Highly Efficient Red Emissive Heteroleptic Cyclometalated Iridium(III) Complexes Bearing Two Substituted 2-Phenylquinoxaline and One 2-Pyrazinecarboxylic Acid

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Received September 20, 2012, Accepted October 25, 2012

A series of highly efficient red phosphorescent heteroleptic iridium(III) complexes 1-6 containing two cyclometalating 2-(2,4-substituted phenyl)quinoxaline ligands and one chromophoric ancillary ligand were synthesized: (pqx)Ir(mpz) (1), (dmpqz)Ir(mpz) (2), (dfpqx)Ir(mpz) (3), (pqx)Ir(prz) (4), (dmpqz)Ir(prz) (5), (dfpqz)Ir(prz) (6), where pqx = 2-phenylquinoxaline, dfpqx = 2-(2,4-difluorophenyl)quinoxaline, dmpqz = 2-(2,4-dimethoxyphenyl)quinoxaline, prz = 2-pyrazinecarboxylate and mpz = 5-methyl-2-pyrazinecarboxylate. The absorption, emission, electrochemical and thermal properties of the complexes were evaluated for potential applications to organic light-emitting diodes (OLEDs). The structure of complex 2 was also determined by single-crystal X-ray diffraction analysis. Complex 2 exhibited distorted octahedral geometry around the iridium metal ion, for which 2-(2,4-dimethoxyphenyl)quinoxaline N atoms and C atoms of orthometalated phenyl groups are located at the mutual trans and cis-positions, respectively. The emission spectra of the complexes are governed largely by the nature of the cyclometalating ligand, and the phosphorescent peak wavelengths can be tuned from 588 to 630 nm with high quantum efficiencies of 0.64 to 0.86. Cyclic voltammetry revealed irreversible metal-centered oxidation with potentials in the range of 1.16 to 1.89 V as well as two quasi-reversible reduction waves with potentials ranging from −0.94 to −1.54 V due to the sequential addition of two electrons to the more electron-accepting heterocyclic portion of two distinctive cyclometalated C=N ligands.

Key Words: Iridium(III) complexes, Photoluminescence, Highly efficient red phosphorescence, Color tuning

Introduction

Phosphorescent heavy-metal complexes as emitters in organic light-emitting diodes (OLEDs) have attracted increasing attention because they can fully utilize both singlet and triplet excitons through the strong spin-orbital coupling of heavy-metal ions.1 Most recently, considerable effort has been focused on the design of OLEDs based on phosphorescent cyclometalated iridium complexes owing to their relatively short excited-state life time, high photoluminescence efficiency and excellent wavelength tunability over the entire visible spectrum, and an internal phosphorescence quantum efficiency (\(\eta_{\text{ip}}\)) as high as ~100% can theoretically be achieved.2 On the other hand, there are a few red-emitting iridium complexes, which are important for the realization of RGB full-color displays and the creation of white organic light-emitting devices (WOLEDs).3 Compared to green and blue phosphorescent iridium complexes, red emitting iridium complexes tend to have limited quantum yields4 due to the energy gap law. Increasing the vibrational overlap between the excited and ground states causes an increase in non-radiative rates \(k_{n}\) and a decrease in the radiative rates \(k_{r}\) for longer wavelength emission, resulting in lower quantum efficiency in red emitters. Therefore, the synthesis of new highly efficient red emitting materials is generally based on the design of rigid cyclometalated ligands with a low degree of freedom for vibrational loss. Recently, the highly efficient heteroleptic cyclometalated iridium(III) complexes bearing nitrogen containing 2-phenylquinoxaline-based ligands with a low degree of freedom were reported.5 The reported complexes emitted from red-orange to deep red phosphorescence with high emission quantum yields (\(\Phi = 0.58-0.78\)) were found to be dependent on the substituent of cyclometalated ligands, and were suggested to be good triplet phosphors for OLEDs applications.

