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Communication

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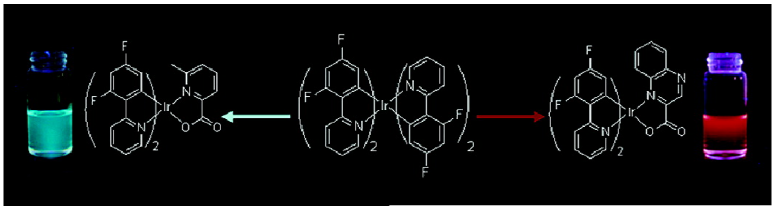

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Inter-Ligand Energy Transfer and Related Emission Change in the Cyclometalated Heteroleptic Iridium Complex: Facile and Efficient Color Tuning over the Whole Visible Range by the Ancillary Ligand Structure

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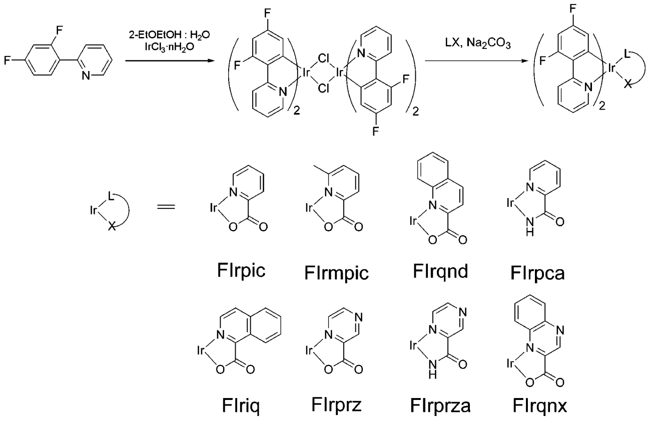
Initiated by the pioneering work of the Thompson and Forrest group,[1] enormous advances in cyclometalated iridium complexes have been made in pursuit of a highly efficient electrophosphorescent organic light-emitting diode (OLED). Many different classes of homoleptic (Ir(III)(C∧N)$_3$) and heteroleptic (Ir(III)(C∧N)$_2$ (LX)) iridium complexes have been developed, where (C∧N) is a monoanionic cyclometalating ligand (e.g., 2-phenylpyridine, 2-phenylbenzothiazole) and (LX) is an ancillary ligand (e.g., acetyl acetonate, picolinate). It has been well demonstrated that structural changes in the skeletal as well as the substituent groups of the cyclometalating ligand (C∧N) afford significant color tuning of electrophosphorescence. Therefore, the design and synthesis of novel cyclometalating ligands have been enthusiastically investigated as the main strategy of phosphorescence color tuning.[2,3]

Unfortunately, however, the synthesis of an electrophosphorescent iridium complex from the newly synthesized cyclometalating ligand (C∧N) is not always feasible because the chloride-bridged iridium dimer intermediate, (C∧N)$_2$Ir(μ-Cl)$_2$Ir(C∧N)$_2$, is often difficult to prepare for steric and electronic reasons. Therefore, at least, in principle, emission color tuning by the ancillary ligand structure in the heteroleptic iridium complex of the already known cyclometalating ligand (C∧N) is considered a much easier, efficient, and competitive approach. In this regard, heteroleptic iridium complexes incorporating ancillary ligands, such as acetylacetonate, picolinate, *N*-methylsalicylimine, triazolate, and tetrazolate derivatives, have been investigated by many groups. However, discouragingly, it was found that the emission color was largely governed by the nature of the cyclometalating ligand, while the ancillary ligand operated insignificant control.[3,4]

Recently, observation and calculational prediction of some color tuning (over the 532−603 nm range) in heteroleptic iridium complexes with 1-isoquinolinate and 3-isoquinolinate as emitting ancillary ligands were reported.[5] In addition to the small range of color tuning and low phosphorescence quantum yield ($<$0.14), however, no viable mechanism explaining the photophysical processes based on inter-ligand energy transfer (ILET)[6] was suggested.

