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electroluminescence of iridium 1-(2,6-*bis*(trifluoromethyl)pyridin-4-4-(2,6-*bis*(trifluoromethyl)pyridin-4-

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Cite

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Two novel iridium(III) complexes, $Ir(tfmpiq)_2(acac)$ (tfmpiq = 1-(2,6-bis(trifluoromethyl)pyridin-4vl)isoquinoline, acac = acetylacetone) and $Ir(tfmpqz)_2(acac)$ (tfmpqz = 4-(2,6*bis*(trifluoromethyl)pyridin-4-yl)quinazoline), were synthesized and thoroughly investigated. Both complexes emit orange-red photoluminescence with high quantum yields (Ir(tfmpiq)2(acac): Amax: 587 nm, η_{PL} : 42%; Ir(tfmpqz)₂(acac): λ_{max} : 588 nm, η_{PL} : 91%). Furthermore, the complex containing quinazoline shows higher electron mobility than that with isoquinoline. The organic light-emitting diodes (OLEDs) with single- or double-emitting layers (EML) were fabricated using two new emitters. The double-EML device using Ir(tfmpqz)₂(acac) with the structure of ITO (indium-tinoxide) / MoO₃ (molybdenum oxide, 3 nm) / TAPC (di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane, 50 nm) / Ir(tfmpqz)₂(acac) (1 wt%): TcTa (4,4',4''-tris(carbazole-9-yl)triphenylamine, 10 nm) / Ir(tfmpqz)₂(acac) (1 wt%): 26DCzPPy (2,6-bis(3-(carbazol-9-yl)phenyl)pyridine, 10 nm) / TmPyPB (1,3,5-tri(m-pyrid-3-yl-phenyl)benzene, 50 nm) / LiF (1 nm) / Al (100 nm) displays good electroluminescence performances with a maximum luminance of 96 609 cd m⁻², a maximum current efficiency of 59.09 cd A⁻¹ and a maximum external quantum efficiency of 20.2%, a maximum power efficiency of 53.61 lm W⁻¹, respectively, and the efficiency roll-off ratio is mild.

Introduction

The green and red phosphorescent iridium(III) complexes have been used in commercial organic light-emitting diodes (OLEDs) because of their high quantum efficiency and the wide range of emission colors.¹ Quite high efficiency has been obtained for green phosphorescent devices, while the highest efficiency that has been reported for red emitters based devices is still much lower. Red emission is a crucial monochromatic light and also a pivotal constituent for the development of full-color display.² Most red emitters are subjected to the heavy concession on the color purity and device efficiency. Because the characteristic emission is in the spectral zone where eyes are insensitive, luminosity of red devices is lower. Moreover, the difference between the host with wide bandgap and the red-emitting guest with narrow bandgap is quite enormous in the level of the highest occupied molecular orbital (HOMO) and/or lowest unoccupied molecular orbital (LUMO). Therefore, the guest molecule should be used as a deep trap for the electron and hole in an emitting layer, leading to an enhancement of the driving voltage. In addition, for red dopants, the self-quenching and triplet-triplet annihilation are too serious to be ignored especially when the doping concentrations are high. Thus, from perspective of reality,

solving the above issues via the design of materials or/and the optimization of device is inevitable.³⁻⁹

It is well-known that the balance of the electron-hole injection and transport is necessary for high-efficiency OLEDs using the Ir(III) emitters because both the charge carrier balance deterioration and nonradioactive quenching processes increase will cause a serious efficiency roll-off. Since the majority of holetransporting materials' hole mobility is much higher than the electron-transporting materials' electron mobility, the OLEDs performances depend on electron transport's capability. Therefore, the use of ambipolar host materials is essential to gain phosphorescent OLEDs with low efficiency roll-off, as well as the synthesis of dopants with excellent electron mobility.¹⁰

From our previous work, we found out that the bulky CF_3 substituents can affect the molecular packing and the steric protection surrounding the metal would restrain the selfquenching impact, and the C-F bond with low vibrational frequency can reduce radiationless deactivation rate.¹¹ It is known that the replacement of hydrogen atoms by fluorine can heavily alter the physical and chemical properties of compounds. Thanks to its electronegativity and electron density distribution, fluorine can have a great influence on inter- and intramolecular forces.

