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Synthesis, photophysical properties and DFT studies of the pyridineimidazole (PyIm) Cu(I) complexes: Impact of the pyridine ring functionalized by different substituents



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ABSTRACT

A series of the pyridine-imidazole (PyIm) Cu(I) complexes with different substituents (bromide (P1), methyl (P2), and phenyl (P3)) attached on the pyridine ring are synthesized and characterized. All the complexes show the typical metal-to-ligand charge transfer (MLCT) absorption in the visible region. Complex P1 with an electron-withdrawing substituent on the pyridine ring, e.g., a bromine group, shows a red shift of the emission wavelength. Conversely, an electron-donating substituent on the pyridine ring in complex P2, e.g., a methyl group, shifts the emission to longer wavelength. Similarly, complex P3 containing the extended π -conjugation system of the ligand also exhibits a red shift of the emission wavelength. All of the complexes exhibit efficient green-yellow emission in PMMA films at room temperature with emission wavelength of 547-569 nm and quantum yields of 24.8-53.0%. Meanwhile, DFT and TDDFT methods were employed to explain the photophysical properties.

1. Introduction

Copper(I) complexes have drawn special attention due to their structural diversities and rich photophysical properties as well as promising applications in numerous areas such as catalysis, organic lightemitting devices (OLEDs), dye-sensitized solar cells (DSSCs) [1-7]. The combination of electron rich metal centers, conjugated organic ligands and high degree of inherent covalence in soft acid-base bonding can produce low energy electronic interactions between the metal center and the ligands and the resulting compound possesses interesting optical and electronic properties. However, the traditional tetrahedral copper(I) complexes display weak emission, low quantum yields and short excited state lifetimes because of the excited-state distortion, which accelerates nonradiative decay of the emissive excited state [8-10]. To improve the photophysical properterties of the Cu(I) complexes, the heteroleptic [Cu(N^N)(P^P)] + complexes, where N^N denotes diimine ligands and P^P represents diphosphine ligands, have been designed and synthesized with rich luminescence properties [11-14].

Among the various N^N ligand systems, the imidazole ligand and its derivatives have been frequently employed in the syntheses of the luminescence Cu(I) complexes due to the electron-rich nature of the fivemembered imidazole ring and the facile N-alkylation of the NH group of the imidazole ring [15-19]. It is demonstrated that the imidazole ligands with different functional groups have great effects on the photophysical properties of Cu(I) complexes. Recently, Wang and coworkers reported a series of the emissive Cu(I) complexes bearing the quinolyl-benzimidazole ligands, exhibiting bright yellow-orange luminescence in the solid states with quantum yields in the range of 0.12-0.16 and emission lifetimes in the range of 16-54 µs [20]. Notably, by employing the pyridine-imidazole (PyIm) as diimine ligand, adachi and co-workers synthesized a green-emitting Cu(I) complex displaying improved luminescence properties with 25% quantum yield and lifetime of 15.5 µs in the solid state [21]. Most recently, our group has prepared a series of the PyIm-based Cu(I) complexes, showing tunable optical and electronic properties modulated by different organic chromophore groups [22].

Excellent photophysical properties possessed with these imidazolebased Cu(I) complexes encouraged us to explore the luminescent properties of analogous Cu(I) complexes of this type. As an extension of our works, we report herein the synthesis and characterization of a few PyIm-based Cu(I) complexes with different substituents such as bromide, methyl, and phenyl groups attached onto the position A in the pyridine ring of the PyIm ligand (see Fig. 1). The photophysical

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Fig. 1. Structures of the Cu(I) complexes in this study.

properties of the resulting complexes were systematically investigated both experimentally and theoretically. We believed that these findings are useful for the development of highly efficient luminescent materials of the PyIm-based Cu(I) complexes.

2. Experimental section

2.1. Materials and method

All reagents were obtained from commercial sources, unless otherwise stated. Complex P0 was prepared according to our previous report [22]. NMR spectra were recorded on a Bruker AV400 MHz spectrometer. UV-vis absorption spectra were measured with a Perkin Elmer Lambda-900 spectrophotometer. Elemental analyses of the complexes were carried out on an Elementar VarioEL cube analyzer. Fluorescence spectra were determined with a Hitachi F-4600 fluorescence spectrophotometer. Photoluminescence (PL) quantum yields were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C11347). Fluorescent lifetimes were measured with a compact fluorescent lifetime spectrometer (Hamamatsu, C11367, Japan).

