Tris(cyclometalated) Iridium(III) Phosphorescent Complexes with 2-Phenylthiazole-Type Ligands: Synthesis, Photophysical, Redox and Electrophosphorescent Behavior


Keywords: Iridium / Phosphorescence / Thiazole / Photochemistry / Organic light-emitting diodes / Luminescence

Tris(cyclometalated) iridium(III) phosphorescent emitters with 2-phenylthiazole-type ligands have been designed and synthesized. Their photophysical properties, electrochemical behavior and electroluminescent (EL) performance can be influenced by introducing fluorine atoms to the phenyl moiety of the thiazole-based ligands. The phosphorescent emission maxima can be shifted from 546 nm to 517 nm by increasing the number of the fluorine atoms attached to the ligands of the iridium(III) complexes. Furthermore, the HOMO levels for these phosphorescent complexes exhibit a gradual decrease from -5.28 eV to -5.59 eV with the introduction of fluorine atoms. Owing to the character of their electronic structures, the phosphorescent emitters are preferentially excited by means of a host-guest energy-transfer process in the organic light-emitting diodes (OLEDs). Accordingly, their EL performance is strictly restricted by the triplet energy level difference between the phosphorescent dopant and the host materials. The thiazole-based cyclometalated iridium(III) triplet emitters can exhibit maximum EL efficiencies with \( \eta_{\text{ext}} = 7.87\% \), \( \eta_L = 23.62 \text{ cdA}^{-1} \) and \( \eta_p = 13.46 \text{ lmW}^{-1} \).

Introduction

Recently, substantial research work has been carried out on the design and synthesis of organometallic molecules of Ru\(^{II}\), Os\(^{II}\), Pt\(^{II}\), Re\(^I\) and Ir\(^{III}\) for their unique photophysical features, which would meet the requirements in the research frontiers of organic light-emitting diodes (OLEDs),\(^{[1]}\) organic photovoltaic cells,\(^{[2]}\) chemosensors\(^{[3]}\) etc. Owing to the heavy-atom effect induced by the transition-metal centers, the triplet excited states can be easily formed to induce triplet emission, i.e. phosphorescence, in these organometallic molecules.\(^{[4]}\) Among them, Ir\(^{III}\) complexes chelated with 2-phenylpyridine (ppy) type anionic ligands exhibit unique phosphorescent characteristics, such as high phosphorescent quantum yield (\( \Phi_P \)), tunable emission color and a relatively short triplet-state lifetime (\( \tau_P \)).\(^{[5]}\) Hence, highly efficient monochromatic OLEDs and white OLEDs (WOLEDs) have been constructed by employing these phosphorescent emitters, indicating their great potential in bringing OLEDs into practical applications.\(^{[6]}\)

Based on the photophysical and electroluminescent (EL) studies of the Ir\(^{III}\) ppy-type triplet emitters, it can be clearly seen that their properties such as emission color, \( \Phi_P \), \( \tau_P \), charge carrier injection/transporting properties etc. can be greatly affected by the electronic structures of the chelated organic ligands.\(^{[7]}\) This can be ascribed to the fact that the organic ligands have participated in the excited states of the Ir\(^{III}\) ppy-type phosphors, which has been confirmed by the substantial contribution from the \( \pi \) orbitals of the organic ligands to both the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs).\(^{[8]}\) Hence, tuning the chemical structures of the ppy-type organic ligands has become a prevalent strategy...
for optimizing the photophysical and EL properties of the corresponding Ir$^{III}$ ppy-type phosphors. It is well accepted that the thiazolyl group can be considered as a hybrid of the electron-deficient pyridyl moiety and electron-rich thiophenyl ring,[9] and this provides a distinct electronic structure to the thiazole with respect to the traditional pyridyl-type electron-deficient block in the ppy-type ligands. Hence, introducing a thiazolyl group to the ppy-type ligands should represent a new outlet for the development of Ir$^{III}$ ppy-type phosphors with unique photophysical and EL features. However, the potential of the thiazole ring in the phosphorescent cyclometalate chemistry remains relatively underexplored.[10] By combining a thiazolyl ring with triphenylamine and naphthalene groups, we have successfully obtained new thiazole-based ppy-type phosphors with unique features, including high EL efficiencies, tunable phosphorescent color, and balanced charge carrier injection/transporting traits. All of these encouraging results clearly indicate that the thiazole ring can play a critical role in furnishing valuable properties in the Ir$^{III}$ ppy-type phosphors to advance the field of OLEDs. Bearing this in mind, another series of Ir$^{III}$ ppy-type phosphorescent emitters with relatively simple thiazole-based ligands has been developed for investigating their photophysical properties, electronic structures, and EL performance. The results presented in this paper will provide not only valuable information about the optoelectronic properties of these thiazole-based phosphorescent Ir$^{III}$ complexes but also an assessment of the critical role that the thiazole group plays in phosphorescent emitters.

