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Orange to red iridium(III) complexes possessing good electron mobility with a pyrimidine-4-carboxylic acid ligand for high-performance solution-processed OLEDs with an EQE over 31%†

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Three novel iridium(III) complexes with pyrimidine carboxylic acid as the auxiliary ligand were designed, showing adjustable emission peak wavelengths from 559 nm to 610 nm with relatively high photoluminescence quantum yields (PLQYs) of 58–89% in CH_2Cl_2. The structures of the title complexes were confirmed by single-crystal X-ray diffraction (XRD), nuclear magnetic resonance spectroscopy (NMR), and high-resolution mass spectrometry (HRMS). Their electronic states were investigated using time-dependent density functional theory (TD-DFT) calculations. When employing these emitters to fabricate solution-processed organic light-emitting diodes (OLEDs), the obtained orange and red OLEDs exhibit prominent performances with the maximum current efficiencies of 95.4 cd A^{-1} and 39.8 cd A^{-1}, and the maximum external quantum efficiencies (EQE_{max}) of 31.3% and 24.7%, both of which are ranked among the highest values for orange and red solution-processed OLEDs.

Introduction

Organic light-emitting diodes (OLEDs) have the advantages of thin thickness, high brightness, high flexibility, fast response speed, *etc.*, which are ideal for the new generation of flat panel displays and energy-saving solid-state light sources.[1–10] Light-emitting materials are the core of OLEDs, especially phosphorescent metal complexes, which have high photoluminescence quantum yields (PLQYs) and suitable device performance.[11–13] Among them, iridium(III) complexes are the essential emitters and have the advantages of easy chemical structure modification, flexible control of photophysical properties, high luminescence efficiency, and relatively low phosphorescence lifetimes.[14]

In general, the hole-transporting capacity of most hole-transporting materials in OLEDs is much higher than the electron-transporting capacity of most electron-transporting materials, and in order to balance carrier injection and transport in the emissive layer, the introduction of electron-transporting groups into the ligand is an effective way to improve the electron mobility of a complex.[15] Nitrogen heterocyclic pyrimidines can improve the electron transfer ability of complexes and increase the device efficiency, so we propose the use of pyrimidine carboxylic acid as an auxiliary ligand and the introduction of nitrogen heterocycles into primary ligands, which improve the device efficiency and reduce the efficiency roll-off.[16]

Since the invention of high-efficiency organic light-emitting diodes in 1987, the initial technique for fabricating each functional layer in a device has involved vapor deposition by thermal evaporation. However, high temperature and a vacuum are required in this process, so using evaporation treatments can be more expensive than other treatments.[17] Solution processing has emerged as a new technology that utilizes liquid solutions of materials to deposit functional layers in devices at room temperature. This method opens the door to molecules with high molecular weights, high sublimation temperatures, or poor thermal stability. Due to their relatively

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low cost and ease of manipulating large-area displays, more and more attention has been given to developing these devices from both commercial and academic communities.[18–22] For example, by using the solution-processed method, Liu *et al.* synthesized a boron-containing 2-phenylpyridine (ppy) type ligand as the primary ligand with an EQE_{max} of 28.1%.[23] Gong *et al.* synthesized a dibenzo[*b*,*d*]thiophene-*S*,*S*-dioxide primary ligand, with an EQE_{max} of 16.6%.[24] Sun *et al.* synthesized a 5-(dimesitylboranyl)-2-phenylpyridine primary ligand with an EQE_{max} of 23.2%.[25] So far, solution-processed OLEDs with EQE_{max} over 30% have been rarely reported.

Combined with the above characteristics, we synthesized three new iridium complexes: $(4\text{-tfmpq})_2Ir(4\text{-pca})$, $(4\text{-tfmptp})_2Ir(4\text{-pca})$, and $(4\text{-pq})_2Ir(4\text{-pca})$. Their maximum emission wavelengths in CH_2Cl_2 ranged from 559 to 610 nm. Among them, $(4\text{-pq})_2Ir(4\text{-pca})$ showed a PLQY of 57.6% for the standard red CIE (0.67,0.33); $(4\text{-tfmpq})_2Ir(4\text{-pca})$ showed a better PLQY of 83.6%; $(4\text{-tfmptp})_2Ir(4\text{-pca})$ showed a maximum current efficiency ($\eta_{c,max}$) of 95.4 cd A^{-1} with the best PLQY of 88.5%, a maximum power efficiency ($\eta_{p,max}$) of 54.5 lm W^{-1}, and an EQE_{max} of 31.3%.

