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Syntheses, Photoluminescence, and Electroluminescence of Iridium(III) Complexes with Fluorinated 2-Phenylpyridine as Main Ligands and Tertraphenylimidodiphosphinate as Ancillary Ligand

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Three green-emitting heteroleptic iridium complexes with 2-(4,5,6-trifluorophenyl)pyridine, 2-(3,4,6-trifluorophenyl)pyridine, and 2-(3,4,5-trifluorophenyl)pyridine as main ligands and tetraphenylimidodiphosphinate (tpip) as the ancillary ligand were synthesized and characterized. The positions of the three fluorine atoms on the phenyl ring affect the emission properties of the complexes, and the application of Htpip as the ancillary ligand improves the electron mobility of the complexes to make it comparable to that of the popular electron transport material tris(8-hydroxyquinolinato)aluminium (Alq₃) under the same electric fields. The organic light-emitting diodes (OLEDs) based on the above phosphorescent emitters {indium tin oxide (ITO)/1,1-bis[4-(di-p-tolyl-amino)phenyl]cyclohexane (TAPC), 30 nm/Ir complex (x wt.-%)/ N,N'-dicarbazolyl-3,5-benzene (mCP), 15 nm/1,3,5-tri(1-

phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenyl (TPBi), 45 nm/LiF (1 nm)/Al (100 nm)} exhibited good performances. The device doped with bis[2-(3,4,6-trifluorophenyl)pyridine](tetraphenylimidodiphosphinato)iridium [Ir(F_{3,4,6}ppy)₂(tpip)] (8 wt.-%) showed superior performance with a peak current efficiency (η_c) of 66.36 cd A⁻¹ and a peak external quantum efficiency (η_{ext} , EQE) of 25.7% at 5.8 V, a maximum power efficiency (η_p) of 48.20 lm W⁻¹ at 4.4 V, and a maximum luminance (L_{max}) of 47627 cd m⁻² at 12.6 V. Notably, the electroluminescence (EL) efficiency roll-off effects at relatively high current density in all devices are very mild, which helps them to obtain high efficiency at brightness. The results suggest that the three complexes, [Ir(F_{3,4,6}ppy)₂(tpip)] especially, would have potential applications in OLEDs.

Introduction

In recent decades, organic light-emitting diodes (OLEDs) have evolved because of their low power consumption and the possibility to fabricate large and brilliant flat panel displays at moderate prices, illuminating wallpapers, and microdisplays for all types of applications.^[1] As the emitters, phosphorescent Ir^{III} complexes play an important part in the fabrication of efficient OLEDs owing to their high quantum efficiency and the short lifetimes of their triplet

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excited states.^[2] These Ir^{III} complexes have very strong spin–orbit coupling, which introduces intersystem crossing to mix the singlet and triplet exited states and changes the spin-forbidden radiative relaxation from the triplet exited state to be allowed. As a result, both singlet and triplet excitons can be harvested for light emission, and the internal quantum efficiency of the Ir^{III} complexes can theoretically achieve 100%.

In particular, Ir^{III} complexes based on 2-phenylpyridine (ppy) derivatives have drawn much more attention because they emit red, green, and blue light, which can be tuned by modifying the ppy main ligands as well as by introducing diverse ancillary ligands.^[3] Different substituents at the different positions of the ppy ring in these Ir^{III} complexes will result in various spectral characteristics. For example, Ir^{III} complexes that carry fluorinated phenylpyridine ligands were reported to have good performances,^[4] which suggests that the introduction of the electron-withdrawing groups improves the performance of OLEDs; the conversion of the C–H bonds in these complexes to C–F bonds may have sev-

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eral potential benefits, such as reduction of irradiative exciton decay, enhancement of photoluminescence (PL) efficiency, and electron mobility.^[5] In 2010, Chi and Chou gave a critical review on advanced methodologies for the systematic preparation of Ir^{III}-based phosphors that show latent applications in the field of OLEDs.^[6] In 2006, Naso and De Cola reported the synthesis and performance of OLEDs of blue homoleptic $[Ir(F_nppy)_3]$ and heteroleptic $[(F_nppy)_2-$ Ir(acac)] complexes $[n = 3, F_3ppy = 2-(3,4,6-trifluoro$ phenyl)pyridine; n = 4, $F_4ppy = 2-(3,4,5,6-tetrafluoro$ phenyl)pyridine; acac = acetylacetonate].^[5d] Tao and Lee also reported highly efficient blue and white phosphorescent OLEDs based on an iridium complex with 2-(3,4,5trifluorophenyl)pyridine and 2-(4,5,6-trifluorophenyl)pyridine as main ligands and 2-picolinic acid (pic) as ancillary ligand.^[5j,5k] As the electron effects are believed to be one of the ways to finely tune the color of the emission of Ir^{III} complexes, the position and number of the fluorine atoms substituted at the phenyl ring will mainly affect the emitting properties of Ir^{III} complexes.^[5j,5k] Indeed, these complexes were expected to show a shift of the emission to higher frequency, owing to the presence of electron-withdrawing fluorine substituents on the chelating ligands, which should decrease the energy of the highest occupied molecular orbital (HOMO) and, as a consequence, increase the HOMO-LUMO (lowest unoccupied molecular orbital) energy gap.

