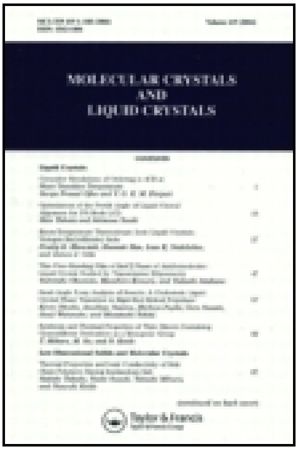

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Synthesis and Photophysical Studies of Iridium Complexes of Fluorinated Phenylisoquinolines

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*There have been reported materials emitting green color in both fluorescence and phosphorescence with great success, however efficient red luminescence materials are rare. Recently, it has been reported iridium (III) complexes of 1-(phenyl)isoquinoline (**piq**) and 1-(4′-fluorophenyl) isoquinoline (**piq-F**) show strong electroluminescence (EL) brightness and efficiency, even at high currents. These complexes show the strong intensity of band around 450 nm assigned to the spin-forbidden ^{3}MLCT (metal to ligand charge transfer) transition [1]. In this study, Ir(III) complexes of fluorinated piqs (**piq-F, piq-2F, piq-CF$_3$**) as cyclometalated ligand were prepared and photonic properties were investigated to improve the EL efficiency. The Ir(III) complex with **piq-CF$_3$** ligands exhibits the largest emission efficiency with maximum at 612 nm. The result of ab. Initio calculation using the Time-dependent density functional theory (TD-DFT) shows that the strong ^{3}MLCT transition of the complex is due to the strong coupling between the 5d orbital of the Ir atom and the highest occupied molecular orbitals (HOMOs) of ligands.*

Keywords: DFT; Ir complex; Ir(piq-CF$_3$)$_2$(acac); OLED; phosphorescence; red

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1. INTRODUCTION

Electroluminescent (EL) organic materials have received a great deal of attention due to their potential for application in flat-panel displays because of their luminous efficiency and the simplicity to obtain low cost device fabrication. Recently, Forrest and Thompson have developed electro-phosphorescent OLEDs with high efficiency approaching 100% of internal quantum efficiency which utilize both singlet and triplet excitons occurring at the emitting layer doped with the phosphorescent dopants [2,3]. The heavy metal forms such as Ir or Pt in the complex were known to induce the intersystem crossing by strong spin-orbit coupling, leading to mixing of the singlet and triplet excited states. Spin-forbidden nature of radiative relaxation from the triplet excited state then changed to be allowed, resulting in high phosphorescent efficiencies. Thus, Ir complexes were known to have high photoluminescence efficiency and relatively short excited state lifetime which minimizes quenching of triplet emissive states [4,5].

