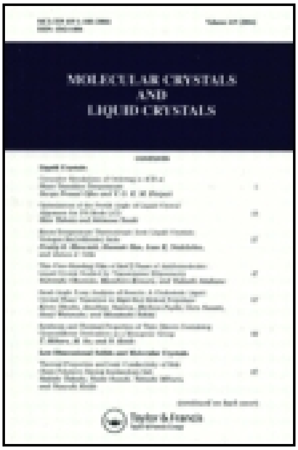

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Iridium(III) Complexes with 6-Pentafluorophenyl-2,4-Diphenylquinolines for Red OLEDs

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Iridium(III) Complexes with 6-Pentafluorophenyl-2, 4-Diphenylquinolines for Red OLEDs

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Novel red electrophosphorescent devices were fabricated by doping perfluorophenyl substituted iridium(III) complex, bis[1-(6-Pentafluorophenyl-2,4-diphenyl)quinolinato-N,$C^{2'}$] iridium(III) (acetylacetonate) [Ir(PF-dpq)$_2$(acac)] for the application in organic light-emitting diodes (OLEDs). The maximum electroluminescent (EL) wavelengths of Ir(dpq)2(acac) and Ir(PF-dpq)$_2$(acac) have shown at 614 nm and 620 nm, respectively. The device using Ir(PF-dpq)$_2$(acac) showed red emission with 1931 CIE chromaticity coordinates ($x = 0.640$, $y = 0.342$) at 12 V. The perfluorophenyl substituent on the quinoline ring as electron withdrawing group decreased the lowest unoccupied molecular orbital (LOMO). As a result, the energy gap is reduced, leading to red-shift the emission wavelength. The ab initio calculation using the time-dependent density function theory (DFT) showed in agreement with the experimental results. However, the iridium complex of PF-dpq underwent a weak MLCT transition because of the weak coupling between the 5d-orbital of the iridium atom and HOMO of the substituted ligand. Thus, the luminous efficiency of the device using Ir(dpq)2(acac) and Ir(PF-dpq)$_2$(acac) are 4.36 cd/A and 3.13 cd/A, respectively, at the current density of 3.38 mA/cm^2 and 1.11 mA/cm^2.

Keywords: DFT; 2,4-diphenylquinoline ligand; iridium complex; OLED; phosphorescence; red

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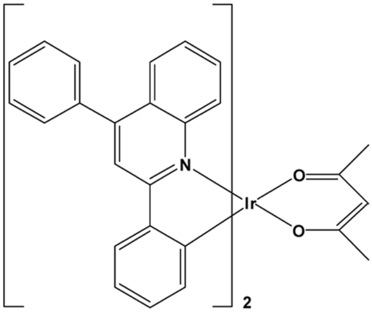
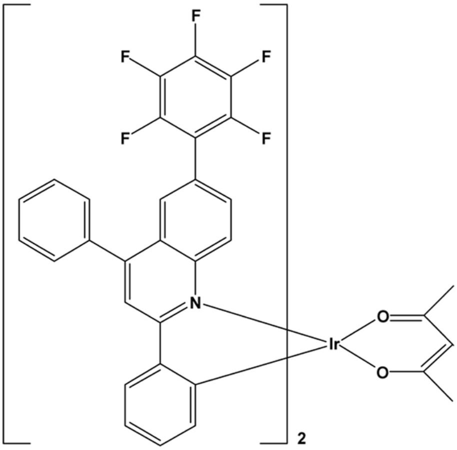
1. INTRODUCTION

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 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%. Thompson *et al.* 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 bis[2,4-diphenylquinolinato-N,$C^{2'}$] iridium(III) (acetylacetonate) [Ir(dpq)$_2$(acac)] showed a high luminous efficiency of nearly 11.61 cd/A at turn on voltage 7.1 V, whose EL emission band is at 606 nm [10,11]. Unlike other Ir(III) red phosphor complexes, the 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, these complex emit an impure red emission wavelength, we have designed and synthesized Ir(PF-dpq)$_2$(acac) as shown in Figure 1. By introducing a pentafluorophenyl substituent into Ir(dpq)$_2$(acac), photoluminescence (PL) and electroluminescence (EL) spectra exhibited longer wavelength due to the electron-withdrawing nature of the substituent [12]. It is found that a pentafluorophenyl substituent leads to red-shift of electroluminescence (EL) wavelength and change in luminous efficiency. Further support on such emission peak shift is provided by theoretical calculation.



