Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, characterization, crystal structures, and photophysical properties of a series of room-temperature phosphorescent copper(I) complexes with oxadiazole-derived diimine ligand

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ARTICLE INFO

Article history: Received 2 February 2010 Received in revised form 20 April 2010 Accepted 25 April 2010 Available online 5 May 2010

Keywords: Cu(1) complexes Single crystal Pi-stacking Luminescence

ABSTRACT

In this paper, we report four phosphorescent Cu(I) complexes of $[Cu(OP)(PPh_3)_2]BF_4$, $[Cu(Me-OP)(PPh_3)_2]BF_4$, $[Cu(OP)(POP)]BF_4$, and $[Cu(Me-OP)(POP)]BF_4$ with oxadiazole-derived diimine ligands, where OP = 2-(5-phenyl-[1,3,4]oxadiazol-2-yl)-pyridine, Me-OP = 2-(5-p-tolyl-[1,3,4]oxadiazol-2-yl)-pyridine, POP = bis(2-(diphenylphosphanyl)) ether, and $PPh_3 = triphenylphosphane$, including their synthesis, crystal structures, photophysical properties, and electronic nature. The Cu(I) center has a distorted tetrahedral geometry within the Cu(I) complexes. Theoretical calculation reveals that all emissions originate from triplet metal-to-ligand-charge-transfer excited state. It is found that the inter-molecular sandwich structure triggered by inter- and intra-molecular pi-stacking within solid states, and thus greatly enhances the photoluminescence (PL) performances, including PL quantum yield improvement, PL decay lifetime increase, and emission blue shift.

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1. Introduction

Recently, the development of practical components for chemical sensors, display devices, biological probes, phototherapy, and solar-energy conversion has sparked a great interest in transition metal complexes, especially heavy metal complexes such as Ru(II) and Re(I) complexes [1,2]. At the same time, the strong appeal of replacing the expensive compounds based on heavy metal ions with cheap ones, as well as the need for a deeper understanding on the correlation between molecular structures and photophysical properties, has pushed a continuous progress in the design of luminescent first-row transition metal complexes. Phosphorescent Cu(I) complexes, as a new class of optoelectrical material, have drawn much attention due to their advantages of less toxic, low cost, redundant resource, and environmental friendliness.

Generally, emission signals from charge-transfer (CT) excited states of copper(I) complexes are typically weak and short lived because the lowest energy CT state of a d¹⁰ system involves excitation from a metal–ligand d σ^* orbital [3,4]. An important consequence is that the excited state typically prefers a tetragonally flattened geometry whereas the ground state usually adopts a tetrahedral-like coordination geometry appropriate for a closed-shell ion. Aside from reducing energy content, the geometric relaxation that occurs in excited states facilitates relaxation back to ground state.

McMillin firstly reported this type of exciplex quenching, and by now, many other studies have confirmed this mechanism [5,6].

Mixed-ligand systems involving triphenylphosphane seem to be promising because they exhibit long excited state lifetimes in solid state and frozen solutions [7,8]. A series of new mixed-ligand copper(I) complexes such as $[Cu(N-N)(POP)]^+$ [POP = bis(2-(diphenylphosphanyl)phenyl) ether] which are superior emitters have been synthesized. It is found that the exciplex quenching is relatively inefficient for the CT excited state in this POP system. In addition, the introduction of sterically blocking ligands can impede geometric relaxation as well as solvent attack [9]. Here, steric effects cooperate to effectively block excited state close to groundstate geometry, which has been proved by the theoretical studies finished by Feng and coworkers on $[Cu(N-N)(P-P)]^+$ system [10]. For a typical phosphorescent [Cu(N–N)(POP)]⁺ complex, the highest occupied molecular orbital (HOMO) has predominant metal Cu d character, while, the lowest unoccupied orbital (LUMO) is essentially π^* orbital localized on the diimine ligand. The photoluminescence (PL) corresponds to the lowest triplet T1 and is thus assigned as a character of metal-to-ligand-charge-transfer ³MLCT $[d(Cu) \rightarrow \pi^*(diimine ligand)]$. The photophysical properties of [Cu(N–N)(POP)]⁺ complexes are usually sensitive towards both ligands structures and environment surroundings.