Results and Discussion

Synthesis and Characterization

The synthetic procedure for the thiazole-based Ir$^{III}$ ppy-type phosphors is shown in Scheme 1. The thiazole group was introduced to the organic ligands $L_1$, $L_2$, and $L_3$ by a Suzuki cross-coupling reaction between 2-bromothiazole and the corresponding phenylboronic acid with Pd(PPh$_3$)$_4$ as the catalyst. All the ligands can be easily obtained in good yields (>80%). All the phosphorescent Ir$^{III}$ complexes were prepared according to the well-established two-step strategy from the cyclometalation of IrCl$_3$·$n$H$_2$O with the corresponding organic ligands to form, initially, the μ-chloro-bridged dimers, followed by coordination of the acetylacetone (acac) anion in the presence of Na$_2$CO$_3$.[11] The complexes were purified by silica chromatography to furnish Ir$^{III}$ complexes in high purity as air-stable orange to yellow powders. Their well-defined chemical structures were confirmed by NMR spectroscopy and FAB-MS.

Single Crystal Structure Analyses

Good-quality crystals of Ir-Tz2 were grown by slow diffusion of hexane into a CHCl$_3$ solution of Ir-Tz2 at room temperature. The geometry of Ir-Tz2 was characterized by X-ray crystallography (Figure 1). The crystal structure of Ir-Tz2 reveals that the iridium center is coordinated by two anionic C∧N ligands of $L_2$ and one chelating acac anion. The coordination around the Ir$^{III}$ center is distorted octahedral, with cis-O,O, cis-C,C and trans-N,N chelate disposi-
tions (Figure 1 and Table S1 in the Supporting Information). Ir-Tz2 crystallizes in the $P\overline{3}21$ space group with half of the complex in the asymmetric unit. Hence, the two Ir–N bonds show the same bond length of 2.035(3) Å in Ir-Tz2. The same results were observed for the Ir–C bond [1.990(4) Å] and the Ir–O bond [2.138(3) Å]. The N–Ir–N bond angle is 173.4(2)°. Moreover, the involvement of electron-attracting F atoms on the anionic $C\equiv N$ ligand strengthens the distortion of the coordination sphere of the central Ir$^{III}$ ion, which can be shown from the dihedral angles of 78.3(2)° between the two almost coplanar $C\equiv N$ ligands despite those of 89.2(2)–90.8(2)° between each $C\equiv N$ ligand and the acetylacetone anion ligand.

Figure 1. Perspective drawing of Ir-Tz2. Only selected atoms are labeled, and all H atoms are omitted for clarity.

A detailed examination of the crystal packing in complex Ir-Tz2 reveals that six sets of intermolecular complementary hydrogen bonds C12–H12···F1a [C12 from Me group of acac, 3.543(6) Å and 130.6(2)°] in each molecule surrounded by six others lead to the formation of a 2D layered network, as shown in Figure 2a. On the other hand, as depicted in Figure 2b, a bi-layer framework has been formed through weak π···π interactions [centroid-to-centroid distance 3.871(3) Å] between two adjacent 2D layers, and two adjacent bi-layer frameworks are closely aligned through intermolecular complementary C8–H8···O1 [3.472(8) Å and 168.0(2)°] hydrogen bonds resulting in the 3D network.

Table 1. Photophysical and thermostability data for the thiazole-based Ir$^{III}$ ppy-type phosphors.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption (298 K)</th>
<th>Emission (298 K)</th>
<th>$\Phi_P$</th>
<th>$\tau_P$</th>
<th>$\tau_r$</th>
<th>$\Delta T_{5%/T_g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-Tz1</td>
<td>285 (4.67), 291 (4.67), 308 (4.57), 347 (4.14), 389 (3.92), 420 (3.83), 466 (3.54)</td>
<td>546</td>
<td>0.35</td>
<td>0.49</td>
<td>1.40</td>
<td>320/102</td>
</tr>
<tr>
<td>Ir-Tz2</td>
<td>280 (4.55), 292 (4.59), 305 (4.55), 334 (4.13), 372 (3.91), 405 (3.81), 434 (3.65)</td>
<td>530</td>
<td>0.40</td>
<td>0.54</td>
<td>1.35</td>
<td>318/104</td>
</tr>
<tr>
<td>Ir-Tz3</td>
<td>280 (4.75), 302 (4.68), 331 (4.21), 362 (4.10), 390 (4.01), 428 (3.31)</td>
<td>517</td>
<td>0.68</td>
<td>0.56</td>
<td>0.82</td>
<td>316/109</td>
</tr>
</tbody>
</table>

[a] Measured in CH$_2$Cl$_2$ at a concentration of 10$^{-5}$ M with log ε values shown in parentheses. [b] Measured in CH$_2$Cl$_2$ at a concentration of 10$^{-5}$ M. [c] In degassed CH$_2$Cl$_2$ relative to fac-[Ir(ppy)$_3$]$_2$ ($\Phi_P = 0.40$), $\lambda_{ex} = 360$ nm. [d] Measured in degassed CH$_2$Cl$_2$ solutions at a sample concentration of ca. 10$^{-6}$ M with the excitation wavelength set at 355 nm for all the samples at 298 K. [e] The triplet radiative lifetimes ($\tau_r$) were deduced from $\tau_r = \tau_P/\Phi_P$.

Thermal and Photophysical Properties

Under nitrogen, the thermal properties of the thiazole-based phosphorescent Ir$^{III}$ complexes were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results indicate their good thermal stability with the 5% weight-reduction temperature ($\Delta T_{5%/T_g}$) of around ca 320 °C (Table 1). The DSC traces for the thiazole-based complexes revealed their high glass-transition temperatures ($T_g$) in the range from 102 to 109 °C,
and this is desirable for high-performance OLEDs. Hence, all the thiazole-based phosphorescent IrIII complexes possess thermal properties good enough to guarantee the fabrication of OLEDs by the vacuum-deposition method and the operational stability of the devices prepared thereof.

