

## Review

# Phosphorescent cyclometalated complexes for efficient blue organic light-emitting diodes

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## Abstract

Phosphorescent emitters are extremely important for efficient organic light-emitting diodes (OLEDs), which attract significant attention. Phosphorescent emitters, which have a high phosphorescence quantum yield at room temperature, typically contain a heavy metal such as iridium and have been reported to emit blue, green and red light. In particular, the blue cyclometalated complexes with high efficiency and high stability are being developed. In this review, we focus on blue cyclometalated complexes. Recent progress of computational analysis necessary to design a cyclometalated complex is introduced. The prediction of the radiative transition is indispensable to get an emissive cyclometalated complex. We summarize four methods to control phosphorescence peak of the cyclometalated complex: (i) substituent effect on ligands, (ii) effects of ancillary ligands on heteroleptic complexes, (iii) design of the ligand skeleton, and (iv) selection of the central metal. It is considered that novel ligand skeletons would be important to achieve both a high efficiency and long lifetime in the blue OLEDs. Moreover, the combination of an emitter and a host is important as well as the emitter itself. According to the dependences on the combination of an emitter and a host, the control of exciton density of the triplet is necessary to achieve both a high efficiency and a long lifetime, because the annihilations of the triplet state cause exciton quenching and material deterioration.


Keywords: OLED, phosphorescent emitter, iridium complex, cyclometalated complex

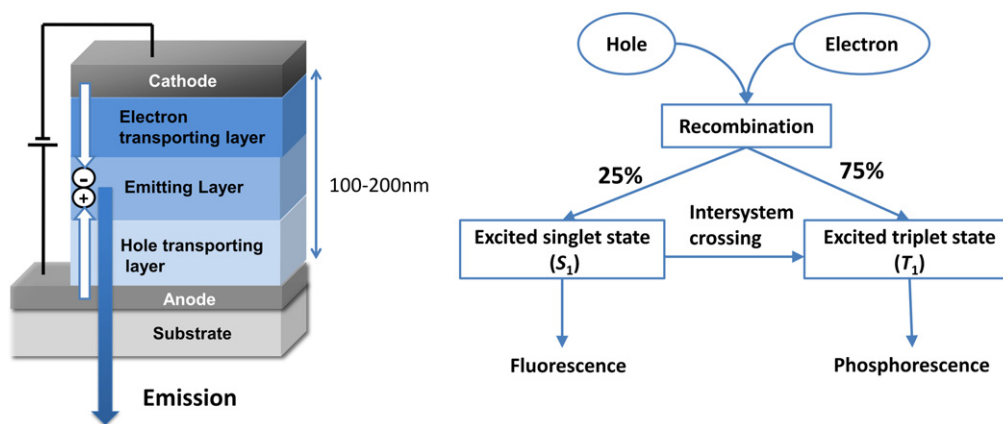
## 1. Introduction

Approximately 20% of electric power worldwide is used for lighting. This proportion is even higher when the power consumed by displays is considered; therefore, the efficiency of optical devices that convert electricity into light is extremely important. Research and development of organic light-emitting

diodes (OLEDs) as the next generation of light-emitting devices are being actively pursued because unlike fluorescent lamps, OLEDs do not contain any toxic substances such as mercury, and they can also be manufactured in a highly efficient and flexible manner through a wet process. The three methods that have been proposed to increase the efficiency of the OLEDs are the use of high-efficiency luminescent materials, reduction of the input voltage, and the use of light out-coupling technology. Phosphorescent emitters are important materials for highly efficient light-emitting diodes (LEDs).

The OLED is a light-emitting device that uses excitons generated by the recombination of injected holes and

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**Figure 1.** Device structure and luminescence process.

electrons in the emitting layer. The most significant difference from excitons generated by optical excitation is in the generating ratios of the excited singlets to that of the excited triplets. Except for some compounds that exhibit transitions directly from the ground state to the triplet state, only the excited singlet states are generated immediately after optical excitation. In this respect, the excitons generated by a charge injection have a singlet-to-triplet ratio of 1:3 [1].

The efficiency of the OLED can be increased using phosphorescent materials because in addition to the 75% excited triplet state generated during recombination, the remaining 25% excited singlet state can be converted into the excited triplet state through an intersystem crossing (figure 1). Furthermore, the efficiency of extracting light from inside the device to the air (light out-coupling efficiency) is ~20–25%. The limit of external quantum efficiency is 20–25% using a phosphorescent emitter. However, using a fluorescent emitter, the limit of external quantum efficiency is 5–6.25%.

Most organic compounds emit phosphorescence only at cryogenic temperatures. Phosphors that can emit at room temperature are mostly metal complexes. The excited states of the metal complexes can be largely categorized as the charge-transfer (CT) transition, the ligand-centered (LC) transition, and the metal-centered (MC) transition. Representative examples of complexes that exhibit the MC transition include complexes of lanthanides such as Eu or Nd, while metalloporphyrin can be cited as a representative example of the LC transition. Such complexes have been applied to OLEDs, but high efficiencies that approach the theoretical limit have not been pursued [2]. Meanwhile, phosphorescent metal complexes that exhibit the CT transition have achieved extremely high efficiencies.

Baldo *et al* conducted epoch-making research in 1999, which resulted in an external quantum efficiency (EQE) exceeding 8% with the iridium complex Ir(ppy)<sub>3</sub>, which emits green light [3]. Efficiency at theoretical limits has been achieved with cyclometalated Ir-complexes [4–6], and [7]. Highly efficient iridium complexes primarily emit phosphorescence by metal-to-ligand charge transfer (MLCT) or MLCT mixed with LC. Yellow and red phosphorescent emitters with extended conjugation ligands are reported [8–11], and [12], and these phosphorescent emitters such as Ir(ppy)<sub>3</sub> and Ir

(piq)<sub>3</sub> achieved the long operation lifetime [13, 14]. On the other hand, a blue phosphorescent emitter is needed to advance toward practical use.