In this paper, we report four phosphorescent Cu(I) complexes with oxadiazole-derived diimine ligands and phosphorous ligands, including their synthesis, crystal structures, photophysical properties, and electronic nature. The Cu(I) center has a distorted





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tetrahedral geometry within the Cu(I) complexes. Theoretical calculation reveals that all emissions originate from triplet metalto-ligand-charge-transfer excited state. It is found that the intermolecular sandwich structure triggered by inter- and intra-molecular π -stacking within solid state Cu(I) complexes is highly effective on restricting the geometric relaxation that occurs in excited states, and thus greatly enhances the PL performances, including PL quantum yield improvement, PL decay lifetime increase, and emission blue shift.

2. Experimental

A synthetic procedure for the two oxadiazole-derived diimine ligands of 2-(5-phenyl-[1,3,4]oxadiazol-2-yl)-pyridine (referred as OP) and 2-(5-p-tolyl-[1,3,4]oxadiazol-2-yl)-pyridine (referred as Me-OP), as well as their corresponding Cu(1) complexes, is shown in Scheme 1.

4-Methyl-benzoyl chloride, benzoyl chloride, sodium azide, zinc bromide, Cu(BF₄)₂, bis(2-(diphenylphosphanyl)phenyl) ether (referred as POP), triphenylphosphane (referred as PPh₃), polyvinylpyrrolidone (PVP), and 2-cyanopyridine were purchased from Aldrich Chemical Co., and used without further purifications. The starting materials of [Cu(CH₃CN)₄]BF₄ and 2-(2H-tetrazol-5-yl)pyridine (referred as TP) were synthesized according to the literature procedures [7,11]. All organic solvents were purified using standard procedures.

2.1. Synthesis of diimine ligands

OP. The mixture of 20 mmol of TP, 22 mmol of benzoyl chloride, and 30 mL of pyridine was brought to reflux under N₂ atmosphere for 3 days. The mixture was then poured into cold water and filtered. The obtained crude product was purified by column chromatography. Yield: 62%. ¹H NMR (CDCl₃): δ 7.48 (1H, m), 7.54 (3H, m), 7.90 (1H, m), 8.22 (1H, t), 8.24 (1H, t), 8.33 (1H, d, *J* = 6.0), 8.83 (1H, d, *J* = 3.6). *Anal.* Calc. for C₁₃H₉N₃O: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.89; H, 4.12; N, 18.71%. IR (KBr pellet): 3051, 1618, 1543, 1484, 1446, 1382, 1139, 1071, 1029, 791, 710 cm⁻¹.

Me-OP. Me-OP was synthesized by a method similar to that of OP, except that benzoyl chloride was replaced by 4-methylbenzoyl chloride. Yield: 51%. ¹H NMR (CDCl₃): δ 2.45 (3H, s), 7.31 (2H, d, *J* = 6.0), 7.47 (1H, t), 7.90 (1H, t), 8.10 (2H, d, *J* = 6.0), 8.31 (1H, d, *J* = 3.6). *Anal.* Calc. for C₁₄H₁₁N₃O: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.95; H, 4.77; N, 17.58%. IR (KBr pellet): 3051, 2927, 2859, 1603, 1548, 1481, 1454 1381, 1142, 1076, 1037, 818, 784, 719 cm⁻¹.

2.2. Synthesis of Cu(I) complexes

All the Cu(I) complexes were synthesized according to the classic literature procedure [7]. Their identity was confirmed by ¹H NMR, elemental analysis, IR spectra, and single crystal XRD.