Ir(dpq)$_2$(acac)



Ir(PF-dpq)$_2$(acac)

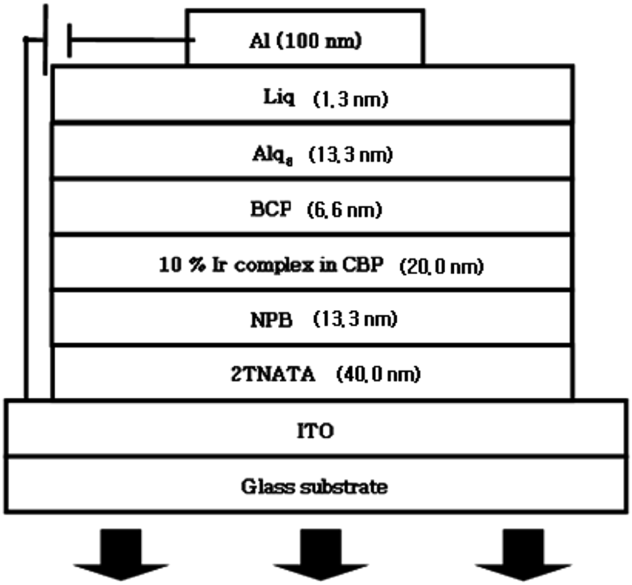


FIGURE 1 Molecular structures of iridium complexes and the device configuration.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Iridium Complexes

The 2,4-diphenyl-quinoline [dpq] and 6-chloro-2,4-diphenyl-quinoline [dpq-Cl] ligands were prepared from Friedlander Reaction [10]. Concentrated sulfuric acid (1.0 ml) was added to a solution of 2-aminobenzophenone (1.972 g, 10.0 mmol) [5-chloro-2-aminobenzophenone (2.31 g, 10.0 mmol) for dpq-Cl ligand] and acetophenone (1.169 g, 10.0 mmol) in 30 ml of glacial acetic acid. The solution was heated to reflux for 20 h. The reaction mixture was then cooled and dripped slowly with stirring into an ice cold solution of 15 ml of concentrated ammonium hydroxide in 40 ml of water. The resultant yellow precipitate was filtered, washed with water. The solid was chromatographed on a silica gel column with dichloromethane (CH_2Cl_2).

The PF-dpq ligand was prepared according to Suzuki coupling reaction with modification [13,14]. 6-chloro-2,4-diphenyl-quinoline (1.733 g, 5.5 mmol), pentafluorophenyl boronic acid (1.06 g, 5 mmol) and tetrakistriphenylphospine palladium(0) (0.196 g, 0.17 mmol) were placed in a mixture of toluene (20 ml), ethanol (10 ml) and 2N sodium carbonate aqueous solution (20 ml). The reaction mixture was heated to reflux for 15 hr at 135°C. The mixture was cooled to room temperature and extracted with 20 ml of ethyl acetate. The organic fraction was dried over anhydrous $MgSO_4$, filtered and pumped dry. The residue was chromatographed on a silica-gel column with ethyl acetate/hexane (1:7). The product was collected and dried in vacuum to yield a white solid. The general procedure for synthesis of iridium complexes via cyclometalated iridium μ-chloro-bridged dimmer $[(L)_2Ir\ (\mu\text{-}Cl)_2Ir(L)]$ can be found in many literature [10].

