Heteroleptic Cyclometalated Iridium(III) Complexes Displaying Blue Phosphorescence in Solution and Solid State at Room Temperature

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A series of heteroleptic Ir(III) metal complexes 1−3 bearing two N-phenyl-substituted pyrazoles and one 2-pyridylpyrazole (or triazole) ligands were synthesized and characterized to attain highly efficient, room-temperature blue phosphorescence. The N-phenylpyrazole ligands, dfpzH 1-(2,4-difluorophenyl)pyrazole, fpzH 1-(4-fluorophenyl)-pyrazole, dfmpzH 1-(2,4-difluorophenyl)-3,5-dimethylpyrazole, and fmpzH 1-(4-fluorophenyl)-3,5-dimethylpyrazole, show a similar reaction pattern with respect to the typical cyclometalated (C–N) chelate, which utilizes its ortho-substituted phenyl segment to link with the central Ir(III) atom, while the second 2-pyridylpyrazole (or triazole) ligand, namely, fppzH 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole, fptzH 3-(trifluoromethyl)-5-(2-pyridyl)triazole, and hptzH 3-(heptafluoropropyl)-5-(2-pyridyl)triazole, undergoes typical anionic (N–N) chelation to complete the octahedral framework. X-ray structural analyses on complexes [(dpzp)2Ir(fppz)] (1a) and [(fmpz)2Ir(hptz)] (3d) were established to confirm their molecular structures. Increases of the \( \pi^* \) energy gaps of the Ir(III) metal complexes were systematically achieved with two tuning strategies. One involves the substitution for one or two fluorine atoms at the N-phenyl segment or the introduction of two electron-releasing methyl substituents at the pyrazole segment of the H(C–N) ligands. Alternatively, we have applied the more electron-accepting triazolate in place of the pyrazole segment for the third (N–N)H ligand. Our results, on the basis of steady-state, relaxation dynamics, and theoretical approaches, lead to a conclusion that, for complexes 1−3, the weakening of iridium metal–ligand bonding strength in the T1 state plays a crucial role for the fast radiationless deactivation. For the case of [(fmpz)2Ir(hptz)] (3d), a thermal deactivation barrier of 4.8 kcal/mol was further deduced via temperature-dependent studies. The results provide a theoretical basis for future design and synthesis of the corresponding analogues suited to blue phosphorescent emitters.

One of the most important research subjects in the development of organic light-emitting diodes (OLEDs) is the development of phosphorescent metal complexes showing all three primary colors for full-color displays. Among phosphorescent complexes, green-emitting complexes have been known for years and have been successfully fabricated as green OLEDs with ~100% internal quantum efficiency.1

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Recently, red-emitting complexes have become accessible through selective incorporation of highly conjugated ancillary ligands.2

groups into the ligand chromophore to extend the triplet-state lifetime as well as to circumvent their intrinsic obstacle, involving rapid nonradiative deactivation predicted by the energy gap law. Presently, researchers have turned their attention to the preparation and characterization of the remaining blue-emitting phosphorescent complexes. This task, however, is even more difficult to achieve than those of the other two cases. One major challenge lies in the selection of suitable chelate ligands that are able to form complexes with sufficiently large ligand-centered \( \pi \pi^* \) transition energies and/or metal-to-ligand charge transfer (MLCT) energies. Such an approach might inevitably raise the ligand-centered transition (or MLCT) to a region very close to the energies. Such an approach might inevitably raise the ligand-centered transition (or MLCT) to a region very close to the energies. Such an approach might inevitably raise the ligand-centered transition (or MLCT) to a region very close to the energies. Such an approach might inevitably raise the ligand-centered transition (or MLCT) to a region very close to the energies. Such an approach might inevitably raise the ligand-centered transition (or MLCT) to a region very close to the energies.

Heteroleptic Cyclometalated Iridium(III) Complexes

The first series of ligands, denoted as H(C\( \text{N} \)), consist of N-phenyl-substituted pyrazoles, which are expected to show good reactivity with IrCl\( +\text{H}_2\text{O} \) using their phenyl segment to afford products [\( \text{C}(\text{N})\text{IrCl}_2 \) or \( \text{Ir}(\text{C}\( \text{N} \))\( \text{N} \)] (C\( \text{N} \) = cyclometalated ligands). The reaction pattern should be fully consistent with the results documented in earlier papers. Interestingly, the photophysical study of the meridional isomer of [Ir(dpz)\( _2 \)] (\( \text{dpz} = \text{2,4-difluorophenylpyrazole} \)) showed an emission peak wavelength of 412 nm at 77 K, suggesting that Ir complexes incorporating these F-substituted N-phenylpyrazoles may be suitable for the generation of blue phosphorescence at room temperature due to their exceedingly high energy gaps. Moreover, as elaborated in the literature, the second 2-pyridylpyrazole (or triazole), denoted as (N\( \text{N} \)H), possesses a highly acidic NH fragment. Thus, they may display reaction patterns similar to those of typical anion-chelating ligands such as \( \beta \)-diketone or picolate, giving heteroleptic complexes with a formula of [\( \text{C}(\text{N})\text{Ir}(\text{N}\text{N}) \)] upon addition to the chlorine bridged dimer [\( \text{C}(\text{N})\text{IrCl}_2 \)]. In addition to

\[
2\text{IrCl}_3 + 4\text{H}(\text{C}\text{N}) \rightarrow [\text{Ir}(\text{C}\text{N})\text{IrCl}_2] + 4\text{HCl} \tag{1}
\]

where \( [\text{Ir}(\text{C}\text{N})\text{Ir}(\text{N}\text{N})] \) is the intermediate compound. This reaction can be carried out reproducibly with various ancillary ligands in the presence of IrCl\( _3 \) and H\( \text{C}(\text{N}) \). A possible reaction pathway involving these ligands is shown by the following equations:

\[
[\text{Ir}(\text{dpz})\text{IrCl}_2] + 2(\text{N}\text{N})\text{Na} \rightarrow 2[\text{Ir}(\text{C}\text{N})\text{Ir}(\text{N}\text{N})] + 2\text{NaCl} \tag{2}
\]

The synthetic transformation involving these ligands is discussed in more detail in a subsequent section.
their excellent chelating properties, the asymmetric character of these ligands is extended to the HOMO and LUMO of the metal complexes and, hence, would afford a subtle color tuning via substituting either pyrazolate or triazolate sites. On these bases, it is thus anticipated that room-temperature blue phosphorescence may be achieved by attaching both of these specially designed H(C=N) N-phenylpyrazole and (N'=NH) 2-pyridylpyrazole chromophores to the central iridium metal atom.