Consequently, the electron injection is made easier, the materials display a greater resistance against the degradative oxidation processes and organic n-type or ambipolar semiconducting materials may result. Besides that, nitrogen heterocycle would also enhance the electron affinity and the electron mobility of the Ir(III) complexes. Therefore, aiming to get red emitters and devices with high efficiency by improving the electron mobility, both 2,6-bis-trifluoromethyl-pyridine and guinazoline were introduced to replace the widely used phenyl and 1phenylisoquinline (piq) units, respectively. The complexes $Ir(tfmpiq)_2(acac)$ (tfmpiq = 1-(2,6-bis(trifluoromethyl)pyridin-4yl)isoquinoline, acac = acetylacetone) and $Ir(tfmpqz)_2(acac)$ (tfmpqz = 4-(2,6-bis(trifluoromethyl)pyridin-4-yl)quinazoline)display emissions peak at 587 and 588 nm, respectively. The devices based both complexes showed good performances and the device based on Ir(tfmpqz)2(acac) displayed the best performances with a maximum current efficiency ($\eta_{c max}$) of 59.09 $cd A^{-1}$ with low efficiency roll-off.

Experimental section

Materials and measurements

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All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were measured on a Bruker AM 400 spectrometer. Mass spectrometry (MS) spectra were obtained on an electrospray ionization (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) for complexes. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. TG-DSC measurements were carried out on a DSC 823e analyzer (METTLER). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₃CN as the reference electrode, tetra-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc^{+}/Fc as the internal standard, the scan rate was 0.1 V/s. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)₃) and the unknown sample.¹²

Syntheses

All the reagents were used with commercial grade. The ligands and complexes were synthesized under nitrogen atmosphere and the synthetic routes were listed in Scheme 1.

General syntheses of ligands. A stirred solution of 2,6-bis-(trifluoromethyl)pyridine (0.22 g, 10mmol) in diethyl ether (20 mL) was cooled to -78 °C. LDA (lithium diisopropylamide, 6.0

mL, 10 mmol) was added over 20 min and stirred for 1 h, and then B(OPr-i)₃ (2.89mL,12.4mmol) was added. The mixture was warmed to room temperature and stirred for another 1 h. The pH was adjusted to 10 by the slow addition of 10% aqueous NaOH solution (20 mL). After 1 hour, the organic phase was acidified to pH = 4 by the dropwise addition of 3 N HCl. The extraction with ethyl acetate and evaporation of the organic phase gave the crude corresponding aryl boronic acids. 1-Chloroisoquinoline / 4-Chloroquinazoline (10 mmol) and *bis*(diphenylphosphion) ferrocene palladium(II) dichloromethane (0.3 mmol) and the boronic acids were added in 50mL THF. After 20 mL of aqueous 2 N K₂CO₃ was delivered, the reaction mixture was heated at 70 ^oC for 1 day under an nitrogen atmosphere. The mixture was poured into water and extracted with CH_2Cl_2 (10 mL \times 3 times). Finally, silica column purification (PE:EA = 10:1) gave the 1-(2,6-bis(trifluoromethyl)pyridin-4-yl)isoquinoline and 4-(2,6bis(trifluoromethyl)pyridin-4-yl)quinazoline.

1-(2,6-*Bis*(trifluoromethyl)pyridin-4-yl)isoquinoline. 40% yield. MS (ESI): calcd. for M⁺ (C₁₆H₈F₆N₂⁺) m/z = 342.06, found 343.07. ¹H NMR (400 MHz, CDCl₃) δ 8.69 (d, *J* = 5.6 Hz, 1H), 8.26 (s, 2H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.81 (ddd, *J* = 8.2, 5.9, 1.2 Hz, 2H), 7.69 (ddd, *J* = 8.3, 6.9, 1.2Hz, 1H).

4-(2,6-*Bis*(trifluoromethyl)pyridin-4-yl)quinazoline. 30% yield. MS (ESI): calcd. for M⁺ (C₁₅H₇F₆N₃⁺) m/z = 343.05, found 344.06. 1H NMR (400 MHz, CDCl₃) δ 9.49 (S, 1H), 8.30 (S, 2H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.06 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.96 (dd, *J* = 8.4, 0.6Hz, 1H),7.78 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H).