2.2. Theoretical Calculation

Calculations on the electronic ground states of ppy, dpq, PF-py and PF-dpq ligands were carried out using the B3LYP density functional theory (DFT), where ppy and PF-py represent 2-(phenyl)pyridine and 5-(perfluorophenyl)-2-phenylpyridine, respectively. LANL2DZ and 6-31G(d) [15] basis sets were employed for Ir and the other atoms, respectively. For the calculated ground state geometries, the electronic structure is examined in terms of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs). And the electronic populations on the central atom were calculated to show the significant admixture of ligand π character with the amount of metal 5 d character in the occupied molecular orbitals related to those 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, where the basis set of ligands was changed to 6-31 + G(d). The ground-state B3LYP and excited-state TD-DFT calculations were carried out using Gaussian 98 [16].

2.3. Electroluminescence Measurements

The configuration of the devices was ITO/4,4′,4″-tris[2-naphthylphenylamino]triphenylami-ne (2-TNATA) (40 nm)/4,4′-bis[*N*-(naphthyl)-*N*-phenyl-amino]biphenyl (NPB) (13.3 nm)/10% Ir complex in 4,4,*N*,*N*′-dicarbazolebiphenyl (CBP) (20 nm)/bathocuproine (BCP) (6.6 nm)/tris-(8-hydroxy-quinoline) aluminum (AlQ_3)(13.3 nm)/lithium quinolate (Liq) (1.3 nm)/Al (100 nm), as shown in Figure 1. The OLEDs were fabricated by high vacuum (5×10^{-7} torr) thermal deposition of organic materials onto the surface of an indium tin oxide (ITO) coated glass substrate. The ITO glass was chemically cleaned using acetone, methanol, distillated water and isopropyl alcohol. After the fabrication, the current density-voltage (J-V) characteristics of the OLEDs were measured with a source measure unit (Kiethley 236).

3. RESULTS AND DISCUSSION

We have designed and synthesized Ir(PF-dpq)$_2$(acac) by introducing a pentafluorophenyl substituent into Ir(dpq)$_2$(acac) to tune the emission wavelength to be pure red and increase the efficiency. Figure 2 shows that the calculated energy levels of occupied and unoccupied molecular orbitals of the complexes. Ir(ppy)$_2$(acac) and Ir(dpq)$_2$(acac) were known to have high phosphorescence efficiencies in EL emissions near 516 and 614 nm, respectively, because those complexes had a good metal-to-ligand charge transfer (MLCT) characteristics [9,10]. When ppy or dpq ligand combines with an iridium(III) ion, a strong mixing between the t_{2g} orbital of the iridium atom and the π orbital of ligand occurs because their energy levels are close to each other. It can be explained from the calculation of the HOMO's electron population which exists near the iridium atom dominantly. This phenomenon is generally called the π-donation effect.

When the perfluorophenyl group substituted into Ir(dpq)$_2$(acac), the energy gap between HOMO and LUMO decreased as shown in Figure 2. The perfluorophenyl substituent on quinoline ring as

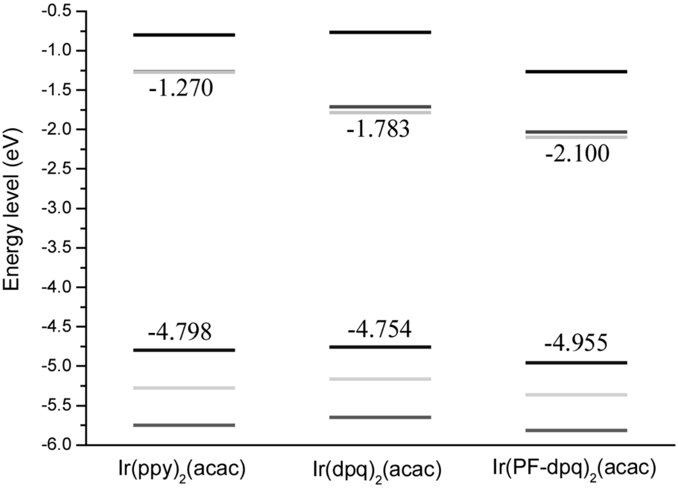


FIGURE 2 HOMO and LUMO energy levels of Ir(ppy)$_2$(acac), Ir(dpq)$_2$(acac) and Ir(PF-dpq)$_2$(acac).

electron withdrawing group strongly affected the LUMO while the substituent effect on the HOMO is small. Thus, the LUMO level of Ir(PF-dpq)$_2$(acac) is effectively decreased by perfluorophenyl substituent more than HOMO level. As a result, the energy gap is reduced, leading to red-shift the emission wavelength. The ab initio calculation using the time-dependent density function theory (DFT) showed in agreement with the experimental results.