 $[Cu(OP)(PPh_3)_2]BF_4$. About 1.0 mmol of $[Cu(CH_3CN)_4]BF_4$ and 2.0 mmol of PPh₃ were dissolved in 10 mL of CH₂Cl₂. The mixture was refluxed for 30 min at room temperature. Then 1.0 mmol of OP was added. The mixture was refluxed for another half an hour. The solvent was removed by rotary evaporation. The crude product was further purified by recrystallization from the mixed solvent of tetrahydrofuran/ether. Yield: 85%. ¹H NMR: δ 7.21 (24H, m), 7.36 (6H, t), 7.586, (4H, m), 8.13 (2H, d, *J* = 5.4), 8.26, (3H, m). *Anal.* Calc. for C₄₉H₃₉BCuF₄N₃OP₂: C, 65.53; H, 4.38; N, 4.68. Found: C, 65.48;



Scheme 1. A synthetic procedure for OP, Me-OP, and their corresponding Cu(I) complexes.

H, 4.41; N, 4.77%. IR (KBr pellet): 3060, 1612, 1557, 1474, 1431, 1158, 1091, 1057, 740 cm⁻¹.

[Cu(Me-OP)(PPh₃)₂]BF₄. [Cu(Me-OP)(PPh₃)₂]BF₄ was synthesized by a method similar to that of [Cu(OP)(PPh₃)₂]BF₄, except that OP was replaced by Me-OP. Yield: 80%. ¹H NMR: δ 2.48 (3H, s), 7.21 (19H, m), 7.25 (5H, m), 7.37 (8H, m), 7.67, (1H, t), 8.04 (2H, d, *J* = 6.0), 8.24 (2H, t), 8.33 (1H, t). *Anal.* Calc. for C₅₀H₄₁BCuF₄-N₃OP₂: C, 65.84; H, 4.53; N, 4.61. Found: C, 65.87; H, 4.44; N, 4.52%. IR (KBr pellet): 3077, 2922, 2863, 1617, 1564, 1434, 1191, 1164, 1086, 1050, 747 cm⁻¹.

[Cu(OP)(POP)]BF₄. [Cu(OP)(POP)]BF₄ was synthesized by a method similar to that of [Cu(OP)(PPh₃)₂]BF₄, except that 2.0 mmol of PPh₃ was replaced by 1.0 mmol of POP. Yield: 82%. ¹H NMR: δ 6.83 (2H, m), 7.00 (6H, m), 7.22 (9H, m), 7.28 (6H, m), 7.30 (5H, m), 7.60 (4H, m), 8.14 (3H, t), 8.38 (2H, m). *Anal.* Calc. for C₄₉H₃₇BCuF₄N₃O₂P₂: C, 65.52; H, 4.09; N, 4.61. Found: C, 65.56; H, 4.13; N, 4.67%. IR (KBr pellet): 3048, 1601, 1549, 1474, 1428, 1389, 1263 (m), 1221, 1180, 1152, 1058, 741 cm⁻¹.

[Cu(Me-OP)(POP)]BF₄. [Cu(Me-OP)(POP)]BF₄ was synthesized by a method similar to that of [Cu(OP)(POP)]BF₄, expect that OP was replaced by Me-OP. Yield: 83%. ¹H NMR: δ 2.45 (3H, s), 6.81 (2H, m), 7.00 (5H, m), 7.21 (11H, m), 7.28, (3H, m), 7.31 (5H, m), 7.37 (3H, d, *J* = 6.3), 7.55 (2H, m), 8.01 (2H, m), 8.14 (1H, d, *J* = 3.6), 8.34 (2H, m). *Anal.* Calc. for C₅₀H₃₉BCuF₄N₃O₂P₂: C, 64.84; H, 4.24; N, 4.54. Found: C, 65.89; H, 4.28; N, 4.41%. IR (KBr pellet): 3051, 2931, 2858, 1617, 1552, 1430, 1261, 1210, 1186, 1157, 1097, 1053, 743 cm⁻¹.

2.3. Methods and measurements

Density functional theory (DFT) and singlet excitation calculations using time-dependent density functional theory (TD-DFT) were performed on the Cu(I) complexes at RB3LYP/SBKJC level. The initial geometries were obtained from their single crystal structures. All computations were finished by GAMESS software package.

