

A Comparative Study of Deep-Blue Ir(III), Pt(II) and Pd(II) Phosphors in Photophysical Properties and OLED Performance

Linfeng Lu

*College of Chemical Engineering, Beijing University of Chemical Technology, Beijing, China
1354040347@qq.com*

Abstract. To date, the main emitters of metal complexes in organic light-emitting diode (OLED) display technology have been the $5d^6$ Ir(III), $5d^8$ Pt(II) and $4d^8$ Pd(II) species. Recently, with the appearance of phosphor-assisted TADF-sensitized fluorescence and the abbreviation pTSF technology, these complexes have found new applications in fourth-generation displays as phosphorescent sensitizers and energy-transfer bridges. However, at present, there are still some problems with the application of luminescent metal complexes in OLEDs. For example, there is an urgent need to continue developing deep-blue-emitting complexes with high colour purity and high efficiency that are also stable in devices. Compare and summarize the photophysical properties and device performance of four representative deep-blue emitters in previous studies in this paper. Among them, Ir(III)- or Pt(II)-luminophores have shown good results, and all devices incorporating them have exhibited external quantum efficiencies (EQEs) exceeding 25%. Pt(II)-based complexes also have a very narrow emission in the device (FWHM = 14 nm) and can meet the high-specification BT.2020 standard. A probable cause of this increase is a relatively rigid structure of the tetradentate ligand. Pd(II)-based diodes have relatively poor performance compared with others; their device efficiencies (EQEmax) are less than 2%, and this is due to weak spin-orbit coupling. To develop high-efficiency deep-blue-emitting materials for OLEDs, we need to understand how metal centres and suitable ligand frameworks are connected better.

Keywords: OLEDs, EQE, tetradentate ligand, metal complexes

1. Introduction

Phosphorescent metal complexes of $5d^6$ Ir(III), $5d^8$ Pt(II) and $4d^8$ Pd(II) are driving the modernisation of OLED displays, such as screens for smart electronic devices, medical devices and vehicles [1, 2]. They can serve as the main materials for emissive layers (EMLs) and also as phosphorescent sensitizers for the new-generation pTSF technology. Most of these widespread applications are due to a heavy-atom effect of certain metals that can cause strong spin-orbit coupling (SOC). It can help achieve efficient and fast intersystem crossing, and thus the device will reach a maximum internal quantum efficiency (IQE) close to 100 per theory [3].

The three types of complexes with Ir(III), Pt(II) and Pd(II) at their centres and their general features have been introduced above. The Earth's crustal abundances of iridium, platinum and palladium are about 0.001, 0.005 and 0.015 ppm, respectively. And interestingly, market prices usually reflect scarcity and thus have the order $\text{Pd} < \text{Pt} < \text{Ir}$. Among them, palladium is relatively inexpensive but has a disadvantage of lower-energy 4d orbitals and weaker spin-orbit coupling; therefore, it exhibits reduced molecular stability and lower intersystem crossing efficiency [4].

Over the long term, Ir(III) and Pt(II) phosphors have continuously been the main directions for OLEDs over the past three decades, and the development of Pd(II) complexes was much later [5]; Ir(III) complexes have achieved excellent device performance, so the corresponding red and green luminophores have been commercialized in phosphorescent OLEDs (PHOLEDs), but blue-emitting species are still not well-developed.

Generally speaking, the present deep-blue triplet emitters have not reached the desired level for key performance indicators, such as colour purity ($\text{CIE}_y < 0.1$), external quantum efficiency (EQE) and operating stability [6]. There are few reports available on deep-blue triplet emitters that can achieve a combination of high colour purity and stable devices.