However, so far satisfactory luminescence efficiency in blue and red phosphorescent material has not been obtained enough to guarantee commercialization. $Ir(btp)_2(acac)$ (**btp** = 2-(2-benzo[4.5-a]thienyl)pyridinato; acac = acetylacetonate) were well known efficient red phosphorescence [6,7], however external quantum efficiency was only about 2.5% at high current (100 mA/cm) because of increase of triplet–triplet (T–T) annihilation phenomenon at high current. Recently, it was reported that $Ir(piq)_2(acac)$ with **piq** representing the 1-(phenyl)-isoquinoline ligand showed high external quantum efficiency of nearly 7.00 at $J = 400\,mA/cm^2$, whose EL emission band at 620 nm [1]. Unlike other Ir(III) red phosphor complexes, remarkably high efficiency could be maintained at high currents with a negligible effect from either the T–T annihilation or saturation of the excited state. The emission spectra for $\mathbf{Ir(btp)_2(acac)}$ closely resemble the phosphorescence spectrum reported for the free organic ligand, supporting the assignment of the lowest energy excited state to be predominantly ligand-based. The vibronic fine structure is clearly observed for the btp ligand [6,7]. However, the emission spectrum of **piq** based iridium complexes are broad and featureless and it denoted that $\mathbf{Ir(piq)_2}$ **(acac)** emits from an excited state that is predominantly due to the MLCT transition [1]. Hence, we wish to synthesize and characterize more efficient red luminance Ir(III) complexes of fluorinated piqs (**piq-F**, **piq-2F**, $\mathbf{piq\text{-}CF_3}$) to improve EL efficiency, where **piq**, **piq-F**, **piq-2F**, and $\mathbf{piq\text{-}CF_3}$ representing 1-(phenyl)isoquinoline, 1-(4′-fluorophenyl)isoquinoline, 1-(3,5-difluorophenyl)isoquinoline and 1-(4′-trifluoromethylphenyl)isoquinoline). All complexes emit bright red light and the peak of emission wavelengths can be tuned depending on the position of the substituent. In absorption spectra, the ^{1}MLCT and ^{3}MLCT transitions have been resolved and characterized in the range 400–450 nm using the time-dependent density functional theory (TD-DFT) with B3LYP/6-31G(d). The results of the DFT calculation on the ground state of Ir(III) complexes indicated that the 5d orbitals of the Ir atom and the highest occupied molecular orbitals (HOMOs) of ligands were strongly mixed. The strong coupling between the central Ir atom and the HOMOs of ligands allows the strong MLCT transition. The photoluminescent (PL) characteristics for the substituted and the unsubstituted complexes have been compared and discussed.

2. EXPERIMENTAL SECTION

2.1. Synthesis and Characterization

All reagents were purchased from Aldrich Co. except Ir(III) trichloride hydrate($IrCl_3 \cdot H_2O$) which was purchased from Strem Co. and used without further purification. All reactions were carried out under nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-Mesh, Merck. co) Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890 A (capillary column) at Seoul National University, Korea.

2.1.1. Synthesis of Ligands (L=piq-F, piq-2F, piq-CF_3)

Phenylisoquinoline ligands, 1-(4′-fluorophenyl) isoquinoline, 1-(3,5-difluorophenyl) isoquinoline, 1-(4′-trifluoromethylphenyl) isoquinoline were obtained from the reaction of 1-chloroisoquinoline and corresponding phenylboronic acids by Suzuki coupling.

Synthesis of piq-F. 1-chloroisoquinoline (0.899 g, 5.5 mmol), 4-fluorophenylboronic acid (0.699 g, 5 mmol) and tetrakistriphenylphospine palladium(0) (0.196 g, 0.17 mmol) was placed in 20 ml of toluene, 10 ml of ethanol and 20 ml of 2 N sodium carbonate aqueous solution. The mixture were charged with nitrogen atmosphere and heated to reflux for 15hr. The mixture was cooled room temperature and extracted with 20 ml of ethyl acetate. The organic fraction were dried over anhydrous $MgSO_4$, filtered and pumped dry. The residue was chromatographed on silica gel column with ethyl acetate/hexane (1:7). The pure product was collected and dried in vacuum, to afford white powder in 64% yield.

Ligands of **piq-2F** and **piq-CF_3** were prepared from the reaction of 1-chloroisoquinoline and corresponding phenylboronic acids (3,5-difluorophenylboronicacid, 4-trifluoromethylphenyl-boronic acid) by a similar procedure.

piq-F: Yield (0.72 g, 0.64)
piq-2F: Yield (0.82 g, 0.68)
piq-CF_3: Yield (0.78 g, 0.57)

2.1.2. Synthesis of Complexes

*Ir(**L**)$_2$(acac) = Ir(piq-F)$_2$(acac), Ir(piq-2F)$_2$(acac), Ir(piq-CF_3)$_2$ (acac).* Cyclometalated Ir(III) μ-chloro-bridged dimers of general formula, $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$, where ***L*** represents the cyclometalated phenylquinoline derivatives, were synthesized by the method reported by Nonoyama with slight modification. The synthesis of $Ir(\boldsymbol{L})_2$(acac) were described in detail as follows.