In this report, we demonstrate the full potential of a color tuning methodology with an ancillary ligand and suggest its most probable mechanism in heteroleptic iridium complexes. We employ the common cyclometalating ligand 2-(2,4-difluorophenyl)pyridine (*dfppy*) and show the blue to red range emission control in a series of heteroleptic iridium complexes by using novel ancillary ligands. Briefly, excitation from the iridium-centered HOMO to the cyclometalating *dfppy*-centered LUMO (*so-called metal to ligand charge transfer (MLCT) transition*) is followed by efficient inter-ligand energy transfer (ILET) to the “emitting ancillary ligand”, providing a novel channel of phosphorescence color tuning.

Scheme 1. Synthetic Procedure of Heteroleptic Iridium Complexes and Their Structures



Scheme 1 illustrates the chemical structure and synthesis of *dfppy*-based heteroleptic iridium complexes ((*dfppy*)$_2$Ir(LX)) investigated in this work. Ancillary ligands with different band gap energy were designed by changing the fused ring conjugation of pyridine- and pyrazine-based ligand structures. A carboxylate group was included as the metal chelating unit in six ancillary ligands. Synthesis of two amide-containing ligands was accomplished in order to assess the possible perturbation of HOMO levels in iridium complexes.[3e]

Chloride-bridged dimer (*dfppy*)$_2$Ir(μ-Cl)$_2$Ir(*dfppy*)$_2$ was synthesized according to the procedure described in the literature.[3a] A sodium carbonate-mediated ligand exchange reaction with an ancillary ligand was carried out to give a heteroleptic iridium complex in a quantitative yield (see Supporting Information). Photophysical characteristics of seven newly synthesized iridium complexes (see Scheme 1 for designations) together with the already-known complex FIrpic[4c] are summarized in Table 1. Photographs showing the spectral tuning of photoluminescence (PL) and related spectral features are included in Figure 1.[7] It is clearly noted that the emission color is broadly controlled from sky blue (468 nm) to red (666 nm), depending on the ancillary ligand structure, although their absorption spectra were almost the same. This observation implies the presence of a specific energy transfer process, most likely ILET, from the common excited states in a series of these heteroleptic iridium complexes. All the high phosphorescence quantum efficiencies (0.27−0.39) from six carboxylate-containing heteroleptic complexes compare well to that of Ir(*ppy*)$_3$ (0.40), suggesting a highly efficient ILET process. In contrast with our expectations, however, insignificant HOMO level modulation (see Table 1) and much lower phosphorescence efficiencies (0.03 and 0.04 for FIrprza and FIrpca, respectively) were obtained for amide-type ancillary ligands.[8]

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Table 1. Photophysical Properties of Iridium Complexes

	Emission λ_{max} (nm)				
	solution	film	HOMO (eV)	Φ_p	ΔE_{LUMO} (eV)[a]
FIrpic	468, 494	474, 500	5.8	0.42	0.000
FIrmpic	478, 504	479, 501	5.9	0.31	0.000
FIrqnd	573	551	5.9	0.35	−0.048
FIrpca	574	484, 504	5.8	0.04	−0.181
FIriq	581	539, 565	5.8	0.27	−0.196
FIrprz	587	554, 564	5.9	0.31	−0.466
FIrprza	621	554, 569	5.8	0.03	−0.694
FIrqnx	666	615	5.8	0.39	−0.801

[a] Calculated LUMO energy difference relative to FIrmpic.

