

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231642461>

Direct Spectroscopic Observation of Interligand Energy Transfer in Cyclometalated Heteroleptic Iridium(III) Complexes: A Strategy for Phosphorescence Color Tuning and White Light G...

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · FEBRUARY 2007

Impact Factor: 4.77 · DOI: 10.1021/jp0702550

CITATIONS

74

READS

98

5 AUTHORS, INCLUDING:



Kil Suk Kim

Lund University

51 PUBLICATIONS 2,533 CITATIONS

SEE PROFILE



Dongho Kim

Yonsei University

498 PUBLICATIONS 13,486 CITATIONS

SEE PROFILE

Article

Direct Spectroscopic Observation of Interligand Energy Transfer in Cyclometalated Heteroleptic Iridium(III) Complexes: A Strategy for Phosphorescence Color Tuning and White Light Generation

Youngmin You, Kil Suk Kim, Tae Kyu Ahn, Dongho Kim, and Soo Young Park

J. Phys. Chem. C, **2007**, 111 (10), 4052-4060 • DOI: 10.1021/jp0702550

Downloaded from <http://pubs.acs.org> on December 29, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 12 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Direct Spectroscopic Observation of Interligand Energy Transfer in Cyclometalated Heteroleptic Iridium(III) Complexes: A Strategy for Phosphorescence Color Tuning and White Light Generation

Youngmin You,[†] Kil Suk Kim,[†] Tae Kyu Ahn,[†] Dongho Kim,^{*,†} and Soo Young Park^{*,‡}

School of Materials Science & Engineering, Seoul National University, San 56-1,

Shillim-Dong, Kwanak-Gu, Seoul 151-744, Korea, and Center for Ultrafast Optical Characteristics Control and Department of Chemistry, Yonsei University, Seoul 120-749, Korea

Received: January 11, 2007; In Final Form: January 19, 2007

We have characterized a series of highly phosphorescent cyclometalated heteroleptic Ir(III) complexes containing emitting (chromophoric) ancillary ligands with appropriate triplet levels below that of the cyclometalating ligand. We directly observed relatively rapid (ca. 6–7 ns^{−1}) exothermic interligand energy transfer (ILET) from the cyclometalating ligand to the emitting ancillary ligand by time-resolved spectroscopy, which afforded a novel strategy of emission color tuning. Characteristic ILET processes in the heteroleptic Ir(III) complexes were further elucidated by electrochemical measurements and the density functional theory calculations. Facile and efficient generation of white phosphorescence was demonstrated by exploring the ILET process in a mixture of heteroleptic Ir(III) complexes.

1. Introduction

Phosphorescent transition metal complexes are receiving a great deal of attention as excellent emitting materials for organic light-emitting diodes (OLEDs).^{1,2} Strong spin–orbit coupling induced by the transition metal provides large populations of the emitting triplet state, which leads to high phosphorescence quantum efficiencies.^{3–5} Among the phosphorescent metal complexes studied to date, those with d⁶ transition metals (Ru(II),^{6–9} Os(II),^{10–12} and Ir(III)^{13–15}) at the core have been recognized as the most promising candidates for OLEDs due to their exceptionally high phosphorescence quantum efficiencies. Since the report of highly efficient phosphorescent OLEDs based on cyclometalated Ir(III) complexes,¹ the use of these complexes in OLED applications has attracted considerable attention.^{2,16–26}

For practical OLED applications, there have been continuous efforts to develop cyclometalated Ir(III) complexes with finely tuned phosphorescent emissions. To date, the color tuning of cyclometalated Ir(III) complexes has mostly been done by altering the electronic structures of the phenylpyridine-based monoanionic bidentate cyclometalating ligand (C[^]N) (see Chart 1).^{21,27–31} Increasing the π -conjugation length or introducing fused heteroaromatic rings into the cyclometalating ligand caused a red shift in the emission,^{21,27,28,31} whereas lowering the highest occupied molecular orbital (HOMO) by adding an the electron-withdrawing group or raising the triplet state energy by use of a ligand with a strong ligand strength resulted in a blue shift in the emission.^{29,30} Hence, in theory, the color of the emission from cyclometalated Ir(III) complexes can be tuned through the design and synthesis of novel cyclometalating ligands. In practice, however, severe steric hindrance or functional group incompatibility constrain the range of cyclometalating ligands and related Ir(III) complexes that can be synthesized. In addition, the synthesis of homoleptic tris-