General syntheses of iridium complexes. A mixture of $IrCl_3$ (1 mmol) and tfmpiq or tfmpqz (2.5 mmol) in 2-ethoxyethanol and water (20 mL, 3:1, v/v) was refluxed for 24 h. After cooling, the solid precipitate was filtered to give the crude cyclometalated Ir(III) chloro-bridged dimer. Then, the slurry of crude chloro-bridged dimer (0.2 mmol), acac (0.5 mmol) and Na_2CO_3 (0.25 mol) in 2-ethoxyethanol (20 mL) was refluxed for 24 h. The solvent was evaporated at low pressure and the mixture was poured into water and extracted with CH_2Cl_2 , and then chromatographed to give complexes $Ir(tfmpq)_2(acac)$ and $Ir(tfmpqz)_2(acac)$, which were further purified by sublimation in vacuum.

Ir(tfmpiq)₂(acac). 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, J = 8.9 Hz, 2H), 8.51 (s, 2H), 8.08 (d, J = 6.2 Hz, 2H), 7.96 – 7.91 (m, 2H), 7.83 – 7.79 (m, 4H), 7.47 (d, J = 6.4 Hz, 2H), 4.91 (s, 1H), 1.48 (s, 6H). MS(ESI) m/z calcd for $C_{37}H_{21}F_{12}IrN_4O_2$: 974.11 [M]⁺, found 975.12 [M+H]⁺. Anal. Calcd. For $C_{37}H_{21}F_{12}IrN_4O_2$: C 45.64, H 2.17, N 5.75. Found: C 45.30, H 2.53, N 5.83.

Ir(tfmpqz)₂(acac). 27% yield. ¹H NMR (400 MHz, CDCl3) δ 9.49 (s, 2H), 8.60 (s, 2H), 8.31 (s, 4H), 8.25 (d, *J* = 8.5 Hz, 2H), 8.11 - 8.01 (m, 2H), 5.30 (s, 1H), 1.63 (s, 6H). MS(ESI) *m/z* calcd for C₃₅H₁₉F₁₂IrN₆O₂: 976.10 [M]⁺, found 977.21 [M+H]⁺.

Anal. Calcd. For $C_{35}H_{19}F_{12}IrN_6O_2$: C 43.08, H 1.96, N 8.61. Found: C 43.37, H 2.27, N 8.85.

X-ray crystallography

The single crystals of Ir(tfmpiq)₂(acac) was carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT¹³ on all observed reflections. Data were collected 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 using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS¹⁴ supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the program SHELXS-97.15 The positions of metal atoms and their first coordination spheres were located from directmethods E-maps; 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 position and refined as riding atoms with a uniform value of Uiso.

OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15Ω / sq. The deposition rate for organic compounds (TAPC (1,1-*bis*(4-(di-p-tolylamino)phenyl)cyclohexane, TcTa (4,4',4''-*tri*(9-carbazoyl)-triphenylamine), 2,6DCzPPy (2,6-*bis*(3-(carbazol-9-

yl)phenyl)pyridine), TmPyPB (1,3,5-*tri*(m-pyrid-3-yl-phenyl) benzene)) is 1 Å/s. The phosphors and the host TcTa or 2,6DCzPPy were co-evaporated to form emitting layer from two separate sources. The cathode of LiF and Al were deposited with deposition rates of 0.1 and 3 Å/s, respectively. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

Results and discussion

Preparation and characterization of compounds

As shown in Scheme 1, the main ligand tfmpiq and tfmpqz were synthesized using a Suzuki coupling reaction. The iridium complexes were prepared by the reaction of corresponding chloride-bridged dimmers $[(C^N)Ir(\mu-Cl)]_2$ with acac and Na_2CO_3 to give the products Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac). Purification of the mixture by silica gel chromatography provided crude products, which were further purified by vacuum sublimation. All the new compounds were fully characterized by ¹H NMR spectrometry and the crystal structure of Ir(tfmpiq)₂(acac) further confirmed the identity of the complex.