Among the blue-emitting iridium(III) species, it is worth mentioning a typical ligand that can be used to help the metal achieve good stability and blue-light emission: cyclometalated N-heterocyclic carbene (NHC) ligands. Since 2020, Jin and his colleagues have reported a deep-blue NHC-based Ir(III) emitter that meets the NTSC standard ($\text{CIE}_x = 0.149$; $\text{CIE}_y = 0.085$). The corresponding device is optimised with 40 vol% doping, and it has achieved an outstanding EQE of 24.8% and a high luminance of 6453 cd/m^2 [7]. By 2022, the same group released mer-Ir(ptbbp)₃, a new deep-blue Ir(III) emitter for solution-processed PHOLEDs. At a doping concentration of 50 wt%, the corresponding device had an excellent EQE_{max} of 25.3% and a CIE value of (0.16, 0.10) [8]. Building upon the previous work on deep-blue Pt(II) luminophores, Kim et al. have recently developed a rigidity-enhanced emitter named PtCK1 in 2024, which suppresses structural relaxation by incorporating a spirofluorene fusion at the carbazole group [9]; this bottom-emitting OLED exhibits deep-blue emission with an EQE_{max} of 25.3% and a luminescence FWHM of 21 nm. In addition, its top-emitting counterpart had an ultranarrow spectrum (FWHM: 14 nm) and CIE_{x,y} of (0.139, 0.046), which met the requirements of BT.2020 blue standard. Pd(II) complexes with both high efficiency and colour purity in the deep-blue light region are relatively rare. A series of Pd(II) complexes with rigid tetradentate heteroaryl ligands (ppz, ppy, poz) were reported by She and his colleagues in 2020. A relatively rigid structure achieved a high photoluminescence quantum yield (up to 51% in solution and 22% in doped films) and had an excited-state lifetime of less than 100 μs [10]; an optimised device exhibited deep-blue emission with $\text{CIE}_y < 0.10$ and an EQE of only 2.0%, indicating that further research on these materials is warranted. We present the photophysical and electroluminescence properties of the four blue-emitting complexes, mer-Ir(ptbbp)₃, [8] mer-Ir(tfpi_tmBn)₃, [11], PtCK1, [9] and Pd(1-ptz), [10], and discuss their suitability for OLED applications herein.

2. Results and discussion

2.1. Photoluminescence properties

The four metal complexes containing mer-Ir(ptbbp)₃, [8] mer-Ir(tfpi_tmBn)₃, [11] PtCK1, [9] and Pd(1-ptz), [10] had deep-blue photoluminescence in solution at 298 K, with emission maxima at 467 nm (in DCM), 427 nm (in CH₃CN), 454.4 nm (in DCM), and 441 nm (in DCM), respectively, as shown in Table 1. Measurements in DCM at 298 K (Table 1) show that mer-Ir(ptbbp)₃ has a near-

unity photoluminescence quantum yield (96%) and an excited-state lifetime of about 3 μ s (Table 1) [8]. Furthermore, in acetonitrile solution at 298 K, the complex *mer*-Ir(tfpi_tmBn)₃ (Table 1) had a quantum yield of 49% and a lifetime of 2.85 μ s. However, when *mer*-Ir(tfpi_tmBn)₃ was doped with 16.5 wt% in the TSPO1 film, both the quantum yield and the lifetime mentioned above increased significantly to 89% and 3.14 μ s, respectively. This may be due to the limited molecular motion in the solid state, which effectively suppresses non-radiative decay [11]. Furthermore, the PMMA film doped with the Pt(II) complex PtCK1 at a concentration of 5 wt% had a quantum yield close to unity (97%) and a lifetime of 2.95 μ s (as shown in Table 1); on the other hand, the quantum yield of the Pd(II) complex Pd(1-ptz) in DCM solution was significantly lower, at 16%, and in the PMMA film doped with 5 wt%, it was 17%. At the same time, the luminescence lifetimes were significantly extended; they were 37 μ s in solution and 42 μ s in the film (see Table 1) [10]. Compared with Ir(III) and Pt(II) analogues, the different photophysical behaviour mentioned above was characterised by a decrease in luminescence quantum yield and an extension of luminescence lifetime. The main reason was that the SOC constant (1412 cm⁻¹) of Pd(II) (1412 cm⁻¹) was relatively small compared with that of Ir(III) (3909 cm⁻¹) and Pt(II) (4481 cm⁻¹) (Table 1) [4]. Additionally, the emission of Pd(1-ptz) was frequently dominated by the triplet ligand-center (3LC) state in nature, which resulted from the low-energy 4d orbital of palladium. The 4d⁸ electronic structure reduced the overlap between metal-ligand orbitals, weakened the metal-to-ligand charge transfer (MLCT) state, and stabilized the LC state. Thus, the radiative decay is relatively slow and some non-radiative decay occurs to some extent [12].