To a flask containing $IrCl_3{\cdot}H_2O$ (0.298 g, 1 mmol) and ***L*** (piq-F, piq-2F, piq-CF_3 = 2.5 mmol) was added a 3:1 mixture of 2-ethoxyethanol and water. The mixture was refluxed for 12 hr and cooled to room temperature. The mixture solution was evaporated under vacuum slowly to obtain the crude product $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$. The red solid was filtered and washed with ethanol. $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$ (0.3 mmol) was then mixed with Na_2CO_3 (210 mg) in a two-neck flask. 2, 4-pentanedione (0.21 ml, d = 0.975, 2.1 mmol) in 2-ethoxyethanol (10 mL) were added and the mixture was refluxed for 1 hr. The solution was cooled to room temperature and the red solid was filtered. $Ir(\boldsymbol{L})_2$(acac) was obtained after chromatographed using CH_2Cl_2 to afford bright red powder.

***Ir*(*piq-F*)$_2$(*acac*):** Yield (0.335 g, 0.76)MS calced for $C_{35}H_{25}F_2IrN_2O_2$ m/e 735.8, found m/e 736.
***Ir*(*piq-2F*)$_2$(*acac*):** Yield (0.287 g, 0.62)MS calced for $C_{35}H_{23}F_4IrN_2O_2$ m/e 772.13, found m/e 772.
***Ir*(*piq*)-*CF*$_3$)$_2$(*acac*):** Yield (0.302 g, 0.60) MS calced for $C_{37}H_{25}F_6IrN_2O_2$ m/e 836.14, found m/e 836.

2.2. Photoluminescence Property Measurement

UV-Vis absorption spectra were measured on Hewlett Packard 8425 A spectrometer. The PL spectra were measured on Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of ligandsn (***L***) and $Ir(\boldsymbol{L})_2$(acac) were measured in 10^{-5} M dilute solution in CH_2Cl_2.