Excited state lifetimes were obtained with a 355 nm light generated from the third-harmonic-generator pump, using pulsed Nd:YAG laser as the excitation source. The Nd:YAG laser possesses a line width of 1.0 cm⁻¹, pulse duration of 10 ns, and repetition frequency of 10 Hz. A Rhodamine 6G dye pumped by the same Nd:YAG laser was used as the frequency-selective excitation source. All PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. Solid state photoluminescence quantum yields were measured with the Hitachi F-4500 fluorescence spectrophotometer equipped with an integrating sphere [9]. UV-Vis absorption spectra were recorded using a Shimadzu UV-3101PC spectrophotometer. ¹H NMR spectra were obtained with a Varian INOVA 300 spectrometer. Elemental analysis was performed on a Carlo Erba 1106 elemental analyzer. Single crystals data were collected on a Siemens P4 single-crystal X-ray diffractometer with a Smart CCD-1000 detector and graphite-monochromated Mo K α radiation, operating at 50 kV and 30 A at 298 K. All hydrogen atoms were calculated. All data were recorded using single crystal samples in the air at room temperature without being specified.

3. Results and discussion

3.1. Single crystal structures

The crystal structures of $[Cu(OP)(PPh_3)_2]BF_4$, $[Cu(Me-OP)(PPh_3)_2]BF_4$, and $[Cu(OP)(POP)]BF_4$ are depicted in Figs. 1a–d. The selected geometric parameters shown in Table 1 suggest that the Cu(I) center in the three complexes has a distorted tetrahedral



Fig. 1a. Crystal structure of $[Cu(OP)(PPh_3)_2]BF_4.\ BF_4^-$ and hydrogen atoms are not shown for clarity.



Fig. 1b. Crystal structure of $[Cu(Me-OP)(PPh_3)_2]BF_4$. BF_4^- and hydrogen atoms are not shown for clarity.

geometry. The dihedral angles between N–Cu–N and P–Cu–P planes for the three complexes are measured to be 83.85°, 87.47°, and 87.51°, respectively. Cu–N bond lengths of the three Cu(I) complexes localize in a region of 2.1–2.2 Å which are comparable to literature values [6–9]. The Cu–N(pyridine) bond length is longer than the Cu–N(oxadiazole) bond length in PPh₃ system. In POP system, however, the Cu–N(pyridine) bond length is shorter than the Cu–N(oxadiazole) bond length, indicating that the Cu–N bond is affected by phosphorous ligands. In addition, it is observed that Cu–N bond lengths in POP system are usually shorter than those in PPh₃ system, indicating a stronger Cu–N bond in POP system. On the other hand, Cu–P bond lengths of the three Cu(I) complexes are similar to each other. The oxygen atom of POP ligand in [Cu(OP)(POP)]BF₄ localizes at a distance of ~3 Å away from the Cu(I) center and opposite to the coordinated N atoms, indicating



Fig. 1c. Crystal structure of [Cu(OP)(POP)]BF₄. BF₄⁻ and hydrogen atoms are not shown for clarity.



Fig. 1d. Inter- and intra-molecular π -stacking of [Cu(Me-OP)(PPh₃)₂]BF₄.

a weak interaction between oxygen atom and Cu(I) center. Similar $Cu \cdots O$ separations have also been reported in POP-based Cu(I)complexes that contain 1,10-phenanthroline (Phen) and Phenderived ligands [10,12].

N-Cu-N bond angles of the three Cu(I) complexes are quite similar to each other (~79°) with small variations. In contrast, P-Cu-P bond angle varies dramatically from 115.73° for [Cu(OP)-(POP)]BF₄ to 130.40° for [Cu(Me-OP)(PPh₃)₂]BF₄ as shown in Table 1. Considering POP's natural bite angle of 102.2°, with a flexibility range from 86° to 120°, the large P-Cu-P bond angle in [Cu(OP)-(POP)]BF₄ suggests a crowded coordination environment around Cu(I) center [13].

It is also observed that there is inter- and intra-molecular π stacking within solid state [Cu(Me-OP)(PPh₃)₂]BF₄ due to Me-OP's large coplanar conjugation plane, as shown by Fig. 1d. As for solid [Cu(Me-OP)(PPh₃)₂]BF₄, every two molecules are bonded head-to-head, where Me-OP moiety is defined as the "head", due

Table 1
Selected bond lengths (Å) and angles (°) of the three Cu(I) complexes.