All of the thiazole-based IrIII complexes exhibit two distinct absorption bands in their UV/Vis spectra (Figure 3 and Table 1). The strong UV absorption bands below 325 nm were assigned to the spin-allowed S1→S0 transitions of the organic ligands, representing the 1π→π* bands. Conversely, the weaker and low-energy features located beyond 325 nm can be ascribed to both 1MLCT→S0 and 3MLCT→S0 (MLCT = metal-to-ligand charge transfer) excitations. The strong spin–orbit coupling effects induced by the IrIII center are indicated by the similar oscillator strengths for the two MLCT bands (Table 1). Obviously, the energy level for their 3MLCT absorption bands falls in the order Ir-Tz1 (ca. 466 nm) < Ir-Tz2 (ca. 434 nm) < Ir-Tz3 (ca. 428 nm).

Upon UV light irradiation at 360 nm, all the thiazole-based IrIII complexes emit strong bluish-green to yellow phosphorescence in CH2Cl2 (Figure 3 and Table 1). Their photoluminescence (PL) spectra display unstructured line shapes, indicating the predominant MLCT character for the emissive lowest triplet excited states (T1) in all of them. These results are clearly supported by the DFT calculations (Figure 4 and Table 2). The DFT calculation results show that the lowest-energy transitions correspond to HOMO→LUMO transitions with nonzero oscillator strengths in these thiazole-based phosphors, and, hence, the S1 and T1 states are represented by the HOMO→LUMO excitation. Consequently, the characters for the T1 excited states, which are responsible for the phosphorescence in these complexes, will be represented by the HOMO→LUMO transitions. Accordingly, the frontier molecular orbital (MO) compositions represent the features of both the S1 and T1 excited states in Ir-Tz1, Ir-Tz2 and Ir-Tz3. As indicated by the noticeably different contribution to the HOMO and LUMO from the metal dπ orbitals (Table 2 and Figure 4), the lowest-energy excited state T1 shows obvious MLCT features, which lead to the unstructured features in the PL spectra of these thiazole-based IrIII complexes as mentioned before (Figure 3). Similar to those of their analogues in the literature, the HOMOs for Ir-Tz1, Ir-Tz2 and Ir-Tz3 are mainly located on the dπ orbitals of the IrIII center and the π orbitals of the phenyl ring. Hence, introducing the strong electron-withdrawing fluorine atom to the phenyl ring stabilizes the HOMOs, and this should increase the energy associated with the HOMO→LUMO transitions. As mentioned above, the HOMO→LUMO transitions represent the characters of the T1 states showing MLCT features. Therefore, Ir-Tz3 with two F atoms on the

Table 2. Contribution of the metal dπ orbitals to the HOMO and LUMO together with the TD-DFT calculation results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Contribution of metal dπ orbitals to HOMO</th>
<th>Contribution of metal dπ orbitals to LUMO</th>
<th>Largest coefficient in the CI expansion of the T1 state (S0→T1 excitation energy)[a]</th>
<th>Largest coefficient in the CI expansion of the S1 state (S0→S1 excitation energy)[a]</th>
<th>Oscillator strength (f) of the S0→S1 transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-Tz1</td>
<td>Ir 57.1%</td>
<td>Ir 3.83%</td>
<td>H→L: 0.62354 (520 nm)</td>
<td>H→L: 0.69814 (459 nm)</td>
<td>0.0523</td>
</tr>
<tr>
<td>Ir-Tz2</td>
<td>Ir 56.12%</td>
<td>Ir 3.80%</td>
<td>H→L: 0.56978 (500 nm)</td>
<td>H→L: 0.69585 (435 nm)</td>
<td>0.0528</td>
</tr>
<tr>
<td>Ir-Tz3</td>
<td>Ir 57.10%</td>
<td>Ir 3.74%</td>
<td>H→L: 0.52981 (478 nm)</td>
<td>H→L: 0.69534 (416 nm)</td>
<td>0.0503</td>
</tr>
</tbody>
</table>

[a] H→L represents the HOMO-to-LUMO transition; CI stands for configuration interaction.
phenyl ring shows higher $^3$MLCT energy than Ir-Tz2 with one F atom. Also, Ir-Tz1, with no F atoms, possesses the lowest $^3$MLCT energy. The time-dependent (TD) DFT calculation results predicted the energy order of the T1 states ($^3$MLCT) as Ir-Tz1 < Ir-Tz2 < Ir-Tz3 (Table 2), which is in good agreement with the absorption data (Figure 3 and Table 1). Due to the fact that phosphorescence of the Ir$^{III}$ complexes comes from the $^3$MLCT states, the emission wavelength maxima for the thiazole-based complexes follows the order Ir-Tz1 (546 nm) > Ir-Tz2 (530 nm) > Ir-Tz3 (517 nm) (Figure 3 and Table 1). As a result, the theoretical computational results properly support the photophysical properties of the thiazole-based Ir$^{III}$ complexes (Figure 3 and Table 1).