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Fig. 1. Oka Ridge Thermal Ellipsoidal plot (ORTEP) diagrams of $Ir(tfmpiq)_2(acac)$ (CCDC No. 1558320) complex with the atomnumbering schemes. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability level.

Red single crystal of Ir(tfmpiq)₂(acac) was obtained by vacuum sublimation in quadruple prisms. The structure of Ir(tfmpiq)₂(acac) complex was proved via the X-ray diffraction analysis and the crystal diagram is displayed in Fig. 1. The molecular parameters and atomic coordinates are showed in Table S1. From the structure diagram of crystal it can be found that the iridium atom is embraced by C, N and O atoms from tfmpig or acac, with a twisted octahedral coordination geometry. For Ir(tfmpiq)₂(acac), angles of [O-Ir-O] are 89.97(16)°, and the angle of [C-Ir-N] is 80.01(2)° - 106.6(2)°. The lengths of Ir-C bonds range from 2.012(5) - 2.026(5) Å. The Ir-N bonds have the lengths of 2.049(5) - 2.051(5) Å. And the lengths of Ir-O bonds are longer a bit, which are 2.105 (4) - 2.113(4) Å. These results are similar to the parameters of the cyclometalated Ir(III) complexes that have been reported.

Thermal stability

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Fig. 2. The DSC (a) and TGA (b) curves of $Ir(tfmpiq)_2(acac)$ and $Ir(tfmpqz)_2(acac)$.

The thermal stability of the materials is crucial for efficient OLEDs. If a complex can be applied in practical OLEDs, the melting point (T_m) and decomposition temperature (T_d) need to be high enough to guarantee that the complex could be deposited onto the solid face without any decomposition on sublimation. The scanning calorimetry (DSC) and thermogravimetric analysis

(TGA) curves of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) are showed in Fig. 2. From the DSC curves it is can be seen that the melting points of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) are 323 °C and 343 °C, respectively. It can be figured out that there is no loss observed below 320 °C in weight from the curves of TGA, and the decomposition temperature (5% loss of weight) is 340 °C for Ir(tfmpiq)₂(acac) and 349 °C for Ir(tfmpqz)₂(acac), respectively, suggesting that both complexes have the potential application in OLEDs. In general, the efficiency of vacuum-deposited OLEDs is much higher than that of solution-processed devices.

Electrochemical property and theoretical calculation



Fig. 3. (a) The cyclic voltammogram curve of $Ir(tfmpiq)_2(acac)$ and $Ir(tfmpqz)_2(acac)$; (b) Contour plots of $Ir(tfmpiq)_2(acac)$ and $Ir(tfmpqz)_2(acac)$.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the dopants are important for the design of the OLEDs. In order to determine the HOMO/LUMO values of the Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac), the electrochemical properties were investigated by cyclic voltammetry in deaerated CH₃CN (Fig. 3(a)). The HOMO levels were obtained via the oxidation potentials and the LUMO levels were obtained via the redox potentials. During the progress of anodic oxidation, the oxide peak can be observed for both complexes with the oxidation potential in 1.26-1.45 V, which can be ascribed to the metalcentered Ir(III)/Ir(IV) oxide couple, consistent with the cyclometallated Ir(III) system reported.¹⁶ Ir(tfmpiq)₂(acac) exhibits an oxidation potential (1.26 V), an redox potential (-1.31 V) and HOMO/LUMO energy levels are -5.95/-3.54 eV. The oxidation potential of Ir(tfmpqz)₂(acac) increases to 1.45 V and the redox potential is -1.29 V. The HOMO/LUMO energy levels of Ir(tfmpqz)₂(acac) are -6.14/-3.56 eV. From the Table 1, it is observed that the difference of the HOMO values of the two complexes can not be neglected. This means that the introduction of quinazoline has an obvious effect on electrochemical properties of Ir(III) complexes.