The absorption data of Ir(dpq)$_2$(acac) and Ir(PF-dpq)$_2$(acac) in CH_2Cl_2 are shown in Figure 3. The absorption peaks for Ir(PF-dpq)$_2$ (acac) appeared at 440, 490, 528 and 570 nm, respectively. The absorption band below 380 nm can be assigned to the spin-allowed $^1\pi$-π^* transition and the band around 440 nm is a spin-allowed ^{1}MLCT band and the weak bands at long wavelength are associated with both spin-orbit coupling enhanced ^{3}MLCT transition. Strong spin-orbit coupling by the iridium center makes the formally spin-forbidden ^{3}MLCT intensity comparable to the allowed ^{1}MLCT one. The overall profile of absorption spectrum and the peak position of the MLCT absorption of the Ir(PF-dpq)$_2$(acac) are a little shift to long wavelength to those of Ir (dpq)$_2$(acac) by perfluorophenyl ring [17,18].

The PL spectra of the complexes are shown in Figure 4. The emissions of Ir(dpq)$_2$(acac) and Ir(PF-dpq)$_2$(acac) in CH_2Cl_2 exhibit a red color at 600 nm and 621 nm, respectively. Ir(PF-dpq)$_2$(acac) shows bathochromic shifted emission band about 21 nm compared to

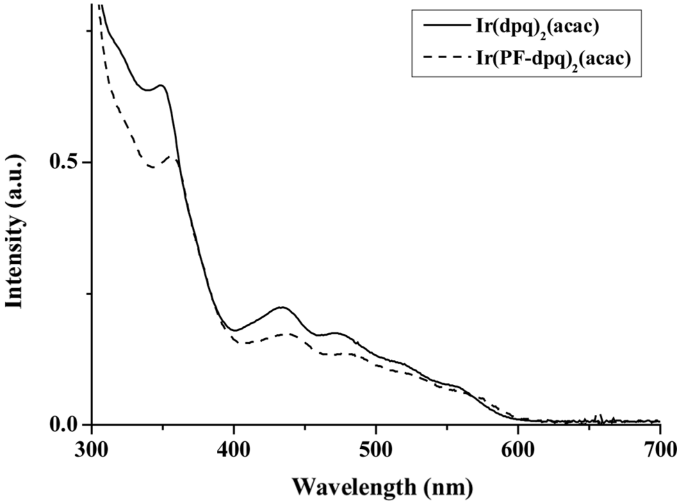


FIGURE 3 UV-vis absorption spectra of Ir(dpq)$_2$(acac) and Ir(PF-dpq)$_2$(acac) in 10^{-5} M CH_2Cl_2 solution at room temperature.

Ir(dpq)$_2$(acac). It is because the energy gap of ligands decreases since the LUMO level decreases due to the withdrawing group like perfluorophenyl ring.

