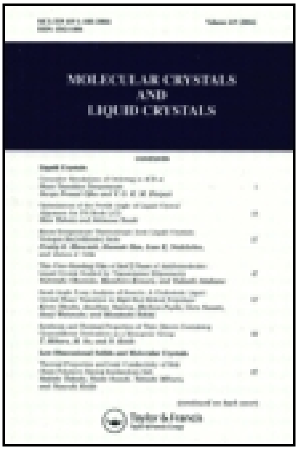

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Theoretical Study of Iridium Complex of New Pentafluorophenyl-Substituted Ligands

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Theoretical Study of Iridium Complex of New Pentafluorophenyl-Substituted Ligands

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In order to tune the emission to be pure red and increase the efficiency, new iridium complex, Ir(PF-piq)$_2$(acac), is designed and studied, where piq, PF-piq and acac represent phenylisoquinoline, 4-(perfluorophenyl)-1-phenylisoquinoline and acetylacetonate, respectively. The Hartree-Fock (HF) method with the 3-21G(d) basis set and density functional theory (DFT) utilizing the B3LYP functional with the 6-31G(d) basis set were used for the geometry optimization and the energy level calculation of the ground state of this complex, respectively. The excited triplet and singlet states are examined using the time-dependent density functional theory (TD-DFT). As a result, it is confirmed theoretically that the wavelength of new iridium complex were shifted toward the red region when introducing a pentafluorophenyl group. The efficiency and brightness of the complex are predicted to increase in comparison with those of Ir(piq)$_2$acac.

Keywords: DFT; Ir complex; OLED; pentafluorophenyl; phosphorescence; red

1. INTRODUCTION

Electroluminescent (EL) organic materials have received much of attention due to their potential application in flat-panel displays due to the rapid progress in material design and device fabrication in recent years. Red, green, and blue emissions of matching efficiencies are required for full-color displays [1–5]. Greater success has been achieved in the development of a green emitter than that of a red one in fluorescent and phosphorescent displays. Organic light-emitting

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diodes (OLEDs) based on phosphorescent materials can significantly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100%. Recently, Forrest, Thompson and coworkers have developed electrophosphorescent OLEDs with a high efficiency approaching 100% of the internal quantum efficiency, which utilize both singlet and triplet excitons produced at the emitting layer doped with the phosphorescent dopants [6,7]. A heavy metal such as Ir or Pt in their complex forms is known to induce intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states. The spin-forbidden nature of radiative relaxation from the triplet excited state has then been changed to allow, resulting in high phosphorescent efficiencies. Thus, Ir complexes are known to have high photoluminescence (PL) efficiency and a relatively short excited state lifetime which minimizes quenching of triplet emissive states [8,9].

Recently, it has been reported that $Ir(piq)_2(acac)$ with piq representing the 1-(phenyl)isoquinoline ligand showed a high external quantum efficiency of nearly 7% at $J = 400\,mA/cm^2$, whose EL emission band is at 620 nm [10]. Unlike that of other Ir(III) red phosphor complexes, markedly high efficiency could be maintained at high currents with a negligible effect from either the T-T annihilation or saturation of the excited state. However, because these complex emit an impure red emission wavelength, we have designed and characterized $Ir(PF\text{-}piq)_2acac$ as shown in Figure 1. By introducing a pentafluorophenyl substituent into the piq ligands of $Ir(piq)_2acac$, photoluminescence(PL) and electroluminescence (EL) spectra could be tuned to longer wavelength due to the electronic accepting nature of the substituent [11]. In order to design the highly efficient Ir(III) complex suitable for red OLED device, we explore the ground and low-lying excited states of Ir(III) complex containing PF-piq ligand and acetylacetonate (acac) as an assistant ligand using density functional approaches.

2. DETAILS OF CALCULATION

The ground and low-lying excited electronic states in the Ir(III) complexes were calculated using the Gaussian 98 package [12]. The 2-(phenyl)pyridine (ppy) ligand has been known as an excellent ligand for metal-to-ligand charge transfer (MLCT) transitions. In order to study the MLCT transition, the highest occupied molecular orbital (HOMO) energy level and the energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO) of the ppy ligand, piq, PF-py