2.2. Synthetic procedure

2.2.1. 5-bromo-2-(1H-imidazol-2-yl)pyridine(L1)

Anhydrous ethanol (25 mL), glyoxal solution (5 mL) were stirred in an ice bath, Then, 5-bromopicolinaldehyde (0.76 g, 4.12 mmol) and concentrated ammonia were added to the mixed solution under nitrogen for 1 h. The mixed solution was cooled to room temperature and allowed to stand for 12 h, extracted with dichloromethane and washed by water until neutral, and evaporated under reduced pressure to remove the solvent. The product was isolated using silica gel column chromatography with EtOAc as the solvent. Recrystallization of the residue from EtOH afforded a brown compound. Yield: 81%. ¹H NMR (400 MHz, DMSO) δ 13.02 (s, 1H), 8.54 (d, *J* = 5.3 Hz, 1H), 8.24 (s, 1H), 7.78–7.63 (m, 1H), 7.26 (s, 2H).

2.2.2. 2-(1H-imidazol-2-yl)-5-methylpyridine(L2)

This compound was prepared via a similar procedure for L0 from 5methylpicolinaldehyde (0.81 g, 5.08 mmol), and glyoxal solution (5 mL). The product was obtained as white solid. Yield: 68%.¹H NMR (400 MHz, DMSO) δ 12.73 (s, 1H), 8.45 (s, 1H), 7.94 (s, 1H), 7.71 (s, 1H), 7.13 (d, J = 60.4 Hz, 2H), 2.36 (s, 3H).

2.2.3. 5-phenylpicolinaldehyde (L3')

5-bromopicolinaldehyde (0.87 g, 4.66 mmol), Pd(PPh₃)₄ (0.65 g, 0.59 mmol) were added to a 20 mL/20 mL anhydrous toluene/THF solution. Then, anhydrous ethanol 10 mL and 2 M K₂CO₃ solution (15 mL) dissolved in H₂O were added to the reaction mixture at 50 °C. Phenylboronic acid (0.68 g, 5.6 mmol) was added after half an hour and the mixture was refluxed for 8 h under nitrogen. After the reaction had finished, the mixture was filtered. The product was isolated using silica gel column chromatography with PE and EtOAc (5:1) as the solvent. The solvent was removed by evaporation. Recrystallization of the residue from EtOH afforded a beige compound. Yield:76%. ¹H NMR (400 MHz, DMSO) δ 10.05 (s, 1H), 9.17 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.54 (dt, *J* = 22.9, 6.8 Hz, 3H).

2.2.4. 2-(1H-imidazol-2-yl)-5-phenylpyridine (L3)

Anhydrous ethanol (25 mL), Glyoxal solution (5 mL) were stirred in an ice bath, Then, **L3'** (0.94 g, 5.15 mmol) and concentrated ammonia were added to the mixed solution under nitrogen for 1 h. The mixed solution was cooled to room temperature and allowed to stand for 12 h, extracted with dichloromethane and washed by water until neutral, and evaporated under reduced pressure to remove the solvent. The product was isolated using silica gel column chromatography with EtOAc as the solvent. Recrystallization of the residue from EtOH afforded a brown compound. Yield: 56%. ¹H NMR (400 MHz, DMSO) δ 12.87 (s, 1H), 8.91 (s, 1H), 8.19 (dd, J = 8.2, 2.2 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.22 (s, 2H).

2.2.5. General procedure for preparation of Im-Py-Cu(I) complexes

Cu(I) complexes were synthesized by the following route: [Cu $(CH_3CN)_4$](PF₆) (0.124 g, 0.4 mmol) and bis(2-(diphenylphosphanyl) phenyl ether (POP) (0.216 g, 0.4 mmol) reacted in dichloromethane (15 mL) at 25 °C for 2 h. Then, the corresponding ligand (0.4 mmol) was dissolved in the degassed dichloromethane solution and injected into the mixed solution for 2 h. The resulting mixture was filtered through a



Scheme 1. The synthetic pathways of the PyIm derivatives and the corresponding Cu(I) complexes.

plug of Celite and concentrated to ca. 1 mL. Addition of Et_2O (10 mL) to the filtrate afforded a pale yellow precipitate, which was collected and washed with Et_2O . And the product was recrystallized with ethanol.

