Characterization of electronic structures and spectral properties of the emitting material molecule Cu(I) complexes containing fluorene moiety: a DFT/TDDFT study

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Abstract. Copper (I) complexes comprise an important class of luminescent materials in organic light emitting diodes (OLED). A Cu(I) complexes, [Cu(POP)(fluPy-Imidazole)]$^+$ (**1**), where fluPy-imidazole = 2-(4,5-dihydro-1H-imidazol-2-yl)-5-(9H-fluoren-2-yl)pyridine, POP= bis[2-diphenylphosphino]-phenyl]ether, was investigated using density functional theory (DFT) and time-dependent density functional theory (TDDFT). The optimized ground structures show that the fluorene ring is not coplanar with the imidazole ring. The HOMO is π character, while the LUMO is π^* orbitals of the Py-imidazole ligands. The lowest lying absorption band of the complexes has the HOMO-1 $\rightarrow$ LUMO transition configurations resulting in the MLCT/LLCT characters

Introduction

Copper(I) complexes have attracted considerable attention since the pioneering work of McMillin on the photoluminescence properties of copper diimine complexes in the 1970s [1]. Highly efficient electroluminescent Cu(I) complexes are required for the application of organic light-emitting diodes (OLEDs) in full-color display and solid-state lighting [2,3]. The emission colors of Cu(I) complexes can be tuned through the judicious choice of ligands. However, advances in the blue emission have not paralleled those for red and green emission [4,5]. Recently, Cu(I) complexes containing pyridine-imidazole ligands have been synthesized and exhibit excellent emissive properties, but, the emission wavelengths are still in the green region [6].
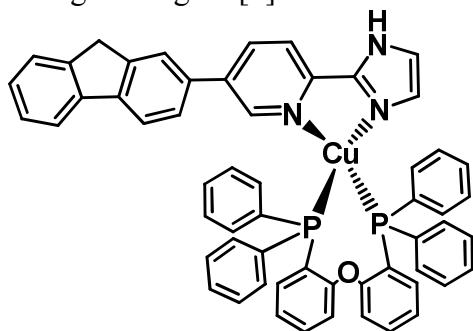

Fig.1 Molecular structure of the studied complex

In this paper, with the aim of further obtaining the blue emission, we report the theoretical studies of the designed Cu(I) complexes, [Cu(POP)(fluPy-Imidazole)]$^+$ (**1**), as shown in Chart 1, fluPy-imidazole = 2-(4,5-dihydro-1H-imidazol-2-yl)-5-(9H-fluoren-2-yl)pyridine, POP= bis[2-diphenylphosphino]-phenyl]ether. The fluorine unit is known to be the electron-rich moiety and should increase the LUMO energy of the corresponding Cu(I) complexes to shift the emission wavelength into the blue region. Electronic structures, and optical absorption spectra of the complexes studied were discussed in detail using density functional theory (DFT) and time-dependent density functional theory (TDDFT).

Computational method

The ground state geometry optimization of **1** was carried out using the B3LYP exchange-correlation functional [7]. A double-ξ quality LANL2DZ basis set [8] was employed for the Cu atom and a 6–31G* type basis set [9] for C, H, N, O, and P atoms. The TDDFT calculations for the simulated UV-vis absorption spectra of **1** were then performed based on the optimized geometries at ground state with the polarized continuum model (PCM) [10]. This functional has been proved to improve the accuracy of excitation energies in metal complexes.

Calculated electronic density plots for the frontier molecular orbitals were prepared using Gauss View 4.1.2 software. All calculations were performed with the Gaussian 09 software package [11].

Results and discussion

Ground state geometries

The optimized ground state geometries of the complexes **1** in the gas phase are presented in Fig. 1. Vibrational frequencies were calculated using the optimized geometries of **1** to verify that those geometries represented a minimum on the potential energy surface.
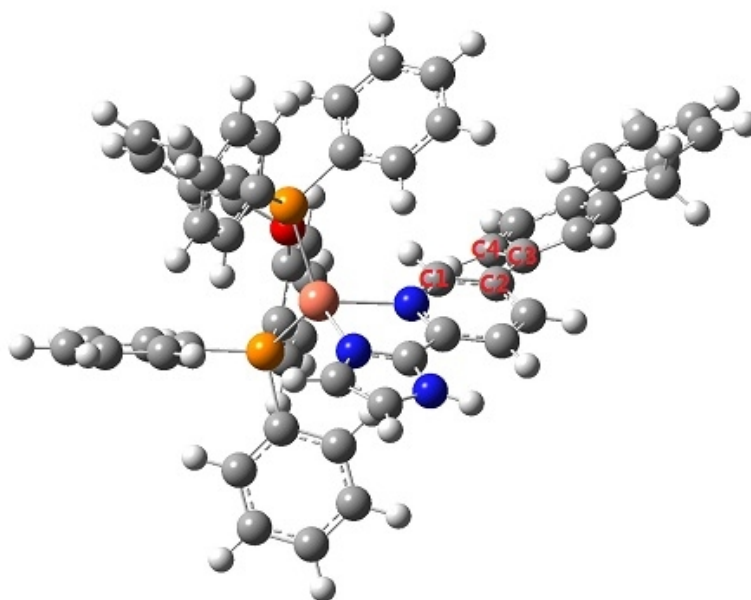

Fig.2 Optimized ground state geometries of **1** at B3LYP/6-31g*/LANL2DZ levels

Copper atom attains almost perfect tetrahedral coordination and bears the two P atoms of POP ligand, two nitrogen atoms of Py-imidazole ligand. The angle between N1Cu1N2 and P1Cu1P2 planes is 90.2°. Additionally, it can be seen that the imidazole ring is not coplanar with the fluorene ring. A 33.7° torsion angle was determined for the C1-C2-C3-C4 unit.