**Experimental Section**

**General Information and Materials.** All reactions were performed under a nitrogen atmosphere using anhydrous solvents or solvents treated with an appropriate drying reagent. Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode or fast atom bombardment (FAB) mode. H and 19F NMR spectra were recorded on Varian Mercury-400 or INOVA-500 instruments. Elemental analyses were conducted at the NSC Regional Instrumentation Center at National Chiao Tung University. 500 instruments. Elemental analyses were conducted at the NSC Impact (EI) mode or fast atom bombardment (FAB) mode. H and 19F NMR spectra were recorded on Varian Mercury-400 or INOVA-500 instruments. Elemental analyses were conducted at the NSC Regional Instrumentation Center at National Chiao Tung University. The nitrogen chelates, 3-(trifluoromethyl)-5-(2-pyridyl)triazole (fppz)H, and 3-(heptafluoropropyl)-5-(2-pyridyl)triazole (hptz)H, were prepared using Pt wire and an Au disk coated with Hg as working electrodes, measurements were performed using a BAS 100 B/W electrochemical instrument. Colorless crystals of [(fmpz)2Ir(fppz)] (1a) were obtained from cooling the mixed solution of CH2Cl2 and methanol at room temperature (61 mg, 0.079 mmol, 75%). The related complexes [(fmpz)Ir(fppz)], [(fmpz)Ir(fptz)], and [(fmpz)Ir(fppz)] (1d) were prepared using similar procedures, yields 56–65%.

**Spectral Data for 1a.** MS (FAB) (obsd m/z [assignment]): 764 [M+], 552 [M+ − fppz]. 

**Spectral Data for 1b.** MS (FAB) (obsd m/z [assignment]): 728 [M+], 516 [M+ − fppz]. 

**Spectral Data for 1c.** MS (FAB) (obsd m/z [assignment]): 820 [M+], 608 [M+ − fppz]. 

**Spectral Data for 1d.** MS (FAB) (obsd m/z [assignment]): 785 [M+], 571 [M+ − fppz]. 

**Preparation of [(fmpz)2IrCl2].** The chloride-bridged complex [(fmpz)2IrCl2] was synthesized from treatment of IrCl3·3H2O (0.81 g, 2.32 mmol) with 1-(4-fluorophenyl)-3,5-dimethylpyrazole (fmpzH, 0.98 g, 5.13 mmol) in 2-ethoxyethanol (40 mL) for 24 h. The solution was treated with water (40 mL) to induce precipitation of a colorless solid. The solid product was then filtered out, washed with diethyl ether, and dried under vacuum (1.12 g, 0.92 mmol, 79%). The complexes [(dfpz)2IrCl2] and [(fppz)2IrCl2] were prepared using similar conditions.

**Preparation of [(dfpz)Ir(fppz)] (1a).** A mixture of [(dfpz)IrCl2] (62 mg, 0.053 mmol), 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole (fppzH, 28 mg, 0.13 mmol), and Na2CO3 (56 mg, 0.53 mmol) in 2-ethoxyethanol (20 mL) was heated to reflux for 12 h. An excess of water was added after the solution was cooled to RT (room temperature). The precipitate was collected by filtration and washed with anhydrous ethanol (10 mL), followed by diethyl ether (10 mL). Colorless crystals of [(dfpz)Ir(fppz)] (1a) were obtained from the resulting mixture of CH2Cl2 and methanol at room temperature (61 mg, 0.079 mmol, 75%).

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Preparation of [(dfpz)₂Ir(hptz)] (2d). Procedures identical with those for 1 were followed, using 120 mg of [(dfpz)₂IrCl₂] (0.099 mmol), 53 mg of dpfHZ (0.248 mmol), and 105 mg of Na₂CO₃ (0.99 mmol) in 25 mL of 2-methoxyethanol. Colorless crystals of [(dfpz)₂Ir(hptz)] (2d) were obtained from cooling the mixed solution of CH₂Cl₂ and methanol at room temperature (50 mg, 0.065 mmol, 33%).

Preparation of [(dfpz)₂Ir(fptz)] (2b). Crystal data and refinement parameters for complexes 1a and 3d are listed in Table 1.

| Table 1. Crystal Data and Refinement Parameters for Complexes 1a and 3d |
|-----------------|--------------|--------------|
| param | 1a | 3d |
| formula | C₂₃H₁₉F₁₇IrN₈ | C₂₂H₁₈F₁₆Cl₁₄Ir |
| Mᵣ | 762.66 | 1053.64 |
| cry system | monoclinic | triclinic |
| space group | P2₁/c | P1 |
| crystal size (Å³) | 2569.46(2) | 1895.27(1) |
| temp (K) | 150(1) | 150(1) |
| GOF | 1.171 | 1.490 |
| Fᵣ (all data) | 0.0348, 0.0696 | 0.0274, 0.0663 |
| F₀ (I > 2σ(I)) | 0.0302, 0.0687 | 0.0279, 0.0673 |
| %R | 1.95 | 1.95 |

Spectral Data for 3d. MS (FAB) (obsd [M⁺] 885 [M⁺ – hptz]). ¹H NMR (500 MHz, CDCl₃, 294 K): δ 8.26 (dd, J₉H = 8.0 Hz, 1H), 7.84 (td, J₉H = 7.8, 1.2 Hz, 1H), 7.56–7.54 (m, 1H), 7.18 (dd, J₉H = 7.2, 2.0, 1.6 Hz, 1H), 6.59–6.53 (m, 1H), 6.48–6.41 (m, 1H), 6.02–6.00 (m, 2H), 5.91 (s, 1H), 5.41 (dd, J₉H = 6.0, 2.4 Hz, 1H), 2.66 (dd, J₉H = 12.0 Hz, 3H), 2.62 (dd, J₉H = 12.0 Hz, 3H), 1.51 (s, 3H), 1.40 (s, 3H). Anal. Calcld for C₂₉H₂₁F₁₆IrN₉: N, 12.18; C, 41.79; H, 2.41. Found: N, 12.24; C, 41.82; H, 2.12.