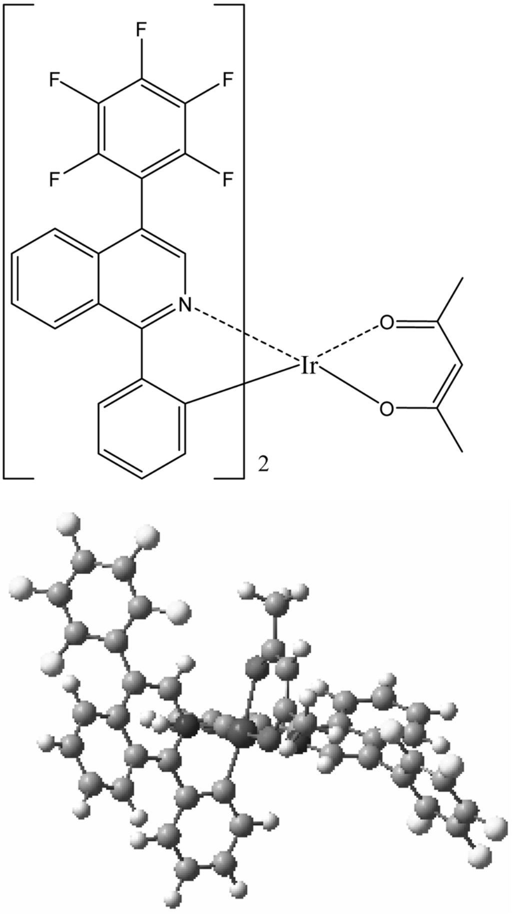


FIGURE 1 Schematic diagram of Ir(III) complex of PF-piq ligand.

and PF-piq, where PF-py represent 5-(perfluorophenyl)-2-phenylpyridine, were compared. The Hartree-Fock (HF) with the 3-21G(d) basis set and the B3LYP with the 6-31G(d) basis set were used for the geometry optimization and the energy level calculation of the ground state of these ligands, respectively. Calculations in the electronic ground states of the Ir(III) complexes such as Ir(PF-piq)$_2$(acac) as well as Ir(piq)$_2$(acac) and Ir(PF-py)$_2$(acac) have been carried out using the same calculation method, except that LANL2DZ basis set was used for the Ir atom. Electronic populations of the central atom were calculated to show the significant admixture of the π character of the ligand and the 5d character of the centric Ir metal in HOMOs related to these

MLCT transitions. To obtain the vertical excitation energies of the low-lying singlet and triplet excited states of the complexes, time-dependent density functional theory (TD-DFT) calculations using the B3LYP functional was performed at the respective ground-state geometry. Typically, the lowest 10 triplet and 10 singlet roots of the non-Hermitian eigenvalue equations were obtained to determine the vertical excitation energies. Recently, in a theoretical paper, an Ir complex having acac has been shown to have ideally three different structural isomers expressed as N−N cis, N−N trans, and N−O trans, where the N−N trans structure was expressed as the most stable one. The same result was also obtained in our calculations [13,14]. Thus, this paper discusses only Ir complexes having the structure of the N−N trans type.

3. RESULTS AND DISCUSSION

In Figure 2, the calculated energy levels of occupied and unoccupied molecular orbitals of some ligands are plotted, where ppy and piq are well-known ligands used to emit highly phosphorescent green and red lights when they exist in the form of the Ir(III) complex. When

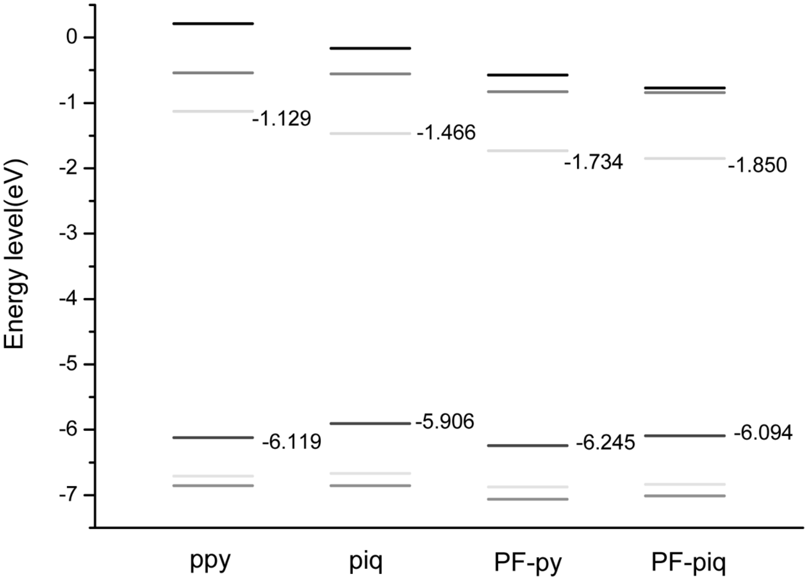
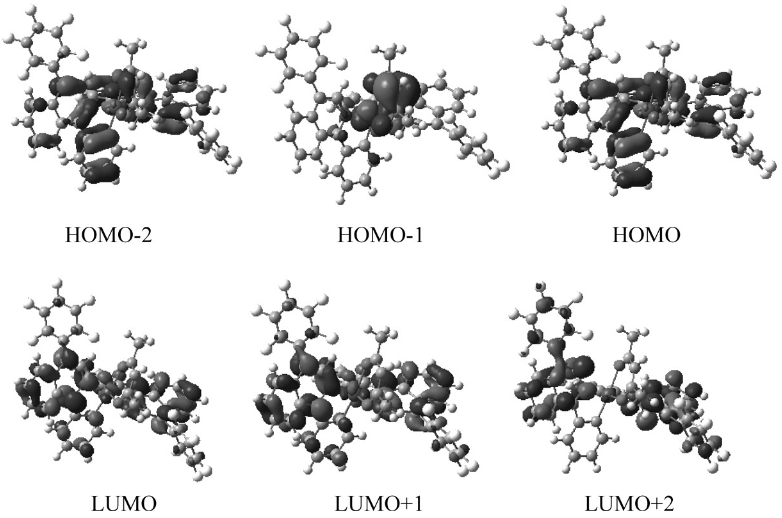


