ISBN: 978-1-948012-12-6

New Materials and Intelligent Manufacturing (NMIM)

DOI : <http://doi.org/10.26480/icnmim.01.2018.133.135>Journal Homepage: <https://topicsonchemeng.org.my/>

THEORETICAL STUDIES ON THE STRUCTURES AND SPECTROSCOPIC PROPERTIES OF IR COMPLEXES WITH THE BIPYRIDYL-PHENYLENEDIAMINE LIGAND

Jianpo Zhang, Ying Wang, Junbo Zang, Yuhe Miao, Yue Sun, Li Jin*

School of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Chengde Street 45#, Jilin, China.

*Corresponding Author Email: lijin@jlicet.edu.cn

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited

ARTICLE DETAILS

Article History:

Received 26 June 2018

Accepted 2 July 2018

Available online 1 August 2018

ABSTRACT

The phosphorescent iridium(III) complexes ($N^{\wedge}C$)₂Ir(bpy-D) (bpy-D = 4-(N-(2-amino-5-methoxyphenyl)aminomethyl)-4'-methyl-2,2'-bipyridine: $N^{\wedge}C$ = F-ppy(1), ppy(2), pq(3), ppe(4); F-ppy = 2-(2,4-difluorophenyl)pyridine, ppy = 2-phenylpyridine, pq = 2-phenylquinoline, ppe = 2-phenylcinchoninic acid methyl ester) were explored using density functional theory (DFT) methods. The optimized geometry structural parameters of the complexes in the ground state agree well with the corresponding experimental values. The lower-lying unoccupied molecular orbitals of complexes **1-4** are dominantly localized on the bidentate ligand, while the higher-lying occupied ones are also composed of bidentate ligand. The lowest energy absorptions at 513, 506, 526, and 569 nm are attributed to a $\pi\pi^*$ transition, while their phosphorescence emission at 551, 619, 642, and 659 nm have similar transition properties. This indicates that the phosphorescent color of lowest-energy emissions of these complexes could be tuned, could be altered by adjusting the π electron-donating ability of $N^{\wedge}C$ ligand.

KEYWORDS

Iridium (III) complexes, Spectroscopic properties, Electronic Structures, TD-DFT

1. INTRODUCTION

In the last few decades, phosphorescent transition-metal complexes have been widely applied in organic light emitting devices, solar energy conversion, luminescence sensing, biotechnology and electroluminescence displays, because of facilitate strong electroluminescence by harnessing both singlet and triplet excitons [1-3]. Among these transition metal complexes, Ir complexes are the most tunable and effective, a lot of Ir complexes such as ($C^{\wedge}N$)₂Ir(O⁺O) have been synthesized by a group researchers [4]. The present results indicate that these complexes exhibit high quantum efficiencies and long radiative lifetime, the lowest-energy absorptions are all assigned to the metal-to-ligand charge transfer transition, and the highest-lying absorption are dominantly assigned to a $\pi\pi^*$ excitation.

Recently, Lo and co-workers have prepared a series of ($N^{\wedge}C$)₂Ir(bpy-D) complexes, they found that these complexes show interesting photophysical behavior and modification of these complexes with an o-phenylenediamine unit will generate a new class of phosphorescent molecular probes for NO [5]. Although there have been many experimental studies on the photophysical and photochemical properties of these luminescent Ir(III) complexes, there are few corresponding theoretical reports on these complexes. Therefore, we performed theoretical calculations on (F-ppy)₂Ir(bpy-D)(1), (ppy)₂Ir(bpy-D)(2), (pq)₂Ir(bpy-D)(3), and (ppe)₂Ir(bpy-D)(4) in the ground- and excited states by DFT method.