P1. The product was a yellow powder. Yield: 82%. ¹H NMR (400 MHz, DMSO) δ 13.76 (s, 1H), 8.43 (s, 1H), 7.95 (s, 1H), 7.62 (d, J = 5.6 Hz, 2H), 7.38 (s, 8H), 7.29 (s, 11H), 7.15–7.02 (m, 5H), 6.87 (s, 3H), 6.68 (s, 2H), ¹³C NMR (100 MHz, DMSO) δ 158.4, 150.1, 144.7, 141.8, 134.3, 134.1, 133.9, 133.4, 132.8, 131.7, 131.5, 131.4, 130.70 129.4, 125.7, 124.1, 124.0, 123.8, 121.9, 120.9. 31P NMR (162 MHz, DMSO) δ -13.36 (s), -144.50 (quint). Anal. Calcd. For C₄₄H₃₄CuBrF₆N₃OP₃ (971.12): C 54.42, H 3.53, N 4.33; found: C 54.61, H 3.12, N 4.53.

P2. The product was a pale yellow powder. Yield: 68%. ¹H NMR (400 MHz, DMSO) δ 13.48(s, 1H), 8.05 (s, 1H), 7.88 (s, 2H), 7.51 (s, 2H), 7.41(s, 1H), 7.38 (d, J = 8.3 Hz, 6H), 7.28 (s, 10H), 7.15 (s, 3H) 7.07 (t, J = 7.4 Hz, 3H), 6.87 (s, 3H), 6.66 (s, 2H), 2.07 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 162.2, 157.8, 149.1, 138.9, 133.6, 132.9, 131.9, 131.3, 131.2, 130.9, 129.9, 128.6, 124.9, 123.7, 123.6, 123.4, 120.9, 120.2, 119.3, 17.6. ³¹P NMR (162 MHz, DMSO) δ -13.64 (s), -144.49 (quint). Anal. Calcd. For C₄₅H₃₇CuF₆N₃OP₃ (906.25): C 59.64, H 4.12, N 4.64; found: C 59.41, H 4.02, N 4.54.

P3. The product was a pale yellow powder. Yield: 51%. ¹H NMR (400 MHz, DMSO) δ 13.78 (s, 1H), 8.36 (d, J = 23.6 Hz, 1H), 8.27 (s, 1H), 8.18 (s, 1H), 7.60 (s, 2H), 7.40 (d, J = 27.1 Hz, 19H), 7.16 (s, 6H), 7.07 (d, J = 6.7 Hz, 3H), 6.81 (s, 3H), 6.66 (s, 2H). ¹³C NMR (100 MHz, DMSO) δ 157.2, 145.7, 145.2, 135.0, 134.4, 132.8, 132.0, 131.4–130.8, 130.0, 129.2, 128.9, 128.7, 126.3, 125.0, 124.3–123.3, 120.4, 119.9–119.7. ³¹P NMR (162 MHz, DMSO) δ -13.42 (s), -144.50 (quint). Anal. Calcd. For C₅₀H₃₉CuF₆N₃OP₃ (968.32): C 62.02, H 4.06, N 4.34; found: C 61.84, H 4.02, N 4.54.

2.3. DFT calculations

The B3LYP exchange-correlation function [23,24] was used to optimize the ground state geometries of all the complexes using the polarized continuum model (PCM) [25] in CH_2Cl_2 media under the Gaussian 09 [26] program package. The 6-31G* basis set [27,28] was used for the C, H, N, O, and P atoms. The LANL2DZ basis set [29] was adopted for the Cu and Br atoms. On the basis of the optimized ground geometries, TDDFT method [30,31] associated with PCM in CH_2Cl_2 media were used to simulate the absorption spectra of the complexes studied. The first 200 singlet vertical excitations were obtained using the TDDFT/B3LYP method to construct the calculated absorption spectra. The calculated emission energies of all the complexes were obtained by the TDDFT method with the M06-2X functional [32] at B3LYP optimized ground state geometry. The calculated electronic density plots for the frontier molecular orbitals were prepared using Multiwfn analyzer soft [33] and VMD program [34].