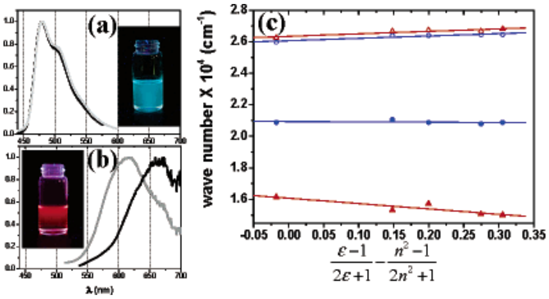

Figure 1. (a) Emission spectra (black for 1.0 × 10^{-5} M in CH_2Cl_2 solution and gray for PMMA film) of FIrmpic (Type I), (b) emission spectra (black for 1.0 × 10^{-5} M in MeCN solution and gray for PMMA film) of FIrqnx (Type II), and (c) a plot of absorption and emission maxima of FIrmpic (Type I, blue) and FIrqnx (Type II, red) as a function of solvent polarity parameter; n and ϵ are the refractive index and dielectric constant of solvent, respectively.

As seen in Figure 1, two different types of phosphorescence emission and related iridium complexes were identified. Type I complexes (FIrmpic, FIrpic) exhibited a blue emission with vibronic structures and showed an invariant spectral emission both in solution and in solid state, as reported earlier for FIrpic. On the other hand, Type II complexes (FIrqnd, FIrpca, FIriq, FIrprz, FIrprza, and FIrqnx) exhibited a broad spectral emission at longer wavelength and a characteristically hypsochromic spectral shift in the solid state compared to the solution state. Furthermore, it is worth noting that the Type II complexes show distinct positive solvatochromism in the phosphorescence emission (see Figure 1c) in contrast that of Type I complexes, indicating that the emitting states of Type II complexes comprise an intramolecular charge transfer (ICT) state.[9]

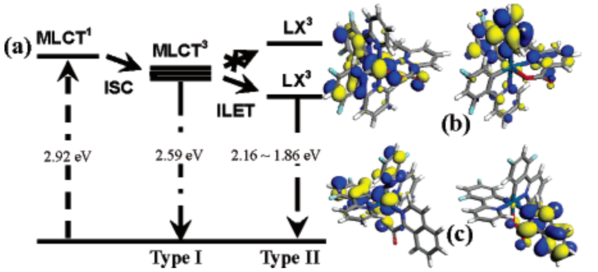

Figure 2. (a) A suggested mechanism of color tuning invoked by the interligand energy transfer (ILET) to ancillary ligand. HOMO (left) and LUMO (right) of (b) FIrmpic and (c) FIriq calculated with BLYP functional and DNP basis set under effective core potential.

On the basis of these experimental observations, the most probable mechanism of phosphorescence emission from the heteroleptic iridium complex is shown in Figure 2a. After the MLCT^1 excitation from iridium to *dfppy* in the singlet manifold, highly efficient inter-system crossing to MLCT^3 occurs due to the strong spin−orbit coupling. This *dfppy*-centered MLCT^3 state has different fates (Types I and II), depending on the triplet energy level of the ancillary ligand (LX^3) compared to that of MLCT^3, as depicted in Figure 2. Type I emission is attributed to the phosphorescent decay from the MLCT^3 state of *dfppy*, which must occur when the level of LX^3 locates higher than that of MLCT^3. On the other hand, ILET to the LX^3 state of the ancillary ligand followed by phosphorescent decay (Type II emission) occurs when the level of LX^3 is lower than that of MLCT^3. This ILET-mediated phosphorescence emission is strongly supported by the relative LUMO energies calculated by the DFT method (see Table 1). It is clearly noted that the LX^3 energies of Type II ancillary ligands are all lower than that of FIrmpic (Type I) and are well correlated with the changes in emission wavelength. Furthermore, DFT calculations show that the LUMO of FIrmpic (Type I) locates largely on the *dfppy* ligand, while that of FIriq (Type II) locates on the isoquinolinate ligand exclusively (see Figure 2). Therefore, tunable emission via the ILET-to-LX^3 scheme and possible solvatochromism of Type II complexes are consistently explained.

In conclusion, we have successfully demonstrated and elucidated the broad range color tuning of heteroleptic iridium complexes via relative energy level (LX^3) control of the ancillary ligand.

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Supporting Information Available: A summary of detailed synthetic procedure, spectral assignment, full absorption and photoluminescence spectra, and characterization methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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