Results and discussion

Synthesis and characterization

The structures of the three complexes are clearly shown in Scheme 1. The Suzuki cross-coupling reaction was employed to prepare three primary ligands. The ancillary ligand, 4-pca (pyrimidine-4-carboxylic acid), is available for direct purchase. The final products, $(4\text{-tfmpq})_2Ir(4\text{-pca})$, $(4\text{-tfmptp})_2Ir(4\text{-pca})$ and $(4\text{-pq})_2Ir(4\text{-pca})$, were synthesized based on a reported two-step method. In the first step, iridium chloride trihydrate reacts with 2.5 equivalents of the primary ligand in 2-ethoxyethanol solution to form a μ-chloro-bridged dimer, and in the second step, the μ-chloro-bridged dimer reacts with a mixture of 4-pca and Na_2CO_3 to give three Ir(III) complexes (Scheme S1†). The crude products of the three complexes were easily purified by column chromatography.

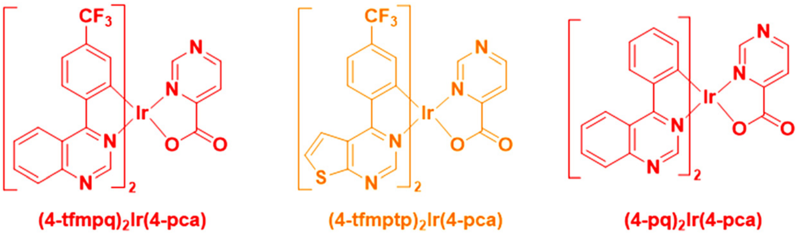
The thermal properties of these Ir(III) complexes were investigated by thermogravimetric analysis (TGA) since the thermal stability of the emitters is crucial for the stability of OLEDs. The results show that the decomposition temperature T_d (5%) values of $(4\text{-tfmpq})_2Ir(4\text{-pca})$ and $(4\text{-pq})_2Ir(4\text{-pca})$ are at excellent levels of 337 °C and 347 °C, respectively, while the T_d value of $(4\text{-tfmptp})_2Ir(4\text{-pca})$ is at a moderate level of 243 °C (Table 1 and Fig. S1†). We speculate that this may be due to the relatively low coordination ability and stability of the thieno[2,3-*d*]pyrimidine unit.

X-ray crystallography analysis

The three new complexes, $(4\text{-tfmpq})_2Ir(4\text{-pca})$, $(4\text{-tfmptp})_2Ir(4\text{-pca})$ and $(4\text{-pq})_2Ir(4\text{-pca})$, were characterized by single-crystal X-ray diffraction. The structures of these complexes are shown in Fig. 1, and the crystallographic data are summarized in Tables S1–S3 (ESI†). An approximate octahedral geometry around the iridium(III) center is observed. The bond lengths of Ir–C (1.987–2.030 Å), Ir–N (2.029–2.148 Å) and Ir–O (2.151–2.171 Å) match with those of other similar Ir(III) complexes.[26–28]

Electrochemical performance

The characterization of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (E_{HOMO}/E_{LUMO}) is of great significance for the electrochemical properties of Ir(III) complexes. They can provide a theoretical basis for the design and fabrication of OLEDs. Cyclic voltammetry (CV) measurements were per-



Scheme 1 Structural drawings of the studied iridium complexes.