As part of an ongoing study of highly efficient red-emitting materials, this paper reports synthesis and characterization of a series of six red-emitting iridium(III) complexes containing two substituted 2-phenylquinoxaline ligands and one 2-pyrazinecarboxylic acid. The energy gap between the ground and lowest excited states can be reduced effectively by either an extension of π electron delocalization of the aromatic ligand chromophore or by emission from a nitrogen containing 2-pyrazinecarboxylate ancillary ligand, giving emitters with highly efficient red color due to an intra-ligand energy transfer (ILET) process.

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Experimental

Materials. All reagents and solvents were obtained commercially from Sigma-Aldrich Chemicals or Acros Organics, and used as received with the exception of tetrahydrofuran (THF), which was distilled from sodium/benzophenone under nitrogen.

Synthesis of Ligands: 2-Phenylquinoxaline (pqx). 2-Phenylquinoxaline (pqx) was prepared from a reaction of 2-chloroquinoxaline and phenylboronic acid. 2-Chloroquinoxaline (3.00 g, 18.2 mmol) and phenylboronic acid (2.00 g, 20.0 mmol) were added to 50 mL of THF. After adding 5 mL of aqueous 4 M K2CO3, the reaction mixture was heated to 80 °C for 24 h. The cooled crude mixture was poured into water, extracted with CH2Cl2 (0.98 g, 0.85 mmol) were added to 50 mL of THF. After degassing, the reaction vessel was maintained under vacuum. The reaction mixture was stirred for 20 h. The resulting dark solution was concentrated under vacuum at 60 °C, and the residues were eluted through a silica column. The solid was filtered and washed with water, hexane and ethanol. After degassing, the reaction vessel was maintained under vacuum. The reaction mixture was stirred for 20 h. The resulting dark solution was concentrated under vacuum at 60 °C, and the residues were eluted through a silica column.

[(pqx)Ir(mpz)] (1). Red solid. Yield: 0.18 g (62%). 1H NMR (CDCl3, 400 MHz) δ 2.52 (s, 3H), 6.12 (d, 2H), 6.7 (t, 2H), 6.83 (dd, 2H), 7.01 (m, 2H), 7.53 (m, 2H), 7.65 (m, 2H), 7.98 (d, 2H), 8.07 (m, 2H), 8.64 (d, 2H), 8.90 (s, 1H), 9.49 (d, 1H).

[(dmpq)x]Ir(mpz) (2). Dark red solid. Yield: 0.16 g (56%). 1H NMR (CDCl3, 400 MHz) δ 2.54 (s, 3H), 3.23 (d, 6H), 3.93 (d, 6H), 5.30 (s, 1H), 5.98 (dd, 2H), 6.93 (m, 2H), 7.06 (d, 1H), 7.42 (dd, 1H), 7.53 (m, 1H), 7.76 (s, 1H), 7.95 (m, 2H), 8.54 (m, 1H), 8.89 (s, 1H), 10.14 (d, 2H).

[(dfpq)x]Ir(mpz) (3). Orange solid. Yield: 0.12 g (42%). 1H NMR (CDCl3, 400 MHz) δ 2.49 (s, 3H), 5.63 (dd, 2H), 6.32 (dd, 2H), 6.61 (m, 2H), 6.69 (m, 1H), 7.02 (dd, 1H), 7.49 (s, 1H), 7.89 (d, 1H), 8.21 (q, 2H), 8.79 (s, 1H), 9.15 (s, 1H), 9.79 (dd, 2H).

[(pqx)Ir(mpz)] (4). Red solid. Yield: 0.14 g (49%). 1H NMR (CDCl3, 400 MHz) δ 6.19 (d, 2H), 6.70 (t, 2H), 6.82 (m, 2H), 7.01 (m, 2H), 7.15 (dd, 2H), 7.55 (m, 2H), 7.85 (m, 2H), 8.01 (d, 2H), 8.10 (m, 1H), 8.64 (m, 1H), 9.08 (s, 1H), 9.50 (d, 2H).