3. Results and discussion

3.1. Synthesis

The synthetic pathways of the ligands and the corresponding Cu(I) complexes are outlined in Scheme 1. The ligands LO–L2 were readily synthesized from commercially available starting materials according to the literature procedure [35]. L3 was prepared in two steps involving the Suzuki coupling reaction [36] of phenylboronic acid with 5-bromopicolinaldehyde, followed by the cyclocondensation reaction of 5-phenylpicolinaldehyde (L3'), oxalaldehyde, and aqueous NH₃ in ethanol. The corresponding Cu(I) complexes were prepared by reacting [Cu(CH₃CN)₄]PF₆ with the corresponding ligands at the rate of 1:1. These Cu(I) complexes were confirmed with H NMR, C NMR, and elemental analysis.

3.2. Photophysical properties

Fig. 2 shows the UV–Vis spectra of **P0–P3** in CH₂Cl₂ solution at room temperature. The corresponding absorbance data are presented in Table 1. All the Cu(I) complexes display intense absorption bands in the region of 250–340 nm, which are assigned to spin-allowed $\pi - \pi^*$ ligand centered (LC) transitions of the diimine and POP ligands. On the other hand, the lower energy bands at the range of 350–425 nm result from spin-allowed metal Cu to ligand charge transfer (MLCT) for all the complexes. It is notable that the MLCT band for **P1** bearing an electron-



Fig. 2. Absorption spectra in dichloromethane ($C = 1 \times 10^{-5}$ mol/L) at 298 K of complexes **P0–P3**.

 Table 1

 Photophysical properties of complexes P0–P3

| notophysical properties of complexes 1 0 10. | | | | | | | | |
|--|---|----------------------------|----------|-----------|-----------------------------|------------------------------|--|--|
| | Absorption | Emission | Emission | | | | | |
| | $\lambda_{abs}\!/nm~(\epsilon\times 10^4M^{-1}cm^{-1})$ | λ_{em} (nm)/E (eV) | τ/μs | $\Phi/\%$ | $k_{\rm r}/10^4{ m s}^{-1}$ | $k_{\rm nr}/10^4{ m s}^{-1}$ | | |
| P0 | 260 (2.5), 291 (2.2), 375 (0.23) | 550/2.25 | 13.9 | 50.4 | 3.63 | 3.57 | | |
| P1 | 271 (3.0), 305 (2.1), 375 (0.35) | 559/2.22 | 13.7 | 46.3 | 3.38 | 3.92 | | |
| P2 | 261 (2.2), 298 (1.8), 375 (0.20) | 547/2.27 | 26.4 | 53.0 | 2.01 | 1.78 | | |
| Р3 | 274 (3.0), 317 (2.3), 375 (0.43) | 569/2.18 | 23.5 | 24.8 | 1.05 | 3.20 | | |
| | | | | | | | | |



Fig. 3. Normalized emission spectra of complexes PO–P3 in PMMA films (10 wt %).



Fig. 4. The energy levels and atomic orbital compositions calculated for the HOMO and LUMO of complexes **P0–P3**.

withdrawing Br substituent is red-shifted compared to that of the parent **P0**. In contrast, the MLCT band for **P2** with an electron-donating methyl substituent is observed at the blue-shifted region. Additionally, a red shift of the MLCT band for **P3** with the extended π -conjugation between the phenyl ring and pyridine-imidazole ligand can be observed compared to that of the parent **P0**. These results indicate that increasing the electron-withdrawing character or extension of the conjugation on the pyridine ring will reduce the energy gap of the complexes, while

introduction of electron-donating substituents will increase the energy gap of the complexes, which agrees with the theoretical results (see below, in Section 3.3, P0:3.96 eV; P1:3.79 eV; P2:4.02 eV; P3:3.83 eV). In addition, complexes P1 and P3 exhibit the enhanced light absorption abilities ($\epsilon_{(375 \text{ nm})} = 3460$ and $4320 \text{ M}^{-1} \text{ cm}^{-1}$, respectively) compared with those of P0 and P2 ($\epsilon_{(375 \text{ nm})} = 2340$ and $2060 \text{ M}^{-1} \text{ cm}^{-1}$, respectively).