	[Cu(OP)(PPh ₃) ₂]BF ₄	[Cu(Me-OP)(PPh ₃) ₂]BF ₄	[Cu(OP)(POP)]BF ₄
Cu(1)-N(1)	2.154	2.175	2.098
Cu(1) - N(2)	2.095	2.129	2.130
Cu(1) - P(1)	2.278	2.274	2.246
Cu(1)-P(2)	2.237	2.229	2.247
Cu···O	N/A ^a	N/A ^a	3.132
N(1)-Cu-N(2)	78.47	78.58	79.24
N(1)-Cu-P(1)	100.37	99.47	109.43
N(2)-Cu-P(1)	109.33	98.60	116.90
N(1)-Cu-P(2)	121.63	112.67	113.98
N(2)-Cu-P(2)	117.69	123.40	115.92
P(1)-Cu-P(2)	120.96	130.40	115.73

^a Not available.

to the π - π attraction between Me-OP rings. The dihedral angle between Me-OP rings is measured to be as small as 6.95° with a distance of ~3.391 Å, which confirms that there is face-to-face π - π stacking between the two Me-OP rings. In addition to this kind of inter-molecular π -stacking interaction, it appears that there is intra-molecular π -stacking interaction between [Cu(Me-OP)- $(PPh_3)_2$]BF₄ molecules, which actually increases $\pi - \pi$ attraction and allows [Cu(Me-OP)(PPh₃)₂]BF₄ molecules to take a more organized geometry. The large P-Cu-P bond angle of [Cu(Me-OP)(PPh₃)₂]BF₄ allows one of PPh₃'s phenyl ring to align almost parallel to Me-OP ring so that their mean planes intersect with an angle of 6.63°, and the approximate distance between PPh_3 phenyl ring and Me-OP ring is only 3.375 Å. No similar π -stacking is observed in POP system, which may be caused by the P-Cu-P bond angle limitation of 120° as mentioned.

3.2. Photophysical properties

The photophysical parameters of the four Cu(I) complexes are summarized in Table 2. Fig. 2 shows the UV-Vis absorption spectra of [Cu(OP)(PPh₃)₂]BF₄, [Cu(Me-OP)(PPh₃)₂]BF₄, [Cu(OP)(POP)]BF₄, and [Cu(Me-OP)(POP)]BF₄ in CH₂Cl₂ solutions with a concentration of 1×10^{-4} mol/L. It can be observed that the four absorption spectra are quite similar to each other due to their similar diimine and phosphorous ligands. Each absorption spectrum is typically composed of a high-energy absorption band ranging from 350 to 220 nm and a low-energy absorption band ranging from 350 to 500 nm. The former one corresponds to ligands $\pi \to \pi^*$ transitions according to literature reports [9,10,12]. While, the latter one is experimentally assigned as MLCT transition absorption. Compared with the absorption spectrum of [Cu(Phen)(POP)]BF₄ ending at \sim 500 nm, it can be seen that the oxadiazole moiety in OP and Me-OP ligand exerts no obvious effect on the absorption edges (λ_{edg}) of their corresponding Cu(I) complexes [9].

As shown in Fig. 3, the four Cu(I) complexes exhibit broad emission spectra (λ_{em}) at room temperature, peaking at 553 nm for $[Cu(OP)(PPh_3)_2]BF_4$, 516 nm for $[Cu(Me-OP)(PPh_3)_2]BF_4$, 569 nm

Table 2
Summarized photophysical parameters of the four Cu(I) complexes

[Cu(N–N)(P–	λ _{edg} a	λ _{em} a	Φ^{b}	τ ^c	$K_{\rm r}$	$K_{\rm nr}$
P)]BF ₄ N–N, P–P =	(nm)	(nm)		(μs)	(×10 ³ s ⁻¹)	(×10 ³ s ⁻¹)
OP, (PPh ₃) ₂	485	553	0.02	3.23	6.2	303.4
Me-OP, (PPh ₃) ₂	485	516	0.95	60.31	15.7	0.88
OP, POP	500	569	0.01	1.28	7.8	773.5
Me-OP, POP	500	560	0.01	3.15	3.2	314.3

^a ±1 nm.