In addition, in most mixed-ligand iridium complexes [Ir(CN)₂(LX)], density functional theory calculations indicate that the HOMO is largely metal-centered, whereas the LUMO is primarily localized on the heterocyclic rings of the cyclometalated ligands. Though the ancillary ligand is not directly involved in the lowest excited state, it can alter the energy of the excited state by modifying the electron density at the metal center^[7] and affect the carrier mobility of the complexes.^[8] Thus, the photophysical, electrochemical, and electroluminescent properties of IrIII complexes can be tuned through controlled functionalization of both the cyclometalated and ancillary ligands. Our group has reported highly efficient green and blue-green phosphorescent OLEDs with tetraphenylimidodiphosphinate (tpip) derivatives as an ancillary ligand.^[8] Compared with the popular acac ligand, Htpip has more polar P=O bonds and four bulky aromatic groups, which may improve the electron mobility and lead to larger spatial separation of neighboring molecules of the Ir^{III} complex to suppress triplet-triplet annihilation (TTA) and triplet-polaron quenching (TPQ) effectively.^[8b] The performances of the devices suggest that Htpip is a useful ancillary ligand for Ir^{III} complexes and benefits OLED performances.^[8] To investigate the effects of the positions of the three fluorine atoms of the phenyl ring of ppy in Ir^{III} complexes on their OLED performance and explore the application of Htpip ligands, we synthesized three bis-cyclometalated Ir^{III} complexes, namely, $[Ir(F_{4.5.6}ppy)_2(tpip)]$ $[F_{4.5.6}ppy = 2-(4,5,6-trifluorophenyl)$ pyridine], $[Ir(F_{3,4,6}ppy)_2(tpip)]$ $[F_{3,4,6}ppy = 2-(3,4,6-tri$ fluorophenyl)pyridine], and [Ir(F_{3,4,5}ppy)₂(tpip)] [F_{3,4,5}ppy = 2-(3,4,5-trifluorophenyl)pyridine], and investigated their **OLED** characteristics.

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Results and Discussion

Single-Crystal Analysis and Thermal Properties

The single-crystal structures of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$ are shown in



Figure 1. ORTEP diagrams of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$.^[9–11] Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

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Figure 1, the corresponding crystallographic data are summarized in Table 3, and selected bond lengths and angles are listed in Tables S1-3. Despite the similarity of the structures of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and [Ir(F_{3,4,5}ppy)₂(tpip)], they crystallize in different space groups. $[Ir(F_{4,5,6}ppy)_2(tpip)]$ and $[Ir(F_{3,4,6}ppy)_2(tpip)]$ belong to the triclinic space group $P2_1/n$, but $[Ir(F_{3,4,5}ppy)_2-$ (tpip)] belongs to the orthorhombic space group $P2_1/c$. The different space groups of the above complexes indicate that the crystal packing is sensitive to the position of the three fluorine atoms in the phenyl ring. For [Ir(F_{4,5,6}ppy)₂(tpip)] and [Ir(F_{3,4,5}ppy)₂(tpip)], the iridium center adopts a distorted octahedral coordination geometry with two CN cyclometalated ligands and an Htpip ancillary ligand (cis-C,C and *trans*-N,N disposition). For [Ir(F_{3,4,6}ppy)₂(tpip)], the geometry of the iridium center is octahedral. The average Ir-C, Ir-N, and Ir-O bond lengths are in agreement with the corresponding parameters described for other simi-

The thermal properties of these iridium complexes were characterized by thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis under a nitrogen stream (Figure S4). The TG-DSC data reveal that all of the complexes have good thermal stability, and the initial decomposition temperatures are in the range 390–404 °C. Furthermore, all of the complexes can be vacuum evaporated easily without degradation and show good film-forming ability, which indicates that the complexes are potential emitting materials for the fabrication of stable OLEDs.

larly constituted complexes (Tables S1–3).

Photophysical Properties

The absorption spectra of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, [Ir(F_{3,4,6}ppy)₂(tpip)], and [Ir(F_{3,4,5}ppy)₂(tpip)] in CH₂Cl₂ were recorded at room temperature (Figure 2, a). Like other phenylpyridine-type heteroleptic iridium complexes, all of these complexes exhibit two major absorption regions. The intense bands at high energy (<340 nm), which resemble the spectra of the free ligands, are assigned to the spinallowed ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions localized on ppy. The relatively weak absorption bands in the range 340-450 nm are attributed to the mixing of ¹MLCT and ³MLCT (metal-to-ligand charge-transfer) states or ligand-to-ligand charge-transfer (LLCT) transitions through strong spin-orbit coupling of iridium atoms (Figure 2, b).^[12] The absorption bands and molar extinction coefficients are listed in Table 1.

At room temperature, all of the complexes in deaerated CH_2Cl_2 solutions show broad emission spectra with maxima in the range 497–513 nm. The emission peaks are slightly different to those of the reported complexes based on 2-(trifluorophenyl)pyridine as main ligands and pic or acac as the ancillary ligands.^[5d,5j,5k] For example, the emission peaks of [Ir(F_{4,5,6}ppy)₂(tpip)] and [Ir(F_{3,4,5}ppy)₂(tpip)] are 499 and 496/526 nm, but [Ir(F_{4,5,6}ppy)₂(pic)] and [Ir(F_{3,4,5}ppy)₂(pic)] emit at 483 and 479/509 nm, respectively. Although tpip has a similar structure to that of acac,



Figure 2. (a) UV/Vis absorption spectra of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$ in degassed CH₂Cl₂, (b) room-temperature and low-temperature (77 K) emission spectra (inset) of complexes in degassed CH₂Cl₂, (c) room-temperature emission spectra of mCP films doped with the complexes.

[Ir(F_{3,4,6}ppy)₂(tpip)] has two emission peaks at 475 and 501 nm, but the emission peaks of [Ir(F_{3,4,6}ppy)₂(acac)] are at 465 and 493 nm, respectively. These results suggest that the ancillary ligands can affect the emission properties of iridium complexes. In general, the emission bands from MLCT states are broad and featureless, whereas a highly structured emission band mainly originates from the ${}^{3}\pi$ - π * state. Accordingly, all of the complexes emit from a mixture of MLCT states and the dominant ligand-based ${}^{3}\pi$ - π * state. Of the three complexes, [Ir(F_{3,4,6}ppy)₂(tpip)] exhibited the broadest spectrum and the highest intensity at the same concentration (10⁻⁵ M). The emission quantum efficiency yields of the three complexes are 28, 13, and 21%, respec-

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Table 1. Thermal, photophysical, electrochemical, and electron mobility data for $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$.