**Electrochemical Characterization**

The electrochemical properties of these thiazole-based Ir$^{III}$ complexes were investigated by cyclic voltammetry (CV) calibrated with ferrocene as the internal standard under nitrogen. All of the complexes show a quasi-reversible oxidation couple between 0.48 and 0.79 V (Table 3). With the increase in the number of F atoms on the phenyl ring, the oxidation potential moves markedly into the more positive direction due to the stabilization of the HOMOs induced by the F atom (vide infra). The reduction potentials for the complexes are spread over the narrow range of −2.55 to −2.60 V, showing the negligible effect of the F atom on the reduction process of the complexes. The irreversibility for the reduction process of the complexes can be ascribed to the electron-rich character of the thiazole group, which makes its reduction more susceptible to other environmental factors.

Table 3. Redox properties of the thiazole-based Ir$^{III}$ ppy-type complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{ox}$ [V]</th>
<th>$E_{1/2}^{red}$ [V]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir-Tz1</td>
<td>0.48</td>
<td>−2.61[a]</td>
<td>−5.28</td>
<td>−2.19</td>
</tr>
<tr>
<td>Ir-Tz2</td>
<td>0.63</td>
<td>−2.58[a]</td>
<td>−5.43</td>
<td>−2.22</td>
</tr>
<tr>
<td>Ir-Tz3</td>
<td>0.79</td>
<td>−2.55[a]</td>
<td>−5.59</td>
<td>−2.25</td>
</tr>
</tbody>
</table>

[a] Irreversible.

Figure 5. General configuration of electrophosphorescent OLEDs made from Ir-Tz1 to Ir-Tz3 and molecular structures of the relevant compounds used in these devices together with energy level diagram.
Electrophosphorescent Characterization

Due to their strong triplet emissions, the electrophosphorescent properties of Ir-Tz1 to Ir-Tz3 were characterized by making OLEDs with the configuration of ITO/m-MTDATA (40 nm)/NPB (20 nm)/x wt.-% Ir:CBP (20 nm)/BCP (10 nm)/Alq3 (30 nm)/LiF:Al (0.5:100 nm). Figure 5 depicts the structures of the multi-layer OLEDs and the chemicals involved in the fabrication of devices together with the energy-level diagram. The layer of tris(4-[3-methylphenyl](phenyl)amino]phenyl)amine (m-MTDATA) was firstly deposited on the pre-cleaned ITO surface to form a buffer layer and facilitate hole-injection (HI) for its proper HOMO level lying between that of ITO and NPB {NPB = 4,4'-bis[(1-naphthyl)(phenyl)amino]biphenyl}, while the subsequent NPB layer acts as the hole-transport (HT) layer. For its high triplet energy level and bipolar character, 4,4'-bis(carbazol-9-yl)biphenyl (CBP) serves as a small-molecule host material for the phosphorescent emitters. The hole-