±10%, measured according to the literature method of Ref. [9].

^c ±5%, $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2).$



Fig. 2. UV–Vis absorption spectra of the four Cu(l) complexes in CH₂Cl₂ solutions with a concentration of 1×10^{-4} mol/L. Inset: a magnified view of their absorption edges.



Fig. 3. PL spectra of the four Cu(l) complexes. Inset: a magnified view for $[Cu(OP)(PPh_3)_2]BF_4$, $[Cu(OP)(POP)]BF_4$, and $[Cu(Me-OP)(POP)]BF_4$.

for $[Cu(OP)(POP)]BF_4$, and 560 nm for $[Cu(Me-OP)(POP)]BF_4$, respectively. Those emissions render no vibronic progressions, indicating that the excited states own a CT character. Large Stokes shifts between absorption edges and emission peaks are observed for the Cu(I) complexes (2535 cm⁻¹ for $[Cu(OP)(PPh_3)_2]BF_4$, 2425 cm⁻¹ for $[Cu(OP)(POP)]BF_4$, and 2143 cm⁻¹ for [Cu(Me-OP)-

 $(POP)]BF_4$, except for $[Cu(Me-OP)(PPh_3)_2]BF_4$ (1239 cm⁻¹). The small Stokes shift reveals that the geometric relaxation in $[Cu(Me-OP)(PPh_3)_2]BF_4$ excited state is largely and effectively suppressed.

The PL quantum yields (Φ) are measured to be 0.02 for $[Cu(OP)(PPh_3)_2]BF_4$, 0.95 for $[Cu(Me-OP)(PPh_3)_2]BF_4$, 0.01 for $[Cu(OP)(POP)]BF_4$, and 0.01 for $[Cu(Me-OP)(POP)]BF_4$, respectively. Correspondingly, the PL decay lifetimes (τ) are measured to be 3.23 µs for $[Cu(OP)(PPh_3)_2]BF_4$, 60.31 µs for $[Cu(Me-OP)(PPh_3)_2]BF_4$, 1.28 µs for $[Cu(OP)(POP)]BF_4$, and 3.15 µs for $[Cu(Me-OP)(PPh_3)_2]BF_4$ gives a largely improved PL quantum yield and a largely increased lifetime than the others, which means that its luminescence is greatly enhanced. Based on the quantum yields and lifetime data on hand, the radiative probability and nonradiative probability values, K_r and K_{nr} , are calculated with Formula (1) and Formula (2) as follows.

$$\Phi = \frac{K_{\rm r}}{K_{\rm r} + K_{\rm nr}} \tag{1}$$

$$\frac{1}{\tau} = K_{\rm r} + K_{\rm nr} \tag{2}$$

As shown in Table 2, the radiative probability value of $[Cu(Me-OP)(PPh_3)_2]BF_4$ is typically two times bigger than the corresponding values of the other three Cu(I) complexes. On the other hand, the nonradiative probability value of $[Cu(Me-OP)(PPh_3)_2]BF_4$ is three orders of magnitude smaller than the corresponding values of the other three Cu(I) complexes. Thus, we come to a conclusion that the luminescence enhancement of $[Cu(Me-OP)(PPh_3)_2]BF_4$ is mainly caused by the effective suppression of K_{nr} decay process.

3.3. Theoretical calculations

As mentioned, the emissive state of phosphorescent Cu(I) complexes is usually affected by both ligand electronic nature and coordination geometry. In order to get a further understanding on the electronic nature of the Cu(I) complexes, we perform a DFT/TD-DFT calculation, which has been proved to be a powerful tool to investigate electronic properties of transition metal complexes, on $[Cu(OP)(PPh_3)_2]^+$ and $[Cu(Me-OP)(PPh_3)_2]^+$ at RB3LYP/ SBKJC level [10].