FIGURE 2 Comparison of HOMO and LUMO energy levels of ppy ligand, piq, PF-py and PF-piq.

ppy ligands combines with an Ir(III) ion, a strong mixing between the 5d orbital of the Ir atom and the higher π orbital of the ligand occurs, and π electrons exist near the Ir atom dominantly, which would be theoretically clarified from the calculation of the electron population of higher occupied molecular orbitals. This phenomenon is generally called the "π-donation effect." Originally, the piq ligand is a modified form of the ppy ligand, where an aromatic ring is fused at the side of the pyridine ring to increase the conjugation effect. As a result of the modification, the luminescent color of the Ir complex containing the ligand is changed from green to red. In Figure 2, it is certified that the energy gap of the piq ligand was decreased from 4.99 eV to 4.44 eV as a result of the conjugation effect. Ir complex of the PF-piq ligand, as another substituted form of piq ligand, is newly proposed in this paper to tune the emission wavelength to be pure red and increase the efficiency, by substituting a pentafluorophenyl group into the quinoline ring of the piq ligand. We confirmed that the energy gap between HOMO and LUMO decreases because the LUMO energy level decreases by a pentafluorophenyl substituent which is electronic accepting group into the LUMO position of piq ligand. Also, the pentafluorophenyl substituent reduces the intermolecular interaction of the complexes and enhances the PL by preventing self-quenching. In the case of the Ir(III) complex, it was reported that the fluorination with F radicals suppresses the radiationless deactivation and enhances the photoluminescence efficiency, because C-F bond lower the vibrational frequency. These radicals alter the molecular packing and minimize the self-quenching behavior [15]. They also can enhance the electron mobility of the compound and thus allow the optimization of carrier injection and the tuning of electroluminescent color [16].

In the case of the PF-piq ligand, the energy level of HOMO is very similar to that of the ppy ligand with a small difference of about 0.025 eV. Thus the electronic natures of HOMOs in both Ir complexes may have similar characters. Therefore, in the case of the Ir complex containing PF-piq ligands, it is predicted that the Ir complex has a strong admixing effect between the centric Ir atom and the PF-piq ligand.

After geometry optimization of the molecular structure of this complex using the density functional theory, the d-orbital characteristics of HOMOs and LUMOs were investigated. In Figure 3, contour plots of the three highest HOMOs and three lowest LUMOs of Ir(PF-piq)$_2$(acac) are shown. These orbitals are important because dominant excitations and emissions mainly occur due to the electronic transition among those orbitals. The results of theoretical calculations are summarized in Table 1, where d denotes the electronic population


HOMO-2 HOMO-1 HOMO

LUMO LUMO+1 LUMO+2

FIGURE 3 Contour plots of HOMOs and LUMOs of Ir(PF-piq)$_2$(acac).

of any electrons localized to the centric Ir atom and is a criterion of the 5d character of the orbital. It seems that HOMO is formed by the admixing of the d orbital of an Ir atom and π orbitals localized in

TABLE 1 Calculated HOMO and LUMO Orbital Energies and Electronic Populations of Metallic d Orbital of Ir(III) Complexes