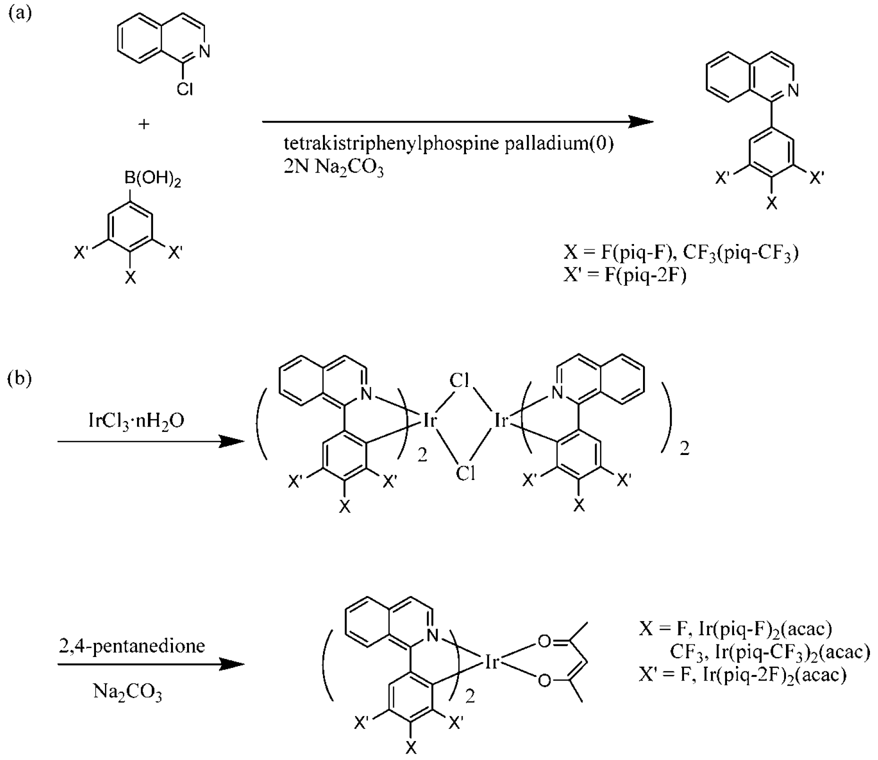
2.3. Computational Method

The ground and low-lying excited electronic states in the Ir(III) complexes were calculated using Gaussian 03 (ab-initio method). The **ppy** (biphenyl pyridine) ligand has been known as an excellent ligand for MLCT transitions. In order to study the MLCT transition, we have compared the HOMO energy level of **ppy** ligand with **piq** ligand derivatives. Density functional theory (DFT) utilizing Hatree-Fork (HF) with 3–21G(d) basic set and B3LYP with the 6–31G(d) basis set were used for the geometry optimization and the energy level calculation of the ground state of those ligands, respectively. The HOMO energy level and the energy gap between HOMO and the lowest unoccupied molecular orbital (LUMO) of **ppy** ligand and **piq** ligand derivatives were compared to explain the strong MLCT transitions. Calculations on the electronic ground states of the Ir(III) complexes have been carried out using the same calculation method and LANL2DZ basis set for Ir atom. Excitation energies of triplet and singlet state were calculated from the TD-DFT utilizing the B3LYP functional with the 6–31G(d) basis set. The electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of metal 5d character in occupied molecular orbitals related to those MLCT transitions [8].

3. RESULTS AND DISCUSSION

Fluorinated **piq** ligands were prepared by palladium (0) catalyzed Suzuki coupling reaction, as illustrated in (a) of Scheme 1. Using the ligands prepared above, the bis-cyclometalated Ir(III) complexes containing an ancillary ligand were synthesized. Ir($\boldsymbol{L}$)$_2$(acac) were obtained via two step synthesis. Ir(III) μ-chloro-bridged dimer, ($\boldsymbol{L}$)$_2$Ir(μ-Cl)$_2$Ir($\boldsymbol{L}$)$_2$ were synthesized according to Nonoyama method. (Scheme 1(b)) Reaction of $IrCl_3 \cdot H_2O$ with **piq** ligand forms chloride-bridged dimer, ($\boldsymbol{L}$)$_2$Ir(μ-Cl$_2$)Ir($\boldsymbol{L}$)$_2$, and the replacement of bridging chlorides with β-diketonate gives Ir($\boldsymbol{L}$)$_2$(acac). Synthetic procedure to make the final monomeric Ir(III) complex with the ancillary ligand required a shorter reaction time than the previously reported time. These reactions result in 60–74% yield of the desired Ir complexes.

Originally, **piq** ligands were modified from **ppy** ligand to decrease the energy gap, increasing the conjugation length which leads to red shift of the emission spectrum to the longer wavelengths. Fluorinated **piq** ligands were designed to decrease the HOMO energy level of **piq** to the HOMO energy level of **ppy**. Because the HOMO of **ppy** and the 5d orbital of the iridium atom have similar orbital energies, it causes



SCHEME 1 Synthesis of ligands and complexes of Ir(***L***)$_2$(acac).

strong coupling between them. Thus, their strong coupling creates MLCT states and gives a strong ^{3}MLCT absorption and emission spectra in the Ir(III) complexes. F-, 2F- or CF_3- were introduced an electron withdrawer in HOMO of **piq** ligand to decrease HOMO level. Figure 1 shows calculated HOMO and LUMO energy levels of ligands. HOMO and LUMO levels of **piq-CF$_3$** were lowered down to −6.179 eV and –1.767 eV from −5.906 eV and –1.466 eV of those of piq, respectively, by the effect of electron withdrawing of CF_3-. The stronger electron withdrawers were introduced, the lower HOMO level of ligand was obtained. HOMO levels of **piq-2F** and **piq-CF$_3$** are much close to the one of **ppy** to induce strong MLCT transition.

Absorption spectra of free ligands and Ir(III) complexes of fluorinated piqs are shown in Figure 2. **Ir(piq-CF$_3$)$_2$(acac)** shows strong MLCT absorption band around 450 nm assigned to the ^{3}MLCT. However, **Ir(piq-2F)$_2$(acac)** shows weak ^{3}MLCT character. This trend was also found in calculation results.

