried out between 20 and 800°C in a static atmosphere of nitrogen. As depicted in Fig. 5, complex **1** is stable up to 223°C, on further hearting, a three-step weight loss was observed between 223 and 800°C, in which the first weight loss between 223 and 317°C is assigned to the removal of one triphenylphosphine ligand (observed, 44.99%; expected, 44.87%). The overall weight loss of 45.08% from the subsequent two steps occurring between 317 and 800°C is due to the decomposition of one Dpq ligand (expected, 39.76%) and the loss of one CN group (expected, 4.45%) [33,34]. In summary, the TGA illustrates that complex **1** possesses good thermal stability and thus render it as potential candidates for practical applications.

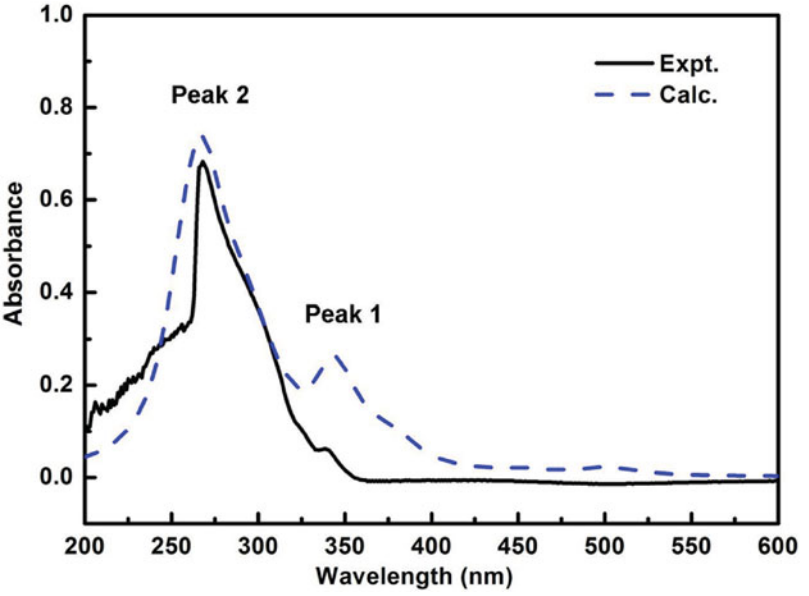


**Figure 3.** Absorption spectra of complex **1** obtained from experimental observations (in black line) and TD-DFT/PCM calculations (in blue dash). For the latter, a Lorentzian function has been adopted with the spectral line width set to be 70 nm. The theoretical spectra are right shifted by 90 nm from TD-DFT/PCM excitation energies, respectively.

### *3.5. Luminescence Behaviors*

Luminescent materials are currently of great interest due to their potentially applications in electroluminescent display and photochemistry [35]. Because of their excellent luminescence properties, the organic-inorganic hybrid coordination complexes constructed from

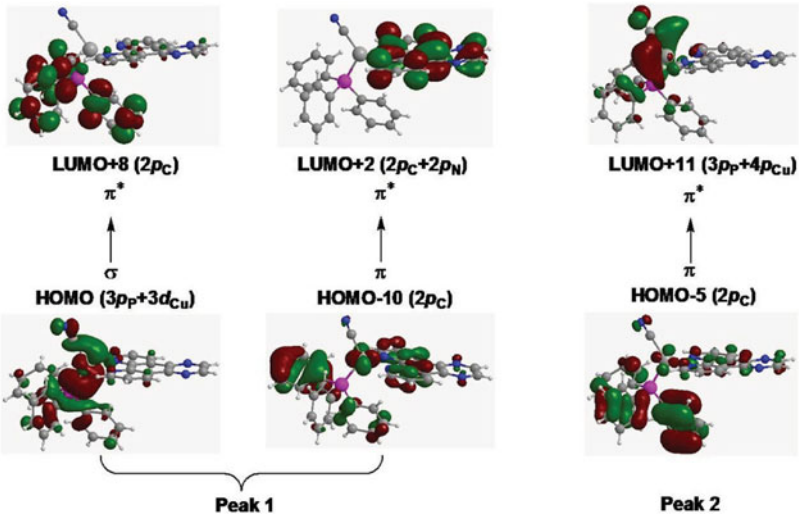


**Figure 4.** The assignment to absorption peaks of complex **1**. The molecular orbitals are obtained through DFT/PCM calculations at the B3LYP/6-31G*+LanL2DZ* level.