Table 1 Photophysical data of Ir(III) complexes

Complex	T_d [a] (°C)	Absorption[b] (λ nm)	Emission[b] (λ_{max} nm)	$\tau_{298\ K}$ [b] (μs)	Φ_p [c] (%)	E_{gap} [d] (eV)	HOMO/LUMO[e] (eV)
$(4\text{-tfmpq})_2Ir(4\text{-pca})$	337	288/341/474/526	604	6.87	83.6	2.10	−5.85/−3.75
$(4\text{-tfmptp})_2Ir(4\text{-pca})$	243	282/441/496	558	5.45	88.5	2.31	−5.85/−3.54
$(4\text{-pq})_2Ir(4\text{-pca})$	347	291/339/475/530	610	7.03	57.6	2.03	−5.60/−3.57

[a] Decomposition temperature. [b] Measured in DCM (10^{-5} M) at 298 K. [c] Measured in DCM (10^{-5} M) under a N_2 atmosphere. Φ: the quantum yields were calculated with the *fac*-$Ir(ppy)_3$ standard in degassed CH_2Cl_2 solution (Φ_p = 40%). [d] Calculated from the UV-vis onset. [e] Calculated from cyclic voltammetry analysis.

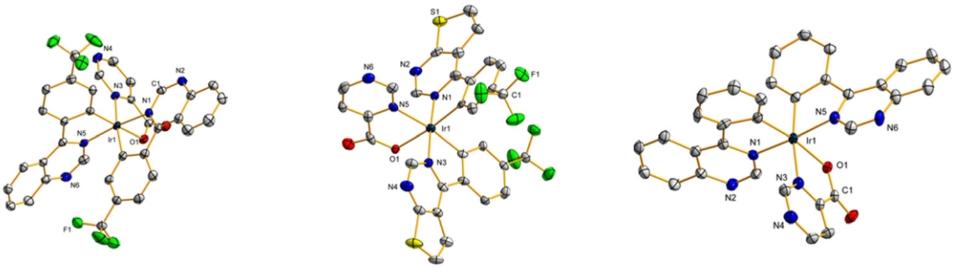


Fig. 1 ORTEP drawing of (4-tfmpq)$_2$Ir(4-pca), (4-tfmptp)$_2$Ir(4-pca) and (4-pq)$_2$Ir(4-pca) with CCDC numbers of 2302907, 2302905 and 2302906,† respectively.

formed in degassed CH_2Cl_2 using ferrocene/ferrocene (Fc^+/Fc) as an internal standard to investigate the redox properties and HOMO/LUMO levels of all Ir(III) complexes (Table 1 and Fig. 2†).[29,30] Previous electrochemical tests with Ir(III) complexes have shown that the reduction process is generally believed to occur mainly in the heterocyclic portion of the C^N ligand. In contrast, the oxidation process mainly involves the iridium center and the auxiliary ligand.

The electrochemical properties of these complexes were examined using cyclic voltammetry in CH_2Cl_2 solution. Based on the formula E_{HOMO} (eV) = $-(E_{\mathrm{ox}} - E_{\mathrm{Fc}/\mathrm{Fc}^+} + 4.8)$ eV, E_{LUMO} (eV) = $E_{\mathrm{HOMO}} + E_{\mathrm{bandgap}}$, the E_{HOMO} of four complexes was deduced, which should be ascribed to the oxidation process of the Ir (III) centers. The HOMO energy level of the Ir(III) complex is estimated from the above equation, and the LUMO energy level is estimated from the sum of the HOMO energy level and

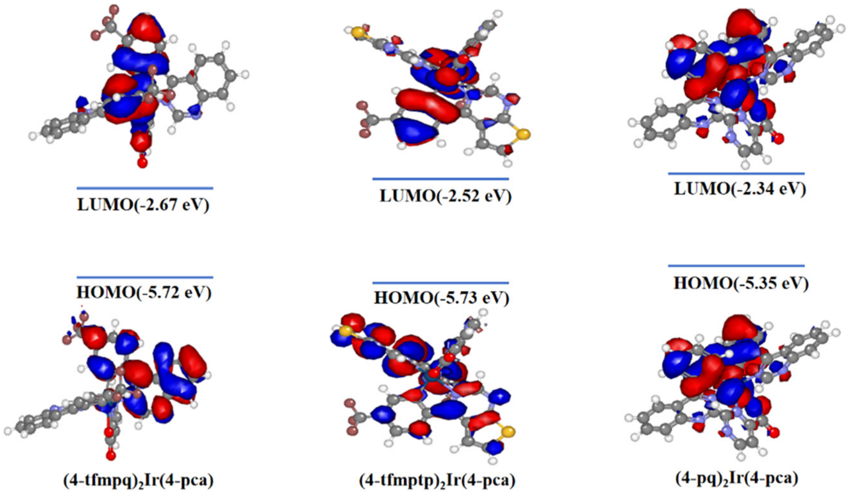


Fig. 2 DFT (HOMO and LUMO surfaces) of the complexes.