X-ray Structural Determination. Single-crystal X-ray diffraction data were recorded on a Bruker SMART CCD diffractometer using λ(Mo Kα) radiation (λ = 0.71073 Å). The data collection was executed using the SMART program. Cell refinement and data reduction were performed with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least squares. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at the calculated positions and included in the final stage of refinements with fixed positional parameters. The crystallographic refinement parameters of complexes 1a and 3d are summarized in Table 1, while the selective bond distances and angles of these complexes are listed in Tables 2 and 3, respectively.

Spectral Measurement. Steady-state absorption and emission spectra were recorded with a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorometer, respectively. Quinine sulfate with an emission yield of Φ ~ 0.57 (λₘₐₓ ~ 460 nm) in 0.1 M
Table 2. Selected Bond Length (Å) and Angles (deg) for Complex 1a

<table>
<thead>
<tr>
<th></th>
<th>Bond Length (Å)</th>
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<tr>
<td>Ir=N(1)</td>
<td>2.004(3)</td>
<td>Ir=N(6)</td>
</tr>
<tr>
<td>Ir=N(3)</td>
<td>2.013(5)</td>
<td>Ir=C(10)</td>
</tr>
<tr>
<td>Ir=N(5)</td>
<td>2.149(4)</td>
<td>Ir=C(10)</td>
</tr>
<tr>
<td>N(1)−Ir=N(3)</td>
<td>173.17(13)</td>
<td>N(5)−Ir=C(10)</td>
</tr>
<tr>
<td>N(6)−Ir=C(1)</td>
<td>172.31(13)</td>
<td>N(1)−Ir=C(1)</td>
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<tr>
<td>N(3)−Ir=C(10)</td>
<td>80.17(16)</td>
<td>N(5)−Ir=N(6)</td>
</tr>
</tbody>
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Table 3. Selected Bond Length (Å) and Angles (deg) for Complex 3d

<table>
<thead>
<tr>
<th></th>
<th>Bond Length (Å)</th>
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<tr>
<td>Ir=N(1)</td>
<td>2.033(3)</td>
<td>Ir=N(6)</td>
</tr>
<tr>
<td>Ir=N(3)</td>
<td>2.024(3)</td>
<td>Ir=C(11)</td>
</tr>
<tr>
<td>Ir=N(5)</td>
<td>2.150(3)</td>
<td>Ir=C(22)</td>
</tr>
<tr>
<td>N(1)−Ir=N(3)</td>
<td>173.09(10)</td>
<td>N(6)−Ir=C(22)</td>
</tr>
<tr>
<td>N(5)−Ir=C(11)</td>
<td>179.78(12)</td>
<td>N(1)−Ir=C(11)</td>
</tr>
<tr>
<td>N(3)−Ir=C(22)</td>
<td>79.91(13)</td>
<td>N(5)−Ir=N(6)</td>
</tr>
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H₂SO₄ served as a standard to calculate the emission quantum yield. An integrating sphere (Labsphere) was applied to measure the quantum yield in the solid state, in which the solid sample film was prepared via the vapor deposition method and excited by a 365 nm Ar⁺ laser line. The resulting luminescence was acquired with a charge-coupled detector (Princeton Instruments, model CCD-1100) for subsequent quantum yield analyses. Nano-second lifetime studies were performed with an Edinburgh FL 900 photon-counting system with a hydrogen-filled/or a nitrogen lamp as the excitation source. Data were analyzed using the nonlinear least-squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of ~200 ps.

Computational Methodology. Calculations on the electronic ground state of complexes 1–3 were carried out using B3LYP density functional theory. A “double-z” quality basis set consisting of Hay and Wadt’s effective core potentials (LANL2DZ) was employed for Ir atom, and a 6-31G* basis, for H, C, N, and F atoms. A relativistic effective core potential (ECP) replaced the inner core electrons of Ir(III), leaving the outer core (5s²5p⁶) electrons and the 5d⁶ valence electrons. Time-dependent DFT (TDDFT) calculations using the B3LYP functional were then performed on the basis of the structural optimized geometries. Typically, the lowest 10 triplet and 10 singlet roots of the non-sequential eigenvalue equations were obtained to determine the vertical excitation energies. Oscillator strengths were deduced from the dipole transition matrix elements (for singlet states only). The ground-state B3LYP and excited-state TDDFT calculations were carried out using Gaussian03.

Results and Discussion

Synthesis and Characterization. Condensation of fluorine-substituted phenylhydrazine hydrochloride with acetylacetone or with 1,1,3,3-tetramethoxypropane gave formation of four H(C≡N) pyrazole ligands, cf. 1-(2,4-difluorophenyl)pyrazole (dfpz)H, 1-(4-fluorophenyl)pyrazole (fpz)H, 1-(heptafluoropropyl)pyrazole (fmpz)H, and 1-(trifluoromethyl)-3-(2-pyridyl)triazole (fptz)H.

A similar synthetic strategy was applied to synthesize other analogues incorporating the triazole ligands, such as 3-(trifluoromethyl)-5-(2-pyridyl)triazole (fptz)H and a heteroleptic complexes containing the C≡N ligand such as CF₃-substituted pyridylpyrazole (fppz)H in the presence of Na₂CO₃ as a proton scavenger. A similar synthetic strategy was applied to synthesize other analogues incorporating the triazole ligands, such as 3-(trifluoromethyl)-5-(2-pyridyl)triazole (fptz)H and 3-(heptafluoropropyl)-5-(2-pyridyl)triazole (hptz)H. These reactions then afforded two more series of iridium complexes: [L₂Ir(fptz)] (1a), [L₂Ir(fpz)] (1b), [L₂Ir(fppz)] (1c), and [IrCl₂(fppz)] (1d), in which (fppz)H = 3-(trifluoromethyl)-5-(2-pyridyl)pyrazole, were then prepared from reactions involving these chloride-bridged complexes and the designated (N≡N)H ligand such as CF₃-substituted pyridylpyrazole (fppz)H in the presence of Na₂CO₃ as a proton scavenger. A similar synthetic strategy was applied to synthesize other analogues incorporating the triazole ligands, such as 3-(trifluoromethyl)-5-(2-pyridyl)triazole (fptz)H and 3-(heptafluoropropyl)-5-(2-pyridyl)triazole (hptz)H. These reactions then afforded two more series of iridium complexes: [L₂Ir(fptz)] (2) and [L₂Ir(hptz)] (3) (L and L’ = dfpz, fpz, dfmpz, and fmpz). Chart 2 summarizes their structural drawings and numbering. It is notable that these iridium complexes are moderately soluble in chlorinated solvents, particularly for the ones with the methyl-substituted N-phenylpyrazole ligands or with the heptafluoropropyl substituent. They also show great thermal stability, as supported by negligible degradation in solution phase over a long period of time. Detailed characterizations were carried out using routine MS and H and F NMR spectroscopy and finally with elemental analysis, among which complexes 1a and 3a were further identified using single-crystal X-ray analysis to establish their three-dimensional structures.