The emission spectra of all the complexes in PMMA film (10 wt%) at room temperature are shown in Fig. 3, exhibiting the emission maxima in the green-yellow region at 550, 559, 547, and 569 nm, respectively. The shapes of the emission spectra are broad and unstructured, indicating the excited state is assigned as the triplet charge transfer character (³CT) in nature. It is clearly seen that the emissive wavelengths can be modulated by an introduction of different substituents on the pyridine ring. For P1, a H atom is replaced with the electronwithdrawing bromide substituent, which resulted in a red shift of the emission maximum of 9 nm in comparison with P0. In contrast, the emission is blue-shifted by 3 nm in P2 where an electron-donating methyl group is attached. Additionally, the emission maximum of P3 is more red-shifted by 19 nm compare to that of P0 due to the efficient π extension caused by the addition of phenyl group in the ligand. The blue or red shift observed in the emission spectra could be explained by the change of the energy level of the lowest unoccupied molecular orbitals (LUMO) of the complex. The addition of donor groups such as methyl group on the pyridine ring destabilizes the LUMO of the complex and ultimately increases the energy gap of the complex, leading to a blue shift of emission. Conversely, the addition of acceptor groups such as bromide group or the extension of π -conjugation on the pyridine ring stabilizes the LUMO of the complex and consequently decreases the energy gap of the complex, thus shifting the emission to longer wavelengths. These results are in good agreement with the theoretical calculations (see below in Section 3.3)

The emission lifetimes (τ) and quantum yields (Φ) of **P0-P3** in PMMA films (10 wt%) are also measured and the corresponding data are provided in Table 1. the τ values of all the complexes are in range of 13.7-26.4 µs, indicating that the emissive behavior is originated from the triplet excited state. The reference complex P0 has a higher quantum yield ($\Phi = 50.4\%$). **P1** with lower emission energy displays slightly lower quantum yield ($\Phi = 46.3\%$), whereas P2 with higher emission energy shows higher quantum yield ($\Phi = 53.0\%$), compared to that of **PO**. This is consistent with the energy gap law [37], i.e., a decrease in emission quantum efficiency with decreasing emission energy. Furthermore, the increase in the nonradiative rate constants (k_{nr}) (see Table 1) across P2 to P0 to P1 supports the present observations. It is worth noting that **P1** and **P3** have similar $k_{\rm nr}$ values (3.92 \times 10⁴ and $3.20 \times 10^4 \text{s}^{-1}$ respectively) but the Φ value of **P3** (Φ = 24.8%) is nearly two times lower than that of P1, which is not enough to be rationalized via the energy gap law alone. The additional decrease in Φ presumably results from the intermolecular π - π stacking interactions, as can be inferred from the extended π -conjugation system in P3

3.3. Theoretical calculations

To provide further insight on the structural and optical properties of the investigated Cu(I) complexes, DFT/TDDFT calculations were



Fig. 5. Comparison of the calculated (red line) and experimental (black line) absorption spectra in CH_2Cl_2 solution for **P0** (a), **P1** (b), **P2** (c), and **P3** (d). Red vertical lines correspond to oscillator strength of calculated singlet-singlet transitions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

performed for these Cu(I) complexes. The energy levels, atomic orbital compositions, and energy gaps of the HOMO and LUMO of the complexes in the optimized ground singlet geometries are shown Fig. 4. The highest occupied molecular orbital (HOMO) of PO-P3 is mainly localized on both the Cu d orbitals (37.2–38.5%) and the π orbitals (57.9-59.4%) on the phenyl ring of POP ligand, while the LUMO is located on the π^* orbitals (82.7–93.1%) of pyridine-imidazole ligand. Therefore, the introduction of substituents onto the pyridine ring would have a significantly influence on the LUMO level. For P1, the LUMO is stabilized by 0.22 eV with respect to the reference complex P0 due to the electron-withdrawing effect of the Br group, while the LUMO of P2 is slightly destabilized by 0.06 eV due to the electron-donating effect of the methyl group. For P3, the electron density of LUMO is delocalized over the whole ligand framework constituted by the pyridyl, carbene and phenyl segments. Thus, the LUMO is stabilized by 0.14 eV compared with that of PO. As expected, the HOMO energies for all the complexes remain almost unaltered. The HOMO-LUMO energy gap increases in the order P2 (4.02 eV) > P0 (3.96 eV) > P3(3.83 eV) > P1 (3.79 eV). This trend is in good agreement with the absorption onset in low energy region observed experimentally.