At first, the excited state of cyclometalated metal complexes, which is important to design emissive materials, is described. Secondly, we focus on the progress of blue phosphorescent emitters. Finally, we show our improvements of efficiency and long life in blue phosphorescent devices.

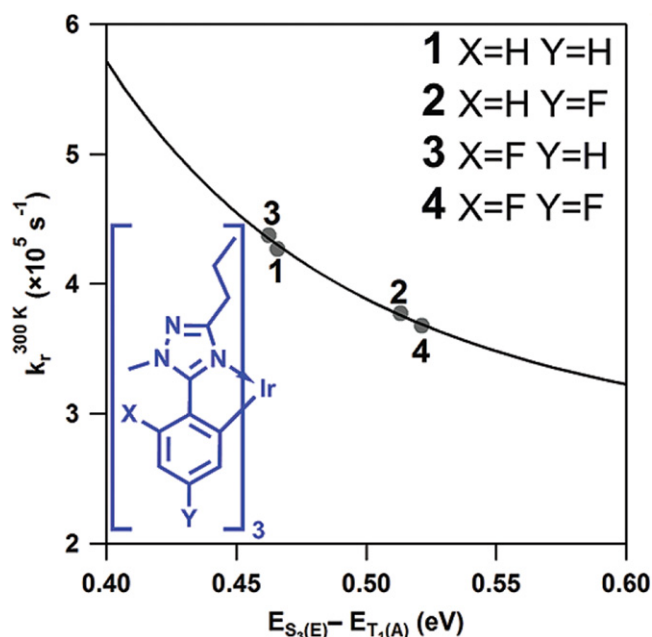
## 2. Excited state of cyclometalated metal complexes

The excited state of emissive cyclometalated metal complexes exhibits MLCT transition. In rare-earth metal complexes such as Eu(TTA)<sub>3</sub>, the color of emission is determined by the central metal because of the involvement of europium 4f orbitals. In the case of cyclometalated metal complexes, it is possible to change the emission color from blue to red by changing the ligand and center metal.

We show here that recent progress of computational analysis contributes to an understanding of the properties of the excited state by clarifying the controlling factors in radiative and non-radiative processes.

### 2.1. Radiative transition of cyclometalated metal complexes

In Ir(ppy)<sub>3</sub> as a representative emissive cyclometalated metal complex, the phosphorescence lifetime was 1.5 μs in the 2-methyltetrahydrofuran at room temperature, which is an extremely short phosphorescence lifetime [15] and [16]. Furthermore, since singlet-triplet (ST) absorption with several thousands M<sup>-1</sup>cm<sup>-1</sup> (a molar extinction coefficient) can be observed directly, it is evident that ST transitions are allowed. This is caused by the spin mixed state in which the excited triplet state is mixed with the excited singlet state in cyclometalated metal complexes such as Ir(ppy)<sub>3</sub> owing to strong spin-orbit coupling by the heavy atoms of the central metal. According to a quantum chemical calculation that takes spin-orbit coupling into consideration, the lowest excited triplet state (T<sub>1</sub>) of Ir(ppy)<sub>3</sub> is known to emit phosphorescence by mixing the strength of the fifth excited singlet state (S<sub>5</sub>), which has significant oscillator strength [17, 18], and [19].



**Figure 2.** Calculated total radiative rate at 300 K for Ir-complexes 1–4, plotted against the calculated energy gap between the scalar TDDFT excitations  $S_3(E)$  and  $T_1(A)$ . Reprinted with permission from A R G Smith *et al* 2012 *Inorg. Chem.* **51** 2821–31. Copyright 2012 American Chemical Society.

The radiative rate ( $k_r$ ) of cyclometalated metal complexes, in which the spin–orbit coupling plays an important role owing to the inclusion of heavy atoms such as iridium or platinum, is proportional to the magnitude of the spin–orbit coupling [20].

In common organic chemical compounds, the three triplet sublevels in the lowest excited triplet state are degenerate, but the cyclometalated metal complexes of MLCT transition split into three different sublevels by the strong spin–orbit coupling. This difference in energy between the sublevels of  $T_1$  is the zero-field splitting, which is one of the indicators of the value of the spin–orbit coupling. From the respective sublevels,  $k_r$  can be derived from experiments based on the temperature dependence of the phosphorescence lifetime.

In  $\text{Ir}(\text{ppy})_3$ ,  $k_r$  from the third sublevel is the fastest and has the largest transition moment at room temperature [21]. In