As depicted in Figure 1, complex 1a reveals a distorted octahedral geometry around the Ir atom with two cyclometalated dfpz (C=N) ligands and one anionic fppz (N\(^{-}\)N) ligand. All three chelate ligands show similar bite angles of 76.8°–80.2° and caused the observed structural distortion. The dfpz ligands adopt mutually an eclipsed configuration with the nitrogen atoms N(1) and N(3) residing at the trans locations, and the Ir—N distances lie between 2.004(3) and 2.013(3) Å. The cyclometalated carbon atoms C(1) and C(10) are mutually cis on the iridium and similar distances, 2.018(3) and 2.011(4) Å. The third fppz ligand displays 2.013(3) Å vs those of the trans-orientated Ir—N distances of the dfpz ligands. This is believed to be caused by the stronger Ir—C bonding interaction of the dfpz ligands, which eventually weakened the Ir—N bonds at their trans-disposition. Moreover, the overall structural arrangement is similar to several previously reported examples, including chloride-bridged dimer complex [(ppy)\(_2\)IrCl] \(_2\),\(^{21}\) the diketonate complexes such as previously reported examples, including chloride-bridged dimer complex [(ppy)\(_2\)IrCl] \(_2\),\(^{21}\) the diketonate complexes such as [(ppy)\(_2\)Ir(acac)] and others,\(^{22}\)\(^{23}\) even and even derivatives with pyrazolyl ancillary ligands,\(^{23}\) confirming that the third fppz ligand entered into the iridium coordination sphere via a simple ligand substitution.

Moreover, the dimethyl-substituted fmpz complex 3d showed an essentially identical structural arrangement (Figure 2). The most notable difference is the slightly elongated Ir—N distances of the cyclometalated fmpz ligands, Ir—N(1) = 2.033(3) and Ir—N(3) = 2.024(3) Å, the results of which could be ascribed to an increase in steric interaction between the methyl group of fmpz ligands and the unique hptz ligand. However, this nonbonding interaction seems to be small, so no apparent influence on the N(1)—Ir—N(3) bond angle was observed between these two complexes.

**Electrochemistry.** The electrochemical behavior of these Ir metal complexes was investigated by cyclic voltammetry using ferrocene as the internal standard. The results are listed in Table 4. During the anodic scan in CH\(_2\)Cl\(_2\), all iridium metal complexes exhibited a reversible oxidation with potentials in the region of 0.69–1.11 V. Upon the switch to the cathodic sweep in THF, one irreversible wave, with potentials ranging from –2.58 to –2.93 V, was detected. It is believed that the oxidation occurred mainly at the Ir metal site, together with minor contributions from the cyclometalated C=N ligand and the third N\(^{-}\)N chelating anion. Accordingly, replacing the 4,6-difluorophenyl with a 4-fluorophenyl moiety and changing from pyrazole to the more electron-donating 3,5-dimethylpyrazole led to the decrease of their oxidation potentials. This is demonstrated by the higher oxidation potential of 1a (0.98 V) vs that of complex 1b (0.83 V), as well as the decrease of oxidation potentials for complexes 1c (0.87 V) and 1d (0.69 V) vs those of 1a, b. Moreover, the oxidation potentials along the series 1a (0.98 V) → 2a (1.11 V) → 3a (1.11 V) and complexes 1d (0.69 V) → 2d (0.78 V) → 3d (0.78 V) revealed that the pyridyltriazolate ligands (i.e. fptz and hptz) are more electron-withdrawing than is their pyrazolate counterpart fppz.

Furthermore, in contrast to the oxidation process, the reduction may occur primarily on the low-lying π* orbitals of the pyridyl segment of the ancillary N\(^{-}\)N ligand. This assignment is supported by the subsequent DFT calculations and by the fact that the reduction potentials of the phenylpyrazolyl complexes fac-Ir(ppz)\(_3\) and fac-Ir(dfppz)\(_3\) are relatively much greater than those of the pyridyl complexes fac-Ir(ppy)\(_2\) and fac-Ir(46dfppy))\(_3\).\(^{26}\) Moreover, the irreversible cathodic peak potentials for the pyrazolate complexes 1a—d occur in the range (–2.72 to –2.93 V), which are notably greater than those of the triazole complexes 2a,d and 3a—d (–2.53 to –2.74 V). This reductive electrochemistry is thus consistent with the pyridylpyrazolate group being significantly more difficult to reduce than its triazole counterparts.

**Photophysical Properties.** Figures 3–5 show the UV/vis absorption and emission spectra of complexes 1–3 in CH\(_2\)Cl\(_2\) and the corresponding emission in solid crystal at 298 K. To gain more insight into the emission properties,
phenyl-to-pyridine interligand ligand charge transfer (ILCT) and a fluorine atom substituted combination of triazolate (or pyrazolate)-to-pyridine intra-bands at theoretical approaches, the origin of broad, structureless the phenyl ring (vide infra). As supported in the later pyrazolate (or triazolate) fragment and, to a small extent, g absorption maximum are calculated to be in the spectral region of 7776 Inorganic Chemistry, aEpc red (298 K). The red trace (b) denotes the emission spectra obtained from solid crystal at room temperature. The blue circle (C) shows the corresponding emission in a 77 K CH$_2$Cl$_2$ matrix.