[(dmpq)x]Ir(mpz) (5). Dark red solid. Yield: 0.16 g (57%). 1H NMR (CDCl3, 400 MHz) δ 3.23 (d, 6H), 3.99 (d, 6H), 5.30 (s, 1H), 5.99 (dd, 2H), 6.93 (t, 2H), 7.04 (d, 2H), 7.39 (t, 1H), 7.52 (m, 1H), 7.95 (m, 2H), 8.51 (m, 1H), 8.65 (d, 1H), 9.01 (s, 1H), 10.14 (d, 2H).

[(dfpq)x]Ir(mpz) (6). Orange solid. Yield: 0.19 g (67%). 1H NMR (CDCl3, 400 MHz) δ 5.61 (dd, 2H), 6.29 (dd, 2H), 6.55 (m, 2H), 6.71 (m, 1H), 6.98 (dd, 1H), 7.52 (s, 1H), 7.96 (d, 1H), 8.11 (q, 2H), 8.56 (d, 1H), 8.75 (s, 1H), 9.05 (s, 1H), 9.83 (dd, 2H).

Instruments. The 1H nuclear magnetic resonance (NMR, Varian Mercury 300 MHz instrument) spectra were recorded and the chemical shifts were referenced to CDCl3 as an internal standard. The UV-visible spectra were recorded on a Jasco V-570 UV-vis. spectrophotometer and the photoluminescence (PL) spectra were recorded at room temperature using an intensified charge-coupled detector. Electrochemical measurements were performed using a Bioanalytical Systems CV-50 W electrochemical analyzer with a three electrode cell assembly. The electrochemical cell consisted of a glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl reference electrode. The oxidation and reduction measurements were recorded in a CH2Cl2 solution containing tetra(n-butyl)ammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 50 mV s⁻¹ under nitrogen conditions. Each oxidation potential was calibrated using ferrocene as the reference. The concentration of the iridium(III) complexes and supporting electrolyte were ~10⁻³ and ~10⁻⁵ M respectively. Thermal analyses were carried out on a meter Toledo TGA/SDTA 815 analyzer under a nitrogen atmosphere at a heating rate
of 10 °C/min.

Crystallography. The X-ray intensity data were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at the temperature of 174 K. The structures were solved using a SHELXS-97 and refined by a full-matrix least-squares calculation on F² using SHELXL-97. All non-hydrogen atoms were refined anisotropically except O atoms of the disordered water molecules. The water H atoms were not found out because of the disordering in the lattice. The other hydrogen atoms were placed in ideal positions and were riding on their respective carbon atoms (Biso = 1.2 Beq and 1.5 Beq).

Results and Discussion

Synthesis and Characterization. The reaction of pqx and IrCl₃·nH₂O in 2-ethoxyethanol afforded the μ-chloro-bridged dimer complex [(pqx)₂Ir(μ-Cl)]. The treatment of [(pqx)₂Ir(μ-Cl)] dimer with a mprz ligand in the presence of Na₂CO₃ yielded the monomeric complex [(pqx)Ir(mprz)] (1). Similarly, complex [(pqx)Ir(prz)] (4) was obtained using prz chelate ligand instead of the mprz ligand. The monomeric iridium(III) complexes, [(dmpqx)Ir(mprz)] (2), [(dfpqx)Ir(mprz)] (3), [(dmpqx)Ir(prz)] (5) and [(dfpqx)Ir(prz)] (6), were also synthesized for subtle tuning of the emission wavelength. Scheme 1 outlines the synthetic protocol for the ligands and phosphorescent iridium(III) complexes. All iridium(III) complexes were highly soluble in chlorinated solvents. ¹H NMR spectral analyses were consistent with the proposed structures. Complex 2 was examined further using single-crystal X-ray analysis to establish its three dimensional structure.

A single crystal of complex 2 was grown by the diffusion of hexane into a concentrated dichloromethane solution and

Figure 1. Molecular structure of (dmpqx)Ir(mprz) (2), showing the atom-numbering scheme. The thermal ellipsoids represent the 30% probability limit. The hydrogen atoms were omitted for clarity.