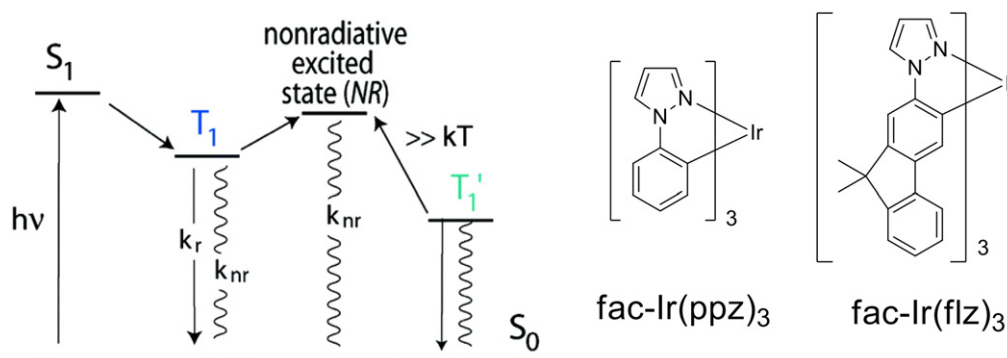
the Amsterdam Density Functional (ADF) package, the time-dependent density functional theory (TDDFT) method based on the zeroth-order regular approximation (ZORA) Hamiltonian is used to calculate the phosphorescence parameters. Younker and Dobbs used the ADF package (ADF 2012.01) to show the results of radiative rates for cyclometalated Ir-complexes. They proposed that radiative rates of cyclometalated Ir-complexes can be calculated at the TD-B3LYP/TZP: DZP level of the theory using the optimized  $S_0$  structures. This calculation for radiative rates has achieved favorable correlations with the experimental values [22]. The similar calculations by ADF were performed by Mori *et al* [23]. They suggested that the consideration of spin–orbit and solvation effects was important in the quantitative prediction of zero-field splitting and phosphorescence lifetime-of-transition metal complexes. They used the symmetry-lowered  $T_1$ -optimized structures in obtaining the physical properties.

Figure 2 shows that the magnitude of radiative rates of iridium complexes is influenced by the fluorine position in the phenyltriazole ligands, as the energy gap changes according to the substitution position [24].

On the other hand, the radiative rate constant  $k_r$  is also governed by the magnitude of the singlet–triplet splitting ( $\Delta E_{st}$ ). The value of  $k_r$  increases as the energy of  $\Delta E_{st}$  decreases [20]. In the case of iridium complexes for which the ligand is carbene derivative, the values calculated with TDDFT show a favorable correlation with the experimental values [25].

## 2.2. Non-radiative transition of cyclometalated metal complexes

Controlling the relationship between the triplet MLCT and other energy levels of excited states is important to achieve high phosphorescence yield. An example of an iridium complex coordinated fluorenyl pyrazole ligands ( $\text{Ir}(\text{Flz})_3$ ) is shown in figure 3 [26]. In  $\text{Ir}(\text{ppz})_3$  containing phenyl pyrazole ligands, the thermal deactivation process is dominant at room temperature, because the  $d-d$  transition level or the  $n-\pi^*$  level of the ligands (non-radiative level) is close to the MLCT. In the case of  $\text{Ir}(\text{Flz})_3$  with extended conjugation, emission from the triplet MLCT at room temperature can be observed due to the fact that the energy of the triplet MLCT is much lower than the non-radiative level.



**Figure 3.** Energy level scheme for emissions from  $\text{fac-Ir}(\text{ppz})_3$  ( $T_1$ ) and  $\text{fac-Ir}(\text{flz})_3$  ( $T_1'$ ). The two compounds are expected to have non-radiative excited states (NR) with similar energies. Reprinted with permission from T Sajoto *et al* 2005 *Inorg. Chem.* **44** 7992–8003. Copyright 2005 American Chemical Society.

Treboux *et al* calculated the potential energy curve for  $T_1$  along the rotation angle for the Ir–N bonding of  $\text{Ir}(\text{ppy})_3$  and  $\text{Ir}(\text{ppz})_3$  using density functional theory calculation [27]. It is known that with  $\text{Ir}(\text{ppy})_3$ , the MLCT state is more stable than the LC state even when the pyridine ring is twisted, but the LC state is more stable than the MLCT state when the pyrazole ring is twisted. It is therefore necessary to consider the energy relationship between the radiative MLCT and the non-radiative  $d-d$  transition and LC transition. However, the structural change between the ground state and the excited state is also a controlling factor for non-radiative rates. The non-radiative rate of *mer*- $\text{Ir}(\text{ppy})_3$  is about 20 times more than *fac*- $\text{Ir}(\text{ppy})_3$ , because the structural change of *mer*- $\text{Ir}(\text{ppy})_3$  between  $S_0$  and  $T_1$  is larger than that of *fac*- $\text{Ir}(\text{ppy})_3$  [19].

It was reported the phosphorescence quantum yield is increased by deuterium substitution. This is an example phosphorescence quantum yield increased as a result of non-radiative process inhibited by deuteration [28].

### 3. Blue phosphorescent cyclometalated metal complexes

There are four principal methods for shortening the wavelength of phosphorescence. They are (i) substituent effect on ligands, (ii) effects of ancillary ligands on heteroleptic complexes, (iii) design of the ligand skeleton, and (iv) selection of the central metal.

#### 3.1. Substituent effect on ligands

In the MLCT transition, the emission wavelength is decided by energy gap between the  $d$  orbital level of metal and lowest unoccupied molecular orbital (LUMO) levels of ligand. The  $d$  orbital level and LUMO level can be controlled by varying the substituents of ligands. For instance, emission peaks of cyclometalated Ir-complexes coordinated with substituted phenyl-pyridine ligands are shown in table 1.

The blue-shift and red-shift of emissions can be controlled by either implementing the electron-donating groups or the electron-withdrawing groups to the respective substitution positions. Electron-donating groups on 4-phenyl position shorten the emission peak, and electron-withdrawing groups on 5-phenyl position also shorten the emission peak.