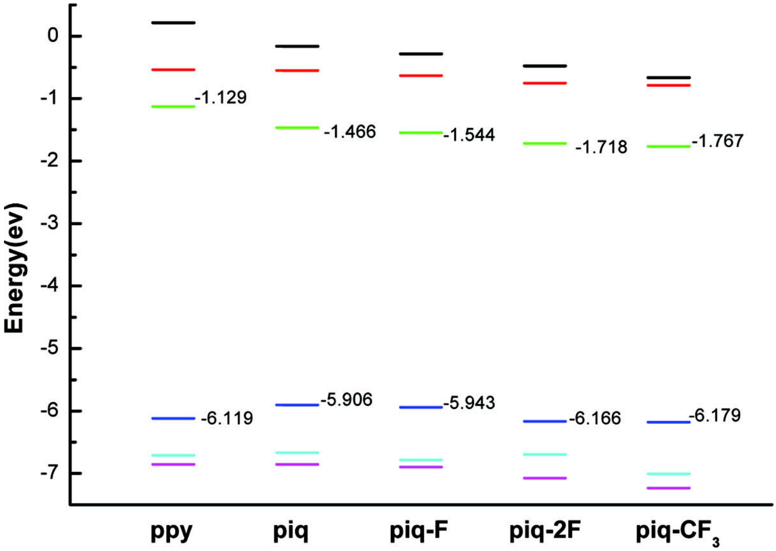


FIGURE 1 Comparison of the HOMO and LUMO energy levels of piq derivatives and ppy ligands.

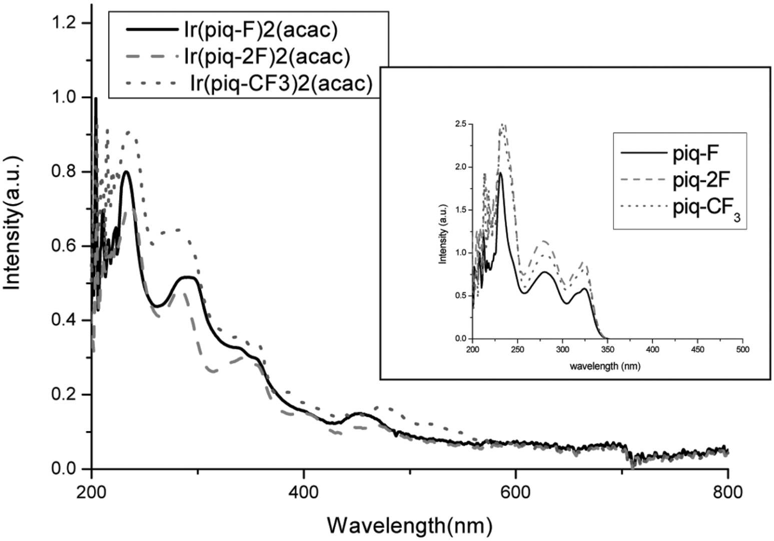


FIGURE 2 Absorption spectra of ligands (inserted) and Ir($\boldsymbol{L}$)$_2$(acac), where L's are -F, -2F, and -CF$_3$.

After optimizations of molecular structures of three ligands, using density functional theory energy levels and d-orbital characteristics of HOMOs and LUMOs of these Ir(III) complexes were investigated. Three highest HOMOs are denoted d_1, d_2, and d_3. HOMOs of these Ir(III) complexes has the strong metallic character of the 5d orbital of the centric Ir atom and the electronic population confined to 5d orbital is more than about 30%. For **Ir(piq)$_2$(acac)**, the resultant 5d character from population analysis are 51%, 48% and 43% for d_1, d_2 and d_3, respectively. Three lowest LUMOs are combinations of the first π^* orbital of **piq**. For the convenience, all virtual π^* orbitals will be labeled starting with π_1^* denote orbitals on **piq** ligand. For **Ir(piq-F)$_2$(acac)**, a population analysis of each orbital shows the following 5d percentages: d_1 (48.4%), d_2 (46.8%), and d_3 (30.9%). As compared with three Ir(III) complexes, **Ir(piq-CF$_3$)$_2$(acac)** has the highest 5d orbital characters, which agrees with the experimental result that **Ir(piq-CF$_3$)$_2$(acac)** shows the highest emission intensity among four Ir(III) complexes.