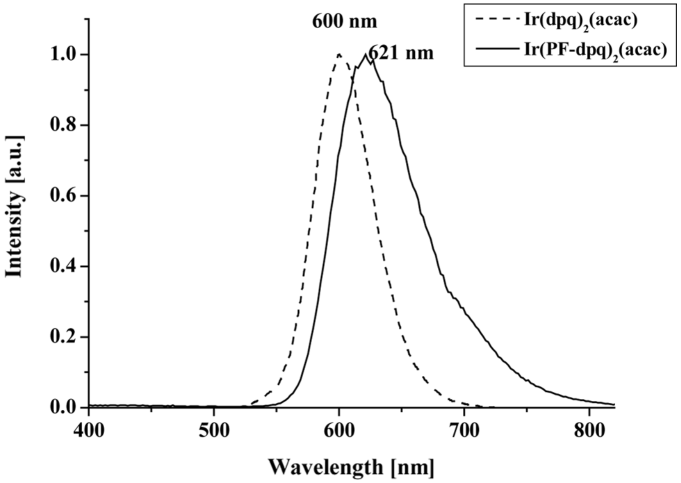


FIGURE 4 PL spectra of Ir(dpq)$_2$(acac) and Ir(PF-dpq)$_2$(acac) in 10^{-5} M CH_2Cl_2 solution.

Figure 5 shows the EL spectra of devices at 12 V. The EL spectra of devices with $Ir(dpq)_2(acac)$ and $Ir(PF\text{-}dpq)_2(acac)$ exhibit at 614 nm and 620 nm, respectively, and the main EL peaks of the devices didn't change with the various applied voltage from 4 V to 14 V. Those Commission Internationale de L'Eclairage (CIE) chromaticity coordinates are (0.629, 0.360) and (0.640, 0.342) at 12 V, respectively.

The luminance of device based on $Ir(dpq)_2(acac)$ and $Ir(PF\text{-}dpq)_2$ (acac) is 8710 cd/m^2 (405 mA/cm^2) and 3240 cd/m^2 (378 mA/cm^2), respectively, as shown in Figure 6. The luminous efficiencies of compounds with respect to current density are shown in Figure 7. The maximum efficiency of the device containing $Ir(dpq)_2(acac)$ and $Ir(PF\text{-}dpq)_2(acac)$ are 4.36 cd/A and 3.13 cd/A, respectively, at the current density of 3.38 mA/cm^2 and 1.11 mA/cm^2.

We have designed and synthesized $Ir(PF\text{-}dpq)_2(acac)$ in order to increase EL efficiency. Because the bulky pentafluorophenyl substituent reduces the intermolecular interaction of the complexes, it can improve the EL efficiency by suppressing the triplet-triplet annihilation. Also, C–F bond lower the vibrational frequency, it can alter the molecular packing and minimize the self-quenching behavior [19]. Furthermore, they can enhance the electron mobility of the compound [20]. However, the luminance and luminous efficiency for device with $Ir(PF\text{-}dpq)_2(acac)$ were against our expectation. It is because the

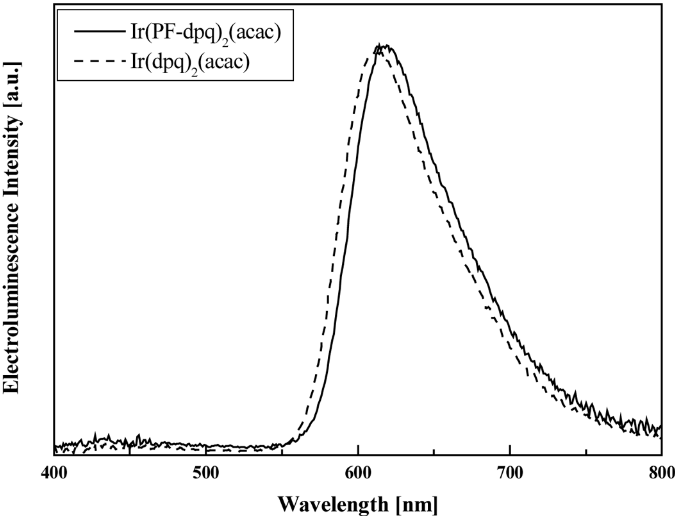


FIGURE 5 EL spectra of the devices fabricated in this study at an applied voltage of 12 V.