This method makes it possible to achieve a highly efficient blue phosphorescent emitter. In cases of devices that require operational stability, however, the substituent effect cannot be considered a good option. The relationship between the relative operating lifetime and the emission peak wavelength of Ir-complexes coordinated with the substituted phenyl-pyridine is shown in figure 4. The device structure is ITO(110 nm)/CuPc(20 nm)/ $\alpha$ -NPD(100 nm)/emitter: mCP(5 wt% 40 nm)/BALq(20 nm)/LiF(0.5 nm)/Al(125 nm), where ITO stands for indium tin oxide, Pc is phthalocyanine,  $\alpha$ -NPD is N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine, mCP is 1,3-Bis(N-carbazolyl)benzene, and BALq is aluminium (III) bis(2-methyl-8-quinolinolato)-4-phenylphenolate.

A correlation can be drawn between the peak wavelength of the emission and the lifetime ( $L50$ ) during continuous operations. This indicates that achieving blue-colored emitters with long life is quite difficult owing to the substituent effect of phenyl-pyridine ligands. Considerations of this correlation are provided.

The first issue has to do with the spectral sensitivity of human eyes, which peaks at about 555 nm. The visual sensitivity for blue light in particular is only about one-fifth that of green light. This means that in order to gain the same level of brightness as green light, it would be necessary to emit five times the amount of power for blue light. Furthermore, it is known that the following relation exists with respect to the lifetime and initial brightness of the OLED:

$$\frac{T_2}{T_1} = \left( \frac{L_1}{L_2} \right)^n \quad (1)$$

$T_1$  is the lifetime when the brightness is  $L_1$ ,  $T_2$  is the lifetime when the brightness is  $L_2$ , and  $n$  is the acceleration factor, which varies depending on the devices but is usually 1.3–1.8.

In a case where the acceleration factor  $n$  is 1.6, for instance, emitting light with five times the power is predicted to shorten the lifetime by about 1/13. This naturally depends on the spectral shape as well, but this makes it evident that based on a simple comparison with the emission of green light, materials with ten times greater stability would be required. The wavelength–lifetime correlation shown in figure 4 indicates that the lifetime has been shortened to less than 1/10 for a blue-emitting device, which reveals that the impact is not solely due to visual sensitivity.

The second issue has to do with energy. The harshest conditions exist at the emitting layer in the organic layers of the OLED. Holes and electrons are injected and transported into the emitting layer, and cation radicals or anion radicals of phosphorescent emitters are generated. This means that there is a demand for electrical stability. Furthermore, the phosphorescence emission occurs through the formation of the excited state of the phosphorescent emitter in the recombination process. This means that there is also a demand for stability of the excited state.

If we were to assume, for instance, that the thickness of the film of the emitting layer is 20 nm, the emitter concentration is 5 mol%, the brightness is  $1000 \text{ cd m}^{-2}$ , and the theoretical emission efficiency is 100%, then for continuous operation of over 10 000 h, the calculation would reveal that the recombination and the light emission are repeated one billion times. Since the film of the OLED is primarily formed by the vacuum evaporation method, hardly any  $\text{H}_2\text{O}$  or  $\text{O}_2$  exists inside the films. This is an ideal environment for organic materials of the OLED. In order to achieve more than one billion turnovers, however, the stability must be extremely high for each instance. The level of energy required is particularly high for blue light compared to green or red light. The typical energy of blue light is 2.6 eV, but the energy of red light is only 2.0 eV. This means that the excited state of a blue emitter has 0.6 eV more energy than a red light emitter,

**Table 1.** Emission peaks of Ir-complexes coordinated with phenyl-pyridine derivative. RT stands for room temperature, Me for methyl, DMSO for dimethyl sulfoxide and THF for tetrahydrofuran.

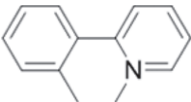
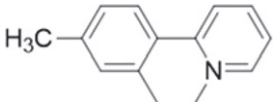
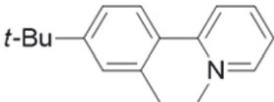
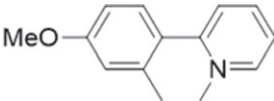
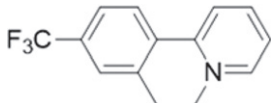
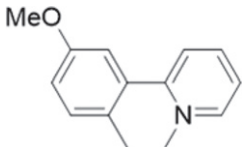
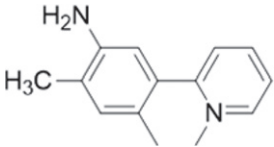
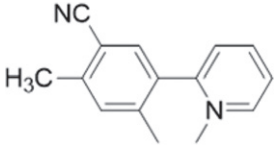
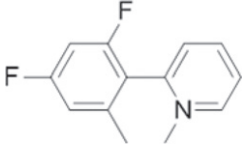
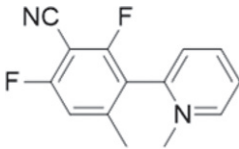
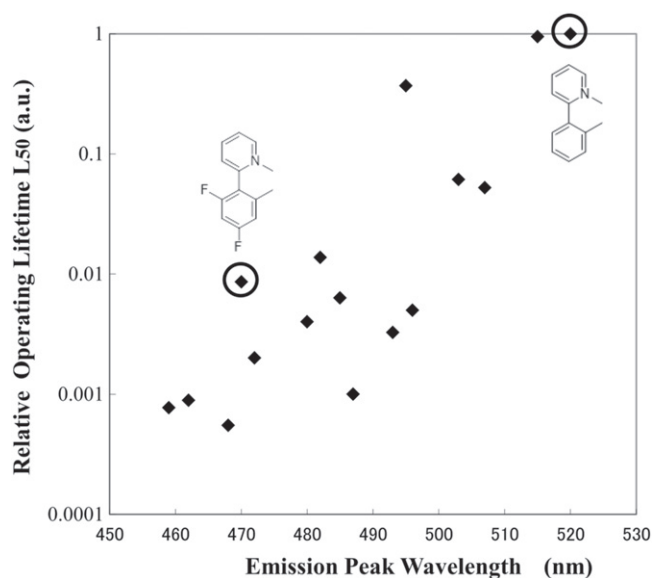
Compound	Ir(C <sup>^</sup> N) <sub>3</sub> C <sup>^</sup> N=	$\lambda_{\max}(\text{nm})$		Ref.
		at RT	at 77 K	
1		510 <sup>a</sup>	494 <sup>d</sup>	[29] [30]
2		510 <sup>a</sup>	493 <sup>d</sup>	[29] [30]
3		—	497 <sup>d</sup>	[30]
4		—	481 <sup>d</sup>	[30]
5		—	494 <sup>d</sup>	[30]
6		—	539 <sup>d</sup>	[30]
7		586 <sup>b</sup>	—	[31]
8		478 <sup>c</sup>	—	[31]
9		468 <sup>a</sup>	450 <sup>a</sup>	[29]