Occupied Molecular Orbital				Unoccupied Molecular Orbital			
No		Energy (eV)	D (%)	No		Energy (eV)	d (%)
Ir(ppy)$_2$(acac)							
116	d_1	−4.798	52.79	117	π_1^*	−1.270	5.25
115	d_2	−5.277	42.66	118	π_2^*	−1.266	5.00
114	d_3	−5.746	66.87	119	π_3^*	−0.798	2.28
Ir(piq)$_2$(acac)							
142	d_1	−4.795	50.74	143	π_1^*	−1.795	4.02
141	d_2	−5.223	43.84	144	π_2^*	−1.715	4.73
140	d_3	−5.613	0.69	145	π_3^*	−0.770	2.25
Ir(PF-py)$_2$(acac)							
196	d_1	−5.022	51.53	197	π_1^*	−1.858	2.17
195	d_2	−5.484	40.28	198	π_2^*	−1.817	2.86
194	d_3	−5.948	51.53	199	π_3^*	−1.198	3.39
Ir(PF-piq)$_2$(acac)							
222	d_1	−5.024	49.44	223	π_1^*	−2.163	3.54
221	d_2	−5.372	37.35	224	π_2^*	−2.081	4.21
220	d_3	−5.802	1.98	225	π_3^*	−1.048	1.78

two PF-piq ligands, where the electronic population localized to the centric Ir atom is 49.44%. However, HOMO-1 and HOMO-2 show rather different characters. The π orbitals take part in the formation of the molecular orbitals belonging to the acac ligand. In cases of Ir(III) complexes, the assistant ligand such as acac was adopted to decrease the dipole moment of the IrL_3 form, where L denotes a ligand, because a rather higher dipole moment would induce unpredictable negative effects such as quenching and dimerization. A more precise description about the assistant ligands was given in our previous paper [13,14]. Three LUMOs show to have orbitals that are localized in PF-piq ligands, where the calculated electron populations in centric Ir atom are only 3.54, 4.21 and 1.78%, as shown in Table 1. Therefore, it would be concluded that two HOMOs and three LUMOs have different characters with respect to each other, as the former has mainly the strong metallic character of the 5d orbital of the centric Ir atom while the latter has the π character of the PF-piq ligand. It shows that the electronic transition between those orbitals would be the MLCT. MLCT has been known to occur when the Ir(III) complex illuminates intensified phosphorescent light [17].

Table 1 shows similar features of other Ir complexes containing piq or PF-py ligands. Among them, $Ir(PF\text{-}piq)_2(acac)$ has a large electron population of 49.44%, which is rather similar to that of $Ir(piq)_2(acac)$. Therefore, it is expected that $Ir(PF\text{-}piq)_2(acac)$ may have a high phosphorescence emitting characteristics.

TD-DFT calculation was employed to examine the low-lying singlet and triplet states of $Ir(PF\text{-}piq)_2(acac)$ and results are shown in Table 2. For Ir(III) complexes, we typically give the vertical excitation energies

TABLE 2 Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillator Strengths Obtained from TD-DFT Calculation of $Ir(PF\text{-}piq)_2(acac)$

Singlet					Triplet			
State	Dominant excitation	Energy (eV)	Wave length (nm)	Oscillator Strength	State	Dominant excitation	Energy (eV)	Wave length (nm)
S_1	$d_1 \rightarrow \pi_1^*$	2.24	553.3	0.0052	T_1	$d_1 \rightarrow \pi_1^*$	1.96	632.1
S_2	$d_1 \rightarrow \pi_2^*$	2.28	542.8	0.0950	T_2	$d_1 \rightarrow \pi_2^*$	2.02	614
S_3	$d_2 \rightarrow \pi_1^*$	2.58	480.5	0.0717	T_3	$d_2 \rightarrow \pi_1^*$	2.26	548.4
S_4	$d_2 \rightarrow \pi_2^*$	2.69	460	0.0031	T_4	$d_2 \rightarrow \pi_2^*$	2.27	547.8
S_5	$d_4 \rightarrow \pi_1^*$	3.04	408.1	0.0158	T_5	$d_2 \rightarrow \pi_1^*$	2.61	474
S_6	$d_4 \rightarrow \pi_2^*$	3.10	399.5	0.0329	T_6	$d_2 \rightarrow \pi_2^*$	2.64	469.1
S_7	$d_3 \rightarrow \pi_1^*$	3.19	388.4	0.1511	T_7	$d_4 \rightarrow \pi_2^*$	2.96	418.6

for the lowest triplet and singlet states calculated at the optimized structure for the ground states. For each of the triplet and singlet excitations, a dominant excitation is achieved among several minor excitations because of a strong d-π mixing if it has the greatest transition probability. Nearly all of these excitations correspond to electron transfer from the two HOMOs with the significant 5d character to virtual MOs with a π^* character. This characteristic is very similar to that of Ir(ppy)$_2$(acac) with only a difference in excitation energy. According to this assessment, it is certain that all excitations calculated in this study are MLCT states. The strong mixing of d orbitals with π orbitals of the PF-piq ligand is shown on the highest two occupied orbitals, as shown in Figure 3.