In order to gain insights into the electronic state and the orbital distribution, the density functional theory (DFT) calculations¹⁷ for both Ir(III) complexes were conducted employing Gaussian09

software with B3LYP function.¹⁸ Plots of the HOMO/LUMO and the molecular orbital energy levels are presented in Fig. 3(b). The basis set used for C, H, N, O and F atoms was 6-31G(d, p) while the LanL2DZ basis set was employed for Ir atoms.¹⁹ The solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum model (C-PCM). It can be observed from the theoretical calculation that nearly all LUMOs are on tfmpiq/ tfmpqz ligands (95.57-95.72%). HOMOs are mostly situated on tfmpiq ligands (46.53%) and *d* orbitals of iridium atom (47.60) for Ir(tfmpiq)₂(acac), while HOMOs are situated on tfmpqz ligands (23.06%), *d* orbitals of iridium atom (37.35%) and acac ancillary ligand (39.59) for Ir(tfmpqz)₂(acac), suggesting that the introduction of quinazoline has an obvious effect.

Photophysical property

The UV-vis absorption and photoluminescence spectra of the two complexes Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) in CH₂Cl₂ $(5 \times 10^{-5} \text{ M})$ are shown in Fig. 4. The absorption spectra of two complexes show broad and intense bands below 320 nm, assigned to the spin-allowed intraligand ¹LC ($\pi \rightarrow \pi^*$) transition of cyclometalated tfmpiq/tfmpqz and acac ligands. The weak bands last to 520 nm can be assigned to spin-allowed metal-ligand charge transfer band (¹MLCT) and spin forbidden ³MLCT transition bands caused by the large spin orbital coupling (SOC) that was introduced by Ir(III) center indicating an efficient spinorbit coupling that is prerequisite for phosphorescent emission.²⁰ The strongest emissions peak at 587 and 588 nm in CH_2Cl_2 , produced by the electronic transition between the lowest triplet excited state and the ground state, which makes Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) orange-red phosphors. The emission in the scope of lower energy around 630 nm for Ir(tfmpiq)₂(acac) may generate by the overlapping vibrational satellites²¹. From Fig. S1

(Supporting Information) and Table 1, it can be seen that the PL spectra of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) at 77 K remain almost the same compared with those at room temperature. In general, the emission bands from the MLCT states are broad and featureless, whereas a highly structured emission band mainly originates from the ${}^{3}\pi$ - π * state. Accordingly, the emission of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) is mainly generated from MLCT states. This indicates that the MLCT characters involved in the emitting T₁ states of different complexes are various but significant, since a dominant MLCT character in T₁ usually leads to large inhomogeneity and low-energy lying metal-ligand vibrational satellites, smearing out the spectrum below the electronic original emission. Furthermore, the complexes show much high quantum efficiency as 0.42 and 0.91 for Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac), respectively. The differences of the absorption and emission profiles between Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) suggest that the introduction of quinazoline does have an obvious effect, and it can increase the quantum efficiency greatly.



Fig. 4. (a) UV-vis absorption and (b) emission spectra of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) complexes in degassed CH_2Cl_2 solutions (5.0 × 10⁻⁵ mol L⁻¹) at room temperature.

	$T_{\rm m}/T_{\rm d}^{\rm a)}$ (°C)	$\lambda_{abs}^{b)}$	$\lambda_{\rm em}^{\rm c)}$ (nm)	Φ ^{d)} (%)	HOMO/LUMO ^{f)}
Complex		(nm)	298K 77K		(eV)
Ir(tfmpiq) ₂ (acac)	340/323	231/353/403	587/632 600/648	42	-5.95/-3.54
Ir(tfmpqz) ₂ (acac)	356/343	233/381/400	588 605	91	-6.14/-3.56

 Table 1. Photophyscial date of Ir(III) complexes.

^{a)} $T_{\rm m}$: melting temperature, $T_{\rm d}$: decomposition temperature; ^{b)} Measured in degassed CH₂Cl₂ solution at a concentration of 5 × 10⁻⁵ mol·L⁻¹ at room temperature; ^{e)} Measured in degassed CH₂Cl₂ solution at a concentration of 5 × 10⁻⁵ mol·L⁻¹ at 298 K and 77 K, respectively; ^{d)} emission quantum yields were measured relative to Ir(ppy)₃ ($\Phi = 0.4$) in degassed CH₂Cl₂ solution at room temperature. ^{e)} Measured in degassed CH₂Cl₂ solution at a concentration of 5 × 10⁻⁵ mol·L⁻¹ at 298 K and 77 K, respectively; ^{d)} emission quantum yields were measured relative to Ir(ppy)₃ ($\Phi = 0.4$) in degassed CH₂Cl₂ solution at room temperature. ^{e)} Measured in degassed CH₂Cl₂ solution at a concentration of 5 × 10⁻⁵ mol·L⁻¹ at room temperature; ^{f)} From the onset of oxidation potentials of the cyclovoltammetry (CV) diagram using ferrocene as the internal standard and the optical band gap from the absorption spectra in degassed CH₃CN solution.