Table 1. (Continued.)

Compound	Ir(C <sup>^</sup> N) <sub>3</sub> C <sup>^</sup> N=	$\lambda_{\max}(\text{nm})$		Ref.
		at RT	at 77 K	
10		—	442 <sup>e</sup>	[32]

Measured in <sup>a</sup> 2-MeTHF, <sup>b</sup> DMSO/H<sub>2</sub>O (1/6), <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub>, <sup>d</sup> ethanol/methanol (1:1) and <sup>e</sup> THF.



**Figure 4.** Relationship between the device-operating lifetime and the emission wavelength of Ir-complexes coordinated with the substituted phenyl-pyridine.

which is disadvantageous with regards to stability. Just about the same thing can also be required about the cation radical state or anion radical state.

Achieving longer-lived blue OLED devices, therefore, would be difficult even when the substituent, which is generally considered to be stable, is implemented. Although it is unknown why the emission wavelength correlates with the device lifetime, as shown in figure 4, achieving a longer lifetime may require other mechanisms.

### 3.2. Impact of ancillary ligand on heteroleptic complexes

Ir-complexes have three bidentate ligands. It is possible to use the heteroleptic complex that coordinates different ligands. For instance, it is focused on Ir-complexes that have the ppy (phenyl-pyridine) and the ppz (phenyl-pyrazole) ligands. It has been reported that iridium complexes Ir(ppy)<sub>3</sub>, Ir(ppy)<sub>2</sub>(ppz), and Ir(ppy)(ppz)<sub>2</sub> are almost unchanged in the peak wavelengths and phosphorescence quantum yields [33].

What this means is that ppz ligands have a high T<sub>1</sub> level and therefore do not contribute to the emission, while the

MLCT transition is surmised to be localized in the ppy ligand. Such non-luminescent ligands shall be referred to as ancillary ligands for our purpose. The important effect of ancillary ligands is that they can control the level of the *d* orbit of iridium. This means that by selecting an electron-withdrawing ligand for the ancillary ligand, the level of the *d* orbit becomes deeper, which makes it possible to derive emissions with shorter wavelengths.

An example is shown in table 2. The effect of these ancillary ligands on the shortening peak wavelength is less than 10 nm. There is a limit to the amount of blue shift attainable with conventional ancillary ligands. Although the approach of ancillary ligands is suitable for the fine adjustment of the emission wavelength, a method for a more fundamental shortening of wavelengths is required.

### 3.3. Design of ligand skeletons

It is considered phenyl-pyridine as our benchmark, the electron-withdrawing ligand would make it possible to deepen the level of the *d* orbital of iridium. Furthermore, shortening of wavelengths is possible by a shallower LUMO level of the ligand. Heterocyclic rings and five-membered heterocyclic rings containing abundant nitrogen have been reported as such ligands (table 3).

As is evident from this, changing the ligand skeleton can dramatically promote shortening of the wavelength. The common point of these Ir-complexes is the heteroaromatic ligand containing more than two nitrogen atoms. Although the transition probability of phosphorescence using these ligands is important, the electron-deficient heteroaromatic ligand is effective to make emission wavelength of MLCT short. The operating lifetimes of many blue phosphorescent emitters have not been reported, but it is surmised that the lifetimes of emitters can be extended by making an appropriate selection of ligands.

### 3.4. Selection of central metals

Platinum (Pt), osmium (Os), and ruthenium (Ru) are well-known central metals of phosphorescence emitters [45] and [46]. Pt in particular has been known to be advantageous for shortening wavelengths because of its strong ligand field.

**Table 2.** Emission peaks and  $\Phi_p$  of Ir-complexes with ancillary ligand at RT.

Ir-complex	Peak wavelength (nm)	$\Phi_p$	Ref.
Ir(F2ppy) <sub>3</sub>	466 <sup>a</sup> 467 <sup>b</sup>	0.98 <sup>a</sup> 0.97 <sup>b</sup>	[34] [35]
Ir(ppz) <sub>2</sub> (F2ppy)	500 <sup>a</sup>	0.55 <sup>a</sup>	[34]
Ir(F2ppz) <sub>2</sub> (F2ppy)	457 <sup>a</sup>	0.6 <sup>a</sup>	[34]
FIr(pic)	471 <sup>b</sup>	0.89 <sup>b</sup>	[35] [36]
FIrtaz	460 <sup>c</sup>	—	[36]
FIrN4	459 <sup>c</sup>	0.13 <sup>a</sup>	[36] [37]

**Table 2.** (Continued.)

Ir-complex	Peak wavelength (nm)	$\Phi_p$	Ref.
FIr6	458 <sup>b</sup>	0.96 <sup>b</sup>	[35]

Measured in <sup>a</sup> 2-MeTHF, <sup>b</sup> dichloroethane and <sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> at RT.