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	$T_{\rm m}/T_{\rm d}^{[\rm a]}$ [°C]	Absorption ^[b] λ [nm] (log ε [M ⁻¹ cm ⁻¹])	$\lambda_{\rm em}^{\rm [c]}$ [nm]	$ au_{\mathrm{p}}^{\mathrm{[d]}}$ [µs]	$arPsi_{ m p}^{[e]}$ [%]	HOMO/LUMO ^[f] [eV]	$\mu_{\rm e}^{\rm [g]} [10^{-6} {\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1}]$
[Ir(F _{4,5,6} ppy) ₂ (tpip)]	304/390	252 (4.14), 298 (3.78), 388 (3.07)	499 (494/525)	2.19 (2.08)	28	-5.59/-3.08	5.00
[Ir(F _{3,4,6} ppy) ₂ (tpip)]	313/404	250 (4.26), 304 (3.88), 379 (3.12)	475/501 (468/500)	2.40 (2.59)	13	-5.70/-2.92	4.61
[Ir(F _{3,4,5} ppy) ₂ (tpip)]	334/391	293 (3.91), 388 (3.19)	496/526 (492/526)	2.52 (2.23)	21	-5.58/-3.05	5.45

[a] $T_{\rm m}$: melting temperature, $T_{\rm d}$: decomposition temperature. [b] Recorded with the complexes in degassed CH₂Cl₂ at room temperature at a concentration of 10⁻⁵ M. [c] Recorded with the complexes in degassed CH₂Cl₂ at a concentration of 10⁻⁵ M at room temperature; the values in parentheses were measured at 77 K. [d] Recorded with the complexes in degassed CH₂Cl₂ at a concentration of 10⁻⁵ M; the values in parentheses are for the solid complexes at room temperature. [e] Φ : emission quantum efficiency yield referenced to *fac*-[Ir(ppy) ₃] ($\Phi_{\rm p} = 0.4$), $\lambda_{\rm exc} = 400$ nm. [f] HOMO/LUMO energy level values calculated based on the cyclovoltammety (CV) diagram with ferrocene as the internal standard and the UV/Vis spectra in degassed CH₂Cl₂. [g] Electron mobility ($\mu_{\rm e}$) values under an electric field of 1300 (V/ cm)^{1/2}.

tively. Compared with [Ir(dfppy)₂(tpip)] [dfppy = 2-(4,6-difluorophenyl)pyridine, $\Phi_p = 4\%$],^[8a] the introduction of more fluorine substituents results in an increase of the phosphorescence quantum yield. There are reports that the replacement of C–H bonds with C–F bonds can bring about a lower vibrational frequency, which leads to an improved PL efficiency.^[4] As *N*,*N'*-dicarbazolyl-3,5-benzene (mCP) is a popular host material in OLEDs, the PL properties of mCP films doped with the three complexes were also investigated. From Figure 2c, it can be seen that all the peaks are similar to those of the Ir^{III} complexes in CH₂Cl₂. The absence of mCP emission suggests a complete energy transfer from the mCP host to the iridium complexes excited by photons. In addition, the [Ir(F_{3,4,6}ppy)₂(tpip)]doped mCP film also shows the highest emission intensity of all the films.

As shown in Figure 2b (inset), the structured emission at 77 K reveals that the mixing between the ³MLCT and the ³LC levels is so effective that an almost ligand-centered emission is observed upon freezing of the matrix. The rigidity of the solvent dramatically affects the stabilization of the charge-transfer states, which shift to higher energy at low temperature, and the electronic mixing of the two states decreases. The rigidochromic effect on some transition metal complexes has been reported.^[13] Owing to the low viscosity of the medium at room temperature, the solvent molecules in the vicinity of the excited-state molecule readily undergo reorientation by dipole-dipole interactions within the lifetime of the excited state, which results in the formation of the fully relaxed excited state. Thus, the room-temperature emission occurs from the fully relaxed excited state. On the other hand, the excited state at 77 K emits before the solvent relaxation occurs, which results in the rigidochromic effects on the emission spectra. Notably, [Ir(F_{3,4,6}ppy)₂-(tpip)] shows green-blue emission with a maximum peak at 468 nm with a blueshift as large as 26 nm relative to the other two complexes.

The phosphorescence lifetime (τ_p) is the crucial factor that determines the rate of triplet-triplet annihilation in OLEDs. Longer τ_p values usually cause greater triplet-triplet annihilation.^[14] The lifetimes of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$ are in the range of microseconds $(2.19-2.52 \,\mu\text{s} \text{ in } \text{CH}_2\text{Cl}_2 \text{ solution}$ and 2.08–2.59 μs in the solid state) at room temperature (Table 1, Figure S5 and S6) and are indicative of the phosphorescent origin for the excited states in each case.

Electrochemistry and Theoretical Calculations

To calculate the HOMO and LUMO energy levels of the present heteroleptic iridium complexes, their electrochemical behaviors were investigated by cyclic voltammetry with ferrocene as the internal standard (Figure 3). During the anodic scan, all of the complexes show reversible Ir^{III}/Ir^{IV} oxidation couples with redox potentials in the region 0.50-1.30 V, which are in accordance with those of previously reported cyclometalated Ir^{III} systems.^[14] The HOMO levels were calculated from the oxidation potentials, and the LUMO levels were obtained from the HOMO data and the band gap (E_g) obtained from the UV/Vis spectra. The HOMO/LUMO energy levels of [Ir(F_{4,5,6}ppy)₂(tpip)], $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$ can be estimated as -5.59/-3.08, -5.70/-2.92, and -5.58/-3.05 eV, respectively (Table 1), from the empirical formulas E_{HOMO} $= -e(E_{\text{ox}} + 4.4)$ and $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$.^[15] Among the complexes, [Ir(F_{3,4.6}ppy)₂(tpip)] shows the lowest HOMO level and the highest LUMO level, in agreement with the



Figure 3. Cyclic voltammograms of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$.

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spectroscopic data. The obvious difference between $[Ir(F_{3,4,6}ppy)_2(tpip)]$ and other two complexes confirms the effects of the position of the fluorine atoms on the phenyl rings.