Table 4. Electrochemical Data (V) and Photophysical Properties of All Iridium Complexes$^a$

<table>
<thead>
<tr>
<th>complexes</th>
<th>$E_{1/2}^{ox}$ ($\Delta E_p$)</th>
<th>$E_{pc}^{red}$ ($\Delta E_p$)</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$10^{-3} \Phi$</th>
<th>$\tau$ (ns)</th>
<th>$k_i$ ($10^3$ s$^{-1}$)</th>
<th>$\tau_{solid}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.98 (100)</td>
<td>-2.72 (irr)</td>
<td>$\sim$295, 349</td>
<td>455$^b$ (451)</td>
<td>6.7$^b$ (130)</td>
<td>42.4</td>
<td>1.6</td>
<td>1834</td>
</tr>
<tr>
<td>1b</td>
<td>0.83 (90)</td>
<td>-2.79 (irr)</td>
<td>$\sim$296, 348</td>
<td>458 (451)</td>
<td>3.5</td>
<td>16.2</td>
<td>2.2</td>
<td>21.8</td>
</tr>
<tr>
<td>1c</td>
<td>0.77 (100)</td>
<td>-2.93 (irr)</td>
<td>297, 352</td>
<td>456 (450)</td>
<td>0.11</td>
<td>1.2</td>
<td>0.9</td>
<td>20</td>
</tr>
<tr>
<td>1d</td>
<td>0.69 (80)</td>
<td>-2.87 (irr)</td>
<td>300, 355</td>
<td>457 (457)</td>
<td>2.1</td>
<td>5.1</td>
<td>4.1</td>
<td>38.1</td>
</tr>
<tr>
<td>2a</td>
<td>1.11 (100)</td>
<td>-2.72 (irr)</td>
<td>300, 349</td>
<td>457 (448)</td>
<td>4.6</td>
<td>8.6</td>
<td>5.4</td>
<td>133</td>
</tr>
<tr>
<td>2d</td>
<td>0.78 (110)</td>
<td>-2.64 (irr)</td>
<td>299, 375</td>
<td>460 (450)</td>
<td>3.3</td>
<td>6.0</td>
<td>5.5</td>
<td>115</td>
</tr>
<tr>
<td>3a</td>
<td>1.11 (100)</td>
<td>-2.53 (irr)</td>
<td>302, 348</td>
<td>455 (447)</td>
<td>4.4</td>
<td>9.3</td>
<td>4.7</td>
<td>133</td>
</tr>
<tr>
<td>3b</td>
<td>0.93 (100)</td>
<td>-2.58 (irr)</td>
<td>306, 349</td>
<td>456 (459)</td>
<td>8.6</td>
<td>8.6</td>
<td>10.0</td>
<td>63</td>
</tr>
<tr>
<td>3c</td>
<td>0.96 (100)</td>
<td>-2.58 (irr)</td>
<td>295, 345</td>
<td>459 (446)</td>
<td>0.34</td>
<td>0.5</td>
<td>6.8</td>
<td>20.4</td>
</tr>
<tr>
<td>3d</td>
<td>0.78 (110)</td>
<td>-2.74 (irr)</td>
<td>302, 353</td>
<td>469 (449)</td>
<td>7.5</td>
<td>5.1</td>
<td>14.7</td>
<td>295</td>
</tr>
</tbody>
</table>

$^a$Epc$^{red}$ ($\Delta E_p$) represents the irreversible cathodic peak potential. $^b$All photophysical data were recorded in degassed CH$_2$Cl$_2$ at room temperature, while data in parentheses show the emission data recorded in solid state at room temperature.

the corresponding emission spectra in a 77 K CH$_2$Cl$_2$ matrix.

Figure 4. UV/vis absorption (a) and emission (b) spectra of complexes 2a–d in CH$_2$Cl$_2$. The red trace (c) denotes the emission spectra obtained from solid crystal at room temperature. The blue circle (D) shows the corresponding emission in a 77 K CH$_2$Cl$_2$ matrix.

the corresponding emission spectra in a 77 K CH$_2$Cl$_2$ matrix were also included. In general, the dominant absorption band in the spectral region of $\leq$280 nm, for which $\epsilon$ values at the absorption maximum are calculated to be $\geq 5 \times 10^8$ M$^{-1}$ cm$^{-1}$, is attributed to the local $\pi\pi^*$ transition of the pyrazolate (or triazolate) fragment and, to a small extent, the phenyl ring (vide infra). As supported in the later theoretical approaches, the origin of broad, structureless bands at $\sim$280–360 nm for 1–3 can be assigned to a combination of triazolate (or pyrazolate)-to-pyridine intraligand charge transfer (ILCT) and a fluorine atom substituted phenyl-to-pyridine interligand $\pi\pi^*$ transition (LLCT) overlapping with the Ir(d$_{xy}$) to pyridyl ligand transition (MLCT) in the singlet manifold. Moreover, the lower lying band that appears in the region of $>380$ nm, as supported by their extinction coefficients of $<1000$ M$^{-1}$ cm$^{-1}$, is tentatively assigned to the $^3$MLCT, mixed with significant $^3\pi\pi$ transition character. For example, the absorptivity of this band, e.g., $\epsilon$ = 200 M$^{-1}$ cm$^{-1}$ at the peak wavelength of $\sim$400 nm for 3d, suggests that the S$_0 \rightarrow$ $^3$MLCT/ $^3\pi\pi$ transition is greatly enhanced and becomes partially allowed due to strong spin-orbit coupling. As supported by the emission spectral feature, the phosphorescence seems to be dominated by the $^3\pi\pi$ transition (vide infra), further detailed assignments for which are firmly supported by theoretical calculations elaborated in the following section.

Complexes 1–3 all exhibit unique blue emission with peak wavelengths at $\sim$450–470 nm in CH$_2$Cl$_2$. The emission spectral profile is reminiscent of the Os(II) 2-pyridylpyrazolate (triazolate) complexes$^{24}$ that, however, are less suitable for OLED application due to the presence of carbonyl ligands and shows additional $\sim$5–10 nm blue shift compared to that of the “almost blue-emitting” Ir(III) complexes.$^{25}$ Varying the substituents on the ligands, such as adding methyl groups on pyrazole of the C$^p$N ligand site (cf. 1a,d), does not show