Molecular orbitals

The contributions of the different molecular fragments to the frontier occupied and virtual orbitals are listed in Table 2. The electron density of the HOMO for **1** is mainly based on Py-imidazole ring with some contribution from fluorine moiety. The HOMO-1 and HOMO-2 are the combination of d orbital of Cu and π orbital of POP ligand. The HOMO-3 is mainly composed of π(fluorene) (99.6%). The HOMO-4 is similar to that of the HOMO-1 and HOMO-2. The LUMO and LUMO+1 are mainly composed of π^*(Py-imidazole) with a few contribution of π^*(fluorene). The LUMO+2, LUMO+3, and LUMO+4 are almost exclusively located on π^* orbital of the POP ligand.

Table 1 Frontier molecular orbital compositions of **1** in CH_3CN at the B3LYP level

Orbital	Energy(eV)	Contribution (%)			
		Cu	POP	Py-imidazole	fluorene
LUMO+4	-0.99	0.78	96.8	1.18	1.28
LUMO+3	-1.16	1.44	97.1	1.27	0.17
LUMO+2	-1.28	1.37	95.2	2.68	0.71
LUMO+1	-1.42	5.68	5.23	69.7	19.4
LUMO	-2.19	1.32	2.69	75.9	20.1
HOMO	-5.94	22.6	32.4	14.9	30.0
HOMO-1	-6.00	21.8	35.2	11.5	31.5
HOMO-2	-6.43	51.2	39.7	8.76	0.32
HOMO-3	-6.51	69.0	8.34	22.3	0.60
HOMO-4	-6.73	6.79	27.8	49.0	16.4

Absorption spectra

The calculated absorption spectra are shown in Fig. 2. It is clearly seen that there are three absorption bands at 200-400 nm regions. The lowest lying distinguishable singlet $\rightarrow$ singlet absorption band at 368.4 nm was mainly assigned as pure HOMO-1 $\rightarrow$ LUMO transition. As mentioned above, the HOMO-1 is mainly d(Cu) orbitals, π(POP), and π(fluorene) in character, while LUMO is composed of Py-imidazole π^* orbitals. Therefore, electronic transitions for the lowest lying absorption band possess the metal-to-ligand charge transfer (MLCT)/ligand-to-ligand charge transfer (LLCT). The middle absorption band centered at 286 nm is composed of multiple combination transitions. The highest absorption band centered at 218 nm are composed of multiple combination transitions, originated from the starting orbitals of the HOMO-1/HOMO-6/HOMO-8/HOMO-10/HOMO-17 to the arriving orbitals of LUMO+3/LUMO+4/LUMO+10/LUMO+16 with MLCT/ILCT/LLCT transition characters.
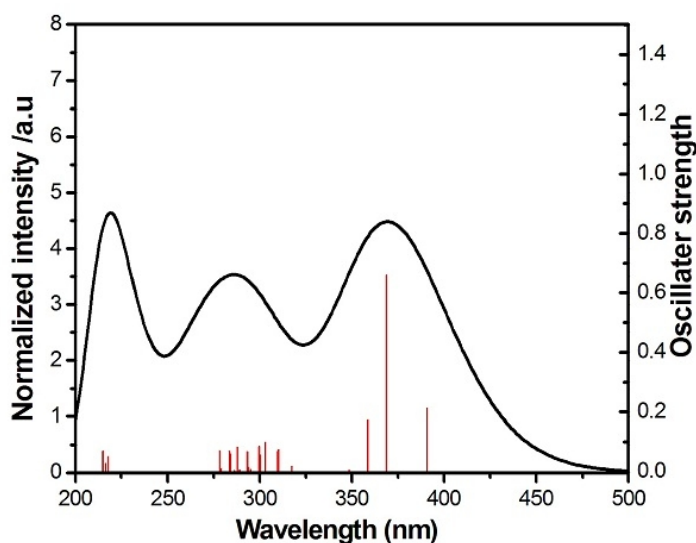

Fig.3 **S**imulated absorption spectra in CH_2Cl_2 at the TDDFT (B3LYP)/6–31g*/LANL2DZ level for **1**. The excited states are shown as vertical bars with height equal to the oscillator strength values (red).

Conclusions

1. A Cu(I) complexes, [Cu(POP)(fluPy-Imidazole)]$^+$, has been investigated using density functional theory (DFT) and time-dependent density functional theory (TDDFT).
2. The calculated results show that the HOMO is π (Py-imidazole) in nature, while the LUMO is mainly located on π* orbital of the Py-imidazole ligand.
3. The lowest lying absorption band of the complexes at 368.4 nm has the HOMO-1 → LUMO transition configurations resulting in the MLCT/LLCT characters.

Acknowledgements

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