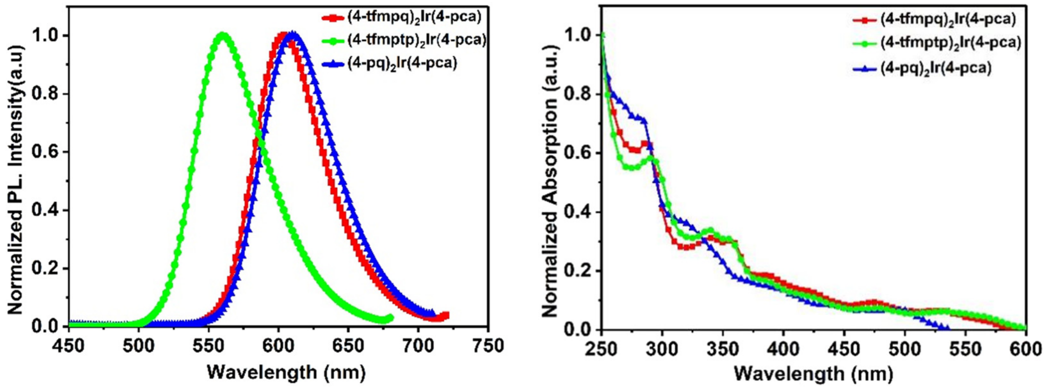
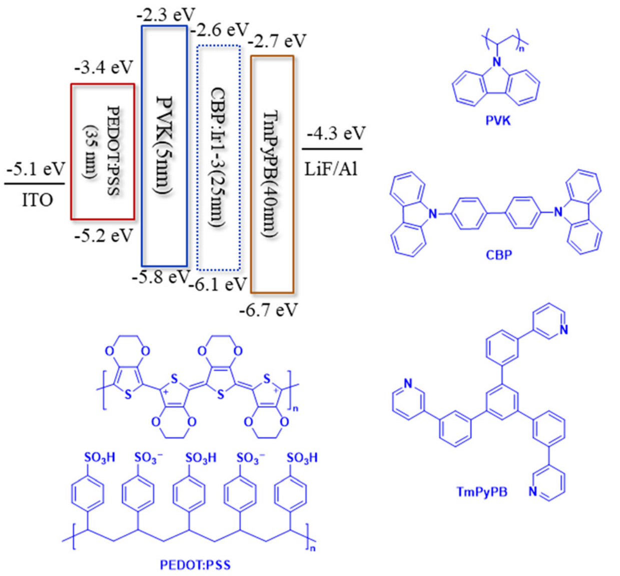


Fig. 3 Photophysical properties of the three complexes measured in DCM solution at 298 K (5 × 10^{-5} M).

the energy bandgap, which is determined from the absorption edge in the absorption spectrum (MLCT). The HOMO/LUMO energy levels are within −5.60 eV–5.85 eV and −3.54 eV–3.75 eV, respectively. When the LUMO energy level is low, it exhibits more electron-transport property, which is favorable for electron trapping. These results demonstrate that an extra nitrogen atom can significantly improve the electron-withdrawing ability and modulate the electrochemical properties and HOMO/LUMO energy levels.[31] The devices based on the three complexes would exhibit better EL performances.[32–34]



Scheme 2 Energy level diagram of the HOMO and LUMO levels of materials investigated and their chemical molecular structures.