Scheme 1. Synthetic route for ligand and iridium(III) complexes 1-6.
Table 1. Crystal data and structure refinement for complex 2

<table>
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<tr>
<th>Complex</th>
<th>(dmpqx):Ir(mprz) (2)</th>
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<tr>
<td>Chemical formula</td>
<td>C_{38}H_{32}N_{16}O_{12}Ir·2CHCl·H_{2}O</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1047.76</td>
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<tr>
<td>Temperature</td>
<td>174(2) K</td>
</tr>
<tr>
<td>Crystal system, Space group</td>
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<tr>
<td>a (Å), α (°)</td>
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</tr>
<tr>
<td>b (Å), β (°)</td>
<td>27.137(5), 94.06(3)</td>
</tr>
<tr>
<td>c (Å), γ (°)</td>
<td>15.071(3), 90</td>
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<tr>
<td>Volume</td>
<td>4360.8(15) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.596 Mg/m³</td>
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<tr>
<td>Absorption coefficient</td>
<td>3.361 mm⁻¹</td>
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<tr>
<td>f(000)</td>
<td>2080</td>
</tr>
<tr>
<td>Crystal size</td>
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<tr>
<td>θ range for data collection</td>
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<tr>
<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
<td>10809 [R_{int} = 0.0811]</td>
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<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R₁ = 0.0623, wR₂ = 0.1502</td>
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<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1300, wR₂ = 0.1817</td>
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<tr>
<td>Data/restraints/parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>2.343 and −1.905 e Å⁻³</td>
</tr>
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**Photophysical Characterization.** Figure 2 shows the UV-vis. absorption and photoluminescence (PL) spectra of the iridium(III) complexes 1-6. Table 3 lists the resulting photophysical properties of the iridium complexes. All the complexes displayed strong absorption bands between 280 and 310 nm, which were assigned to π-π* ligand-centered transitions. In addition, spin-allowed metal-to-ligand charge
transfer (1MLCT) absorption, as evidenced from their molar extinction coefficients in the order $10^{3} - 10^{4} \text{M}^{-1} \text{cm}^{-1}$, and the lowest energy absorption band in combination with broad and structureless spectral features was observed.

Complex 4, (pqx):Ir(prz) [$\lambda_{\text{max}}$ = 628 nm], showed a 10-45 nm red-shift in emission compared to (pqx):Ir(acac) [$\lambda_{\text{max}}$ = 583 nm]$^{35}$, where acac is acetylacetonate and (pqx):Ir(biimdz) [$\lambda_{\text{max}}$ = 618 nm]$^{36}$, where biimdz is bimimidazole. This shows that the ancillary ligand plays an important role in tuning the emission color from the (pqx):Ir moiety and prz is an efficient ancillary ligand in red emission. Furthermore, highly quantum efficiencies of 0.64-0.86 were observed in complexes 1-6. It was reported that a substituted nitrogen atom at the 4-position in 2-pyrazine carboxylate acids decreased the LUMO energy level in heteroleptic iridium complexes containing an ancillary pyrazine carboxylate modulated ligand resulting in a red shift emission.$^{12}$ In addition, the reported iridium complexes showed highly efficient red emissions due to an inter-ligand energy transfer (I LET) process from 1MLCT state to intra-ligand 1LC energy state.$^{12,13}$ On the basis of this reported study and the experimental observation of highly efficient red emissions in complexes (1-6), we suggest that a probable mechanism of phosphorescent emission is a highly efficient I LET process. An efficient intersystem crossing to 1MLCT occurs after 1MLCT excitation from the iridium moiety to the cyclometalating pqx ligand in the singlet manifold, followed by inter-ligand energy transfer to the ancillary ligand.

In addition, the emission bands of all complexes were blue shifted from room temperature to 77 K due to the rigidochromic effect.$^{14}$ The excited state at 77 K emits before solvent relaxation occurs, whereas room temperature emission occurs from the fully relaxed state within the lifetime of the excited state of the emitting molecule.