2. COMPUTATIONAL DETAILS AND THEORY

The structures of iridium complexes **1-4** as shown in Figure 1. The geometry of the ground- and excited state structure is fully optimized by using the density functional theory (DFT) with the Perdew-Burke-Erzenrhof (PBE0) and unrestricted PBE0 functional, respectively [6]. With such calculations, the absorption and emission spectra are obtained by the

time dependent density functional theory (TD-DFT) associated with the polarized continuum model (PCM). This kind of theoretical approach has been proven to be reliable for transition metal complex systems such as [RuL₂(NCS)₂]⁺ complexes. In the calculations, quasirelativistic pseudopotentials of the Ir atom proposed by Hay and Wadt with 17 valence electron were employed, and the 6-31G basis set was adopted for other atoms. All of the calculations were accomplished by using Gauss09 software package on an Sugon A840-G10 server.

3. RESULTS AND DISCUSSION

3.1 The geometries of ground and excited states

For complex **1**, The calculated bond distances of Ir-N(bpy-D), Ir-N(F-ppy), and Ir-C are 2.181, 2.079, and 2.030 Å, the bond angles of N(bpy-D)-Ir-N(bpy-D) are 75.7°, the dihedral angle of N(bpy-D)-N(bpy-D)-Ir-N(F-ppy) is 86.1°, respectively. The three bidentate ligands planes are almost perpendicular to each other with the dihedral angles close to 90°. The analogous structures are also observed in **2-4**.

The geometry parameters of lowest-lying triplet excited state of **1-4**, which show similar tendency, have not vary notably relative compared with their ground state. Take **1** for example, the calculated Ir-N(bpy-D) bond lengths relax by 0.017 Å, but the Ir-N(F-ppy) and Ir-C bond lengths strengthen by 0.006 Å. This indicates that enhance the interaction between Ir atom and bpy-D ligand, and weak the interaction between Ir atom and $N^{\wedge}C$ ligand upon excitation.

Figure 1: The structures of iridium complexes 1-4

3.2 Absorptions spectra of 1-4 in the ground states

From Figure 2, the absorption spectra of **1-4** show three absorption bands, the most representative optical transitions and their oscillator strengths, the main configurations, their assignments are given in Table 1. A detail analysis of the frontier orbital compositions and energies of **1** and **4** is presented in Tables 2 and 3.

Table 1 show the lowest-lying absorptions of **1-4** at 513(2.41), 506(2.45), 526(2.35), and 569 nm (2.18 eV), respectively. With respect to **1**, the excitation of MOs 190→191 is dominantly responsible for the absorption band at 513 nm. Table 2 shows that MOs 190 and 191 are dominantly localized on bpy-D ligand (100% and 94.6%). Thus, the absorption at 513 nm for **1** can be assigned to a $\pi(\text{bpy-D}) \rightarrow \pi^*(\text{bpy-D})$ transition with ILCT transition characters. In the meantime, the transition path of the lowest-energy absorption of **2** is similar to that of **1**. But the absorptions of **3** and **4** at 526 and 569 nm has different character. The only difference is the contributes of the ligand composition from the N⁺C, thus the absorptions

of **3** and **4** can be described as originating from the $\pi(\text{bpy-D}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N})$ excited state with different LLCT character. By comparing the excitation energies of **1-4**, we found that the lowest-lying absorption is red-shifted from **1**~**2**<**3**<**4**, which is consistent with the increasing trend of the π -donating ability.

Figure 2: Gaussian curve simulated absorption spectra of 1-4 in CH₂Cl₂ media

Table 1: Absorptions spectra of 1-4 in CH₂Cl₂ media under TD-DFT calculations, together with experimental values