Density functional theory calculations for [Ir(F_{4.5.6}ppy)₂-(tpip)], $[Ir(F_{3,4.6}ppy)_2(tpip)]$, and $[Ir(F_{3,4.5}ppy)_2(tpip)]$ were conducted to gain insights into the electronic states and the orbital distribution by employing the Gaussian09 software. The effects of substitution on the relative energies of the HOMO and LUMO levels and selected molecular orbitals (MOs) of the complexes are shown in Figure 4. The HOMOs of the three complexes involve contributions from Ir d orbitals (50.43–53.86%) and from a π orbital localized on the fluorine-substituted ppy ligand (39.65-43.71%). Meanwhile, the LUMO is largely dominated by the π^* orbitals of the fluorine-substituted ppy ligand, together with small contributions from Ir and tpip orbitals (Table S4). Therefore, modification of the phenyl ring changes the energy of both the HOMO and the LUMO. The close similarity between the calculated and experimental values reveals the reliability of our computation.



Figure 4. Isodensity plots of the HOMOs and LUMOs for $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$.

Notably, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, which has the lowest HOMO and the highest LUMO, exhibits the largest energy gap compared with the other two complexes. The difference can be attributed to the replacement of a C–H bond with a C–F bond at the 5'-position of ppy, which shows more obvious electron-withdrawing effect than the other substituent positions. Thus, in $[Ir(F_{3,4,6}ppy)_2(tpip)]$, the electron density on the Ir atom decreases and the HOMO level is stabilized. The consistent tendency and small difference (0.14–0.17 eV) between the calculation values and the experimental data reveal the reliability of our theoretical study.

Electron Mobility

As the hole mobility is roughly 2–3 orders of magnitude higher than the electron mobility in OLEDs,^[16] their exci-

tation lifetime relies on the electron transport capability. To obtain phosphorescent OLEDs with low efficiency roll-off, it is necessary to synthesize phosphorescent molecular materials with outstanding electron mobility. As discussed before, compared with the popular acac ligand, Htpip has more polar P=O bonds and four bulky aromatic groups, which may improve the electron mobility and suppress the TTA and TPQ effects effectively.^[8b]

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The electron mobility (μ_e) values of the iridium complexes were determined by the transient electroluminescence (EL) method based on indium tin oxide (ITO)/ 1,1-bis[4-(di-p-tolyl-amino)phenyl]cyclohexane (TAPC, 50 nm)/Ir complex (60 nm)/LiF (1 nm)/A1 (100 nm) with short and rectangular driving voltage pulses.^[8b,17] In transient EL measurements, the time-dependent EL response is monitored upon excitation of the devices with a rectangular voltage pulse. A finite delay time (t_d) , which is between the application of a voltage pulse and the onset of the EL signal, is determined by the arrival of the slower charge carrier of the injected carriers at the emission zone.^[17,18] As shown in Figures 5 and S7, after the t_d , the EL signals gradually rise before reaching the saturated EL intensities. With increasing applied voltage amplitudes from 8 to 10 V, the t_d values decrease. The electron mobility data can be roughly calculated with the equation $\mu_e = d^2/(t_d V)$, in which d is the thickness of the emitting layer, and V is the driving voltage. For [Ir($F_{3,4,6}$ ppy)₂(tpip)], t_d decreased from 1.32 to 0.78 µs, accompanied by a voltage rise from 8 to 10 V. The experimental results show that the electron mobility values in a 30 nm $[Ir(F_{3,4,6}ppy)_2(tpip)]$ layer are $3.41-4.61 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under electric fields from 1150 to 1300 (V/cm)^{1/2}, comparable to that of the popular electron transport material Alq_3 under the same electric fields (4.74 - $4.86 \times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[8b] In addition, [Ir(F_{4,5,6}ppy)₂(tpip)] and [Ir(F_{3,4,5}ppy)₂(tpip)] also have similar electron mobility values to that of [Ir(F_{3,4,6}ppy)₂(tpip)] (Table 1, Figure S7). The good electron transport ability of these complexes facilitates the injection and transport of electrons, which broadens the recombination zone and balances the distribution of holes and electrons, particularly for high doping concentrations, and leads to improved recombination probability and suppressed TTA and TPQ.^[19] Therefore, efficient



Figure 5. Transient EL signals as a function of electrical field for the device based on $[Ir(F_{3,4,6}ppy)_2(tpip)]$.

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OLEDs with suppressed efficiency roll-off are expected at relatively low voltage.

Electroluminescence Devices

The electroluminescence properties of [Ir(F_{4.5.6}ppy)₂-(tpip)], $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$ were investigated in devices comprising ITO/TAPC (30 nm)/Ir complex (x wt.-%):mCP ((15 nm)/1,3,5-tri(1-phenyl-1Hbenzo[d]imidazol-2-yl)phenyl (TPBi, 45 nm)/LiF (1 nm)/Al (100 nm). The energy diagrams of the devices and the molecular structures of the materials used are shown in Figure 6. Clearly, the HOMO and LUMO levels of [Ir(F_{3,4,6}ppy)₂(tpip)], and $[Ir(F_{4,5,6}ppy)_2(tpip)],$ [Ir(F_{3,4,5}ppy)₂(tpip)] are all within the HOMO and LUMO levels of the host material mCP. Therefore, a good carrier trapping is expected in these devices, and this is the dominated EL mechanism. Furthermore, holes and electrons will be well confined within the doped light-emitting layer.



Figure 6. Device structures and energy level diagrams of HOMO and LUMO levels (relative to vacuum level) for materials used in device fabrication.

