Sky-blue and blue-emitting, carbazolyl functionalized, bis-tridentate Ir(III) phosphors Cz-1–Cz-3 with bright emission and short radiative lifetime are successfully synthesized in a one-pot manner. They exhibit very high photostability against UV–vis irradiation in degassed toluene, versus both green and true-blue-emitting reference compounds, i.e., fac-[Ir(ppy)$_3$] and mer-[Ir(pmp)$_3$]. Organic light-emitting diodes (OLEDs) based on Cz-2 exhibit maximum external quantum efficiency (EQE) of 21.6%, EQE of 15.1% at 100 cd m$^{-2}$, and with CIE$_{x,y}$ coordinates of (0.17, 0.25). This study provides a conceptual solution to the exceedingly stable and efficient blue phosphor. It is promising that long lifespan blue OLED based on these emitters can be attained with further engineering of devices suitable for commercial application.
stable and highly efficient blue-emitting bis-tridentate Ir(III) complexes are synthesized according to these three fundamental principles.

The bis-tridentate Ir(III) complexes have been independently reported by Williams and co-workers,[14] De Cola and co-workers,[15] and Esteruelas et al.[16] However, inferior emission efficiency and lack of color tunability were the major weaknesses encountered to these earlier researches. To circumvent these obstacles, we set forth preparation of bis-tridentate Ir(III) complexes using both pincer dicarbene and functional 6-pyrazolyl-2-phenylpyridine (pzpy) as the ancillary and chromophoric chelates, respectively.[17] They were synthesized in a one-pot manner, i.e., heating of a 1:1 mixture of IrCl3·3H2O, carbene pincer pro-chelate, pzyph, and co-workers,[15] and Esteruelas et al. [16] However, inferior emission efficiency and lack of color tunability were the major weaknesses encountered to these earlier researches. To circumvent these obstacles, we set forth preparation of bis-tridentate Ir(III) complexes using both pincer dicarbene and functional 6-pyrazolyl-2-phenylpyridine (pzpy) as the ancillary and chromophoric chelates, respectively.[17] They were synthesized in a one-pot manner, i.e., heating of a 1:1 mixture of IrCl3·3H2O, carbene pincer pro-chelate, pzyph, and excess of potassium acetate in propionic acid.[18] The added metal acetate works as a cyclometalation promoter via a sequence of concerted metalation and deprotonation reaction.[19]

Representative sky-blue and blue-emitting Ir(III) complexes [Ir(mimf)(pzpyF3)] (SB) and [Ir(mimb)(pzpyOH3)] (Px-5) were obtained (cf. Scheme 1), for which the prime difference in structure was the possession of an oxygen spacer in pzytBOhF chelate and (0.18, 0.40), and 20.7% and (0.15, 0.17), respectively.[18] The bis-tridentate Ir(III) complexes have been independently reported by Williams and co-workers,[14] De Cola and co-workers,[15] and Esteruelas et al.[16] However, inferior emission efficiency and lack of color tunability were the major weaknesses encountered to these earlier researches.

UV-vis absorption and emission spectra were recorded in CH2Cl2 solution and the data were provided in Figure 1 and Table 1, respectively. The intense absorption above 330 nm rooted from ligand-centered π* transition, while the absorption at the longer wavelength region 370–450 nm stemmed from both MLCT transitions in singlet and triplet manifolds, respectively. The structureless emission profile of complexes Cz-1-Cz-3 was recorded with peak max. at 486, 473, and 476 nm, and nearly unitary photon emission yield (PLQY) of Cz-1, and turned slightly low to ~83% for both Cz-2 and Cz-3 in degassed CH2Cl2 at room temperature (RT). Surprisingly, the radiative lifetime (τ rad) of emitters Cz-1-Cz-3 (2.77–3.80 µs) was significantly shorter than the previously reported Ir(III) reference complexes SB and Px-5 (τ rad = 5.41 and 12.0 µs).[17,18] manifesting the dominant charge transfer (i.e., both MLCT and LLCT) contribution in these carbazolyl coordinated Ir(III) complexes.