<table>
<thead>
<tr>
<th>Device</th>
<th>Phosphorescent dopant</th>
<th>( V_{\text{turnon}} ) [V]</th>
<th>Luminance ( L ) [cd m(^{-2})]</th>
<th>( \eta_{\text{ext}} ) [%]</th>
<th>( \eta_{\text{l}} ) [cd A(^{-1})]</th>
<th>( \eta_{\text{p}} ) [Im W(^{-1})]</th>
<th>( \lambda_{\text{max}} ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Ir-Tz1 (4 wt.-%)</td>
<td>5.2</td>
<td>16719 (14.3)</td>
<td>2.69 (9.2)</td>
<td>8.02 (8.8)</td>
<td>3.00 (7.8)</td>
<td>548, 584 (0.44, 0.52)</td>
</tr>
<tr>
<td>A2</td>
<td>Ir-Tz1 (6 wt.-%)</td>
<td>5.0</td>
<td>30826 (14.3)</td>
<td>4.74 (9.2)</td>
<td>14.22 (8.8)</td>
<td>5.40 (7.8)</td>
<td>548, 584 (0.45, 0.52)</td>
</tr>
<tr>
<td>A3</td>
<td>Ir-Tz1 (8 wt.-%)</td>
<td>4.1</td>
<td>35451 (13.6)</td>
<td>6.07 (8.2)</td>
<td>18.10 (7.8)</td>
<td>7.83 (7.1)</td>
<td>548, 584 (0.45, 0.52)</td>
</tr>
<tr>
<td>A4</td>
<td>Ir-Tz1 (10 wt.-%)</td>
<td>3.9</td>
<td>38549 (13.2)</td>
<td>7.87 (6.5)</td>
<td>23.62 (6.4)</td>
<td>13.46 (4.8)</td>
<td>548, 584 (0.45, 0.52)</td>
</tr>
<tr>
<td>A5</td>
<td>Ir-Tz1 (12 wt.-%)</td>
<td>4.8</td>
<td>29954 (13.9)</td>
<td>4.76 (8.2)</td>
<td>14.40 (8.2)</td>
<td>5.93 (6.4)</td>
<td>548, 584 (0.45, 0.53)</td>
</tr>
<tr>
<td>B1</td>
<td>Ir-Tz2 (4 wt.-%)</td>
<td>5.3</td>
<td>15491 (13.9)</td>
<td>2.60 (10.2)</td>
<td>8.14 (9.9)</td>
<td>2.77 (8.5)</td>
<td>528, 564 (0.40, 0.56)</td>
</tr>
<tr>
<td>B2</td>
<td>Ir-Tz2 (6 wt.-%)</td>
<td>4.9</td>
<td>22861 (14.6)</td>
<td>3.61 (9.5)</td>
<td>11.33 (9.5)</td>
<td>4.11 (7.8)</td>
<td>532, 568 (0.42, 0.56)</td>
</tr>
<tr>
<td>B3</td>
<td>Ir-Tz2 (8 wt.-%)</td>
<td>4.9</td>
<td>24193 (13.2)</td>
<td>4.59 (8.5)</td>
<td>14.05 (8.5)</td>
<td>5.74 (7.1)</td>
<td>528, 564 (0.40, 0.56)</td>
</tr>
<tr>
<td>B4</td>
<td>Ir-Tz2 (10 wt.-%)</td>
<td>6.3</td>
<td>20160 (14.3)</td>
<td>3.55 (9.5)</td>
<td>11.20 (9.2)</td>
<td>4.21 (7.8)</td>
<td>528, 564 (0.40, 0.56)</td>
</tr>
<tr>
<td>B5</td>
<td>Ir-Tz2 (12 wt.-%)</td>
<td>5.3</td>
<td>15594 (14.6)</td>
<td>2.61 (10.2)</td>
<td>8.30 (9.8)</td>
<td>2.16 (8.2)</td>
<td>532, 564 (0.40, 0.56)</td>
</tr>
<tr>
<td>C1</td>
<td>Ir-Tz3 (4 wt.-%)</td>
<td>4.2</td>
<td>8013 (14.6)</td>
<td>1.47 (10.2)</td>
<td>4.49 (10.2)</td>
<td>1.45 (9.5)</td>
<td>516, 548 (0.35, 0.56)</td>
</tr>
<tr>
<td>C2</td>
<td>Ir-Tz3 (6 wt.-%)</td>
<td>5.3</td>
<td>9200 (14.6)</td>
<td>1.94 (9.8)</td>
<td>6.06 (9.8)</td>
<td>2.02 (8.5)</td>
<td>520, 548 (0.37, 0.56)</td>
</tr>
<tr>
<td>C3</td>
<td>Ir-Tz3 (8 wt.-%)</td>
<td>3.9</td>
<td>11832 (13.9)</td>
<td>3.35 (7.5)</td>
<td>10.48 (7.5)</td>
<td>4.41 (7.5)</td>
<td>516, 548 (0.35, 0.56)</td>
</tr>
<tr>
<td>C4</td>
<td>Ir-Tz3 (10 wt.-%)</td>
<td>4.9</td>
<td>11907 (13.9)</td>
<td>3.79 (7.1)</td>
<td>11.93 (7.1)</td>
<td>5.61 (6.1)</td>
<td>516, 548 (0.36, 0.57)</td>
</tr>
<tr>
<td>C5</td>
<td>Ir-Tz3 (12 wt.-%)</td>
<td>4.9</td>
<td>10484 (14.3)</td>
<td>2.85 (8.5)</td>
<td>8.76 (8.5)</td>
<td>3.52 (7.1)</td>
<td>520, 548 (0.37, 0.56)</td>
</tr>
</tbody>
</table>

[a] Values in parentheses are the voltages at which the data were obtained. [b] CIE coordinates (x, y) are shown in parentheses.

Figure 6. EL spectra for the devices A4, B3 and C4 showing the best EL performance.

Figure 7. Current density (J)–voltage (V)–luminance (L) curves for the devices A4, B3 and C4.
blocking layer of the devices consists of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) due to its low LUMO level. Tris(8-hydroxyquinolinato)aluminum (Alq3) acts as an electron-transporter and LiF as an electron-injection layer. In order to optimize the EL efficiencies, doping-level dependent experiments were also carried out in the range of 4–12 wt.-%.