	Transition and Config	$\lambda_{\text{cal}}(\text{nm})$	Oscillator	Assignment	$\lambda_{\text{expt}}(\text{nm})^{[5]}$
1	190→191(0.70)	513 (2.41)	0.0100	ILCT	
	187→191(0.54)	362(3.42)	0.0690	MLCT/LLCT	366
	187→197(0.45)	260(4.77)	0.2972	MLCT/ILCT	267
2	174→175(0.52)	506(2.45)	0.0009	ILCT	
	171→175(0.62)	385(3.22)	0.1503	MLCT/LLCT	381
	169→179(0.52)	267(4.64)	0.2589	MLCT/ILCT	258
3	200→201(0.70)	526(2.35)	0.0002	LLCT	
	197→201(0.68)	391(3.17)	0.0564	MLCT/ILCT	
	197→206(0.45)	279(4.43)	0.1510	MLCT/LLCT	
4	230→231(0.51)	569(2.18)	0.0302	LLCT	
	225→231(0.66)	392(3.16)	0.1283	MLCT/ILCT	
	227→235(0.58)	292(4.24)	0.1360	MLCT/LLCT	

Table 2: Molecular orbital compositions in the ground state for 1 at the PBE0 level

Orbital	Energy(eV)	Composition (%)			main bond type
		Ir	bpy-D	F-ppy	
197	-1.356	3.4	2.9	93.7	$\pi^*(\text{F-ppy})$
192	-2.144	4.0	3.1	92.9	$\pi^*(\text{F-ppy})$
191	-2.717	3.1	94.6	2.3	$\pi^*(\text{bpy-D})$
HOMO-LUMO Energy Gap					
190	-5.321	0.0	100	0.0	$\pi(\text{bpy-D})$
189	-6.134	0.3	99.6	0.1	$\pi(\text{bpy-D})$
188	-6.214	48.6	3.9	47.5	$d(\text{Ir})+\pi(\text{F-ppy})$
187	-6.726	26.5	3.5	70.0	$d(\text{Ir})+\pi(\text{F-ppy})$

Table 3: Molecular orbital compositions in the ground state for **4** at the PBE0 level

Orbital	Energy(eV)	Composition (%)			main bond type
		Ir	bpy-D	pqe	
235	-1.600	0.4	38.4	61.2	$\pi^*(pqe)+\pi^*(bpy-D)$
232	-3.020	3.6	1.5	94.9	$\pi^*(pqe)$
231	-3.042	3.8	2.1	94.1	$\pi^*(pqe)$
HOMO-LUMO Energy Gap					
230	-5.352	0.0	99.9	0.1	$\pi(bpy-D)$
229	-5.865	47.7	3.4	48.9	$d(Ir)+\pi(pqe)$
228	-6.120	0.1	99.8	0.1	$\pi(bpy-D)$
227	-6.478	30.8	5.0	64.3	$d(Ir)+\pi(pqe)$
225	-6.769	31.9	5.6	62.6	$d(Ir)+\pi(pqe)$

Table 1 shows that the second absorption band of **1-4** are at 362(3.42), 385(3.22), 391(3.17), and 392 nm (3.16 eV), respectively. With respect to **1**, the excitation of MOs 187→191 with the configuration coefficient of 0.54 contributes to the absorption at 362 nm. Table 2 shows that MO 187 has 26.5% d(Ir), and 70.0% $\pi(F-ppy)$, while MO 191 has 94.6% $\pi^*(bpy-D)$ composition. Thus the absorption at 362 nm is mainly attribution to a $[d(Ir)+\pi(F-ppy)] \rightarrow [\pi^*(bpy-D)]$ transition with MLCT/LLCT character, while the absorption of **2** at 385 nm has similar transition character to that of **1** at 362 nm. But the absorptions of **3** and **4** at 391 and 392 nm has different character. The only difference is the contributes of the LUMO orbit from the N[^]C ligand, thus the absorptions of **3** and **4** can be described as originating from the $[d(Ir)+\pi(N^{\wedge}C)] \rightarrow [\pi^*(N^{\wedge}C)]$ excited state with different MLCT/ILCT character.