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Also conducted was the computational approach based on time-dependent density functional theory (TD-DFT) at the B3LYP/LANL2DZ (Ir) and B3LYP/6-31g(d,p) (H, C, N, F, Cl) levels using CH₂Cl₂ as the solvent (see Supporting Information for detail). The calculated energy in terms of wavelengths and assignments of each electronic transition of Ir(III) complexes Cz-1–Cz-3 are listed in Table 2 and Tables S1–S3 in the Supporting Information. Figure 2 and Figures S2–S4 in the Supporting Information depict the frontier orbitals involved in the lower-lying transitions. The calculated wavelengths of the S₀ → S₁ optical transition for Cz-1: 385 nm, Cz-2: 377 nm, and Cz-3: 379 nm were close to the observed onsets of the experimental absorption peaks depicted in Figure 1. The calculated S₀ → T₁ transition wavelengths for Cz-1: 421 nm, Cz-2: 417 nm, and Cz-3: 418 nm were also in good agreement with the trend of the onset of their phosphorescence spectra in Figure 1. Moreover, after geometry optimization, the calculated wavelengths of the T₁ → S₀ emission transitions were at 527, 513, and 510 nm for Cz-1, Cz-2, and Cz-3, respectively. These values are 4~4.5 kcal mol⁻¹ lower in energy than that of the experimentally acquired peak wavelengths (see Figure 1), which is common if one considers that the computational approach is subject to few kcal mol⁻¹ uncertainty, depending on the theoretical levels and basis sets being applied. Nevertheless, the trend of energy gap obtained by the theoretical approach is consistent with that of the experimental result. Therefore, the current TD-DFT simulation works well in predicting the lowest Franck–Condon transition for both absorption and emission based on the optimized ground state (S₀) structure for the studied Ir(III) complexes.

According to the calculation (see Figure 2, Figures S2–S4, Supporting Information and Table 2 and Tables S1–S3, Supporting Information), both S₀ → S₁ (absorption) and T₁ → S₀ (emission) transition for Cz-1–Cz-3 mainly involves highest occupied molecular orbital (HOMO) and LUMO, in which the electron density distributions of HOMO are mainly localized at the central Ir atom (25~33%) and carbazolyl fragment, while LUMO are mostly distributed at the central pyridine of 2-carbazolyl-6-pyrazolylpyridine fragment and very few at the central Ir(III) atom (1~4%). Since we are focusing on the emission property, for more detail, the T₁ → S₀ transition for Cz-1 is mainly assigned to LUMO → HOMO (76%) with minor LUMO → HOMO-2 (13%). For complex Cz-2, the T₁ → S₀ transition is assigned to mainly LUMO → HOMO (65%) with minor LUMO → HOMO-1 (12%) and LUMO → HOMO-3 (11%) contribution. For complex Cz-3, the T₁ → S₀ emissive transition is assigned to mainly LUMO → HOMO (79%) and minor LUMO → HOMO-1 (9%). Note that HOMO-1 (Cz-2 and Cz-3), HOMO-2 (Cz-1), and HOMO-3 (Cz-2) for Cz-1–Cz-3 are mainly located at Ir atom, 3-methylimidazolium and pyrazolyl fragments. Therefore, the T₁ → S₀ transitions for Cz-1–Cz-3 are assigned to MLCT (20~26%) mixed with LLCT. The significant MLCT percentage (>20%) implies fast S₁ → T₁ (or T₃m, m > 1) intersystem crossing, resulting solely in the phosphorescence. This also supports the deduced fast radiative decay rate constant for Cz-1–Cz-3 (vide supra, Table 1) due to the enhancement of spin–orbit coupling.

To confirm this theoretical interpretation, cyclic voltammetry was conducted and showed the reversible oxidation at the metal center and irreversible reduction at the coordinated chelate, for which the graphic and numerical data are depicted in Figure S5 in the Supporting Information and Table 1. The anodic shifts of all electrochemical potentials were observed for Cz-2 and Cz-3 versus that of Cz-1, which are attributed to the electron withdrawing property of CF₃ group in Cz-2 and Cz-3 versus that of electron donating tert-butyl Cz-1 group in on the carbene pincer chelate.