As shown in Table 3, the highest occupied molecular orbital (HOMO) of $[Cu(OP)(PPh_3)_2]^*$ has an evident metal Cu character, admixed with large contributions from the phosphorous ligand, while, the lowest unoccupied molecular orbital (LUMO) of $[Cu(OP)(PPh_3)_2]^*$ is essentially diimine ligand π^* orbital of OP. Similar case is observed in $[Cu(Me-OP)(PPh_3)_2]^*$. The calculated onset transition of $[Cu(OP)(PPh_3)_2]^*$ and $[Cu(Me-OP)(PPh_3)_2]^*$ corresponds to an electronic transition from HOMO to LUMO, and the onset excitation energy value of $[Cu(OP)(PPh_3)_2]^*$ listed in Table 3 correlates quite well with the experimentally recorded

Table 3

Calculated percentage composition of frontier 1 molecular orbitals and the first four singlet excitations of [Cu(OP)(PPh_3)_2]* and [Cu(Me-OP)(PPh_3)_2]* calculated at RB3LYP/SBKJC level.

Orbital/transition	[Cu(OP)(PPh ₃) ₂] ⁺ composition/energy	[Cu(Me-OP)(PPh ₃) ₂] ⁺ composition/energy
LUMO+1 LUMO HOMO HOMO-1 HOMO-2	$\begin{array}{l} Cu(1.6\%)OP(82.8\%)PPh_3(15.7\%) & -3.97 \ eV\\ Cu(2.7\%)OP(88.4\%)PPh_3(8.9\%) & -4.92 \ eV\\ Cu(26.7\%)OP(5.4\%)PPh_3(67.9\%) & -8.04 \ eV\\ Cu(36.9\%)OP(17.0\%)PPh_3(46.0\%) & -8.48 \ eV\\ Cu(45.6\%)OP(34.9\%)PPh_3(19.6) & -8.72 \ eV \end{array}$	Cu(1.1%)Me-OP(88.9%)PPh ₃ (10.1%) -3.90 eV Cu(2.2%)Me-OP(87.7%)PPh ₃ (10.1%) -4.81 eV Cu(26.9%)Me-OP(6.9%)PPh ₃ (66.2%) -8.16 eV Cu(34.6%)Me-OP(18.3%)PPh ₃ (47.0%) -8.42 eV Cu(49.6%)Me-OP(36.0%)PPh ₃ (14.4%) -8.68 eV
$\begin{array}{l} S_{0} \to S_{1} \\ S_{0} \to S_{2} \\ S_{0} \to S_{3} \\ S_{0} \to S_{4} \end{array}$	HOMO → LUMO(99.6%) 2.550 eV HOMO-1 → LUMO(88.9%) 2.769 eV HOMO-2 → LUMO(89.2%) 2.824 eV HOMO → LUMO+1(86.4%) 3.470 eV	HOMO → LUMO(74.7%) 2.690 eV HOMO-1 → LUMO(72.6%) 2.809 eV HOMO-2 → LUMO(89.0%) 2.924 eV HOMO → LUMO+1(85.7%) 3.582 eV



Fig. 4. PL spectra of $[Cu(OP)(PPh_3)_2]BF_4/PVP$ (10 wt.%) and $[Cu(Me-OP)(PPh_3)_2]BF_4/PVP$ (10 wt.%) films. Inset: PL decay curves of the two films.

absorption edge shown in Fig. 2. As for [Cu(Me-OP)(PPh₃)₂]⁺, the calculated onset excitation energy value is slightly bigger than the one calculated from its absorption edge, which may be caused by the distorted geometry of $[Cu(Me-OP)(PPh_3)_2]^+$ triggered by π stacking. It is thus confirmed that the onset electronic transition of [Cu(OP)(PPh₃)₂]⁺ and [Cu(Me-OP)(PPh₃)₂]⁺ is a MLCT one. Correspondingly, the emissive state of [Cu(OP)(PPh₃)₂]⁺ and [Cu(Me- $OP)(PPh_3)_2$ ⁺ is also a MLCT one. Combined with the long excited state lifetimes as mentioned, we come to a conclusion that the emissions of both [Cu(OP)(PPh₃)₂]BF₄ and [Cu(Me-OP)(PPh₃)₂]BF₄ originate from ³MLCT excited states, showing no luminescence mechanism difference. Consequently, the luminescence enhancement of [Cu(Me-OP)(PPh₃)₂]BF₄ is not caused by the electronic nature difference between [Cu(OP)(PPh₃)₂]BF₄ and [Cu(Me-OP)(PPh₃)₂]BF₄.