All the devices emit intense orange electrophosphorescence with maxima at ca. 550 nm for devices A1–A5, ca. 530 nm for devices B1–B5 and ca. 520 nm for devices C1–C5 (Figure 6, Table 4 and Figure S1 in the Supporting Information). The weak EL band centered at ca. 450 nm should come from NPB due to the high LUMO levels of the concerned phosphorescent emitters, which would increase the chance of electron-leaking from the emission layer to the NPB layer.[12] The EL band from NPB remains relatively stable with variation of the doping level and becomes enhanced with an increase of the driving voltage applied to the devices. At higher driving voltages, more electrons will enter the emission layer, which will promote the leaking of electrons into the NPB layer.[12] Hence, the EL band from NPB is enhanced at higher driving voltages. The current density ($J$)–voltage ($V$)–luminance ($L$) curves for the concerned devices are shown in Figures 7 and S2, while the relationships between EL efficiencies and current density for the devices are presented in Figures 8 and S3. From Table 4, it can be clearly seen that device A4 with 10 wt.-% doping level shows the best EL ability of Ir-Tz1. The yellow-emitting device A4 doped with Ir-Tz1 exhibits impressive EL performance with a low turn-on voltage of 3.9 V, a maximum brightness ($L_{\text{max}}$) of 38549 cd m$^{-2}$ at 13.2 V, a peak external quantum efficiency ($\eta_{\text{ext}}$) of 7.87%, a luminance efficiency ($\eta_L$) of 23.62 cd A$^{-1}$ and a power efficiency ($\eta_p$) of 13.46 lm W$^{-1}$ (Figures 7 and 8). The device B3 shows the best EL properties among the devices doped with Ir-Tz2. It can be turned on at ca. 4.9 V, and its light output can reach 24193 cd m$^{-2}$ at 13.2 V with peak EL efficiencies of 4.59%, 14.05 cd A$^{-1}$ and 5.74 lm W$^{-1}$ (Figures 7 and 8). The device C4 emits at 4.9 V, with an $L_{\text{max}}$ of 11907 cd m$^{-2}$ at 13.9 V and maximum EL efficiencies of 3.79%, 11.93 cd A$^{-1}$ and 5.61 lm W$^{-1}$ (Figures 7 and 8). By comparing their EL performances (Table 4 and Figure 8), it is clear that the EL properties generally fall in the order of Ir-Tz1 > Ir-Tz2 > Ir-Tz3. From the energy level diagram (Figure 5), we can see that the HOMO level of the CBP (ca. –6.0 eV) host matches well with that of NPB (ca. –5.5 eV), and its LUMO (ca. –2.9 eV) level is very close to that of both BCP and Alq3 (ca. –3.0 eV). However, the LUMO levels for the phosphorescent emitters (ca. –2.2 to –2.3 eV) are located notably above that of CBP. Such information shows that the phosphorescent emitters are preferably excited by the host-guest energy-transfer process. The triplet energy levels for Ir-Tz1, Ir-Tz2 and Ir-Tz3 are 2.27 eV, 2.34 eV and 2.40 eV, respectively, while that for CBP is 2.56 eV. This result indicates that the energy transfer from the CBP host to Ir-Tz2 and Ir-Tz3 might be inefficient due to the smaller difference between their triplet energy levels, which would lead to endothermic back energy transfer from dopants Ir-Tz2 and Ir-Tz3 to the CBP host. Obviously, the undesired back energy transfer process would adversely affect the EL performance of Ir-Tz2 and Ir-Tz3. Hence, Ir-Tz1 exhibits much better EL properties than Ir-Tz2 and Ir-Tz3. Based on both the triplet energy levels for the phosphorescent dopant and their EL performance mentioned before, it is clear that the closer the triplet energy level of
the dopant to that of the CBP host, the poorer the EL performance will be. This also indicates the validity of ascribing the EL behavior of Ir-Tz1, Ir-Tz2 and Ir-Tz3 to the back energy transfer process. Recently, some carbazole-based IrIII phosphorescent emitters have shown attractive EL efficiencies of 40 cd A−1 and 10 lm W−1 in solution-processed devices with bipolar host materials of poly(N-vinylcarbazole) (PVK) and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD).[6f,6g] As mentioned before, Ir-TZ1 can achieve EL efficiencies of 23.62 cd A−1 and 13.46 lm W−1 in a traditional CBP host. Generally, phosphorescent OLEDs can show much better EL performance by employing a bipolar host to maintain a more balanced charge carrier injection/transport.[6d] So, we would expect better EL performance for our thiazole-based IrIII phosphorescent emitters by doping them in bipolar host materials.

Conclusions

Three thiazole-based cyclometalated IrIII phosphorescent emitters have been successfully prepared and characterized. By introducing fluorine atoms to the phenyl ring of their cyclometalating ligand, the photophysical properties, electrochemistry and EL performance of the concerned metal complexes can be tuned significantly. Owing to the characters of their electronic structures, the phosphorescent emitters are preferably excited through host-guest energy-transfer processes in the EL devices with CBP as the host material, and their EL performances depend on the triplet energy level of the novel phosphorescent emitters. The thiazole-based cyclometalated IrIII emitter exhibit maximum EL efficiencies with \( \eta_{\text{ext}} = 7.87\% \), \( \eta_L = 23.62 \text{ cd} \text{ A}^{-1} \) and \( \eta_p = 13.46 \text{ lm} \text{ W}^{-1} \), indicating their promising potential in the field of OLEDs.

Experimental Section

General Information: All reactions were conducted under nitrogen, and no special precautions were required during workup. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck precoated aluminum plates. Flash column chromatography was carried out by using silica gel (200–300 mesh). FAB mass spectra were recorded with a Finnigan MAT SSQ710 system. NMR spectra were measured in CDCl3 with a Bruker AXS 400 MHz spectrometer with the chemical shifts quoted relative to those of tetramethylsilane.

Physical Measurements: UV/Vis spectra were recorded with a Shimadzu UV-2250 spectrophotometer. The photoluminescence (PL) properties of the complexes were measured with a Hitachi F-4500 fluorescence spectrophotometer. The phosphorescence quantum yields were determined in degassed CH2Cl2 solutions at 293 K against the \( \text{fac}[-\text{Ir(ppy)}_3] \) standard (\( \Phi_p = 0.40 \)). \( \Phi_p \) and the lifetimes were measured with a single photon counting spectrometer from Edinburgh Instruments (FLS-920) with a nanosecond pulse LED excitation source. The data analysis was conducted by iterative convolution of the luminescence decay profile with the instrument response function by using the software package provided by Edinburgh Instruments. DSC was performed with a Netsch DSC 200 PC unit under a nitrogen flow at a heating rate of 10 °C min−1. TGA was conducted with a Netsch STA 409C instrument under nitrogen with a heating rate of 10 °C min−1. Electrochemical measurements were performed by using a Princeton Applied Research 2273A potentiostat. Cyclic voltammetry of the sample solutions was performed at a scan rate of 100 mV s−1 by using a glassy carbon working electrode, a platinum counter electrode and a platinum-wire reference electrode. The solvent was deoxygenated THF, and the supporting electrolyte was 0.1 M [nBu4N][BF4]. Ferrocene was added as a calibrant after each set of measurements, and all potentials are quoted with reference to the ferrocene/ferroenium couple (\( E_{1/2} = +0.27 \text{ V} \) relative to the reference electrode). The oxidation (\( E_{\text{ox}} \)) and reduction (\( E_{\text{red}} \)) potentials were used to determine the HOMO and LUMO energy levels by using the equations \( E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8) \text{ eV} \) and \( E_{\text{LUMO}} = -(E_{\text{red}} + 4.8) \text{ eV} \), which were calculated by using the internal standard ferrocene value of −4.8 eV with respect to the vacuum level.[14]