Examples of blue phosphorescent Pt complexes are shown in table 4.

Pt (II) complexes have planar structures and exhibit long-wavelength phosphorescence from the excimer in high concentration. It is also possible to use a single Pt complex as a white emitter, because the phosphorescence of excimer is highly efficient. A white emitting device with Pt(46dfppy) (acac) as a white excimer emitter achieved high efficiency (maximum EQE; 18%) [50].

Phosphorescence from metal–metal-to-ligand charge transfer (MMLCT) can be derived from the dinuclear complex, Pt<sub>2</sub>(ppy)<sub>2</sub>(pyz), made up of two Pt atoms connected by a bridging ligand [51]. Although the relationship between the excimer phosphorescence of Pt(46dfppy)(acac) and the MMLCT state is unknown, it is possible that this has to do with Pt–Pt interactions.

#### 4. High-efficiency and long-life blue phosphorescent OLED

The device structure is important in order to obtain sufficient performance from the emitter. Particularly, in order to achieve highly efficient devices, inhibiting quenching, dropping the applied voltage, and improving light out-coupling efficiency.

Furthermore, higher efficiency and longer lifetime are possible through a combination of the emitter with the host. This is considered to be due to the inhibition of the annihilation that regulates the exciton density.

##### 4.1. Inhibition of quenching

If a neat film is used for the emitting layer, high EQE is difficult to achieve even with emitters that have high phosphorescence quantum yields because of concentration quenching. Ir-complexes such as Ir(ppy)<sub>3</sub> or FIr(pic) exhibited concentration quenching by Forster resonance energy transfer that is inversely proportional to the sixth power of the distance between emitters [52]. It is necessary to use the host compounds in order to realize a highly efficient device, the T<sub>1</sub> energy of the host materials must be greater than that of the emitter, and they must also have characteristics to transport charges. The carbazole derivatives are often used because of this property, particularly in the case of blue phosphorescent OLEDs (figure 5) [53] and [54].

The recombination zones of the OLED devices are often at the hole-transporting layer/the emitting layer (HTL/EML) boundary surface or the emitting layer/the electron transporting layer (EML/ETL) boundary surfaces, resulting in an energy transfer occurring from the exciton of the emitter to the hole-transporting material or electron-transporting material. It has been reported that high EQE is achieved by the hole transporting materials and the electron transporting materials with high T<sub>1</sub> energy [7], [55] and [56].

##### 4.2. Combination of emitter and host

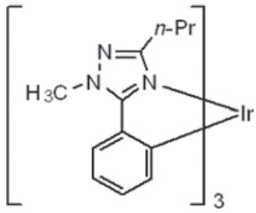
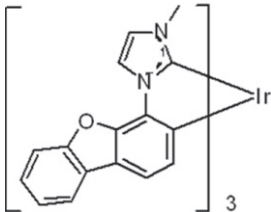
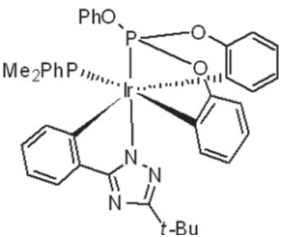
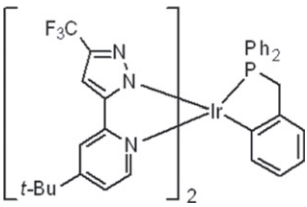
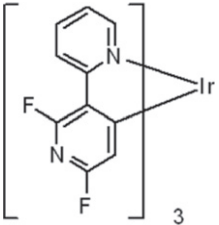
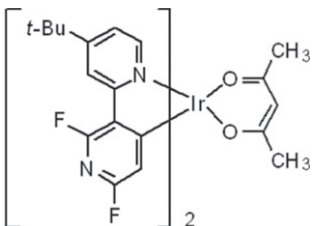
A device performance depends on the combination of an emitter and a host as well as the emitter itself. The relative operating lifetimes of each combination of an emitter (BE-1, BE-2, and BE-3) and a host (A), (B), (C), and (D) as an emission layer are shown in figure 6 [57]. The lifetimes of the three emitters were revealed to be almost the same with host A. Furthermore, the lifetime was also roughly the same with BE-1 for hosts (A), (B), (C), and (D). In contrast, the behavior was radically different for the cases using BE-2 and BE-3. Particularly for the case of BE-2, a five-fold longer lifetime could be achieved by combining it with host C. These hosts were derivatives with identical skeletons, and were satisfied for T<sub>1</sub> energy as well as the highest occupied molecular orbital (HOMO) and LUMO levels. Based on the fact that lifetime varies significantly depending on the emitters and host materials, understanding the appropriate combination of materials and combining the emitters and hosts in the design are the keys for improving lifetime.

The correlation of the operating lifetime and EQE with a combination of various light-blue emitters and hosts is shown in figure 7 [57]. The device structures, except for the emitting layer, were also identical in these devices. An extremely good correlation can be seen with lifetime and EQE. Of particular interest is the fact that a lifetime of 60 000 h is achieved at 300 cd m<sup>-2</sup> and EQE 26%, which is an extremely high efficiency.