Theoretical calculations

To gain insight into the electronic states of the complexes, we performed the time-dependent density functional theory (TD-DFT) calculations. As shown in Fig. 2 and Table S4 (ESI†), the three complexes display a similar orbital charge density distribution profile. Besides the significant contribution (43.77–51.57%) from the primary ligands to the HOMOs, the Ir metal d_π orbitals also contribute considerably (41.19–48.72%) to the HOMOs. The LUMOs are composed of a significant contribution from the primary ligands (92.67–93.44%) and a negligible contribution from the Ir metal d_π orbitals (2.50–4.39%) and the ancillary ligands (2.43–4.06%). Usually, the HOMO–LUMO transitions contribute mainly to both the S_1 and T_1 states. Therefore, the S_1 and T_1 states of these complexes may show an MLCT character with LLCT features.[35–39] The HOMO and LUMO energy levels were also calculated, which turned out to be −5.72/−2.67, −5.73/−2.52 and −4.94/−2.20 eV for

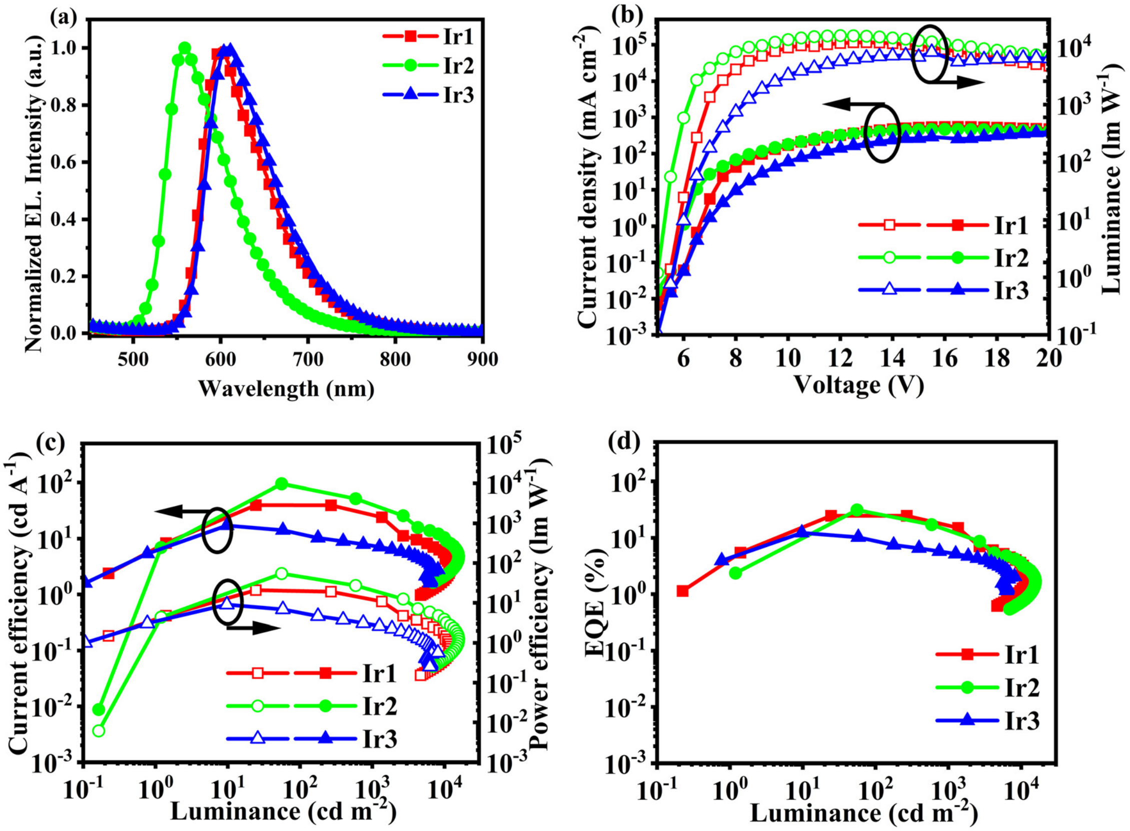


Fig. 4 (a) EL spectra. (b) Current density–voltage–luminance characteristics. (c) η_c and η_p as a function of luminance. (d) Curves of EQE *versus* luminance.

$(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$, $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$ and $(4\text{-pq})_2\text{Ir}(4\text{-pca})$, respectively. The frontier molecular orbital energy levels are significantly more deeper than their counterparts, suggesting that the electron-withdrawing capacity is improved with the increase in the number of nitrogen atoms.