TDDFT method is employed to simulate the absorption spectra of all the complexes using PCM model. As shown in Fig. 5, one can see that the calculated spectra are overall well reproduced the experimental spectra. For all the complexes, the calculated first singlet excited state (S_1) is mainly originated from the HOMO \rightarrow LUMO excitation with MLCT/LLCT character, and this transition is responsible for the lowest lying absorption band in the range 350-425 nm in experiment. The calculated absorption bands in the 250-320 nm range are much pronounced, which are composed of a mixture of several of the excitation transitions. For example, for P0, the mixed transitions of the S_6 and S_7 dominantly contribute to the calculated absorption bands centered at 293 nm with $(\pi \rightarrow \pi^*)$ /MLCT character (see Table 2), correlating well with the experimental shoulders centered at 291 nm. The highest energy absorption bands centered at 263 nm calculated mainly originate from the mixed transitions of the S₂₈ and S₃₁ with MLCT/LLCT/ ($\pi \rightarrow$ π^*) character, which are coincident with the absorption band of 260 nm observed experimentally. The detailed assignments of the transitions for the other complexes are provided in Table 2.

Since the nature of the lowest absorption bands for all the complexes has a ¹MLCT/¹LLCT character, we reasoned that the nature of the emitting state from the lowest lying triplet excited state would also have ³MLCT/³LLCT character. In order to investigate the origin of the emitting state for these complexes, the calculated emission energy is obtained using the TDDFT method. The B3LYP functional seems to underestimate the emission energy of the investigated Cu(I) complexes, while the M06-2X functional gives more satisfactory results (see Table 5S in the Supporting Information). Therefore, we have employed the M06-2X functional using 6-31G(d)/LANL2DZ level for further emission energy calculations. The calculated emission energy, wavelength, and transition nature are complied in Table 3, along with the experimental values. The involved molecular orbital compositions are provided in Table 5S (Supporting Information). As can be noticed, the calculated emission energies are in excellent agreement with the experimental values and decrease in the order P2 > P0 > P1 > P3 along with the same order of the experimental results. For all the complexes, the lowest energy emissions are mainly from the transitions of LUMO \rightarrow HOMO. For P0, from an analysis of the electron density distribution of HOMO and LUMO, the emitting state of PO can be assigned as ${}^{3}MLCT/{}^{3}LLCT$ character. The emitting states of P1 and P2