For the comparison of calculation results with experimental data, the absorption spectra of Ir(PF-py)$_2$(acac) are replotted in Figure 4, [18] which were originally reported by Su *et al*. [10]. In their study, the wavelengths of the lowest 10 singlet and triplet states calculated by the TD-DFT method are marked “S” and “T”. In the higher region of wavelength, there commonly exist small and elongated tails that are always shown in absorption spectra of phosphorescent Ir complexes. we have thought that those tails are due to the lower triplets such as T1 and T2 [13,14]. These triplets having lower energies are very important because their transition states are related to the luminescence. Also, they play a role in setting the criterion that predicts the position of the luminescent wavelength through the comparison.

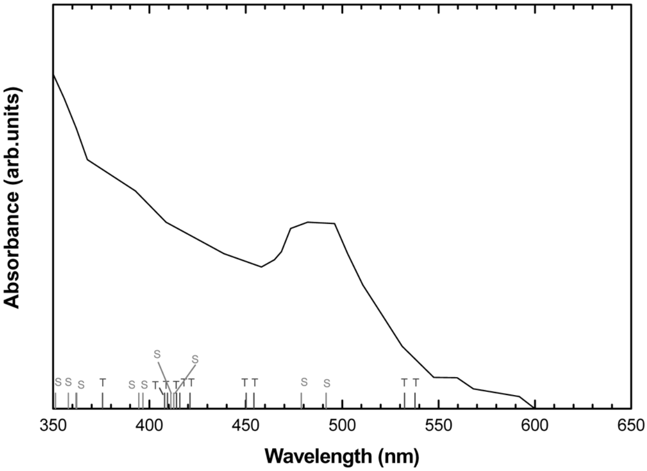


FIGURE 4 Absorption spectra of Ir(PF-py)$_2$(acac). Spectra are replotted from Ref. 11 for comparison of calculated data.

TABLE 3 Photophysical Data and Calculation Results of Ir(III) Complexes

Complex	Energy gap (eV)	Emission wavelength (nm)	Calculation result(nm) (TD-DFT)
$Ir(ppy)_2acac$	3.527	516	493
$Ir(piq)_2(acac)$	3.000	622	601
$Ir(p\text{-}PF\text{-}py)_2(acac)$	3.164	537	559
$Ir(p\text{-}PF\text{-}piq)_2(acac)$	2.862		632.1

In the case of $Ir(PF\text{-}py)_2acac$, the measured value mostly agrees with calculated value.

As shown in Table 3 [10], we confirmed that the trend of the calculated result agrees with one of the experimental value, by comparing the calculated excitation data and the experimental emitting wavelength data of Ir complexes. All of the Ir complexes in this paper show a wavelength difference of about 20 nm between above two data.

From the TD-DFT calculation, the value of the lowest triplet excitation of $Ir(PF\text{-}piq)_2(acac)$ is 632 nm, which is 31 nm longer than that of $Ir(piq)_2(acac)$. Therefore, it is possible to expect that the emission wavelength of $Ir(PF\text{-}piq)_2(acac)$ will be about 650 nm in the region of pure red color. From the calculation of the electronic population of some HOMOs and LUMOs, it is predicted that a strong MLCT transition promising intensified emissive efficiency will exist in the electronic transition of $Ir(PF\text{-}piq)_2(acac)$.

4. CONCLUSIONS

To enforce a red shift and improve the luminescence efficiency of Ir(III) complexes, $Ir(PF\text{-}piq)_2acac$ is newly proposed in this paper by introducing pentafluorophenyl substituent into the position of the quinoline ring of the piq ligand. The pentafluorinated substituent reduces the energy gap between HOMO and LUMO by withdrawing the LUMO energy level due to the electronic accepting nature of the substituent. Also, it reduces the intermolecular interaction of the complexes and enhances the PL by preventing self-quenching. Authors confirmed theoretically that the energy level of PF-piq ligand have very similar to that of ppy ligand and the energy gap decreases by a pentafluorophenyl group. Therefore the wavelength of $Ir(PF\text{-}piq)_2$ acac would appear pure red region about 650 nm with more intensified efficiency. All of the low-lying excitations calculated in this study are categorized as ^{3}MLCT transitions for $Ir(PF\text{-}piq)_2(acac)$ because the 5d characters of the two highest MOs are considerably high. The calculated result shows that the strong ^{3}MLCT transition of the complex is due to the strong mixing between the 5d orbital of the Ir atom and the HOMOs of ligands.

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