much effect on the spectral feature in terms of e.g. peak wavelengths and the associated vibronic structures. The results may indicate that pyrazole on the C’N site plays a minor role in the lower lying transitions. Likewise, substitution of pyrazole on the N’N ligand site of complex 1a by triazole, forming complexes 2a or 3a, gives rise to slight spectral changes. For the case of free pyridylpyrazolate ligand, the lowest transition normally takes place from pyrazolate (HOMO) to pyridyl sites (LUMO). Assuming spectral changes. For the case of free pyridylpyrazolate (0.1 ..., with quantum yields measured to be in the range of 5.4 ± 3b fluorine substituents, complex further, in comparison to complex 3a, possessing two fluorine substituents, complex 3b, bearing only one fluorine atom on the C’N ligand, undergoes a small bathochromic shift of 3–5 nm. Accordingly, the cyclometalated phenyl ring, to a certain extent, also contributes to the lowest T1 – S0 transition, in which the fluorine substituent at the metal center acts as an electron withdrawing group to further lower the HOMO energy level, resulting in an increase of the energy gap.27 However, the <5 kcal/mol decrease in the phosphorescence gap from difluorine-substituted 3a to monofluorine-substituted complex 3b is rather small, supporting the proposed mechanism in that the S0 – T1 transition may concurrently incorporate various ligand chromophores. Further evidence of these viewpoints is given by computational results (vide infra).

The emission intensities of 1–3 are all relatively weak, with quantum yields measured to be in the range of $\Phi = (0.1–8.6) \times 10^{-3}$ in degassed CH2Cl2. The quantum efficiencies of complexes 1–3 were measured under the condition of 10–5–10–6 M, and there was no concentration dependence on the quantum efficiency and the corresponding lifetime. For all cases, negligible changes of the emission intensity were observed upon aerating the CH2Cl2 solution. The nearly O2-independent emission intensities can be supported by their corresponding emission lifetimes of as short as <50 ns in both degassed and aerated solution (see Table 4). Accordingly, a radiative decay rate constant $k_r$ of $\sim 10^8$ s⁻¹ was deduced for 1–3 (e.g., 1.6 × 10^8 s⁻¹ for 1a, 5.4 × 10^8 s⁻¹ for 2a; see Table 4). The >1 µs radiative lifetime (i.e., $k_r < 10^8$ s⁻¹), in combination with vibronic spectral features, leads us to assign the emission originating from the triplet manifold, in which the $^3Π\pi^*$ configuration may have a greater contribution to the transition than that of MLCT. Further support was given by the photophysical measurements in the solid state. In the solid crystal, a slight or negligible spectral blue shift was observed for all complexes (see Figures 3–5 and Table 4). Moreover, as depicted in Figures 3–5, in comparison to that measured in room-temperature solid, the vibronic spectral feature remains unchanged at 77 K for complexes 1–3. The results unambiguously conclude that $^3Π\pi$ is the lowest lying triplet state for the studied complexes. In comparison to that in solution, all complexes have the tendency to increase emission yield and hence the observed lifetime in the solid. For complex 1a, the quantum efficiency $\Phi_p$ was measured to be ~0.13, with a lifetime of 1.8 µs in the solid state at 298 K. The quantum efficiency of all others was too low (<0.02) to give a reliable value on the basis of the integrating-sphere method (see Experimental Section).

One intriguing feature lies in that the quantum yields of blue-emitting complexes 1–3 are much smaller than most of the highly emissive, red-emitting Ir complexes reported in the literature, for which the pyridylpyrazolate (triazolate) ligands served only as the ancillary N cyclometalated ligands of the molecule.28 The nonradiative rate constants $k_{nr} + k_{a}(T)$ (vide infra), calculated according to $k_{nr} + k_{a}(T) = (k_p/\Phi_p) - k_r$, were deduced to be in the range $10^6$ s⁻¹. Since the heteroleptic (i.e. tris-bidentated) structure of complexes 1–3 is considered to be rigid, a major radiationless deactivation associated with large amplitude skeletal motion seems to be very unlikely. Note that complexes 1–3 show very good photostability.29 Thus, the radiationless pathway resulting from any photochemistry30 should be considered as a very minor deactivating channel. In addition, both emission quantum yield and observed lifetime are only slightly dependent on pendant substituents such as Me, CF3, or C6F5. Likewise, the role of torsional motion participating in the radiationless deactivation can be discarded.31

We further performed temperature-dependent experiments in an attempt to gain insight into the deactivation mechanism on the complexes studied. A prototype used in this study is complex 3d due to its good solubility in methycyclohexane; a solvent that has a low freezing point of 145 K is suited to the temperature-dependent approach. As shown in Figure 6, the phosphorescence of 3d revealed strong temperature dependence. The quantum yield increased from 1.0 × 10⁻³ at 298 K to a plateau ($\Phi_p = 0.46$) at ~140 K and remained constant at lower temperatures. Temperature-dependent relaxation dynamics also correlate well with respect to the steady-state approaches. The lifetime followed the steady-
state pattern, increasing significantly from 1.94 ns at 298 K to as long as 890 ns at 138 K. Assuming a temperature-independent radiative decay rate \( k_r \) for the phosphorescence, the observed temperature-dependent decay rate \( k_{\text{obs}} \) can be expressed as \( k_{\text{obs}} = k_r + k_{\text{nr}} + k_{\text{nr}}(T) \), in which \( k_{\text{nr}}(T) \) represents the temperature-dependent nonradiative deactivation rate and \( k_{\text{nr}} \) denotes the temperature-independent radiationless decay rate constant, possibly involving intersystem crossing, etc. Accordingly, the measured quantum yield is deduced to be

\[
\Phi_p = \frac{k_r}{k_r + k_{\text{nr}} + k_{\text{nr}}(T)}
\]  

(3)

The temperature-dependent radiationless decay rate constant \( k_{\text{nr}}(T) \) can be further expressed as an Arrhenius type of thermally deactivated pathway of \( k_{\text{nr}}(T) = Ae^{-E/RT} \), which is then substituted into eq 3 to obtain eq 4:

\[
\ln\left(\frac{1}{\Phi_p} - 1 - \frac{k_{\text{nr}}}{k_r}\right) = \ln A - \frac{E_a}{RT}
\]  

(4)