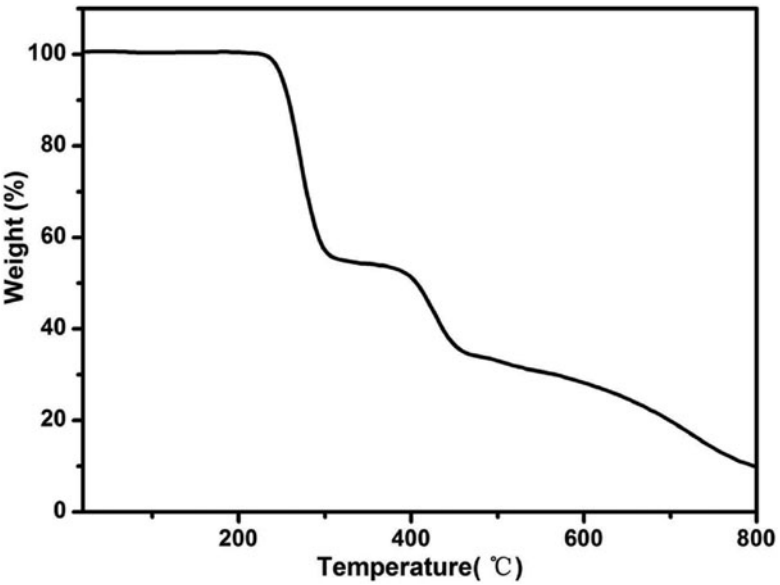


**Figure 5.** TGA curve of complex **1**.

$d^{10}$ transition metal centers and conjugated organic ligands have been the research focus and developed for the potential luminescent materials [36]. In order to examine the fluorescent properties of this copper(I) complex, the fluorescence spectra of complex **1** in DMF solution was measured. As shown in Fig. 6, the complex **1** produces an emission peak

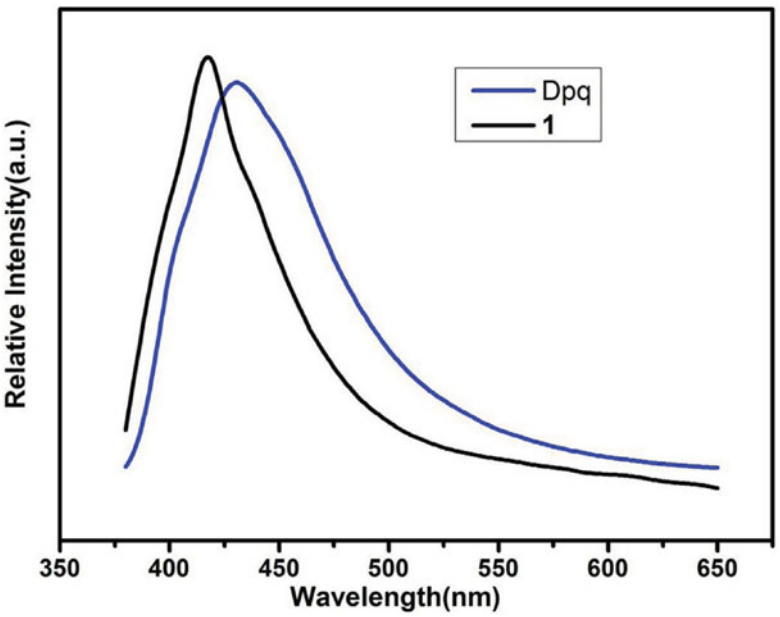


**Figure 6.** The emission spectra of complex **1** and Dpq ligand in DMF solution at room temperature.

at 417 nm when excited at 370 nm. To further study the relative luminescence between the free ligand and its complex, the photoluminescent spectrum of free Dpq ligand was also investigated in DMF solution at room temperature (Fig. 6). Upon excitation at 370 nm, the free Dpq ligand exhibits an emission peak at 430 nm, which may be attributed to the $\pi \rightarrow \pi^*$ transition [37]. By comparing the profiles and locations of the emission peak of complex **1** with the corresponding free Dpq, we can presume that emission peak at 417 nm of complex **1** should originate from intraligand $\pi \rightarrow \pi^*$ transitions, the blue shift of the peak in **1** is presumably a result of coordination of the relevant ligands to a metal atom, the $\pi$-system is altered and therefore also the transition energy [38].

## 4. Conclusions

In summary, a new luminous copper(I) complex based on dipyrido[3,2-f:2′,3′-h]-quinoxaline (Dpq) ligand has been synthesized and characterized. X-ray crystal analysis reveals that complex **1** display a favorable pairwise $\pi$-$\pi$ stacking. It is demonstrated that the introduction of the second auxiliary ligand, such as triphenylphosphine and pseudo halogen group, has an important effect on both the molecular structure and luminescence behavior of this Cu(I) complex. The theoretical absorption spectra of **1** obtained from DFT and TD-DFT calculations are in good agreement with the experimental observations. The intense fluorescent property of the title complex suggests that it may be used as potential luminescent materials. More efforts will focus on the construction of mononuclear copper(I) complexes based on dipyrido[3,2-f:2′,3′-h]-quinoxaline.

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