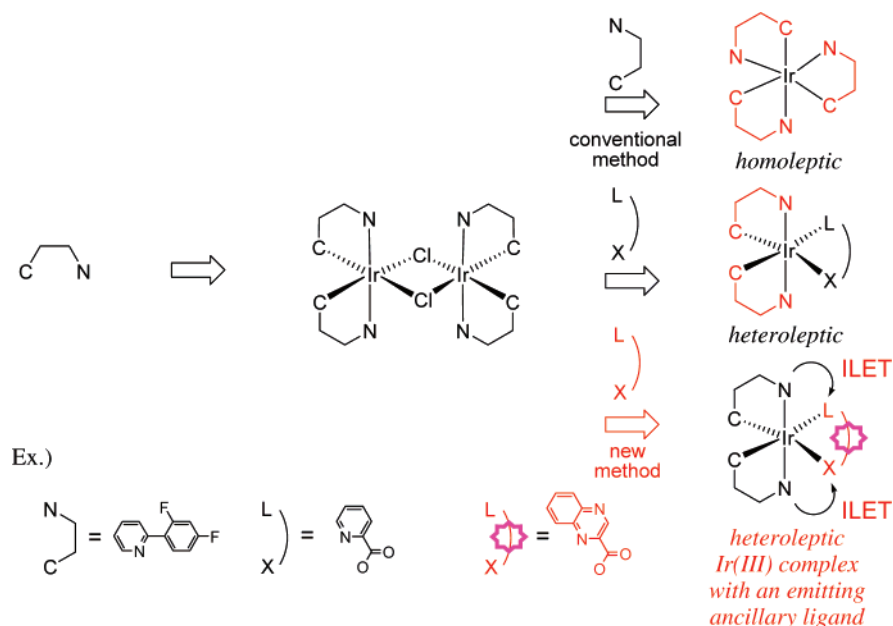
cyclometalated Ir(III) complexes (i.e., complexes with three identical ligands), which have generally been used in previous studies, involves harsh reaction conditions and tedious purification procedures due to the presence of geometric isomers (*fac*) and meridional (*mer*) isomers.³² Most of all, the benefits to be derived from developing new homoleptic Ir(III) complexes are seriously limited by the fact that only a single cyclometalated Ir(III) complex is formed for each new cyclometalating ligand.

Various heteroleptic Ir(III) complexes, comprised of an ancillary ligand (LX) together with the cyclometalating ligands, have been synthesized with use of acetylacetonate (*acac*), picolinate (*pic*), triazolate, tetrazolate, and *N*-methylsalicylimine as ancillary ligands.^{27,33–38} In contrast to the tendency of homoleptic Ir(III) complexes to form *fac* and *mer* isomers, heteroleptic Ir(III) complexes with one ancillary ligand have been synthesized as a single isomer.^{39,40} Moreover, heteroleptic Ir(III) complexes exhibit facile and versatile synthetic derivatization,²⁷ enabling easy color tuning, at least in principle. However, because the ancillary ligands employed to date did not have a profound effect on the phosphorescence color of the Ir(III) complexes, they have been recognized only as blind parts of the complexes. For example, Thompson et al. reported the systematic color-tuning of Ir(III) complexes by using bis-(pyrazolyl)borate, diphosphine, *tert*-butylcyanide, and *N*-heterocyclic carbene ligands as ancillary ligands.^{41,42} For these complexes, the change in phosphorescence color with varying the ancillary ligand was attributed to the degree of perturbation of the metal-to-ligand charge transfer (MLCT) transition by the excited-state interaction between the cyclometalating ligand centered (LC) state. However, the variation in emission wavelength achieved was rather narrow (<54 nm) because the emissive state was still largely associated with the cyclometalating ligand.