Photophysical properties

The ultraviolet-visible absorption (UV-vis) and photoluminescence (PL) spectra of Ir(III) complexes in dichloromethane (DCM, 10^{-5} M) at room temperature are shown in Fig. 3. The relevant data are listed in Table 1. All these complexes show intense absorption bands below 375 nm due to the spin-allowed ligand-centered singlet π–π* transitions. The weaker absorption bands between 375 and 600 nm can be assigned to the singlet and triplet metal–ligand charge transfer (^{1}MLCT and ^{3}MLCT) and triplet ligand-centered charge transfer (^{3}LC) absorptions.[40] Due to the strong spin–orbit coupling of iridium atoms, Ir(III) complexes undergo a mixture of singlet and triplet states, which may enhance their quantum efficiency, and differences in the primary ligands also affect the quantum efficiency of Ir(III) complexes.[41,42]

Due to the primary ligand's relative rigidity and large planar structure, the three complexes show higher PLQYs in CH_2Cl_2 solution. They are 83.6% for $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$, 88.5% for $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$, and 57.6% for $(4\text{-pq})_2\text{Ir}(4\text{-pca})$, respectively. This result shows that OLEDs with these emitters can exhibit better performances. Introduction of $-CF_3$ will enhance the electron-withdrawing ability of the primary ligands and weaken the conjugated system, thereby increasing the quantum yields. In contrast, the PLQYs of complexes without $-CF_3$ will be reduced.[18,43] In addition, the change of substituents on the primary ligands also affects the CIE properties of different emitters measured in CH_2Cl_2 solution. They include CIE (0.66, 0.34) for $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$, CIE (0.67, 0.33) for $(4\text{-pq})_2\text{Ir}(4\text{-pca})$, and CIE (0.41, 0.58) for $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$. All the complexes in degassed DCM solution exhibit quite short phosphorescence lifetimes, which are 6.87 μs for $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$, 5.45 μs for $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$, and 7.03 μs for $(4\text{-pq})_2\text{Ir}(4\text{-pca})$, respectively (Table 1).

Table 2 Device performances based on the three complexes at a 1 wt% dopant ratio

Device	EL_{max} λ (nm)	$V_{turn\text{-}on}$ [a] (V)	L_{max} (cd m^{-2})	$\eta_{c,max}$ (cd A^{-1})	$\eta_{p,max}$ (lm W^{-1})	$\eta_{ext,max}$ (%)
D1	601	5.5	11 959	39.8	20.8	24.7
D2	558	5.0	15 673	95.4	54.5	31.3
D3	607	5.5	8094	17.2	8.90	12.3

[a] At 1 cd m^{-2}.

Electroluminescent devices

By comparing the phosphorescence quantum efficiencies, the devices using $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$, $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$, and $(4\text{-pq})_2\text{Ir}(4\text{-pca})$ as the emitters for the solution-processed OLEDs are named D1, D2, and D3, respectively. The devices have a simple structure of ITO/PEDOT:PSS (35 nm)/PVK (5 nm)/Ir (1 wt%): CBP (25 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (120 nm), in which PEDOT is poly(3,4-ethylenedioxythiophene), PSS is polystyrene sulfonic acid, PVK is poly(*N*-vinylcarbazole), CBP is 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl, and TmPyPB is 1,3,5-tri[(3-pyridyl)phen-3-yl]benzene. Due to the carrier transport equilibrium, CBP was chosen as the hybrid host material, PEDOT:PSS as the hole-transport layer (HTL) and electron-blocking layer (EBL), and TmPyPB as the electron-transport layer (ETL) and hole-blocking layer (HBL) material (Scheme 2).[44–46] The luminescence peaks of D1, D2, and D3 at 601 nm, 558 nm, and 607 nm, respectively, are close to those measured in CH_2Cl_2 solution, indicating that the EL emission of the devices originates from Ir(III)