To optimize the device efficiency, concentration-dependence experiments were performed in the range 6–10 wt.-% to give green-emitting OLEDs named as AG1 (x = 6 wt.-%), AG2 (8 wt.-%), and AG3 (10 wt.-%) for [Ir(F_{4.5.6}ppy)₂- (tpip)], BG1 (x = 6 wt.-%), BG2 (8 wt.-%), and BG3 (10 wt.-%) for $[Ir(F_{3,4,6}ppy)_2(tpip)]$, CG1 (x = 6 wt.-%), CG2 (8 wt.-%), and CG3 (10 wt.-%) for [Ir(F_{3.4.5}ppy)₂-(tpip)]. The key performance parameters of the devices with different dopants and concentrations are listed in Table 2. With $[Ir(F_{4,5,6}ppy)_2(tpip)]$ and $[Ir(F_{3,4,6}ppy)_2(tpip)]$ as the emitters, the devices with 8 wt.-% doped concentration (AG2 and BG2) showed superior device efficiencies than those with other doping concentrations. However, for $[Ir(F_{3,4.5}ppy)_2(tpip)]$, the device (CG1) with 6 wt.-% doped concentration exhibited the best device efficiency. Figure 7 shows the EL spectra, current and power efficiency vs. current density (η_c -J and η_p -J) curves, and current densityvoltage and luminance-voltage (J-V and L-V) characteristics for devices AG2, BG2, and CG1. All the devices have turn-on voltages ($V_{turn-on}$) below 3.5 V, and the maximum emission peaks for [Ir(F_{4,5,6}ppy)₂(tpip)], [Ir(F_{3,4,6}ppy)₂-(tpip)], and [Ir(F_{3,4,5}ppy)₂(tpip)] devices are located at 497, 497, and 495 nm, respectively. The Commission Internationale de l'Eclairage (CIE) color coordinates are x = 0.17, y = 0.60 for AG2, x = 0.17, y = 0.50 for BG2, and x = 0.17, y = 0.57 for CG1. The similarity of the EL and PL emission spectra indicates that the EL is caused by emission from the triplet excited states of the iridium complexes. The absence of residual emission from mCP suggests a complete energy transfer from the mCP host to the iridium complexes in these devices.

For the $[Ir(F_{4,5,6}ppy)_2(tpip)]$ -based devices, AG2 showed a peak current efficiency of 43.95 cd A⁻¹, an external quantum efficiency (η_{ext} , EQE) of 15.1% at 5.1 V, and a maximum power efficiency of $28.51 \text{ lm } \text{W}^{-1}$ at 4.6 V. The peak η_{ext} was obtained from the current efficiency, EL spectrum, and the human photopic sensitivity. Of all six devices, AG3 has the maximum luminance (L_{max}) of 57193 cd m⁻² at 9.2 V. [Ir(F_{3,4,6}ppy)₂(tpip)]-based BG2 exhibited the best efficiency: a peak current efficiency of 66.36 cd A⁻¹ and external efficiency of 25.7% at 5.8 V, a power efficiency (η_p) of 48.20 lm W⁻¹ at 4.4 V, and a maximum luminance of 47627 cd m⁻² at 12.6 V. Perhaps the broad emission spectrum and the high intensity of the $[Ir(F_{3,4,6}ppy)_2(tpip)]$ doped mCP film combine to improve the efficiency of the devices. The devices with [Ir(F_{3,4.5}ppy)₂(tpip)] as the emitter showed relatively poor performances with a maximum current efficiency of 37.36 cd A⁻¹ and external efficiency of

Table 2. Device performances of [Ir(F_{4,5,6}ppy)₂(tpip)], [Ir(F_{3,4,6}ppy)₂(tpip)], and [Ir(F_{3,4,5}ppy)₂(tpip)] doped OLEDs.

Device	V _{turn-on} [V]	$L_{\rm max}^{[a]} [{\rm cd} {\rm m}^{-2}]$	$\eta_{c,max}^{[a]} [cd A^{-1}] (V)$	$\eta_{\rm p,max}{}^{[a]} [{\rm lm} {\rm W}^{-1}] ({\rm V})$	$\eta_{\rm ext,max}^{[a]} [\%]$	$\lambda_{\max}^{[b]}$ [nm]
AG1	3.3	55826	43.62 (5.3)	26.29 (5.4)	15.0	
AG2	3.3	38827	43.95 (5.1)	28.51 (4.6)	15.1	497 (0.17, 0.60)
AG3	3.2	57193	24.46 (5.4)	15.44 (4.7)	8.4	
BG1	3.3	40028	36.43 (5.2)	23.94 (4.5)	14.1	
BG2	3.3	47627	66.36 (5.8)	48.20 (4.4)	25.7	497 (0.17, 0.50)
BG3	3.3	32533	36.58 (6.7)	20.03 (5.5)	13.9	
CG1	3.2	40319	37.36 (6.5)	19.11 (5.1)	12.8	495 (0.17, 0.57)
CG2	3.2	34276	34.83 (6.5)	17.78 (5.7)	12.1	
CG3	3.4	31250	32.97 (6.4)	18.11 (5.8)	11.5	

[a] Maximum values of the devices; the values in parentheses are the corresponding driving voltages. [b] Values were collected at 8 V, and CIE coordinates (x, y) are shown in parentheses.

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Figure 7. Charts for the three devices AG2, BG2, and CG1 doped with [Ir(F_{4,5,6}ppy)₂(tpip)], [Ir(F_{3,4,6}ppy)₂(tpip)], and [Ir(F_{3,4,5}ppy)₂-(tpip)], respectively. (a) Normalized EL spectra, (b) current efficiency as a function of current density, (c) power efficiency as a function of current density, and (d) current density-voltage and luminance-voltage curves.

12.8% at 6.5 V, a maximum power efficiency of 19.11 lm W⁻¹ at 5.1 V, and a maximum brightness of 40319 cd m⁻² at 12.7 V. The results show that the positions of the three F atoms on the phenyl ring can influence both the PL properties and EL performances of the IrIII complexes.

Notably, the EL efficiency roll-off effects at relatively high current density in these devices are very mild. For BG2, the η_c values at practical luminances of 100 and 1000 cd m⁻² are 67.55 and 64.37 cd A⁻¹, respectively, which help to obtain the high efficiency and brightness. This mild roll-off should be attributed to fluorination of the ppy ligand and the application of Htpip as the ancillary ligand, which can decrease self-quenching and improve the holeelectron balance in charge injection. Good electron mobility of the phosphorescent emitters would facilitate the injection and transport of electrons and, therefore, broaden the recombination zone and balance the distribution of holes and electrons, particularly at high doping concentrations; this leads to suppressed TTA and TPQ and improved recombination probability, high device efficiency, and low efficiency roll-off effect.[19,20]