General Procedure for the Synthesis of L1, L2 and L3: Under nitrogen, 2-bromothiazole and the corresponding phenylboronic acid (1.2 equiv.) were added to toluene and 2 M Na2CO3 (1:1, v/v). Pd(PPh3)4 (5 mol.-%) was then added to the solution. The resultant mixture was stirred at 110 °C for 24 h and was then cooled to room temperature and extracted with CH2Cl2. The combined organic phases were dried with anhydrous MgSO4. The solvent was then removed, and the residue was purified by column chromatography by eluting with CH2Cl2/hexane (2:1, v/v). All the ligands were obtained in high yields of ca. 85%.

L1: Yield: 86%. 1H NMR (400 MHz, CDCl3): \( \delta = 7.95–7.80 \text{ (m, 2 H, Ar)}, 7.86 \text{ (d, } J = 3.2 \text{ Hz, 1 H, Ar)}, 7.44–7.42 \text{ (m, 3 H, Ar)}, 7.31 \text{ (d, } J = 4.8 \text{ Hz, 1 H, Ar)}) \text{ ppm}.

13C NMR (100 MHz, CDCl3): \( \delta = 168.38, 143.63, 133.55, 129.94, 129.81, 126.54, 118.76 \text{ ppm}.

FAB-MS: \( m/z = 161 \text{ [M]}^+ \text{ C} 9\text{H}7\text{NS} \text{ (161.03) : calcd. C} 60.32, \text{ H} 3.37, \text{ N} 7.82 \text{; found C} 60.02, \text{ H} 3.05, \text{ N} 7.42 \text{ ppm.} \)

L2: Yield: 83%. 1H NMR (400 MHz, CDCl3): \( \delta = 7.96–7.93 \text{ (m, 2 H, Ar)}, 7.84 \text{ (d, } J = 3.2 \text{ Hz, 1 H, Ar)}, 7.31 \text{ (d, } J = 3.2 \text{ Hz, 1 H, Ar)}, 7.15–7.11 \text{ (m, 2 H, Ar)}) \text{ ppm}.

13C NMR (100 MHz, CDCl3): \( \delta = 167.17, 165.03, 162.54, 143.65, 129.95, 129.92, 128.48, 128.40, 118.76, 116.10, 115.88 \text{ ppm}.

FAB-MS: \( m/z = 179 \text{ [M]}^+ \text{ C} 9\text{H}6\text{FNS} \text{ (179.02) : calcd. C} 68.41, \text{ H} 3.78 \text{; found C} 68.32, \text{ H} 3.78, \text{ N} 7.82 \text{; found C} 60.56, \text{ H} 3.78 \text{; N} 7.68 \text{.} \)

L3: Yield: 85%. 1H NMR (400 MHz, CDCl3): \( \delta = 8.33–8.27 \text{ (m, 1 H, Ar)}, 7.92 \text{ (s, 1 H, Ar)}, 7.45–7.44 \text{ (m, 1 H, Ar)}, 7.03–6.93 \text{ (m, 2 H, Ar)}) \text{ ppm}.

13C NMR (100 MHz, CDCl3): \( \delta = 164.76, 164.63, 162.24, 162.12, 161.32, 161.20, 159.92, 159.68, 158.79, 158.67, 142.55, 130.06, 130.02, 129.79, 129.93, 120.00, 119.92, 118.10, 112.36, 112.33, 112.15, 112.11, 104.47, 104.41, 104.15 \text{ ppm}.

FAB-MS: \( m/z = 197 \text{ [M]}^+ \text{ C} 9\text{H}6\text{FNS} \text{ (197.90) : calcd. C} 54.81, \text{ H} 2.56, \text{ N} 7.10 \text{; found C} 54.63, \text{ H} 2.75, \text{ N} 6.95 \text{.} \)

General Procedure for the Synthesis of Iridium Complexes: Under nitrogen, each appropriate organic ligand and IrCl3·nH2O (0.5 equiv.) were heated to 110 °C in a mixture of 2-ethoxyethanol and water (3:1, v/v) for 16 h. The reaction mixture was then cooled to room temperature, and water was added. The cyclometalated IrIII µ-chlorido-bridged dimer was formed as a precipitate, which was collected and dried under vacuum. Subsequently, the precursor complex, acetylactone (5 equiv.) and Na2CO3 (10 equiv.) were added to 2-ethoxyethanol under nitrogen, and the mixture was heated to 110 °C for 12–16 h. After cooling to room temperature and the addition of water, the colored precipitate was collected by
filtration and washed with water and dried. The crude product was purified on a silica column by using an appropriate eluent to produce a pure sample of each of the title iridium complexes after solvent evaporation and drying.