TD-DFT calculation was employed to examine the low-lying singlet and triplet states of the complexes and results are shown in Table 1. For those molecules, we typically give the vertical excitation energies for the lowest ten triplet and singlet states calculated at the optimized structure for the ground states. For each of triplet and singlet excitations, a dominant excitation is achieved among several excitations. All correspond to excitations from an electron in the three HOMOs with the significant 5d character to virtual MOs with π^* character. According to this assessment, it is certain that every excitations calculated in this study are MLCT states. For the comparison with experimental data, we plotted the results obtained through the TD-DFT in the absorption spectra of the **Ir(piq-CF$_3$)$_2$(acac)** having the highest oscillation strengths, as shown in Figure 3. It is certain that peaks distributed from 374 nm to 602 nm would be assigned to MLCT absorptions that singlets ($S_1 \sim S_7$) and triplets ($T_1 \sim T_7$) are separately located in the region of 374 nm $\sim$ 507 nm and 444 nm $\sim$ 602 nm, respectively. **Ir(piq-2F)$_2$(acac)** has weak MLCT character because energy transfer from the carbon atom linked iridium atom to the metal atom was hindered by F atom at para position.

Particularly, the strong intensity of band around 450 nm was shown spin-forbidden ^{3}MLCT. Measured and calculated values are similar, as shown in Figure 3. The emission spectra of complexes are shown in Figure 4. The emission wavelength of **Ir(piq-F)$_2$(acac)**, **Ir(piq-CF$_3$)$_2$(acac)** in CH_2Cl_2 was 597 nm and 612 nm, respectively. The PL spectrum of **Ir(piq)$_2$(acac)** shows emission band at 622 nm in CH_2Cl_2 [3], whereas Ir(III) complexes of fluorinated piqs were blue

TABLE 1 Calculated Excitation Energies, Dominant Orbital Excitation, and Oscillator Strengths Obtained from TD-DFT Calculations for Ir(piq-CF_3)$_2$(acac)

Singlets					Triplets			
States	Dominant excitation	Energy (eV)	Wave-length (nm)	Oscillator strengths	States	Dominant excitation	Energy (eV)	Wave-length (nm)
S_1	$d_1 \rightarrow \pi_1^*$	2.44	507	0.015	T_1	$d_1 \rightarrow \pi_1^*$	2.06	602
S_2	$d_1 \rightarrow \pi_2^*$	2.52	491	0.054	T_2	$d_1 \rightarrow \pi_1^*$	2.19	567
S_3	$d_2 \rightarrow \pi_1^*$	2.62	473	0.003	T_3	$d_2 \rightarrow \pi_2^*$	2.36	526
S_4	$d_2 \rightarrow \pi_2^*$	2.74	453	0.073	T_4	$d_1 \rightarrow \pi_2^*$	2.43	509
S_5	$d_3 \rightarrow \pi_2^*$	3.00	414	0.043	T_5	$d_2 \rightarrow \pi_2^*$	2.69	460
S_6	$d_3 \rightarrow \pi_2^*$	3.08	402	0.036	T_6	$d_2 \rightarrow \pi_3^*$	2.78	446
S_7	$\pi_1 \rightarrow \pi_3^*$	3.32	374	0.007	T_7	$d_5 \rightarrow \pi_2^*$	2.79	444