Complex 3 bearing the 2,4-difluorophenyl group showed a ~32 nm hypsochromic shift in emission compared to complex 1, which can be rationalized qualitatively by a decrease in the HOMO energy level due to the stronger electron-withdrawing character of the fluorine atom at the ortho- and para- positions.$^{13}$ Moreover, complex 2 resulted a 8 nm blue shift in emission peak maximum ($\lambda_{\text{max}}$) than complex 1. In complexes 2 and 5, the electron releasing substituent (-OCH$_3$) did not have a significant impact on emission comparing to complexes 3 and 6. Similar phenomena were also observed in the iridium(III) complexes containing substituted quinoline, regardless of whether the substituents in the 2-phenyl ring of the quinoline unit were electron-withdrawing -F or electron-releasing -OCH$_3$ groups.$^{15}$

The thermal stability of complexes 1-6 were probed by thermogravimetric analysis (TGA), and exhibited 5% weight loss in the 209 to 262 °C range under a nitrogen atmosphere, as shown in Table 3, supporting its suitability for electronic device applications.

**Electrochemical Properties.** The electrochemical properties of the complexes were characterized by cyclic voltammetry (CV) in a methylene chloride solution to provide insight into the highest occupied molecular orbital (HOMO) energy levels of the complexes. All the iridium complexes showed irreversible oxidation potentials in the 1.16 to 1.89 V range and double quasi-reversible reduction waves with potentials ranges from –0.94 to –1.36 V and from –1.22 to –1.54 V. Oxidation occurred mainly at the iridium metal ion sites together with a contribution from the cyclometalated phenyl fragment, which led to a loss of electrochemical
the phenyl ring led to a marked increase in the oxidation potential and a concomitant decrease in the reduction potential, whereas the electron releasing -OCH$_3$ group on the phenyl ring decreased the oxidation potential and increased the reduction potential. This shows that the introduction of electron withdrawing groups on the phenyl ring reduces the HOMO energy level, resulting in a blue shift in an emission. The presence of electron donating -CH$_3$ group at the 5-position on the mprrz ligand shifts the oxidation potentials to lower values than the prz ligand. Accordingly, the electron enrichment of the metal centered redox site destabilized the HOMO energy level, resulting in making the iridium(III) metal ion easier to oxidize.

Conclusions

A series of six heteroleptic cyclometalated iridium(III) complexes 1-6 bearing 2-(2,4-substituted phenyl)quinoxaline and 2-pyrazinecarboxylate (prz) or 5-methyl-2-pyrazinecarboxylate (mprrz) ligands as red triplet emitters were synthesized. The complexes incorporated two substituted cyclometalated ligands with an extended π system with fused heteroaromatic rings and one chromophoric ancillary ligand to counterbalance the energy gap suited for red emission. The optical and electrochemical properties were examined and compared with those reported for (pqx)$_2$Ir(L-$^X$), where L-$^X$ = acetylacetonate (acac) or biimidazole (bim)d complexes. The prz ancillary ligand plays an important role in the redshifted emission in the heteroleptic cyclometallated iridium complexes due to the ILET process. X-ray diffraction of complex (dmpqx)$_2$Ir(prz) (2) showed that the complex exists as a descriptive monomer showing a distorted octahedral symmetry around the iridium metal ion with no intermolecular interactions in the solid. These complexes exhibited high emission quantum yields (Φ = 0.64-0.86) suitable for red emitting phosphors for OLEDs applications. The color tuning of heteroleptic cyclometalated iridium(III) complexes was achieved by relative energy level control of the main and ancillary ligands.

Supplementary Material

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-671926 for [(dmpqx)$_2$Ir(mprz)] (2)). The data can be obtained free of charge via www.ccdc.cam.ac.uk/deposit (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-01223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments. This work was supported by the research fund of Samsung Display, Korea.

References

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