Electron mobility

According to our previous studies, an excellent electron mobility of emitters could benefit electron transport and improve the device efficiency.²² To determine the two complexes' electron mobility, the transient electroluminescence

(TEL) measurement was carried out via the devices with a structure of ITO (indium-tin-oxide) / TAPC (50 nm) / Ir complexes (60 nm).²³ The Ir(III) complexes act as not only the emissive layer (EML) but also electron-transport layer. The experimental results (Fig. 5 and Fig. S2) indicated that the electron mobilities of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac)

are 8.57-8.65 × 10⁻⁶ cm² V⁻¹ s⁻¹ and 9.47-10.23 × 10⁻⁶ cm² V⁻¹s⁻¹, respectively, under the electric field from 1040 (V cm⁻¹)^{1/2} to 1300 (V cm⁻¹)^{1/2}, higher than that of the widely used electron transport material Alq₃ (aluminum 8-hydroxyquinolinate, 4.74-4.86 ×10⁻⁶ cm² V⁻¹s⁻¹).²⁴ Additionally, the electron mobility of Ir(tfmpqz)₂(acac) is better than that of Ir(tfmpiq)₂(acac) suggesting that quinzoline has the strong impact on the enhancement of the electron flow. The result is exactly fitting our design intent to improve the electron transport ability of the emitter by introducing more nitrogen atoms. The good electron transport ability of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) will reinforce the recombination chance of electrons and holes, so that their devices may have good performances, especially for that using Ir(tfmpqz)₂(acac).



Fig. 5. Electric field dependence of charge electron mobility in the thin films of Ir(tfinpiq)₂(acac) and Ir(tfinpqz)₂(acac) and Alq₃.

OLEDs performance

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Fig. 6. Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work and their molecular structures.

To evaluate the EL performances of two complexes, single emitting layer (EML) devices named G1 and G2 using Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) as the emitters, respectively, were fabricated with the structure of ITO (indiumtin-oxide)/ MoO₃ (molybdenum oxide, 3 nm)/ TAPC (50 nm)/ Ir complexes (x wt%) : 26DCzPPy (10 nm)/ TmPyPB (50 nm)/ LiF (1 nm)/Al (100 nm). MoO₃ and LiF served as hole- and electron-inject interface modified materials, respectively. TAPC owning high hole mobility $(1 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and high-lying LUMO level (-2.0 eV) was used as hole transport/electron block layer (HTL/EBL), while TmPyPB with high electron mobility $(1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and low-lying HOMO level (-6.7 eV) was used as electron transport/hole block layer (ETL/HBL). Ambipolar material 26DCzPPy was chosen as the host because its' nearly equal electron mobility (μ_e) and hole mobility (μ_h) values $(1.8 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under an electric field between 6.0 $\times 10^5$ and 1.0×10^6 V cm⁻¹), which benefits the electron-hole balance in the EML.²⁵ The chemical structures of the materials mentioned above as well as the device structure and energy level diagrams are depicted in Fig. 6.

Theoretically speaking, the stepwise HOMO levels of TAPC (-5.50 eV), TcTa (-5.70 eV), and 2,6DCzPPy (-6.05 eV) are beneficial for the injection and transport of holes, while the stepwise LUMO levels of TmPyPB (-2.70 eV), 2,6DCzPPy (-2.56 eV) and TcTa (-2.4 eV) are beneficial for the injection and transport of electrons. Therefore, balanced distribution of carriers (holes and electrons) and wide recombination zone could be expected. More importantly, the LUMO level of TAPC is 0.6 eV higher than that of TcTa while the HOMO level of TmPyPB is 0.6 eV lower than that of 2,6DCzPPy; thus, holes and electrons are well confined within EMLs and the triplet excitons quenching of the dopants will be effectively avoided. In single EML devices, the optimized Ir(III) complexes with 2 wt% doped concentrations for Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac).

