

DFT/TDDFT studies of electronic structures and spectral properties of Cu(I) complexes containing pyridine-imidazole ligand tethered with fluorene moiety

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Keywords: Copper(I) complexes; Luminescent materials; Organic light emitting diodes; Blue light

Abstract. Copper (I) complexes have received significant attention because of their potential applications in a broad range of fields, including organic light emitting diodes (OLED), bioimages, sensors, and photocatalysis. A Cu(I) complexes, [Cu(POP){(Py-Imidazole)(CH₂)₂(2-Fluorene)}]⁺ (**1**), where Py-Imidazole(CH₂)₂(2-Fluorene) = 5-(2-(9H-fluorene-2-yl)ethyl)-2-(1H-imidazol-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 parallel to 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]. A number of different Cu(I) complexes are synthesized in the literature, and much has been learned about their photophysical properties[2-6]. However, the weak absorption in visible region and short-lived lifetimes of Cu(I) complexes prevent Cu(I)-based materials from actual application in the fields of OLED, sensors, and photocatalysis. A related method for improving the absorption in the visible region has focused on attaching strong light harvesting groups into Cu(I) complexes. Unfortunately for those Cu(I) complexes, the corresponding excited state lifetimes were relatively short[7-9]. It is difficult to develop these Cu(I) complexes with both strong absorption and long excited state lifetimes. In 1992, Ford and Rogers presented a strategy by the incorporation of organic chromophores to extend excited-state lifetimes of Ru(III) complexes from 0.8 to 11.2 μ s[10]. Following the same principle, through the addition of strong absorptive organic chromophores, it is possible to obtain Cu(I) complexes with strong absorption in the visible region while maintaining longer excited state lifetimes.

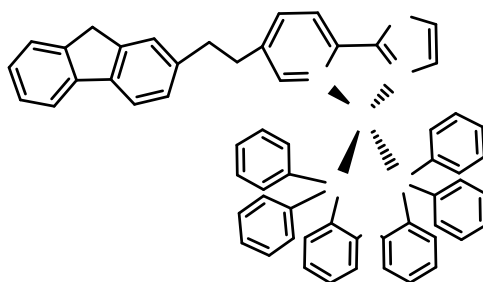


Chart.1 Molecular structure of the studied complex **1**

Herein, we report the theoretical studies of the designed Cu(I) complexes, [Cu(POP){(Py-Imidazole)(CH₂)₂(2-Fluorene)}]⁺ (**1**), as shown in Chart 1, where

Py-Imidazole)(CH₂)₂(2-Fluorene) = 5-(2-(9H-fluoren-2-yl)ethyl)-2-(1H-imidazol-2-yl) pyridine, POP= bis[2-diphenylphosphino]-phenyl]ether. The fluorine unit is known to be the electron-rich moiety and should increase absorption in visible region of the corresponding Cu(I) complexes. 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 [11] in the gas phase. A double- ξ quality LANL2DZ basis set [12] was employed for the Cu atom and a 6-31G* type basis set [13] 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) [14]. 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 [15].

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.

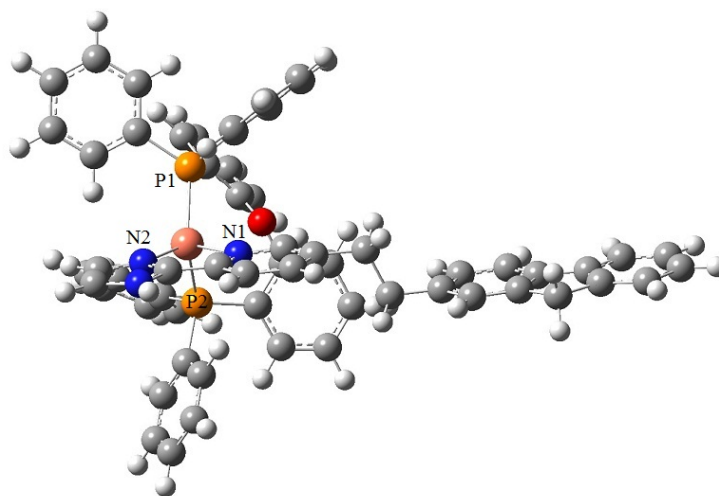


Fig.1 Optimized ground state geometries of **1** at B3LYP/6-31g*/LANL2DZ levels

Complex **1** exhibits the slightly distorted tetrahedral geometry and the angle between N1Cu1N2 and P1Cu1P2 planes is 88.3°. Additionally, it can be seen that the pyridine-imidazole ring is parallel to the fluorene ring.