**Ir-Tz1**: Yield: 33%. 1H NMR (400 MHz, CDCl3): δ = 7.67 (d, J = 3.2 Hz, 2 H, Ar), 7.48 (dd, J = 7.6, 1.2 Hz, 2 H, Ar), 7.36 (d, J = 3.6 Hz, 2 H, Ar), 6.80–6.76 (m, 2 H, Ar), 6.71–6.67 (m, 2 H, Ar), 6.30 (d, J = 7.2 Hz, 2 H, Ar), 5.22 (s, 1 H, acac), 1.82 (s, 6 H, acac) ppm. 19F NMR (376 MHz, CDCl3): δ = –109.34 (1 F) ppm. FAB-MS: m/z = 612 [M]+. C32H14Ir2N2O2S2 (612.05): calcd. C 42.48, H 2.92, N 4.13.

**Ir-Tz2**: Yield: 30%. 1H NMR (400 MHz, CDCl3): δ = 7.61 (d, J = 3.5 Hz, 2 H, Ar), 7.47 (dd, J = 8.4, 5.6 Hz, 2 H, Ar), 7.37 (d, J = 3.5 Hz, 2 H, Ar), 6.55–6.50 (m, 2 H, H), 5.88 (dd, J = 9.8, 2.5 Hz, 2 H, Ar), 5.24 (s, 1 H, acac), 1.83 (s, 6 H, acac) ppm. 13C NMR (100 MHz, CDCl3): δ = 185.14 (acac), 177.42, 164.06, 161.54, 148.36, 139.17, 137.51, 125.65, 125.55, 120.10, 119.93, 119.96, 108.48, 108.24 (Ar), 100.54, 28.35 (acac) ppm. 19F NMR (376 MHz, CDCl3): δ = –109.34 (1 F) ppm. FAB-MS: m/z = 648 [M]+. C52H29F2Ir3N2O6S2 (648.03): calcd. C 42.65, H 2.65, N 4.32; found C 42.48, H 2.92, N 4.13.

**Ir-Tz3**: Yield: 29%. 1H NMR (400 MHz, CDCl3): δ = 7.63 (dd, J = 3.6, 1.7 Hz, 2 H, Ar), 7.49 (d, J = 3.6 Hz, 2 H, Ar), 6.38–6.33 (m, 2 H, Ar), 6.56 (dd, J = 9.0, 2.2 Hz, 2 H, Ar), 5.26 (s, 1 H, acac), 1.84 (s, 6 H, acac) ppm. 13C NMR (100 MHz, CDCl3): δ = 185.28 (acac), 172.27, 172.21, 164.76, 164.65, 162.22, 162.11, 160.41, 160.18, 157.85, 157.71, 148.82, 148.75, 138.52, 118.02, 105.35, 28.41 (acac) ppm. 19F NMR (376 MHz, CDCl3): δ = –106.40 (1 F), –108.42 (1 F) ppm. FAB-MS: m/z = 684 [M]+. C62H12F2Ir3N2O6S2 (684.06) was recorded by using a Keithley 2400/2000 source meter, and the luminous efficacy was measured by using a PR650 SpectraScan spectrometer.

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**Supporting Information** (see footnote on the first page of this article): Crystal data for Ir-Tz2; EL spectra for the phosphorescent OLEDs made from the thiazole-based triplet emitters; J–V–L curves for the concerned phosphorescent OLEDs; EL efficacy–luminance curves for all the phosphorescent OLEDs.

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**OLED Fabrication and Measurements**: The precleaned ITO glass substrates were treated with ozone for 20 min. The m-MTDATA layer was then deposited on the surface of ITO glass to form a 40 nm thick hole-injection layer. A 20 nm thick hole-transporting layer of NPB was then constructed. The 20 nm doped emission layer was deposited by co-evaporation of the Ir|| complex and the CBP host. After that, the BCP (15 nm), Alq3 (40 nm), LiF (0.5 nm) and Al cathode (100 nm) were successively evaporated. All the evaporation processes were conducted at a base pressure less than 10–6 Torr. The EL spectra and CIE coordinates were measured with a PR650 Spectra colorimeter. The J–V–L curves of the devices were recorded by using a Keithley 2400/2000 source meter, and the luminance was measured by using a PR650 SpectraScan spectrometer. All the experiments and measurements were carried out under ambient conditions.

**X-ray Crystallography**: X-ray diffraction data were collected at 293 K by using graphite-monochromated Mo-Kα radiation (λ = 0.7073 Å) with a Bruker Axa SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT+,[15] and an absorption correction (SADABS)[16] was applied to the collected reflections. The structure was solved by direct methods (SHELXTL)[17] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F2. Hydrogen atoms were generated in their idealized positions, and all non-hydrogen atoms were refined anisotropically. CCDC-931996 (Ir-Tz2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

**Theoretical Computation Details**: Density functional theory (DFT) calculations by using B3LYP were performed for all the Ir|| complexes, and their geometries were obtained by theoretical optimization during the computation. The basis set used for the C, H, F, N and O atoms was 6-31G, while effective core potentials with a LanL2DZ basis set were employed for S and Ir atoms.[18] The energies of the excited states of the complexes were computed by time-dependent (TD) DFT (TD-DFT) based on all the ground-state geometries. All calculations were carried out by using the Gaussian 09 program.[19] Mulliken population analyses were performed by using MulliPop.[20] Frontier molecular orbitals obtained from the DFT calculations were plotted by using the Molden 3.7 program.[21]