Table 2

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|--|

| | Excited state | Transition | Coeff | E(eV)/(nm) | Oscillator | Assign | Exptl/nm |
|----|-----------------------|---|-----------------|------------|------------|---|----------|
| PO | S ₁ | $H \rightarrow L$ (188–189) | 0.69998(98.0%) | 3.32/374 | 0.0752 | $MLCT_{(Cu \rightarrow PyIm)}/LLCT_{(POP \rightarrow PyIm)}$ | 370 |
| | S ₆ | $H \rightarrow L + 3$ | 0.47974(46.0%) | 4.16/298 | 0.1299 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 291 |
| | | $H-3 \rightarrow L$ | -0.46027(42.4%) | | | $(\pi \rightarrow *\pi)_{(PyIm)}$ | |
| | S ₇ | $H \rightarrow L + 3$ | 0.49661(49.3%) | 4.17/298 | 0.1451 | $(\pi \rightarrow *\pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 291 |
| | | $H-3 \rightarrow L$ | -0.46027(42.4%) | | | $(\pi \rightarrow *\pi)_{(PyIm)}$ | |
| | S ₂₈ | $H-2 \rightarrow L + 4$ | 0.47326(44.8%) | 4.76/260 | 0.0756 | $MLCT_{(Cu \rightarrow POP)}/LLCT_{(PyIm \rightarrow POP)}$ | 260 |
| | | $H-3 \rightarrow L + 1$ | 0.43145(37.2%) | | | $(\pi \rightarrow *\pi)_{(PyIm)}$ | |
| | S ₃₁ | $H-2 \rightarrow L + 4$ | 0.35091(24.6%) | 4.78/259 | 0.0386 | $MLCT_{(Cu \rightarrow POP)}/LLCT_{(PyIm \rightarrow POP)}$ | 260 |
| | | $H-3 \rightarrow L + 1$ | -0.34494(23.8%) | | | $(\pi \rightarrow \pi)_{(PyIm)}$ | |
| | | $H-10 \rightarrow L$ | -0.25967(13.5%) | | | $MLCT_{(Cu \rightarrow POP)}/LLCT_{(POP \rightarrow PyIm)}$ | |
| P1 | S_1 | $\mathrm{H} \rightarrow \mathrm{L} \; (191192)$ | 0.70189(98.5%) | 3.14/395 | 0.0747 | $MLCT_{(Cu \rightarrow PyIm)}/LLCT_{(POP \rightarrow PyIm)}$ | 380 |
| | S ₅ | $H-3 \rightarrow L$ | 0.65028(84.6%) | 3.96/331 | 0.2281 | $(\pi \rightarrow *\pi)_{(PyIm)}$ | 305 |
| | S ₆ | $H \rightarrow L + 2$ | 0.67343(90.7%) | 4.00/310 | 0.0476 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow PyIm)}$ | 305 |
| | S ₈ | $H \rightarrow L + 3$ | 0.67711(91.7%) | 4.10/303 | 0.0936 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow PyIm)}$ | 305 |
| | S ₁₈ | $H-3 \rightarrow L + 1$ | 0.44244(39.2%) | 4.49/276 | 0.2100 | LLCT _(PyIm→POP) | 271 |
| | | $H \rightarrow L + 6$ | -0.38064(29.0%) | | | $MLCT_{(Cu \rightarrow Br)}/LLCT_{(POP \rightarrow PyIm)}$ | |
| | S ₂₃ | $H \rightarrow L + 8$ | 0.60143(72.3%) | 4.55/273 | 0.0781 | $(\pi \rightarrow *\pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 271 |
| P2 | S_1 | $H \rightarrow L$ (192–193) | 0.70113(97.4%) | 3.34/371 | 0.0787 | $MLCT_{(Cu \rightarrow PyIm)}/LLCT_{(POP \rightarrow PyIm)}$ | 360 |
| | S ₆ | $H \rightarrow L + 3$ | 0.63880(81.6%) | 4.07/304 | 0.0910 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 298 |
| | S ₇ | $H-3 \rightarrow L$ | 0.59681(71.2%) | 4.11/302 | 0.2050 | $(\pi \rightarrow *\pi)_{(PyIm)}$ | 298 |
| | S ₈ | $H \rightarrow L + 4$ | 0.69391(96.3%) | 4.17/298 | 0.0666 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 298 |
| | S ₉ | $H \rightarrow L + 5$ | 0.68682(94.3%) | 4.24/292 | 0.0923 | $(\pi \rightarrow \pi)_{(POP)}/MLCT_{(Cu \rightarrow POP)}$ | 298 |
| | S ₂₄ | $H-5 \rightarrow L$ | 0.47572(45.3%) | 4.67/265 | 0.0578 | $LLCT_{(POP \rightarrow PyIm)}$ | 261 |
| | | $H-3 \rightarrow L + 2$ | -0.28425(16.2%) | | | $(\pi \rightarrow \pi)_{(PyIm)}/LLCT_{(PyIm \rightarrow POP)}$ | |
| | | $H-11 \rightarrow L$ | -0.26250(13.8%) | | | $MLCT_{(Cu \rightarrow PyIm)}/LLCT_{(POP \rightarrow PyIm)}$ | |
| | S ₂₅ | $H-3 \rightarrow L + 2$ | 0.50053(50.1%) | 4.71/263 | 0.1140 | $(\pi \rightarrow \pi)_{(PyIm)}/LLCT_{(PyIm \rightarrow POP)}$ | 261 |
| | | $H-5 \rightarrow L$ | 0.23497(11.0%) | | | LLCT _(POP→PyIm) | |
| P3 | S_1 | $H \rightarrow L$ (208–209) | 0.70115(98.3%) | 3.23/383 | 0.0778 | MLCT _(Cu→PyIm) /LLCT _(POP→PyIm) | 375 |
| | S ₄ | $H-1 \rightarrow L$ | 0.56539(63.9%) | 3.85/322 | 0.5463 | LLCT _(Phenyl→PyIm) | 317 |
| | S ₁₅ | $H-1 \rightarrow L + 1$ | 0.40967(33.6%) | 4.43/280 | 0.1816 | $(\pi \rightarrow \pi)_{(PyIm)}/LLCT_{(Phenyl \rightarrow PyIm)}$ | 274 |
| | | $H-2 \rightarrow L + 1$ | -0.26447(14.0%) | | | MLCT _(Cu→PyIm) /LLCT _(POP→PyIm) | |
| | | $H-9 \rightarrow L$ | -0.23228(10.8%) | | | LLCT _(Phenyl→PyIm) /LLCT _(POP→PyIm)) | |