As for the stability, thermal gravimetric analysis data illustrated in Table 1 showed Tₐ of Cz-1–Cz-3 exceeding 380 °C, which are common to most Ir(III) emitters documented in literature. However, the hot excited states generated by triplet–triplet annihilation of blue emitters possess an energy of ~6 eV [23], meaning that these Tₐ concepts are not suitable in estimating the material stability of blue emitters. To cope with this deficiency and provide better assessment on material

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**Table 1.** Essential photophysical and relevant data of Ir(III) complexes Cz-1–Cz-3.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz-1</td>
<td>289(33), 324.5(24), 358(15)</td>
<td>486</td>
<td>100</td>
<td>80.3</td>
<td>2.77</td>
<td>2.77</td>
<td>3420</td>
<td>0.55 (0.09)</td>
<td>−2.98</td>
<td>423</td>
<td></td>
</tr>
<tr>
<td>Cz-2</td>
<td>287(31), 316(15)</td>
<td>473</td>
<td>83.5</td>
<td>86.9</td>
<td>3.20</td>
<td>3.83</td>
<td>3440</td>
<td>0.69 (0.08)</td>
<td>−2.81</td>
<td>448</td>
<td></td>
</tr>
<tr>
<td>Cz-3</td>
<td>287(31), 322(19), 363.5(15)</td>
<td>476</td>
<td>82.7</td>
<td>95.6</td>
<td>2.7</td>
<td>3.26</td>
<td>3400</td>
<td>0.68 (0.09)</td>
<td>−2.79</td>
<td>386</td>
<td></td>
</tr>
</tbody>
</table>

ᵃAll photophysical data were recorded in CH₂Cl₂ with a conc. of 10⁻² M at RT, ɛ is in M⁻¹ cm⁻¹;ᵇEmission was measured with excitation at 375 nm and in reference to Coumarin 102 in MeOH (Φ = 80%);ᶜMeasured in doped film (10 wt% in DPEPO matrix);ᵈFull width at half-maxima of PL in cm⁻¹;ᵉTₑ = [(Eₑₓ − Eₑᵣ)/2] and ΔEₑ = [Eₑₓ − Eₑᵣ] in eV, while Eₑₓ and Eₑᵣ are defined as the anodic and cathodic peak potentials referenced to Fc⁺/Fc;⁹Eᵣ is the temperature with 5% of weight loss in thermogravimetric analysis.
stability, there are a number of literature reports on the use of either 400 nm LED or UV irradiation to test photostability of OLED emitters in solution and in a solid organic matrix. The photostabilities studies of bis-tridentate Ir(III) complexes remain rare in comparison to the corresponding tris-bidentate phosphors. Within this context, we attempted similar photodegradation experiment for Cz-1–Cz-3 in deaerated toluene using the standard Atlas Suntest CPS+ Xenon Test Instrument. Figure 3 provides the plot of ln($A_t/A_0$) versus irradiation time of Ir(III) emitters Cz-1–Cz-3. For a fair comparison, the relevant data for [fac-Ir(ppy)$_3$] and [mer-Ir(pmp)$_3$], that are known to be the best green and true-blue emitters, are also shown in Figure 3. From this diagram, the rate constant of photodegradation was estimated to be 1.9, 2.8, and $2.5 \times 10^{-3}$ h$^{-1}$ for Cz-1, Cz-2, and Cz-3, and 2.6 and $12 \times 10^{-3}$ h$^{-1}$ for [fac-Ir(ppy)$_3$] and [mer-Ir(pmp)$_3$], using the integrated first-order rate law:

$$\ln \left( \frac{A_t}{A_0} \right) = -kt$$

These rate constants clearly verified the superior photostability of the bis-tridentate emitters Cz-1–Cz-3, for which all samples were dissolved in deaerated toluene, placed in argon-filled PL cuvette, followed by the simulated solar irradiation at 620 W m$^{-2}$ and 35 °C.