As indicated by steady-state and time-resolved measurements, the lifetime and intensity of the emission at <140 K are nearly temperature independent. Thus \( k_{\text{nr}}(T) \) is assumed to be negligible, and \( \Phi_p \) expressed in eq 3 can be simplified to \( k_r/(k_r + k_i) \), which was measured to be ~0.46 at 138 K. On the other hand, \( k_{\text{nr}} \) was resolved to be 1.12 \( \times \) 10\(^6\) s\(^{-1}\) at 138 K. Accordingly \( k_r \), and \( k_{\text{nr}} \) were deduced to be 5.16 \( \times \) 10\(^4\) and 6.07 \( \times \) 10\(^5\) s\(^{-1}\), respectively. With all parameters provided, the plot of \( \ln \left( (1/\Phi_p) - 1 - k_{\text{nr}}/k_r \right) \) as a function of the reciprocal of the temperature reveals a straight line, and \( E_a \) was deduced to be 4.43 kcal/mol with a frequency factor \( A \) of 1.25 \( \times \) 10\(^{12}\) s\(^{-1}\) (see insert of Figure 6). The results provide a quantitative estimate of the energy difference between ground vibrational level (\( \nu = 0 \)) of \( T_1 \) and a specific channel (or state) that initiates the main deactivation process. Discussion regarding a plausible deactivation pathway will be elaborated in the next section, on theoretical approaches.

Figure 6. Temperature-dependent emission spectra of 3d in methylcyclohexane. Insert: linear graphical plot of \( \ln k \) versus \( 1/T \), where \( k = \ln((1/\Phi_p - 1 - k_{\text{nr}}/k_r) \); see text for the definition.

**Theoretical Approaches**

To further rationalize the photophysical properties of complexes 1–3, ab initio approaches (DFT; see Experimental Section) on the corresponding molecular orbitals involved in the transitions were carried out. The results, according to the chromophores contributing to the frontier orbitals (vide infra), show similar patterns for all complexes 1–3. To avoid redundancy, only the results of 3d are elaborated here, due to its easily accessible temperature-dependent spectroscopic/dynamic data (vide supra). The features of the frontier orbitals of 3d mainly involved in the electronic transitions are depicted in Figure 7, while the descriptions and the energy gap of each transition are listed in Table 5. Apparently, the electron densities of the singlet and triplet states of complex 3d for the HOMO, HOMO–1, HOMO–2, and HOMO–3 are mainly based on the triazole, fluorine-substituted phenyl moieties and Ir atom, while those of the LUMO, on the contrary, are almost completely distributed on the pyridyl moiety, although there are also minor contributions from nonbonding d orbitals of Ir metal. The lowest singlet absorption at 406 nm (transition 1, HOMO → LUMO) corresponds to a transfer of electron density from 4-fluorophenyl to pyridine (ligand to ligand charge transfer, LLCT) and Ir metal to pyridine (MLCT) in character.

At ~355 nm, there is another electronic transition with high oscillator strength, the major contributions of which are ascribed to HOMO–2 and HOMO–1 → LUMO, and the charge density is similar to that calculated for the 406 nm transition, except for an additional contribution from C,F\(_7\)-substituted triazole. Another highly allowed transition is located at ~329 nm, which mainly incorporates HOMO–3 → LUMO and HOMO–4 → LUMO, corresponding to transfer of electron density mainly from Ir metal to pyridine or pyrazole and dimethyl-substituted fmpz or 4-fluorophenyl to pyridine and pyrazole of another ligand. Qualitatively, most of the allowed transition peaks for complex 3d, neglecting the contribution from vibronic transition (i.e., the Franck–Condon envelope), are in good agreement with the observed absorption spectral profiles, supporting the validity of this approach.

For all complexes studied, in contrast to the pure HOMO → LUMO as the lowest singlet transition, frontier orbitals associated with the lowest triplet state are rather complicated, involving HOMO, HOMO–1, HOMO–2, and HOMO–5 to LUMO (see Table 5 for the case of complex 3d). Similar results were obtained for complexes 1–3, but they are somewhat different from those of Ir(ppy)\(_3\) and its derivatives, which could be reasonably attributed to a \( \pi\pi* \) manifold, mixed to a great extent with the MLCT character.\(^{32}\) For complexes 1–3, it is apparent, however, that electron densities of the resulting \( S_0 \rightarrow T_1 \) transition state are completely located at the pyridyl moiety, the electron densities of which are contributed from pyrazolate (or triazole in the anionic N=\( \pi\)N ligand), phenyl moieties, and the Ir atom (d\(_z^2\) orbitals). On the other hand, the pyrazole in cyclometalated C=\( \pi\)N ligand of 1a–d has little contribution.

believe that the Ir metal center in $^2\text{N}$ electron deficient than that of a $^2\text{dd}$ transition, which normally results in weakening of the associated photophysical properties, rationalizing the lack of substituent effect on the $^2\text{N}$-phenylpyrazole chromophore (i.e. $^2\text{C}^\text{N}$ ligand). However, for the triazolate complexes $3\text{a}$–$\text{d}$, addition of methyl groups has slightly red shifted the emission by 3–12 nm in both fluid and solid states (Table 4). We believe that the Ir metal center in $3\text{a}$–$\text{d}$ is relatively more electron deficient than that of $1\text{a}$–$\text{d}$ due to the better $\pi$-accepting effect of the triazole vs that of the pyrazolate $^2\text{N}$ ligand. This electron deficiency then makes the electron donation ability of the methyl substituents on the $^2\text{N}$-phenylpyrazole chromophore more obvious by raising the $^2\text{d}$ energy at the Ir metal center. Moreover, because $^2\text{HOMO}$–$^2\text{LUMO}$, $^2\text{HOMO}$–$^2\text{LUMO}$+1, $^2\text{HOMO}$–$^2\text{LUMO}$+2, and $^2\text{HOMO}$–$^2\text{LUMO}$+3 orbitals that are mainly involved in $^2\text{S}_0$–$^2\text{T}_1$ transition consist of the frontier orbitals among pyrazolate (or triazole in anionic $^2\text{N}$ ligand), phenyl moieties, and the Ir atom, substitution on each single moiety is diluted and should cause little effect on the associated photophysical properties, rationalizing the experimental results.