Conclusions

Three heteroleptic iridium complexes with 2-(4,5,6-trifluorophenyl)pyridine, 2-(3,4,6-trifluorophenyl) pyridine, and 2-(3,4,5-trifluorophenyl)pyridine as the main ligands and tetraphenylimidodiphosphinate (tpip) as the ancillary ligand were synthesized. All of the complexes are green emitters ($\lambda_{max} = 496-501$ nm) with PL quantum efficiency yields of 13-28%. Electrochemistry and DFT calculation results reveal that the HOMO and LUMO levels [Ir(F_{3,4,6}ppy)₂(tpip)], of $[Ir(F_{4,5,6}ppy)_2(tpip)],$ and [Ir(F_{3,4,5}ppy)₂(tpip)] are well within the HOMO and LUMO levels of the mCP host material; therefore, good carrier trapping is expected in devices containing these complexes. Owing to the good electron mobility values of the Ir^{III} complexes, which are improved by the tpip ancillary ligand $[3.41-4.61 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under electric fields from 1150 to 1300 (V/cm)^{1/2}], all the devices show good performances. The device based on [Ir(F_{3,4,6}ppy)₂(tpip)] with 8 wt.-% concentration exhibited superior performance to the others and has a peak external quantum efficiency (η_{ext}) of 25.7%, a peak current efficiency (η_{c}) of 66.36 cd A⁻¹ at 5.8 V, and a maximum power efficiency $(\eta_{\rm p})$ of $48.20 \text{ lm } \text{W}^{-1}$ at 4.4 V. The EL efficiency roll-off effects at relatively high current density in these devices are very mild, which helps to obtain high efficiency and high brightness.

Experimental Section

General Information: All commercial chemicals were used without further purification, except for anhydrous toluene. All reactions were conducted under a nitrogen atmosphere. ¹H NMR spectra were recorded with a Bruker AM 500 spectrometer. Mass spectrometry (MS) spectra were obtained with an electrospray ioniza-

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tion (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) for ligands and a matrix-assisted laser desorption/ionization timeof-flight (MALDI-TOF) mass spectrometer (Bruker Daltonic Inc.) for complexes. Elemental analyses for C, H, and N were performed with an Elementar Vario MICRO analyzer. TG-DSC measurements were performed with a DSC 823e analyzer (Mettler). Absorption and emission spectra were measured with a Shimadzu UV-3100 spectrophotometer and a Hitachi F-4600 luminescence spectrophotometer, respectively. The quantum efficiency measurements were performed at room temperature with degassed toluene solutions and *fac*-[Ir(ppy)₃] ($\Phi_p = 0.4$) as a reference.^[21] Low-temperature (77 K) emission spectra were recorded with a Hitachi F-4600 luminescence spectrophotometer with samples in 5 mm diameter quartz tubes, which were placed in a liquid nitrogen Dewar equipped with quartz walls. Samples and standard solutions were degassed with at least three freeze-pump-thaw cycles. PL lifetime measurements were performed by using an excitation line (370 nm) of a laser delivering pulses of 25 ns time duration at 20 Hz repetition rate with an Edinburgh FSL-920 spectrophotometer. Cyclic voltammograms were recorded at a scan rate of 100 mV/s at room temperature with CH₂Cl₂ solutions under nitrogen by using a three-electrode cell equipped with a Pt disk working electrode, a Pt wire counterelectrode, and a Pt wire pseudoreference electrode with a computer-controlled IM6ex electrochemical and chemiluminescent system (Zahner); tetrabutylammonium perchlorate (nBu₄N-ClO₄, 0.1 M) was used as the supporting electrolyte. All potentials are calibrated with ferrocene in acetonitrile as a reference.

X-ray Crystallographic Analysis: Crystals of the iridium complexes were obtained by vacuum sublimation. The diffraction data were collected with a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) by using monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. The cell parameters were retrieved by using SMART software and refined by using SAINT^[22] on all observed reflections. The data were collected by using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced by using SAINT and corrected for Lorentz and polarization effects.

Absorption corrections were applied by using SADABS.^[23] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the program SHELXS-97.^[24] The positions of metal atoms and their first coordination spheres were located from direct methods; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with uniform U_{iso} values (Table 3).

Computation Study:^[13] The singlet ground-state geometry of the iridium complexes has been optimized at the density functional theory (DFT) level from the X-ray crystallographic data. B3LYP geometry optimizations were performed with the LANL2DZ basis set for Ir and the 6-31G(d) basis set for C, H, N, O, F, and P atoms. The characterization of the lowest-lying singlet and triplet excited states based on the ground-state geometry used the same functional and basis set. All the geometries were confirmed as stationary structures by the presence of only real frequencies at the same level of the theory. All calculations were performed with the Gaussian09 software.

OLED Fabrication and Measurement:^[8,14] All OLEDs with an emission area of 0.1 cm² were fabricated on prepatterned ITO-coated glass substrates with a sheet resistance of $15 \Omega \text{ sq}^{-1}$. The substrate was cleaned by ultrasound in organic solvents followed by ozone treatment for 20 min. All materials used for EL devices were sublimed in vacuo (2.2×10^{-4} Pa) prior to use. The 30 nm hole transport material of 1,1-bis[4-(di-*p*-tolyl-amino)phenyl] cyclohexane (TAPC) film was first deposited on the ITO glass substrate. The phosphor (*x* wt.-%) and host (mCP, *N*,*N*'-dicarbazolyl-3,5-benzene) were co-evaporated to form 15 nm emitting layer from two separate sources. Successively, 1,3,5-tri(1-phenyl-1*H*-benzo-