Table 1. Photophysical properties and corresponding device parameters of *mer*-Ir(ptbbp)₃, [8] *mer*-Ir(tfpi_tmBn)₃, [11] PtCK1, [9] and Pd(1-ptz) [10]

	<i>mer</i> -Ir(ptbbp) ₃ [8]	<i>mer</i> -Ir(tfpi_tmBn) ₃ [11]	PtCK1 [9]	Pd(1-ptz) [10]
SOC / cm ⁻¹		3909 (Ir) [4]	4481 (Pt) [4]	1412 (Pd) [4]
$\lambda_{\max}$ / nm (in solution, 298 K)	467 (DCM)	427 (CH ₃ CN)	454.4 (DCM)	441 (DCM)
QY	96% (DCM)	49% (CH ₃ CN) 89% (16.5% wt.% in TSPO1)	97% (5 wt.% in PMMA)	16% (DCM) 17% (5 wt.% in PMMA)
lifetime / μ s	~3	2.85 (CH ₃ CN) 3.14 (16.5% wt.% in TSPO1)	2.95 (5 wt.% in PMMA)	37 (DCM) 42 (5 wt.% in PMMA)
λ_{EL} (FWHM) / nm	443	424 (66)	460 (21, bottom) 460 (14, top)	445 (44)
CIE	(0.156, 0.102)	(0.16, 0.08)	(0.132, 0.108) (bottom) (0.139, 0.046) (top)	(0.149, 0.079)
$EQE_{\max}$	25.3%	14.9%	25.3% (bottom)	~2%
EQE @ 100 cd/m ²	21.8%	11.7%	--	--

2.2. OLED performance

The electroluminescence spectra of light-emitting devices based on *mer*-Ir(ptbbp)₃, *mer*-Ir(tfpi_tmBn)₃, PtCK1 and Pd(1-ptz) showed blue emission at 443, 424, 460 and 445 nm, respectively (Table 1). Among them, the device using Pt(II)-complexed PtCK1 (see Table 1) as the

EML material had a very narrow emission spectrum. Notably, the FWHM was only 21 nm for the bottom-emitting device and reduced further to 14 nm in the top-emitting configuration [9]; as expected, these were much narrower than the emission spectra of mer-Ir(tfpi_tmBn)₃ (FWHM = 66 nm) and Pd(1-ptz) (FWHM = 44 nm) (Table 1). The very narrow emission of PtCK1 was attributed to the excellent coupling of the carbazole and benzofuran groups in its tetradentate ligand, which thus increased molecular rigidity.

As shown in Table 1, both devices with mer-Ir(ptbbp)₃ and mer-Ir(tfpi_tmBn)₃ had deep-blue electroluminescence, with chromaticity coordinates of (0.156, 0.102) and (0.16, 0.08), respectively [8, 11]. The complex PtCK1 showed different electroluminescence properties in the devices with different structures (Table 1): the CIE coordinates of the bottom-emitting device were (0.132, 0.108), and the top-emitting one reached (0.139, 0.046). The performance of the latter device (CIE_y < 0.05) showed ultra-high colour purity and met the commercialised BT.2020 blue standard [9]. Another remarkable feature was a high Blue Index (BI) of up to 397 (cd/A)/CIE_y. The PHOLED devices containing Pd(II) complex, Pd(1-ptz), were also able to achieve deep-blue emission with a CIE_{x,y} of (0.149, 0.079) (Table 1), and the corresponding devices showed narrowband deep-blue electroluminescence [10].

The OLED based on mer-Ir(ptbbp)₃ has achieved a high efficiency of nearly 25.3% and shows low efficiency roll-off; it maintains an efficiency of 21.8% at an actual brightness of 100 cd/m² (Table 1). However, devices with mer-Ir(tfpi_tmBn)₃ only reached a maximum EQE of 14.9%. It should also be pointed out that the Pt(II) complex PtCK1 had very good performance, comparable to mer-Ir(ptbbp)₃, and achieved an EQE_{max} of 25.3% in the bottom emission configuration (Table 1). Devices doped with Pd(1-ptz), on the other hand, showed a large drop in efficiency and had an EQE_{max} of only about 2% (Table 1). This also showed that Pd(II) complexes had certain deficiencies in OLEDs at present [10].