The EL spectra, luminance-voltage-current density (*L-V-J*) curves, current efficiency-luminance (y_c -*L*) curves, power efficiency-luminance (y_p -*L*) curves for **G1** and **G2** are shown in Fig. 7. And the crucial EL data are shown in Table 2. The peaks of EL emission are 584 and 579 nm for **G1** and **G2**, respectively, and the emission spectra are almost invariant of the current density and there is no dependence on concentration. From the Fig. 7(a), it is can be seen that the EL spectra are almost identical to the PL spectra of the complexes, suggesting that the devices' EL emissions come from the triplet excited states of the phosphors. The Commission Internationale de 1'Eclairage (CIE) color coordinates of **G1** and **G2** are (0.561, 0.432) and (0.525, 0.446), respectively.

For the device **G1**, a maximum current efficiency ($\eta_{c,max}$) of 22.46 cd A⁻¹ with a maximum external quantum efficiency (EQE_{max}) of 7.7%, a maximum power efficiency ($\eta_{p,max}$) of 19.59 lm W⁻¹ and a maximum luminance (L_{max}) of 36 945 cd m⁻²

were obtained. **G2** exhibits much better performances with a maximum luminance of 66 716 cd m⁻², a maximum current efficiency ($\eta_{c,max}$) of 43.76 cd A⁻¹, a maximum external quantum efficiency (EQE_{max}) of 14.8%, and a maximum power efficiency ($\eta_{p,max}$) of 38.17 lm W⁻¹. Moreover, **G2** can remain high efficiency even at relatively high luminance and the EL

efficiency roll-off is rather low. For instance, the current efficiency for the device **G2** still keeps as high as 36.59 cd A^{-1} at the brightness of 1 000 cd m⁻² and 28.64 cd A⁻¹ at the brightness of 5 000 cd m⁻², respectively, suggesting that this complex is a promising material for OLEDs.



Fig. 7. Characteristics of devices of G1 and G2: (a) electroluminescence spectra at 8 V; (b) luminance – voltage – current density (L - V - J) curves; (c) current efficiency – luminance $(\eta_c - L)$ curves; (d) power efficiency – luminance $(\eta_p - L)$ curves.

The double-EMLs device could achieve better performances than the single-EML device in common because a better balance of carries and a wider recombination zone within EMLs could be gotten by the double-EMLs device. Thus, to confirm our assumption, we researched the devices **G3** and **G4** using Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) emitters, respectively, with a structure of ITO / MoO₃ (3 nm) / TAPC (50 nm) / Ir complex (x%): TcTa (10 nm) / Ir complex (x%): 26DCzPPy (10 nm) / TmPyPB (50 nm) / LiF (1 nm) / Al (100 nm) (Fig. 4). The optimal device performances are achieved at doping level of 1 wt% for Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac).

The EL spectra, luminance-voltage-current density (*L-V-J*) curves, current efficiency-luminance (y_c -*L*) curves, power efficiency-luminance (y_p -*L*) curves for **G3** and **G4** are shown in

Fig. 8. And the crucial EL data are shown in Table 2. Similar with devices **G1** and **G2**, the peaks of EL emission are 584 and 578 nm for **G3** and **G4**, respectively, and the emission spectra are almost invariant of the current density and there is no dependence on concentration. For the device **G3**, a maximum current efficiency ($\eta_{c,max}$) of 21.30 cd A⁻¹ with a maximum external quantum efficiency of 7.6%, a maximum power efficiency ($\eta_{p,max}$) of 17.60 lm W⁻¹ and a maximum luminance (L_{max}) of 34 521 cd m⁻² were obtained. **G4** exhibits much better performances with a maximum luminance of 96 609 cd m⁻² at 10.3 V, a maximum current efficiency of 59.09 cd A⁻¹, a maximum power efficiency ($\eta_{p,max}$) of 53.61 lm W⁻¹. Moreover, **G4** can remain high efficiency even at relatively high luminance

and the EL efficiency roll-off is rather low. For instance, the current efficiency still keeps as high as 54.55 cd A^{-1} at the

brightness of 1 000 cd m^{-2} and 46.74 cd A^{-1} at the brightness of 5 000 cd m^{-2} , respectively.