Table 3.	Crystallographic	data and structure	refinement for [Ir(F4,5,6ppy)2(tpip)], [$Ir(F_{3,4,6}ppy)_2(tpip)],$	and $[Ir(F_{3,4,5}ppy)_2(tpip)].$
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	$[Ir(F_{4,5,6}ppy)_2(tpip)]$	[Ir(F _{3,4,6} ppy) ₂ (tpip)]	[Ir(F _{3,4,5} ppy) ₂ (tpip)]	
Formula	C46H30F6IrN3O2P2	$C_{46}H_{30}F_{6}IrN_{3}O_{2}P_{2}$	$C_{46}H_{30}F_6IrN_3O_2P_2$	
FW	1024.87	1024.87	1024.87	
<i>T</i> [K]	296(2)	296(2)	296(2)	
Wavelength [Å]	0.71073	0.71073	0.71073	
Crystal system	triclinic	orthorhombic	triclinic	
Space group	$P\overline{1}$	Pbca	$P\overline{1}$	
a [Å]	10.9896(4)	20.5929(10)	10.4740(5)	
<i>b</i> [Å]	12.5364(6)	18.8926(9)	12.2002(6)	
<i>c</i> [Å]	16.0015(3)	20.9574(10)	17.6273(4)	
a [°]	90.4480(10)	90.00	105.2140(10)	
β [°]	104.177(2)	90.00	91.522(2)	
γ [°]	107.0080(10)	90.00	112.7750(10)	
V [Å ³]	2036.38(13)	8153.5(7)	1983.19(14)	
Ζ	2	8	2	
$\rho_{\text{calcd.}} [\text{g/cm}^3]$	1.665	1.670	1.710	
μ (Mo- K_{α}) [mm ⁻¹]	3.426	3.424	3.518	
<i>F</i> (000)	1004	4032	1004	
Range of transmission factors [°]	1.70-26.00	1.76-28.29	2.29-28.35	
Reflections collected	12433	10120	7774	
Unique reflections	7969	7452	6404	
GOF on F^2	1.038	1.038	1.051	
$R_1,^{[a]} w R_2^{[b]} [I > 2\sigma(I)]$	0.0520, 0.1350	0.0262, 0.0573	0.0520, 0.1261	
R_1 , ^[a] wR_2 ^[b] (all data)	0.0577, 0.1370	0.0472, 0.0669	0.0591, 0.1279	

[a] $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma F_0|$. [b] $wR_2 = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)]^{1/2}$.

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[d]imidazol-2-yl)phenyl (TPBi, 45 nm) as electron transport material, LiF (1 nm) as electron injection material, and Al (100 nm) as the cathode were evaporated. The vacuum was less than 1×10^{-5} Pa during the deposition of all materials. The current density–voltage (J-V) and luminance–voltage (L-V) characteristics, current efficiency vs. current density (η_c-J) , and power efficiency vs. current density (η_c-J) curves of the devices were measured with a computer-controlled Keithley 2400 source meter with a calibrated silicon diode in air without device encapsulation. The EL spectra were measured with a Hitachi F-4600 photoluminescence spectrophotometer. On the basis of the uncorrected PL and EL spectra, the CIE coordinates were calculated by using a test program of the Spectra Scan PR650 spectrophotometer.

Syntheses: Htpip, F-ppy ($F_{4,5,6}$ ppy, $F_{3,4,6}$ ppy, and $F_{3,4,5}$ ppy), [(F-ppy)₂Ir(μ -Cl)]₂, and [Ir(F-ppy)₂(tpip)] were obtained according to previously published literature procedures.^[8,15] The synthesis scheme is shown in Scheme 1. Purified [Ir($F_{4,5,6}$ ppy)₂(tpip)], [Ir($F_{3,4,6}$ ppy)₂(tpip)], and [Ir($F_{3,4,5}$ ppy)₂(tpip)] were obtained by vacuum-evaporation after silica column chromatography.



Scheme 1. The synthetic route for the ligands and $[Ir(F_{4.5,6}ppy)_{2^{-1}}(tpip)]$, $[Ir(F_{3,4,6}ppy)_{2}(tpip)]$, and $[Ir(F_{3,4,5}ppy)_{2}(tpip)]$. (i) Pd(PPh₃)₄, K₂CO₃, THF/H₂O, 80 °C, 24 h; (ii) IrCl₃·3H₂O, 2-EtOCH₂CH₂OH/H₂O, reflux, 24 h; (iii) toluene, 105 °C, 6 h; (iv) H₂O₂, THF; (v) KOH, methanol; (vi) 2-EtOCH₂CH₂OH, N₂, 120 °C, 24 h.

General Synthesis Procedure for F-ppy: The three ligands $[F_{4,5,6}ppy: 2-(4,5,6-trifluorophenyl)pyridine, F_{3,4,5}ppy: 2-(3,4,6-trifluorophenyl)pyridine, F_{3,4,5}ppy: 2-(3,4,5-trifluorophenyl) pyridine] were prepared in good yields through Suzuki coupling reactions. 2-Bromopyridine (2.40 mL, 25 mmol), trifluorophenyl boronic acid (5.28 g, 30 mmol), K₂CO₃ (16.56 g, 120 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.35 g, 0.3 mmol) were dissolved in a tetrahydrofuran/H₂O (THF/H₂O) mixture (80/60 mL). The solution was heated at 80 °C and monitored with TLC. The THF was removed by vacuum concentration, and then the cooled crude mixture was poured into water and extracted with CH₂Cl₂ (30 mL × 3). Finally, silica column purification (petroleum ether/EtOAc 10:1) gave a white solid.$

F_{4,5,6}ppy: Yield 78%. ¹H NMR (500 MHz, [D₆]acetone): $\delta = 8.74$ (d, J = 4.7 Hz, 1 H), 7.95 (td, J = 7.9, 1.6 Hz, 1 H), 7.92–7.82 (m, 2 H), 7.48–7.40 (m, 1 H), 7.39–7.29 (m, 1 H) ppm.

F_{3,4,6}ppy: Yield 82%. ¹H NMR (500 MHz, [D₆]acetone): $\delta = 8.74$ (d, J = 4.7 Hz, 1 H), 8.03 (ddd, J = 11.7, 9.2, 7.2 Hz, 1 H), 7.94 (td, J = 7.7, 1.7 Hz, 1 H), 7.90–7.86 (m, 1 H), 7.47–7.37 (m, 2 H) ppm.

F_{3,4,5}**ppy:** Yield 87%. ¹H NMR (500 MHz, [D₆]acetone): δ = 8.69 (d, *J* = 4.7 Hz, 1 H), 8.02 (d, *J* = 8.0 Hz, 1 H), 8.00–7.90 (m, 3 H), 7.46–7.37 (m, 1 H) ppm.