Table 2. The calculated wavelengths, transition probabilities and main charge characters of the lowest optical transitions $S_1$ and $T_1$ for Ir(III) complexes Cz-1–Cz-3 in CH$_2$Cl$_2$ solution.

<table>
<thead>
<tr>
<th>Complex</th>
<th>State</th>
<th>$\lambda$ [nm]</th>
<th>$f$</th>
<th>Main assignments</th>
<th>MLCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz-1</td>
<td>$T_1$</td>
<td>421.7</td>
<td>0</td>
<td>HOMO $\rightarrow$ LUMO (43%)</td>
<td>21.60%</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>384.9</td>
<td>0.0405</td>
<td>HOMO $\rightarrow$ LUMO (97%)</td>
<td>29.94%</td>
</tr>
<tr>
<td>Cz-2</td>
<td>$T_1$</td>
<td>417.5</td>
<td>0</td>
<td>HOMO $\rightarrow$ LUMO (33%)</td>
<td>22.38%</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>377.4</td>
<td>0.0552</td>
<td>HOMO $\rightarrow$ LUMO (88%)</td>
<td>28.09%</td>
</tr>
<tr>
<td>Cz-3</td>
<td>$T_1$</td>
<td>418.5</td>
<td>0</td>
<td>HOMO $\rightarrow$ LUMO (34%)</td>
<td>22.29%</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>379.4</td>
<td>0.0497</td>
<td>HOMO $\rightarrow$ LUMO (88%)</td>
<td>28.77%</td>
</tr>
</tbody>
</table>

Figure 2. Frontier molecular orbitals for the ground state $S_0$ of Ir(III) complexes Cz-1–Cz-3 in CH$_2$Cl$_2$. "Ir" indicates the relative electron density distribution at the iridium atom.

Figure 3. Photodegradation responses of Ir(III) emitters SB, Pz-5, Cz-1–Cz-3, [fac-Ir(ppy)$_3$], and [mer-Ir(pmp)$_3$], for which all samples were dissolved in deaerated toluene, placed in argon-filled PL cuvette, followed by the simulated solar irradiation at 620 W m$^{-2}$ and 35 °C.
19.6%; CE: 39.5 cd A⁻¹; PE: 37.6 lm W⁻¹; Commission Internationale de l’éclairage (CIE) coordinates of (0.19, 0.34), while the Cz-2- and Cz-3-based devices exhibited the blue emission and impressive performances, with max. EQE of 21.6% and 19.6%, CE of 31.7 and 33.8 cd A⁻¹, PE of 29.3 and 31.2 lm W⁻¹, and CIEₓᵧ coordinates of (0.17, 0.25) and (0.17, 0.26) respectively. These characteristics are clearly superior to those displayed by other relevant bis-tridentate Ir(III) emitters[18,29] and fall in the ranking column of typical tris-bidentate blue-emitting Ir(III) phosphors.[30] The recorded CIE coordinates are still deviated from the NTSC blue standard (0.14, 0.08), e.g. National Television System Committee USA. However, this shortcoming can be fixed by employment of microcavity effect and/or using color filter in commercial OLEDs.

However, serious efficiency roll-off was obtained as increasing luminance (Figure 4 and Table 3), especially at above 1000 cd m⁻², which seems contradicting the better photophysical robustness of emitters. However, it should be noted that the chemical stability is not the solely factor in determining the OLED stability and efficiency roll-off. Other device parameters such as the exciton interaction, exciton–polaron interaction, field-induced quenching, and charge carriers imbalance also need to be considered.[31] In an effort to unveil this efficiency roll-off, a 2 nm thick, red-emitting [Ir(piq)₂(acac)] dopant was co-deposited to the emitting layer, at a conc. of 2 wt% but with variable distances (x = 10, 15, and 20 nm) from the emitting layer (EML)/mCP interface. [32] As shown in Figure S8 in the Supporting Information, the electroluminescence decreases with increase of x, indicating the close association of the EML/mCP interface and recombination zone (RZ). Furthermore, the red luminescence of device with x = 10 nm turned lowered upon increasing current and