3.4. Analysis on luminescence enhancement

As above mentioned, the luminescence enhancement is mainly caused by the suppression of K_{nr} decay process. McMillin and coworker's reports confirm that the dominant nonradiative decay process is the geometric relaxation that occurs at excited state from a tetragonally flattened geometry to a tetrahedral-like one [3,5–7]. Since the crystal data suggest that [Cu(Me-OP)(PPh₃)₂]BF₄ molecules adopt the "head-to-head" dual-molecular structure due to the inter- and intra-molecular π -stacking within solid state [Cu(Me-OP)(PPh₃)₂]BF₄, and this bonded dual-molecule structure is believed to be a rigid structure to some extent, it is thus expected that this geometric relaxation is somehow suppressed by the bonded dual-molecule structure, resulting in the enhanced luminescence of [Cu(Me-OP)(PPh₃)₂]BF₄ [14].

In order to confirm this hypothesis, we disperse [Cu(Me-OP)(PPh₃)₂]BF₄ crystal into PVP film, so that the inter-molecular π - π stacking can be suppressed or even eliminated. With the disappearance of the rigid dual-molecule structure, the rigid sandwich structure in [Cu(Me-OP)(PPh₃)₂]BF₄ is expected to be destroyed, leading to the absence of luminescence enhancement.

The emission spectrum of $[Cu(Me-OP)(PPh_3)_2]BF_4/PVP$ film (10 wt.%) is presented in Fig. 4. It can be seen that the emission of $[Cu(Me-OP)(PPh_3)_2]BF_4/PVP$ film (534 nm) red-shifts by 18 nm compared with that of $[Cu(Me-OP)(PPh_3)_2]BF_4$ crystal, along with the sharply decreased emission intensity. Correspondingly, the luminescence decay lifetime of $[Cu(Me-OP)(PPh_3)_2]BF_4/PVP$ film

(3.48 μ s) is nearly twenty times shorter than that of [Cu(Me-OP)(PPh_3)_2]BF_4 crystal. For comparison, we also disperse [Cu(OP)(PPh_3)_2]BF_4 crystal into PVP film and its omission space

 $[Cu(OP)(PPh_3)_2]BF_4$ crystal into PVP film, and its emission spectrum is also shown in Fig. 4. The $[Cu(OP)(PPh_3)_2]BF_4/PVP$ film exhibits a blue shifted emission peaking at 533 nm compared with $[Cu(OP)(PPh_3)_2]BF_4$ crystal with a luminescence decay lifetime of 3.27 µs. This slightly enhanced luminescence should be caused by the rigid surrounding environment of PVP [15,16].

The photophysical properties comparison between pure and dispersed samples indicates that the absence of inter-molecular π - π stacking breaks down the rigid sandwich structure, and consequently causes the obvious red-shifted emission, reduced emission intensity, together with the greatly shortened excited state lifetime, which can be served as a powerful evidence for our hypothesis demonstrated above.

4. Conclusion

In this paper, we report four phosphorescent Cu(I) complexes with oxadiazole-derived diimine ligands and phosphorous ligands, including their syntheses, crystal structures, photophysical properties, and their electronic nature. The Cu(I) center has a distorted tetrahedral geometry within the Cu(I) complexes. Theoretical calculation reveals that all emissions originate from ³MLCT excited state. It is found that the inter-molecular sandwich structure triggered by inter- and intra-molecular π -stacking within solid state Cu(I) complexes is highly effective on restricting the geometric relaxation that occurs in excited states, and thus greatly enhances the PL performances, including PL quantum yield improvement, PL decay lifetime increase, and emission blue shift. This finding may be useful when designing high-performance phosphorescent Cu(I) complexes.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [No. 90202034] and Youth Foundation of China University of Mining and Technology (2007A051).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.04.041.

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