3. Conclusion

Comparison of deep-blue phosphorescent emitters based on Ir(III), Pt(II) and Pd(II) centres shows that their structures and properties, as well as photophysical and electroluminescent characteristics, are related. First, for the Ir(III) emitters, mer-Ir(ptbbp)₃ and mer-Ir(tfpi_tmBn)₃ have reported photoluminescence quantum yields as high as 96% in solution at 298 K. These devices, when used in OLEDs, have relatively high external quantum efficiencies, close to a maximum of 25.3%, due to strong spin-orbit coupling of iridium(III) and fast intersystem crossing; thus, singlet excitons can be fully utilized [8, 11]. However, they have slightly wider emission spectra and a high cost of iridium metal, so they are not suitable for high-definition OLED displays.

However, the above discussions show that the Pt(II) complex PtCK1 (see Table 1) has achieved good results compared with the iridium complex. The Pt(II) complex PtCK1 is comparable in performance to the Ir(III) complex mer-Ir(ptbbp)₃; it has a PLQY close to 1 (specifically 97%) and an EQE_{max} of 25.3% in devices, as well as narrow-band emission (FWHM = 14 nm) that meets the strict requirements of BT.2020 blue standards [9]. This excellent colour purity is due to the highly rigid tetradentate-fused ligand scaffold, and Pt(II) emitters are now considered promising materials for the next generation of OLED displays.

In addition to the above, palladium(II) complexes are also relatively promising emitters for OLEDs and have received more and more attention recently. Due to the inherent limitations of metal, the complex Pd(1-ptz) has a relatively low PLQY (~17%) and a poor EQE_{max} (~2%) (Table 1) [10]. This is because of weak spin-orbit coupling and a dominant ligand-centered triplet state, which enhances the rate of non-radiative decay. Although Pd(II) complexes can achieve deep-blue

emission, their application in OLEDs remains impractical; without proper ligands to enhance the proportion of metal-to-ligand charge transfer states or suppress losses due to molecular vibrations, it is not feasible.

In short, Ir(III) complexes have set a high-efficiency benchmark for OLEDs; Pt(II) systems are more suitable for the future of narrowband blue emitters; and Pd(II) is still being explored for good ligand engineering.

4. Future perspective

In addition to the luminescent materials themselves, several other promising research directions for the noble-metal-based complexes mentioned above have been identified.

First of all, noble-metal complexes have shown good prospects for application in blue-light sensitisation systems, particularly pTSF systems. In the sensitization system, the inherent luminescent profiles of Pd(II) complexes are not the main reasons; instead, the energy level matching with fluorescent materials and a good exciton capture ratio are more significant indicators to be considered. Future work will rationally design ligands to modify the energy levels and increase the rigidity of the molecule, reduce non-radiative decay, and thus improve the overall efficiency of the device.

Second, circularly polarised luminescent (CPL) materials are also a new field of study. Ir(III) and Pt(II) complexes have a heavy-atom effect and excellent photophysical properties that are suitable for building high-efficiency circularly polarised organic light-emitting diodes (CP-OLEDs). To achieve CPL emission with good colour purity and device efficiency, chiral elements such as stereocentres, axial chirality or helical chirality can be added to current blue emitters, or strategies for chiral induction can be used.

Exploration of luminescent composites based on earth-abundant metals is needed to achieve the sustainable development of OLED technology after precious-metal systems. Copper(I), manganese(II), chromium(III), nickel(II) and cobalt(II/III) are all relatively abundant in the crust and have various coordination geometries and rich excited-state profiles of their complexes. However, due to their weak inherent spin-orbit coupling and fast non-radiative decay induced by low-energy metal-centered states, a high demand has been placed on ligand design. The two main ways to create strong coordination environments and introduce rigid ligands for improving the luminescence of low-cost metal-based luminescent materials are now well-known.

In short, metal complexes continue to have various applications in OLEDs at present, such as emitters, sensitizers and components for CPL luminescence.

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