Molecular orbitals

The contributions of the different molecular fragments to the frontier occupied and virtual orbitals are listed in Table 1. The electron density of the HOMO for **1** is mainly based on fluorene ring. 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 d(Cu) with some contribution from π (Py-imida). The HOMO-4 is π (Py-imida) character. The LUMO and LUMO+1 are mainly composed of π^* (Py-imidazole). 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 CH₃CN at the B3LYP level

Orbital	Energy(eV)	Main bond nature	Contribution (%)			
			Cu	POP	Py-imidazole	Fluorene
LUMO+6	-0.97	π^* (Flu)	0.25	0.51	4.09	88.5
LUMO+4	-1.08	π^* (POP)	0.86	97.6	0.71	0.24
LUMO+3	-1.16	π^* (POP)	1.35	95.6	1.99	0.17
LUMO+2	-1.26	π^* (POP)	1.39	88.9	7.96	0.89
LUMO+1	-1.32	π^* (Py-imida)	5.14	13.3	76.5	1.77
LUMO	-1.95	π^* (Py-imida)	2.46	3.73	88.0	1.43
HOMO	-5.93	π (Flu)	1.44	1.81	2.77	87.9
HOMO-1	-5.97	d(Cu)+ π (POP)	37.7	56.1	3.18	1.77
HOMO-2	-6.44	d(Cu)+ π (POP)	52.8	36.1	10.3	0.07
HOMO-3	-6.51	d(Cu)+ π (Py-imida)	68.7	7.45	21.0	0.05
HOMO-4	-6.58	π (Py-imida)	3.10	2.15	89.0	2.15

Absorption spectra

The calculated absorption spectra are shown in Fig. 2. It is clearly seen that there are four absorption bands at 250-400 nm regions. The lowest lying distinguishable absorption band at 368 nm was mainly assigned as HOMO-1 \rightarrow LUMO transition. As mentioned above, the HOMO-1 is mainly d(Cu) orbitals and π (POP) 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 absorption band centered at 341 nm was originated from the transition of HOMO [π (Flu)] \rightarrow LUMO [π^* (Py-imida)] with LLCT character. The 299 nm absorption band was mainly assigned as HOMO-4 [π (Py-imida)] \rightarrow LUMO [π^* (Py-imida)] transition with intraligand charge transfer (ILCT) character. The highest absorption band centered at 273 nm was originated from the HOMO [π (Flu)] \rightarrow LUMO+6 [π^* (Flu)] with ILCT transition character

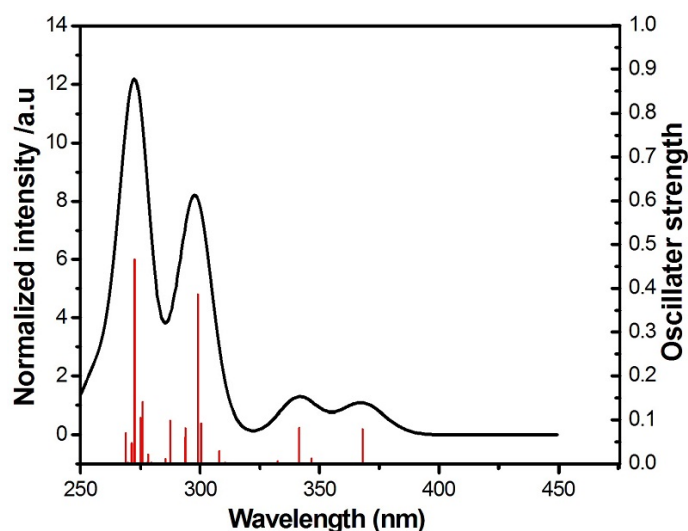


Fig.2 Simulated absorption spectra in CH₂Cl₂ at the TDDFT (B3LYP)/6-31g*/LANL2DZ level for **1**. The excited states are shown as vertical bars with height equal to the oscillator strength values (red).

Summary

A Cu(I) complexes, [Cu(POP){(Py-Imidazole)(CH₂)₂(2-Fluorene)}]⁺, has been investigated using density functional theory (DFT) and time-dependent density functional theory (TDDFT).

The calculated results show that the HOMO is π (Flu) in nature, while the LUMO is mainly located on π^* orbital of the Py-imidazole ligand.

The lowest lying absorption band of the complexes at 368 nm has the HOMO-1 \rightarrow LUMO transition configurations resulting in the MLCT/LLCT characters.

Acknowledgements

The authors acknowledge financial support by the National Natural Science Foundation of China (No.21443010). They thank the Guizhou University High Performance Computation Chemistry Laboratory (GHPCC) for help with computational studies.

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