**Table 3. Key performance data for the OLED devices.**

<table>
<thead>
<tr>
<th>Emitter</th>
<th>Device types</th>
<th>V_on [V]</th>
<th>λ_EL [nm]</th>
<th>CEₐ [cd A⁻¹]</th>
<th>PEₐ [lm W⁻¹]</th>
<th>EQEₐ [%]</th>
<th>CIEₓᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cz-1</td>
<td>Uniform</td>
<td>3.3</td>
<td>484</td>
<td>39.5, 34.7, 29.1</td>
<td>37.6, 24.3, 15.1</td>
<td>19.6, 15.5, 12.9</td>
<td>0.19, 0.34</td>
</tr>
<tr>
<td></td>
<td>Graded</td>
<td>3.3</td>
<td>484</td>
<td>41.3, 36.2, 32.0</td>
<td>39.3, 24.3, 16.0</td>
<td>21.5, 16.5, 14.2</td>
<td>0.19, 0.34</td>
</tr>
<tr>
<td>Cz-2</td>
<td>Uniform</td>
<td>3.5</td>
<td>468</td>
<td>31.7, 27.1, 19.9</td>
<td>29.3, 17.8, 9.80</td>
<td>21.6, 15.1, 11.0</td>
<td>0.17, 0.25</td>
</tr>
<tr>
<td></td>
<td>Graded</td>
<td>3.5</td>
<td>468</td>
<td>32.5, 30.8, 24.0</td>
<td>29.1, 20.3, 11.6</td>
<td>21.0, 17.1, 13.2</td>
<td>0.17, 0.25</td>
</tr>
<tr>
<td>Cz-3</td>
<td>Uniform</td>
<td>3.4</td>
<td>472</td>
<td>33.8, 29.4, 21.5</td>
<td>31.2, 21.0, 10.6</td>
<td>19.6, 15.9, 11.7</td>
<td>0.17, 0.26</td>
</tr>
<tr>
<td></td>
<td>Graded</td>
<td>3.5</td>
<td>472</td>
<td>32.7, 32.1, 25.8</td>
<td>27.6, 21.3, 12.5</td>
<td>19.5, 17.7, 14.0</td>
<td>0.17, 0.26</td>
</tr>
</tbody>
</table>

*Data at max. and @ 100 and 1000 cd m⁻², respectively. †@ 100 cd m⁻². Device structure: uniformly doped: ITO/MoO₃ (1 nm)/TCTA (30 nm)/mCP (10 nm)/DPEPO: 10 wt% dopant (35 nm)/3TPYMB (50 nm)/LiF (1 nm)/Al (120 nm); graded doping: ITO/MoO₃ (1 nm)/TCTA (30 nm)/mCP (10 nm)/DPEPO: 15–6 wt% dopant (40 nm)/3TPYMB (50 nm)/LiF (1 nm)/Al (120 nm).
driving voltage, meaning that the RZ is further shifting closer to the EML/mCP interface.\(^{[6c,32,33]}\) Therefore, in this case, the poor carrier balance in EML has resulted in a narrowed RZ and with highly concentrated excitons, causing the inferior efficiency roll-off. This problem can be partially alleviated by adapting gradient-doping technique,\(^{[57]}\) as shown in Figure S9 in the Supporting Information. For completely resolving this undesirable issue, bipolar host material with highly concentrated excitons, causing the inferior poor carrier balance in EML has resulted in a narrowed RZ.

In conclusion, stability remains to be one key issue for the development of robust and efficient blue-emitting OLEDs, for which both the material-related and the extrinsic fabrication issues were considered to be two main factors that gave the undesirable fast device degradation. The high photostability displayed by these new bis-tridentate Ir(III) emitters Cz-1–Cz-3 mainly eliminates the material-related factor. This, together with the decent OLED architecture to optimize and/or balance the carrier transport and stability of hole and electron transporting materials, would eventually provide a solution aimed at the long lifespan blue-emitting OLED phosphors for commercial applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bis-tridentate, carbazole, iridium, N-heterocyclic carbene (NHC), pyrazolato

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