For the third absorption band, the most representative absorption of **1-4** are between 260-292 nm, which have the largest oscillator strength of 0.1~0.3. According to above analysis, these absorptions is attributed to the $[d(Ir)+\pi(N^{\wedge}C)] \rightarrow [\pi^*(N^{\wedge}C)]$ or $\pi^*(bpy-D)$ transition with MLCT/ILCT or LLCT characters. In comparison with those of **1**, the absorptions of **2-4** are red shifted to some extent. This is due to the strong π -conjugation effects in **2-4** compared to those of **1**.

3.3 Emission spectra of 1-4 in the excited states

The calculated phosphorescence values of four complexes are at 551(2.25), 619(2.00), 642(1.93), and 659 nm (1.88 eV) for **1-4**, respectively. The excitation of LUMO→HOMO-1 dominates the emissions of **1-4**. Upon the above discussion on the frontier molecular orbitals, these emission can be described as a $^3[\pi(N^{\wedge}N) \rightarrow \pi^*(C^{\wedge}N)]$ or $\pi^*(bpy-D)$ transition with $^3\pi\pi^*$ character, which are consistent with the low-energy absorptions in term of transition characters. The energy differences between the calculated low lying absorptions and corresponding phosphorescences are 0.16, 0.45, 0.42, and 0.30 eV for **1-4**, respectively, which is consistent with the little change between the ground- and excited-states structures.

4. CONCLUSIONS

In this paper, we investigated the geometry structures, absorptions, and phosphorescent properties of four Ir(III) bipyridyl-phenylenediamine complexes theoretically. Often, the phosphorescent excited state is relevant to both the metal and the ligands, and the frontier molecular orbitals of HOMO and LUMO are dominantly localized on the metal and

ligands, respectively. However, in this work, the HOMO are dominantly localized on N[^]N ligand (100%), while LUMO is contributed by $\pi^*(bpy-D)$ or $\pi^*(C^{\wedge}N)$ with the 94.1% composition, therefore, this kind of complex different from traditional transition metal complexes. By comparing the excitation energies of complexes **1-4**, we found that the lowest-energy emissions is red-shifted, which is consistent with the increasing trend of the π -donating ability. At last, we hope that these theoretical studies will assist in the design of highly efficient phosphorescent materials.

ACKNOWLEDGEMENTS

This work was financially supported by the foundation of state key laboratory of theoretical and computational chemistry (No. 20130023) and the national natural science foundation of china (No. 21405058).

REFERENCES

- [1] Xin, H., Li, F.Y., Shi, M., Bian, Z.Q., Huang, H, C. 2003. Efficient electroluminescence from a new terbium complex [J]. Journal of the American Chemical Society, 125, 7166-7167. doi: 10.1021/ja034087a*
- [2] Yeh, S.J., Wu, M.F., Chen, C.T., Song, Y.H., Chi, Y., Ho, M.H. 2005. New dopant and host materials for blue-light-emitting phosphorescent organic electroluminescent devices [J]. Advanced Materials, 17 (3), 285-289. doi:10.1002/adma.200401373*
- [3] Castellano, F.N., Lakowicz, J, R. 1998. A water-soluble luminescence oxygen sensor [J]. Photochemistry and Photobiology, 67, 179-183.
- [4] Lakowicz, J.R., Castellano, F.N., Dattelbaum, J.D., Tolosa, L., Rao, G., Gryczynski, I. 1998. Low-frequency modulation sensors using nanosecond fluorophores [J]. Analytical Chemistry, 70, 5115-5121.
- [5] Law, W.H., Leung, K.K., Lee, L.C. 2014. Cyclometalated iridium (III) bipyridyl-phenylenediamine complexes with multicolor phosphorescence: synthesis, electrochemistry, photophysics, and intracellular nitric oxide sensing [J]. Chemmedchem, 9 (6), 1316-1329. doi:10.1002/cmdc.201400040*
- [6] Adamo, C., Barone, V. 1999. Toward reliable density functional methods without adjustable parameters: the pbe0 model. Journal of Chemical Physics, 110, 6158-6170. doi: DOI: 10.1063/1.478522*