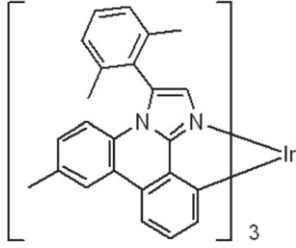
In order to achieve high efficiency in general, the exciton in the emitting layer is enclosed by a carrier blocking layer or an exciton-blocking layer. However, the phosphorescence lifetimes of phosphorescent emitters are over 1 μs, which is about 1000 times longer than in fluorescent emitters. For this reason, the efficiency is known to decrease via triplet–triplet annihilation and triplet–carrier annihilation. Moreover, these



**Table 3.** Photo-physical properties and EQE of Ir-complexes.

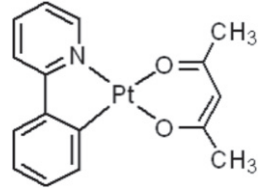
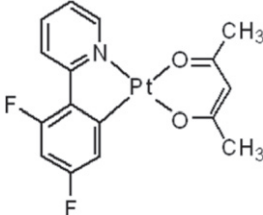
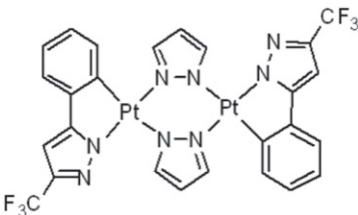
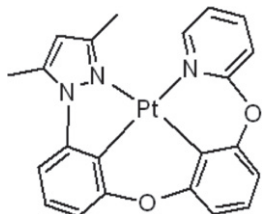
Ir-complex	Photo-physical properties in solution		Device property		
	Peak wavelength (nm)	$\Phi_p$	EQE <sub>max</sub> (%)	Ref.	
	449, 479 <sup>a</sup>	66 <sup>a</sup>	—	[38]	
Ir(dbfmi) <sub>3</sub>		445	—	18.6	[39]
	451,473,498 <sup>b</sup>	0.97 <sup>c</sup>	11	[40]	
Ir(fbppz) <sub>2</sub> (dfbdp)		428,455 <sup>b</sup>	0.57 <sup>c</sup>	11.7	[41]
Ir(dfppy) <sub>3</sub>		438, 463 <sup>b</sup>	0.71 <sup>b</sup>	—	[42]
FK306		454 <sup>d</sup>	0.78 <sup>c</sup>	17	[43]

**Table 3.** (Continued.)

Ir-complex	Photo-physical properties in solution		Device property	
	Peak wavelength (nm)	$\Phi_p$	EQE <sub>max</sub> (%)	Ref.
	464 <sup>e</sup>	—	11	[44]

Measured in <sup>a</sup> toluene, <sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub>, <sup>c</sup> film and <sup>d</sup> CHCl<sub>3</sub> at RT <sup>e</sup> Electroluminescence emission peak.

**Table 4.** Emission peaks and  $\Phi_p$  of Pt-complexes.

Pt-complex	Peak wavelength (nm)	$\Phi_p$	Ref.
Pt(ppy)(acac) 	486 <sup>a</sup>	0.15	[47]
Pt(46dfppy)(acac) 	466 <sup>a</sup>	0.02	[47]
[Pt(fppz)(μ-pz)] <sub>2</sub> 	446, 476, 502 <sup>b</sup>	0.55	[48]
PtOO1 	430, 456 <sup>a</sup>	0.83	[49]

Measured in <sup>a</sup> 2-MeTHF and <sup>b</sup> doped poly(methyl methacrylate) film at RT.

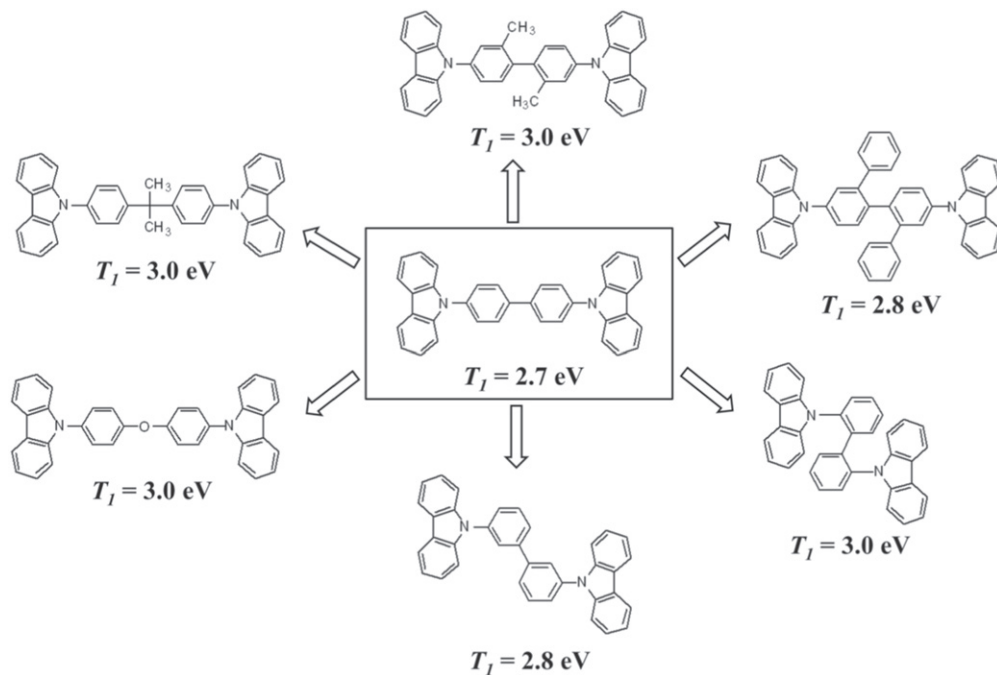


Figure 5. Carbazole derivatives as a host in EML.