Fig. 8. Characteristics of devices of G3 and G4: (a) electroluminescence spectra at 8 V; (b) luminance – voltage – current density (L - V - J) curves; (c) current efficiency – luminance $(\eta_c - L)$ curves; (d) power efficiency – luminance $(\eta_p - L)$ curves.

Table 2. EL	performances o	f single-EML	devicesG1,	G2 and double	-EMLs devices	G3, G4.
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Device	V _{turn-on} ^{a)} (V)	$L_{\rm max}^{\rm b)}$ (cd m ⁻²)	$ \begin{array}{c} \eta_{\mathrm{c,max}} ^{\mathrm{c})} \\ (\mathrm{cd} \mathrm{A}^{-1}) \\ (EQE_{\mathrm{max}} ^{\mathrm{d}}) \end{array} $	$\eta_{c,L1000}^{e)} (cd A^{-1}) (EQE_{L1000}^{f)})$	$\eta_{\rm p,max}^{g)}$ (lm W ⁻¹)	$CIE^{h)} (x,y)$
G1	3.3	36 945	22.46 (7.7%)	14.23(5.1%)	19.59	0.561,0.432
G2	3.1	66 716	43.76(14.8%)	36.58 (11.7%)	38.17	0.525,0.446
G3	3.7	34 521	21.30 (7.6%)	17.04 (6.1%)	17.60	0.558,0.429
G4	3.2	96 609	59.09(20.2%)	54.55 (18.3%)	53.61	0.520,0.448

^{a)} turn-on voltage recorded at a luminance of 1 cd m⁻², ^{b)} maximum luminance, ^{c)} maximum current efficiency, ^{d)} maximum external quantum efficiency (*EQE*); ^{e)} current efficiency at 1 000 cd m⁻²; ^{f)} *EQE* at 1 000 cd m⁻²; ^{g)} maximum power efficiency, ^{h)} Commission Internationale de l'Eclairage coordinates (CIE).

Conclusions

In conclusion, we reported two *bis*-cyclometalatted iridium complexes Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) with 1-(2,6-*bis*(trifluoromethyl)pyridin-4-yl)isoquinoline (tfmpiq) and 4-(2,6-*bis*(trifluoromethyl)pyridin-4-yl)quinazoline (tfmpqz) as

main ligands. Both complexes emit orange-red phosphorescence with high quantum efficiency. Through the comparison with the device using Ir(tfmpiq)₂(acac), the device using Ir(tfmpqz)₂(acac) displays better EL performances and lower efficiency roll-off. Furthermore the double-EMLs device based

on Ir(tfmpqz)₂(acac) shows the best device performances with a L_{max} of 96 609 cd m⁻², a $\eta_{c,\text{max}}$ of 59.09 cd A⁻¹, an EQE_{max} of 20.2% and a $\eta_{p,\text{max}}$ of 53.61 lm W⁻¹, respectively, which may be beneficial to white OLEDs with high performance. Meanwhile, the results also suggest that the Ir(III) complexes with quinazoline units are potential phosphorescent materials for OLEDs, which has instructional significance to the design of the red emitters in some degree.

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Notes and references

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 \pm Electronic Supplementary Information (ESI) available: the transient EL signals for the device structure of ITO/ TAPC (50 nm)/ Ir complexes (60 nm)/ LiF/ Al under different applied fields of Ir(tfmpiq)₂(acac) and Ir(tfmpqz)₂(acac) and the crystallographic data, selected bonds and angles of complex Ir(tfmpiq)₂(acac).

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Graphical abstract



Two red iridium complexes with high quantum yield and good electron mobility were applied in efficient OLEDs showing a maximum luminance of 96 609 cd m⁻², a maximum current efficiency and a maximum power efficiency of 59.09 cd A^{-1} and 53.61 lm W^{-1} , respectively, with low efficiency roll-off.