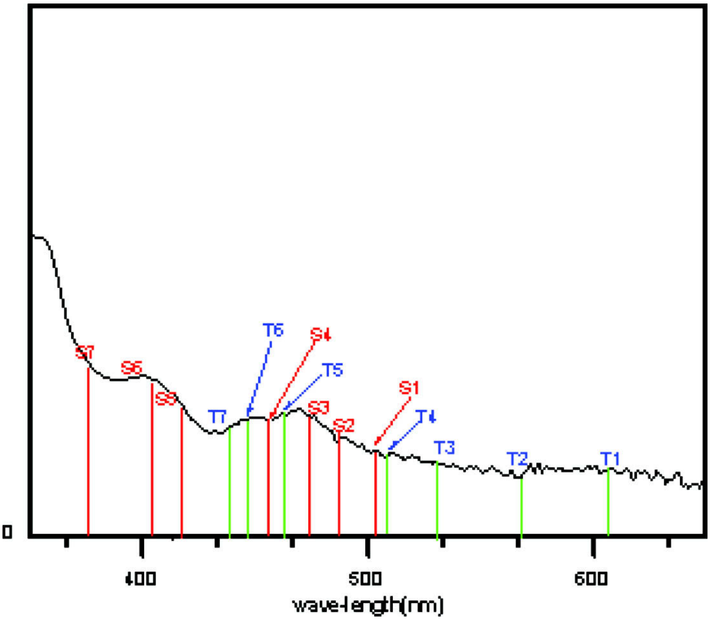


FIGURE 3 Comparison of absorption spectrum and values of TD-DFT calculations for Ir(piq-CF_3)$_2$(acac).

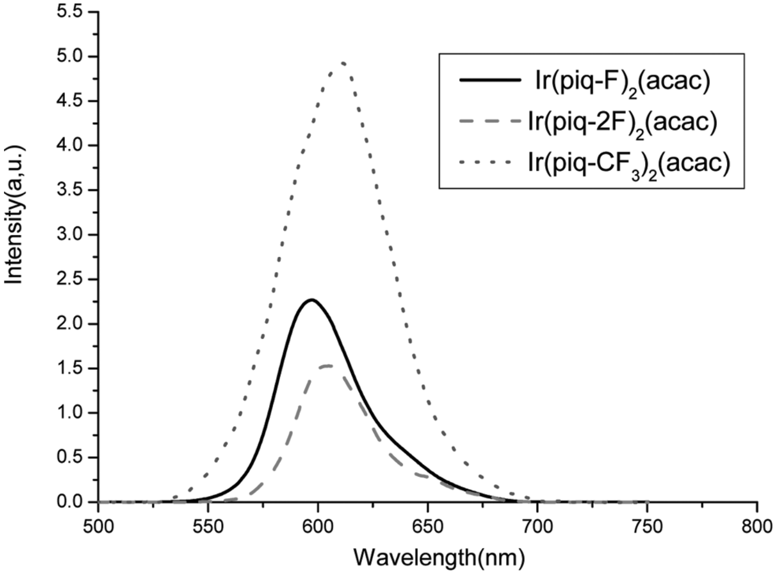


FIGURE 4 PL spectra of Ir(***L***)$_2$(acac), where L's are -F, -2F, and -CF_3.

shifted. It is because the energy gap of ligands increase as HOMO level goes down due to withdrawer like as F and CF_3.

4. CONCLUSION

To improve luminescence efficiency of reported piq-based Ir(III) complexes, we have designed and synthesized fluorinated piq ligands such as piq-F, piq-2F, and piq-CF_3 to decrease the HOMO energy level of **piq** to the HOMO energy level of **ppy**. Because the HOMO of **ppy** and the 5d orbital of the iridium atom have similar orbital energies, it causes strong coupling between them. Thus, their strong coupling creates MLCT states and gives a strong ^{3}MLCT absorption and emission spectra in the Ir(III) complexes. Complexes containing these ligands were prepared and photophysical properties were investigated. Among these two complexes, **Ir(piq-CF_3)$_2$(acac)** exhibits the largest emission efficiency with maximum emission at 612 nm. All of the low-lying transitions calculated in this study are categorized as ^{3}MLCT transitions for **Ir(piq-CF_3)$_2$(acac)** because the metal 5d character of three highest MOs are considerably high as 52.8%, 47.7% and 49.1%, respectively. The calculational result shows that the strong ^{3}MLCT transition of the complex is due to the strong coupling between the 5d orbital of the Ir atom and the HOMOs of ligands.

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