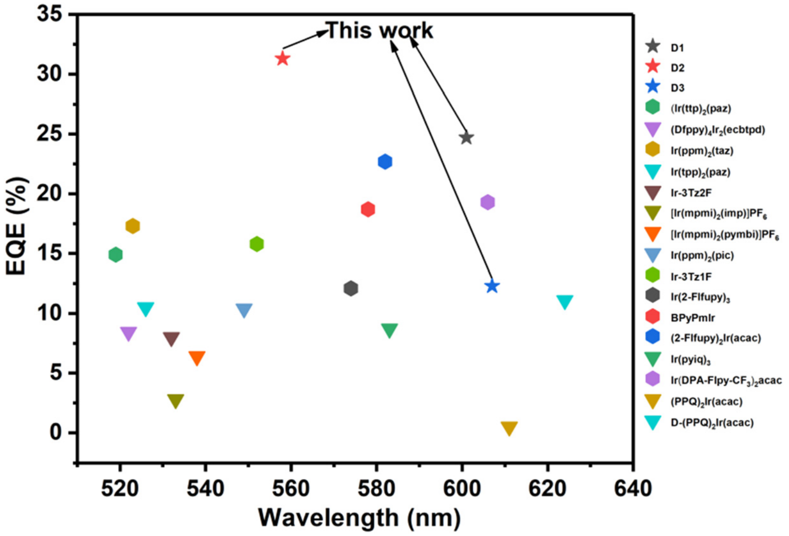


Fig. 5 The EQEs of solution-processed OLEDs using Ir complexes with emission at 510–630 nm are summarized, and their chemical names are summarized in Table S5.†

complexes. No prominent EL emission bands from the host material are observed in these devices, which suggests that the energy transfer from the host material to Ir(III) complexes in the emissive layer is efficient.

As can be seen from Fig. 4 and Table 2, device D1 based on $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$ outperforms device D3 employing $(4\text{-pq})_2\text{Ir}(4\text{-pca})$, which correlates with the Φ_{PL} of these phosphorescent emitters. Device D1 has a turn-on voltage of 5.5 V, $L_{\max}$ of 11 959 cd m^{-2}, $\eta_{\text{c,max}}$ of 39.8 cd A^{-1}, $\eta_{\text{p,max}}$ of 20.8 lm W^{-1}, and $\text{EQE}_{\max}$ of 24.7%. In contrast, the device performance of D1 is superior to that of D3, mainly due to the introduction of $-\text{CF}_3$ into the primary ligand, which improves the PLQY of $(4\text{-tfmpq})_2\text{Ir}(4\text{-pca})$ and also reduces the triplet–triplet annihilation (TTA) and triplet–polaron annihilation (TPA) effects.[47,48] The device D2 has a start-up voltage of 5 V, the maximum luminance ($L_{\max}$) of 15 673 cd m^{-2}, $\eta_{\text{c,max}}$ of 95.4 cd A^{-1}, $\eta_{\text{p,max}}$ of 54.5 lm W^{-1}, and $\text{EQE}_{\max}$ of 31.3%. The excellent performance of the $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$-based device may stem from the fact that the heavy atom effect of S atoms can enhance the spin–orbital coupling (SOC) of the Ir(III) complexes, which can also improve the EL performance.[49] The rigid structure of the primary ligand and a large number of nitrogen heterocyclic structures endow the three emitters with enhanced electron transport capabilities to achieve a balance between carrier injection and transport.[6,27] The $\text{EQE}_{\max}$ values of 31.3% and 24.7% for orange and red OLEDs, respectively, are ranked among the highest values for solution-processed OLEDs employing iridium emitters (Fig. 5 and Table S5†).[50–59]

Conclusions

Three phosphorescent bis-cyclometalated iridium complexes with rigid nitrogen heterocyclic structures have been successfully developed. Notably, varying the primary ligand moiety can modulate the iridium complexes' color and PLQY properties. In addition, the high PLQY and charge carrier mobility endow these iridium complexes with excellent EL efficiencies to prepare OLEDs in solution. In particular, the solution-processed OLED based on $(4\text{-tfmptp})_2\text{Ir}(4\text{-pca})$ exhibits the most prominent performance with the peak η_{c} and EQE of 95.4 cd A^{-1} and 31.3%, respectively, which are among the highest values for orange solution-processed OLEDs. This research reveals the profound relationship between the iridium structure and optoelectronic properties. It provides an effective strategy for developing efficient iridium complexes and the corresponding solution-processed OLEDs.

Conflicts of interest

The authors declare no conflict of interest.

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