[(F-ppy)₂Ir(µ-Cl)]₂: A solution of chlorodiphenylphosphine (4.40 g, 20 mmol) and hexamethyldisilazane (1.77 g, 11 mmol) in anhydrous toluene (30 mL) was heated to reflux under nitrogen for 6 h, and then the byproducts and toluene were removed at reduced pressure. A solution of H₂O₂ (2.5 mL, 30 wt.-% in H₂O) in THF (5 mL) was added in an ice bath. The solution was stirred for 2 h and then added to diethyl ether (50 mL), whereupon a white precipitate was obtained. The solid was washed with water and recrystallized from methanol to give the desired product Htpip in 50% yield. ¹H NMR [500 MHz, (CD₃)₂SO]: δ = 7.73 (dd, *J* = 11.3, 7.8 Hz, 1 H), 7.52 (t, *J* = 7.2 Hz, 20 H), 7.44 (t, *J* = 6.6 Hz, 1 H) ppm. ³¹P NMR (500 MHz, CDCl₃): δ = 19.34 (s) ppm. ESI-MS: *mlz* = 416 [M]⁻.

To a suspension of Htpip (2.09 g, 5 mmol) in methanol (20 mL) was added a solution of KOH (2.85 g, 5.2 mmol) in methanol (5 mL), and the mixture was stirred for 2 h at room temperature. Concentration in vacuo precipitated a white solid, which was recovered by filtration and washed with diethyl ether to yield Ktpip (1.65 g, 73%).

General Synthesis of $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$: $[(F-ppy)_2Ir(\mu-Cl)]_2$ (0.2 mmol) and Ktpip (0.27 g, 0.6 mmol) in 2-EtOCH₂CH₂OH (10 mL) were heated at 120 °C for 24 h. The 2-EtOCH₂CH₂OH solvent was removed by vacuum, and the crude product was chromatographed on a silica column with an elution gradient (petroleum ether/EtOAc 10:1–7:1) to produce a brilliant yellow sample of each iridium complex. Further purification was achieved by gradient sublimation in vacuo, and yields of 28–35% were obtained.

[Ir(F_{4,5,6}ppy)₂(tpip)]: Yield 32%. ¹H NMR (500 MHz, CDCl₃): δ = 9.02 (d, *J* = 5.6 Hz, 2 H), 8.05 (d, *J* = 8.3 Hz, 2 H), 7.77 (dd, *J* = 12.3, 6.9 Hz, 4 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.44–7.30 (m, 10 H), 7.18 (t, *J* = 7.4 Hz, 2 H), 7.01 (td, *J* = 7.6, 2.8 Hz, 4 H), 6.68 (t, *J* = 6.6 Hz, 2 H), 5.66–5.42 (m, 2 H) ppm. MALDI-TOF: *m/z* = 1024.93 [M]⁺. C₄₆H₃₀F₆IrN₃O₂P₂ (1024.92): calcd. C 53.90, H 2.95, N 4.10; found C 53.86, H 2.93, N 4.12.

[Ir(F_{3,4,6}ppy)₂(tpip)]: Yield 35%. ¹H NMR (500 MHz, CDCl₃): δ = 9.02 (d, *J* = 5.5 Hz, 2 H), 8.05 (d, *J* = 8.3 Hz, 2 H), 7.77 (dd, *J* = 12.3, 6.9 Hz, 4 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 7.43–7.30 (m, 10 H), 7.18 (t, *J* = 7.4 Hz, 2 H), 7.18 (t, *J* = 7.4 Hz, 2 H), 7.18 (t, *J* = 7.4 Hz, 2 H), 7.01 (td, *J* = 7.6, 2.8 Hz, 4 H), 6.68 (t, *J* = 6.5 Hz, 2 H) ppm. MALDI-TOF: *m*/*z* = 1025.03 [M]⁺. C₄₆H₃₀F₆IrN₃O₂P₂ (1024.92): calcd. C 53.90, H 2.95, N 4.10; found C 53.70, H 2.98, N 4.05.

[Ir($F_{3,4,5}ppy$)₂(tpip)]: Yield 28%. ¹H NMR (500 MHz, CDCl₃): $\delta = 9.03$ (d, J = 5.6 Hz, 2 H), 7.77 (dd, J = 12.3, 7.0 Hz, 4 H), 7.50 (d, J = 8.1 Hz, 14 H), 7.50 (d, J = 8.1 Hz, 2 H), 7.17 (t, J = 7.3 Hz, 2 H), 7.00 (td, J = 7.6, 2.8 Hz, 4 H), 6.56 (t, J = 6.5 Hz, 2 H) ppm. MALDI-TOF: m/z = 1024.79 [M]⁺. C₄₆H₃₀F₆IrN₃O₂P₂ (1024.92): calcd. C 53.85, H 2.92, N 4.30; found C 53.86, H 2.93, N 4.12.

Supporting Information (see footnote on the first page of this article): ¹H NMR spectra, MALDI-TOF spectra, selected bond lengths and angles, TG-DSC thermograms, photoluminescence life-

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times of solids and CH_2Cl_2 solutions, and transient EL signals under different electric fields of iridium complexes $[Ir(F_{4,5,6}ppy)_2(tpip)]$, $[Ir(F_{3,4,6}ppy)_2(tpip)]$, and $[Ir(F_{3,4,5}ppy)_2(tpip)]$.

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Ir-Based OLEDs

Syntheses, Photoluminescence, and Electroluminescence of Iridium(III) Complexes with Fluorinated 2-Phenylpyridine as Main Ligands and Tertraphenylimidodiphosphinate as Ancillary Ligand

Keywords: Iridium / Luminescence / Organic light-emitting diodes / Fluorinated ligands



A light-emitting diode based on $[Ir(F_{3,4,6}ppy)_2(tpip)]$ $[F_{3,4,6}ppy = 2-(3,4,6-trifluorophenyl)pyridine, tpip = tetraphen$ ylimidodiphosphinate] exhibited good per $formance with a peak <math>\eta_{ext}$ of 25.7% and a peak η_c of 66.36 cd A⁻¹ at 5.8 V and a peak η_p of 48.20 lm W⁻¹ at 4.4 V.