Table 3

Emission energies and transition natures of **P0–P3** calculated by TDDFT method using M062X/6-31G(d)/LANL2DZ level, as well as the experimental values.

| | $\lambda_{em}^{Calc}(nm)/E_{em}^{Calc}$ (eV) | Configuration | Assignment | $\lambda_{em}^{Expl}(nm)/E_{em}^{Expl}$ (eV) |
|----|---|----------------------------|--------------------------------------|---|
| P0 | 511/2.43 | $L \rightarrow H (81.1\%)$ | ³ MLCT/ ³ LLCT | 550/2.25 |
| P1 | 530/2.34 | $L \rightarrow H (82.1\%)$ | ³ MLCT/ ³ LLCT | 559/2.22 |
| P2 | 500/2.48 | $L \rightarrow H (80.7\%)$ | ³ MLCT/ ³ LLCT | 547/2.27 |
| P3 | 581/2.14 | $L \rightarrow H (92.5\%)$ | ³ LLCT | 569/2.18 |

have similar character to that calculated for **P0**, see Table 3. With respect to **P3**, the HOMO is localized on the PyIm moiety (73.7%) and the phenyl ring (30.9%) whereas the LUMO is also localized on the PyIm

moiety (82.2%) and the phenyl ring (15.1%), thus, the transition characters of the emission can be described as ³LLCT [$\pi^*(PyIm) \rightarrow \pi(Phenyl)$] character.

To support our assignments of the emitting state, a spin density analysis has been calculated and the corresponding spin density distributions are shown in Fig. 6. As shown in Fig. 6, the unpaired electron spin-density distributions in the lowest lying triplet excited state for **P0–P2** are similar (Cu, 0.54e; POP, 0.32e; PyIm, 1.15e for **P0**; Cu, 0.53e; POP, 0.33e; PyIm, 1.14e for **P1**; Cu, 0.54e; POP, 0.31e; PyIm, 1.14e for **P2**) and clearly demonstrate the higher contribution of the d (Cu) to the PyIm ligand with some contribution of POP ligand to the PyIm ligand, confirming the emission behavior of ³MLCT/³LLCT character. With respect to complex **P3**, the unpaired electrons in the emission state are localized on both PyIm ligand and the Phenyl ring (Cu,



Fig. 6. Spin density distribution contours (isovalue = 0.004) for the lowest triplet state T₁ of complexes **P0–P3**. The values of the unpaired-electron spin-density population are depicted together with the electronic nature of the states.

0.027e; POP, 0.007e; PyIm, 1.57e; Phenyl, 0.42e), indicating that the emitting state of P3 has a ³LLCT character originating from the Phenyl group to PyIm ligand.

4. Conclusion

In summary, the preparation, structural characterization, and photophysical properties, as well as theoretical investigation of a new class of the Cu(I) complexes based on the pyridine-imidazole as ligands are reported. All the complexes exhibit efficient green-yellow emission in PMMA films at room temperature with emission wavelength of 547-569 nm and quantum vields of 24.8-53.0%. The addition of substituents onto the pyridine moiety has a direct influence on the energy of the emitting states of the resulting Cu(I) complexes, thus leading to the blue or red shift observed in the emission wavelength. DFT and TDDFT studies reproduce well the experimental data and perfectly explained the photophysical properties.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https:// doi.org/10.1016/j.ica.2019.01.005.

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