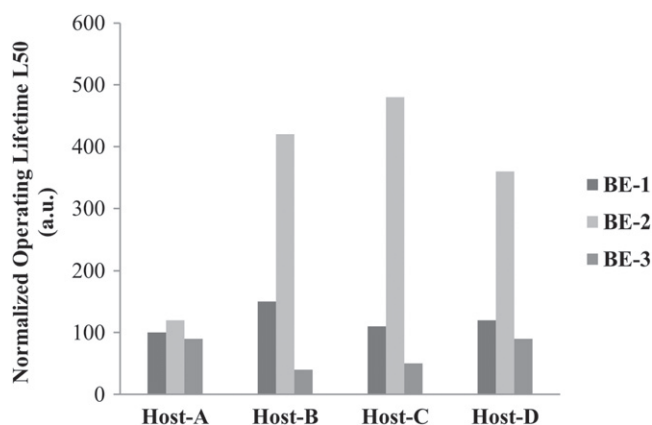


Figure 6. Relative operating lifetimes with light-blue phosphorescent emitter BE-1, BE-2, and BE-3 [57].

annihilations tend to cause the materials deterioration, so the operating lifetime decreases. When the recombination zone is concentrated in the boundary face of EML and the layer adjacent to EML, the exciton density of the triplet becomes high. In order to achieve both a high efficiency and long operating lifetime, it is necessary to control the position and the distribution of the recombination zone. This means that the recombination zone must be broadened to inhibit the annihilations. The tendency shown in figure 7 is such that the exciton density can be controlled by varying the host.

4.3. Improving the out-coupling efficiency with an oriented phosphorescent complex

It is possible to increase the light out-coupling efficiency by using molecular-oriented emitters. For instance, a planar Pt complex has been reported [58]. Although the

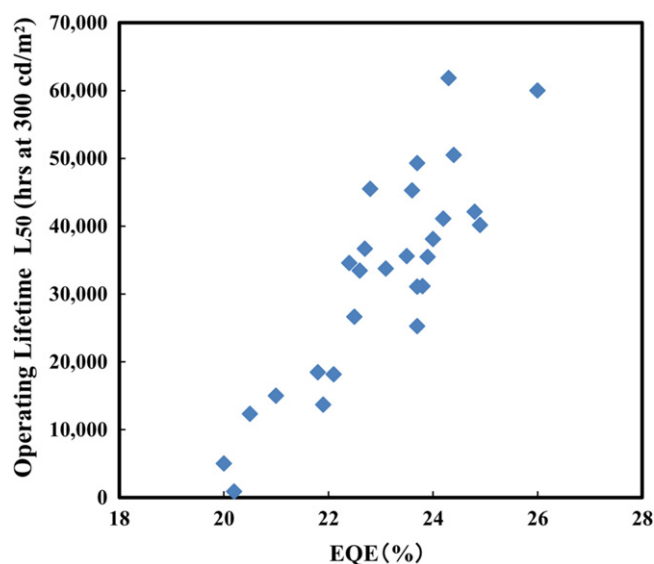


Figure 7. Correlation between the operating lifetime and EQE in various light-blue emitters and hosts [57].

photoluminescence quantum yield of the Pt complex was 50%, the maximum EQE was 15.8%. This leads to the estimation of the out-coupling efficiency to be at least 32%. Furthermore, together with optical analysis, the conclusion has been drawn that Pt complex was oriented parallel to the substrate.

Similar examinations have been conducted with heteroleptic Ir-complexes such as Ir(MDQ)<sub>2</sub>(acac) and Ir(ppy)<sub>2</sub>(acac). The orientation of Ir(MDQ)<sub>2</sub>(acac) has been verified in the parallel versus perpendicular ratio of 2:0.63 (2:1 in random cases) [59] and [60]. In Ir(ppy)<sub>2</sub>(acac) devices, roughly an identical level of orientation has been confirmed.

Furthermore, light out-coupling simulations have been conducted, which indicated that EQE reaches 46% when a 100% orientation of the emitter and 100% photoluminescence quantum yield (PLQY) are achieved [61].

Since the OLED is a planar light source, out-coupling is more difficult to achieve in comparison with an LED, which is a point light source. This can be considered an important technology in the pursuit of super-high efficiency.

## 5. Conclusions

In this review, we summarized cyclometalated complexes as the phosphorescent emitter for OLEDs. In particular, this paper focuses on blue phosphorescent emitters.

The excited state of highly efficient iridium complexes is MLCT or MLCT mixed with LC, the radiative transitions are allowed. TDDFT calculation for radiative rate of Ir complex has achieved favorable correlations with the experimental values. The quantum chemical calculation is useful to design the new emitters, and that is expected to estimate non-radiative rate precisely.

We also summarized the control of phosphorescence emission peak: (i) substituent effect on ligands, (ii) effects of ancillary ligands on heteroleptic complexes, (iii) design of the ligand skeleton, and (iv) selection of the central metal. We showed the relationship between the relative operating lifetime and the emission peak of Ir-complexes coordinated with the substituted phenyl-pyridine. It indicates that the shorter the emission peak wavelength, the shorter the operating lifetime. It would be difficult to achieve long lifetime in blue OLEDs using cyclometalated Ir-complexes with the substituted phenyl-pyridine ligands. Other methods are expected to achieve a longer operation lifetime in the blue device.

The combination of emitter and host is quite important to get high performances. We indicated the correlation of the operating lifetime and EQE with a combination of various light-blue emitters and hosts. The appropriate combination of emitter and host achieves high efficiency and long life because the exciton density of the triplet and the position of the recombination zone are controlled.

It is possible to increase the out-coupling efficiency by using molecular-oriented emitters. EQE reaches 46% if 100% orientation of the emitter and 100% PLQY are achieved. It is considered that the molecular orientation technology is of importance to achieve super-high efficiency.

## Acknowledgments

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