As for the radiationless deactivation pathways, it is noteworthy that because there is no involvement of the $^2\text{d}_\pi^*$ orbital up to $^2\text{LUMO}+5$ in complexes $1$–$3$, a popularly adopted deactivation mechanism incorporating metal-centered $^2\text{dd}$ transition, which normally results in weakening of the metal–ligand interaction due to its antibonding character, has been discarded. Alternatively, population at the $^2\text{T}_1$ state causes the shift of the electron density from the metal center, phenyl, and pyrazole of the $^2\text{C}^\text{N}$ ligands to the pyridyl moiety of the unique $^2\text{N}$-$^2\text{N}$ ligand, resulting in the weakening of all Ir–ligand bonding interactions. This, in combination with $^2\text{T}_1$ being in a high-energy blue region, may lead to a shallow potential energy surface (PES) in the $^2\text{T}_1$ state; thus, as for an extreme case, a surface crossing of PES between $^2\text{S}_0$ and $^2\text{T}_1$ is possible. Thus, upon excitation, the $^2\text{T}_1$ state is populated right after fast $^2\text{S}_1$ → $^2\text{T}_1$ ISC, followed by the internal conversion and vibrational relaxation (i.e. solvent deactivation). Subsequently, radiationless deactivations are executed via thermal activation to certain vibrational levels close to the section of the $^2\text{T}_1$–$^2\text{S}_0$ surface through the facile metal–ligand bond stretching discussed above. Particularly, the contribution of the fluorophenyl → pyridyl transition to the $^2\text{T}_1$ state is >40% for complexes $1$–$3$ (see Supporting Information). The resulting transition should weaken the corresponding Ir–phenyl (or Ir–pyridyl) bonds, which, in a sense, may trigger the deactivation process. Although detailed insights into the deactivation mechanism are still

\begin{table}
\centering
\begin{tabular}{|l|l|l|l|}
\hline
state & assgnt & $E$ (eV) & $\lambda$ (nm) \\
\hline
$^2\text{S}_1$ & $^2\text{HOMO}$ → $^2\text{LUMO}$ (+98%) & 3.05 & 406.6 & 0.0002 \\
$^2\text{S}_2$ & $^2\text{HOMO}$–$^2\text{LUMO}$ (+50%); $^2\text{HOMO}$–$^2\text{LUMO}$ (41%) & 3.49 & 355.4 & 0.0281 \\
$^2\text{S}_3$ & $^2\text{HOMO}$–$^2\text{LUMO}$+1 (+86%); $^2\text{HOMO}$–$^2\text{LUMO}$+2 (+5%) & 3.62 & 342.1 & 0.0109 \\
$^2\text{S}_4$ & $^2\text{HOMO}$–$^2\text{LUMO}$+1 (+53%); $^2\text{HOMO}$–$^2\text{LUMO}$+2 (+38%) & 3.67 & 337.9 & 0.0018 \\
$^2\text{S}_5$ & $^2\text{HOMO}$–$^2\text{LUMO}$+2 (+79%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (7%); $^2\text{HOMO}$–$^2\text{LUMO}$ (6%) & 3.75 & 331.0 & 0.0222 \\
$^2\text{S}_6$ & $^2\text{HOMO}$–$^2\text{LUMO}$+3 (+84%) & 3.80 & 326.2 & 0.0302 \\
$^2\text{S}_7$ & $^2\text{HOMO}$–$^2\text{LUMO}$+3 (11%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (12%) & 3.81 & 325.8 & 0.0006 \\
$^2\text{S}_8$ & $^2\text{HOMO}$–$^2\text{LUMO}$+1 (+81%); $^2\text{HOMO}$–$^2\text{LUMO}$+3 (12%) & 3.93 & 315.3 & 0.0123 \\
$^2\text{S}_9$ & $^2\text{HOMO}$–$^2\text{LUMO}$+2 (+44%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (44%) & 3.95 & 313.5 & 0.0388 \\
$^2\text{S}_{10}$ & $^2\text{HOMO}$–$^2\text{LUMO}$+2 (11%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (11%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (+5%) & 3.95 & 313.5 & 0.0006 \\
$^2\text{T}_1$ & $^2\text{HOMO}$–$^2\text{LUMO}$+3 (+49%); $^2\text{HOMO}$–$^2\text{LUMO}$+1 (15%); $^2\text{HOMO}$–$^2\text{LUMO}$+5 (13%) & 2.98 & 415.9 & ~0 \\
\hline
\end{tabular}
\caption{Calculated Energy Levels of the Lower Lying Transitions of Complex $3\text{d}$}
\end{table}
pending for resolution, the experimentally extracted activation energy of 4.43 kcal/mol provides a quantitative estimate of the energy difference between the ground vibrational level of T_1 and the surface crossing section, while the preexponential factor of $1.25 \times 10^{12}$ s$^{-1}$ reflects the vibrational frequency of the weakly bonding modes channeling into the major radiationless pathway.

**Conclusion**

In conclusion, designing a highly efficient blue phosphorescence emitter based on a third-row transition metal is a demanding task. Achieving the phosphorescence toward the blue hue requires pushing either $\pi\pi^*$ or MLCT to a higher energy gap, which normally calls for ligands with an electron-withdrawing substituent or with less extended conjugation. The incorporation of an electron-withdrawing F atom and/or CF$_3$ group at the electron-rich segment of a chelate ligand is expected to increase the ligand-centered $\pi\pi^*$ energy gap and simultaneously destabilized the MLCT transition. On the other hand, the less extended conjugation would make the localization of the excessive energy to specific bonds, i.e., the metal–ligand dative interactive, increasingly significant. Likewise, due to the increase of energy gaps, frontier orbitals contributing to the higher lying HOMOs may spread out to any ligand fragments possessing $\pi$ chromophores, resulting in a mixing of various types (MLCT, ILCT, LLCT) of transitions in the T_1 state. The net results caused the weakening of all corresponding metal–ligand bonds. Both factors are believed to induce radiationless deactivation, as demonstrated in complexes 1–3. While the former is an intrinsic demand in choosing a ligand with $\pi$ chromophores of interest, the latter may be overcome by introducing the strong field auxiliary ligands or the non-$\pi$ electron conjugated ligands so that the LLCT can be reduced significantly. Finally, bright blue phosphorescent emission with quantum efficiency $\Phi_p \sim 0.13$ was observed for complex 1a in the solid state at room temperature. Our results point to the prospect of using this complex as an emitter for blue or even white phosphorescent OLED devices. Focus on this issue is currently in progress.

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**Supporting Information Available:** The calculated energy levels and the associated frontier orbitals of the DFT calculations on complexes 1–3 and X-ray crystallographic data files (CIF) for complexes 1a and 3d. This material is available free of charge via the Internet at http://pubs.acs.org.

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