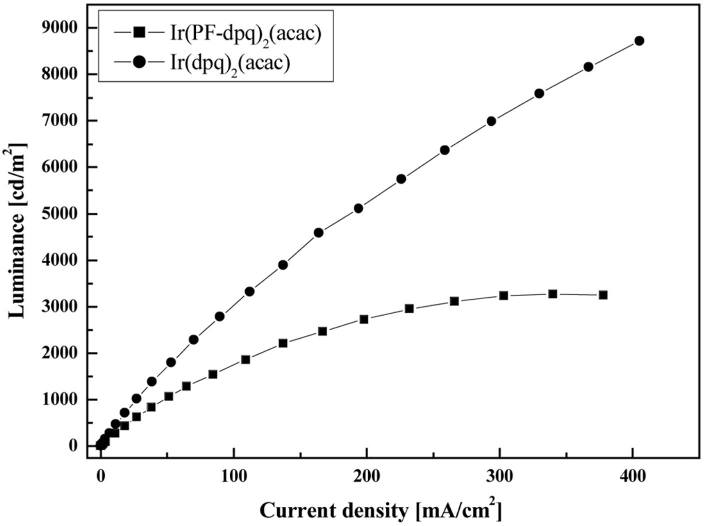


FIGURE 6 The luminance characteristics of the devices fabricated in this study with the applied current densities.

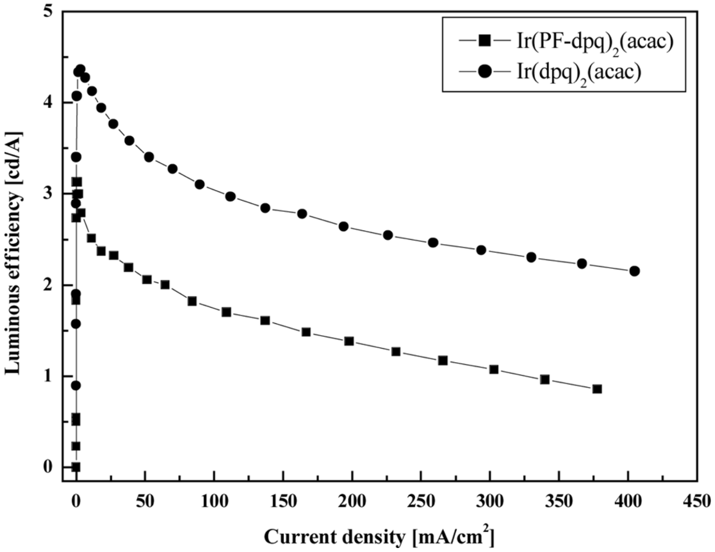


FIGURE 7 The luminous efficiencies of the devices with the applied current densities.

substituent effect on the HOMO decreased the MLCT characteristics. When PF-dpq ligand combines with an iridium ion, the t_{2g} orbital of the iridium atom has a weak coupling with the π orbital of PF-dpq ligand because their energy levels are not close to each other. The HOMO level of Ir(PF-dpq)$_2$(acac) is decreased by perfluorophenyl substituent compared to Ir(ppy)$_2$(acac) and Ir(dpq)$_2$(acac) as shown in Figure 2. For the deep red phosphorescent with high EL efficiency, it need a further study to find a proper substituent which decrease the energy gap as well as increase the MLCT characteristics.

4. CONCLUSION

To enforce a red shift and improve the luminous efficiency of Ir(III) complexes, Ir(PF-dpq)$_2$(acac) is newly proposed in this article by introducing pentafluorophenyl substituent into the position of the quinoline ring of the piq ligand. The pentafluorophenyl substituent reduces the energy gap between HOMO and LUMO by withdrawing the LUMO energy level due to the electronic withdrawing nature of the substituent. Therefore the EL wavelength of Ir(PF-dpq)$_2$(acac) showed more red region at 620 nm with CIE (0.640, 0.342), compared to Ir(dpq)$_2$(acac) at 614 nm. However, the characteristic of device containing Ir(PF-dpq)$_2$(acac) has a rather poor luminous efficiency and luminance because of the weak coupling between the t_{2g} orbital of the iridium atom and the π orbital of PF-dpq ligand.

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