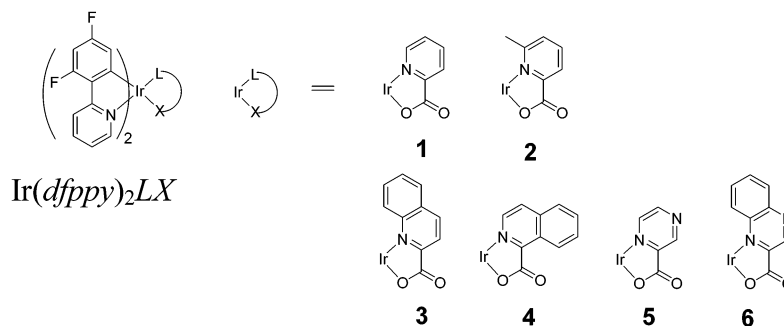
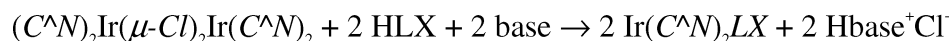
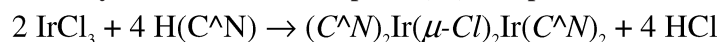
In contrast to the limited range of color tuning achieved by Thompson et al., we recently reported that emission color tuning of heteroleptic Ir(III) complexes over the entire visible range (wavelength = 468–666 nm) could be achieved by changing

[†] Yonsei University. E-mail: dongho@yonsei.ac.kr.

[‡] Seoul National University. E-mail: parksy@snu.ac.kr.

CHART 1: Color Tuning Methods for the Triplet Emission of Ir(III) Complexes^a

SCHEME 1: Reaction Scheme of Cyclometalated Heteroleptic Ir(III) Complexes



the ancillary ligand structure while maintaining the same cyclometalating ligand, (2-(2,4-difluorophenyl)pyridinato (*dfppy*)) (see Scheme 1 for structures).⁴³ Interligand energy transfer (ILET) between the cyclometalating ligand and the ancillary ligand was tentatively proposed as the most probable mechanism underlying the variation in emission color of these complexes, based on their static absorption and photoluminescence properties. Such intramolecular excited-state energy transfer behavior in the transition metal complex has been well explored particularly for Ru(II).^{44–54} Fast energy transfer in the mixed-ligands Ru(II) complex is well understood by fast photophysical studies. However, reports on excited-state ligand interactions in the phosphorescent Ir(III) complexes are extremely rare. In this paper, we report the direct spectroscopic observation of ILET processes for the series of heteroleptic Ir(III) complexes shown in Scheme 1. These findings form the basis of an unambiguous design rule for phosphorescence color tuning of cyclometalated Ir(III) complexes. Notably, for the first time to the best of our knowledge, we reveal the energy transfer process between different ligands in highly phosphorescent cyclometalated heteroleptic Ir(III) complexes. In addition, we provide comprehensive evidence for ILET through photophysical and electrochemical measurements together with quantum chemical

calculations based on density functional theory (DFT). Finally, we propose and demonstrate an innovative strategy for obtaining white phosphorescence that exploits the unique characteristics of the ILET process.

2. Results and Discussion

The structures of the heteroleptic Ir(III) complexes used in this study are illustrated in Scheme 1. To systematically investigate the interactions between different ligands, we selected a series of heteroleptic Ir(III) complexes from **1** (iridium(III) bis[(4,6-difluorophenyl)pyridinato-*N,C*^{2'}]picolinate (Irpic))^{55–57} to **6** (iridium(III) bis[(4,6-difluorophenyl)pyridinato-*N,C*^{2'}]quinoxalinate), in which *dfppy* (defined above) served as the common cyclometalating ligand (C[^]N). In designing these complexes, we aimed to modulate the lowest global triplet state energy level of the Ir(III) complex by varying the ancillary ligand. The main advantage of our synthetic methodology (see Chart 1) is the use of a common intermediate ((*dfppy*)₂Ir(μ-Cl)₂Ir(*dfppy*)₂), which leads to all six products (**1** to **6**) free from (*fac* or *mer*) isomers.

Figure 1a shows the absorption spectra of the Ir(III) complexes **1** to **6**. Each spectrum has a strong spin-allowed ligand-

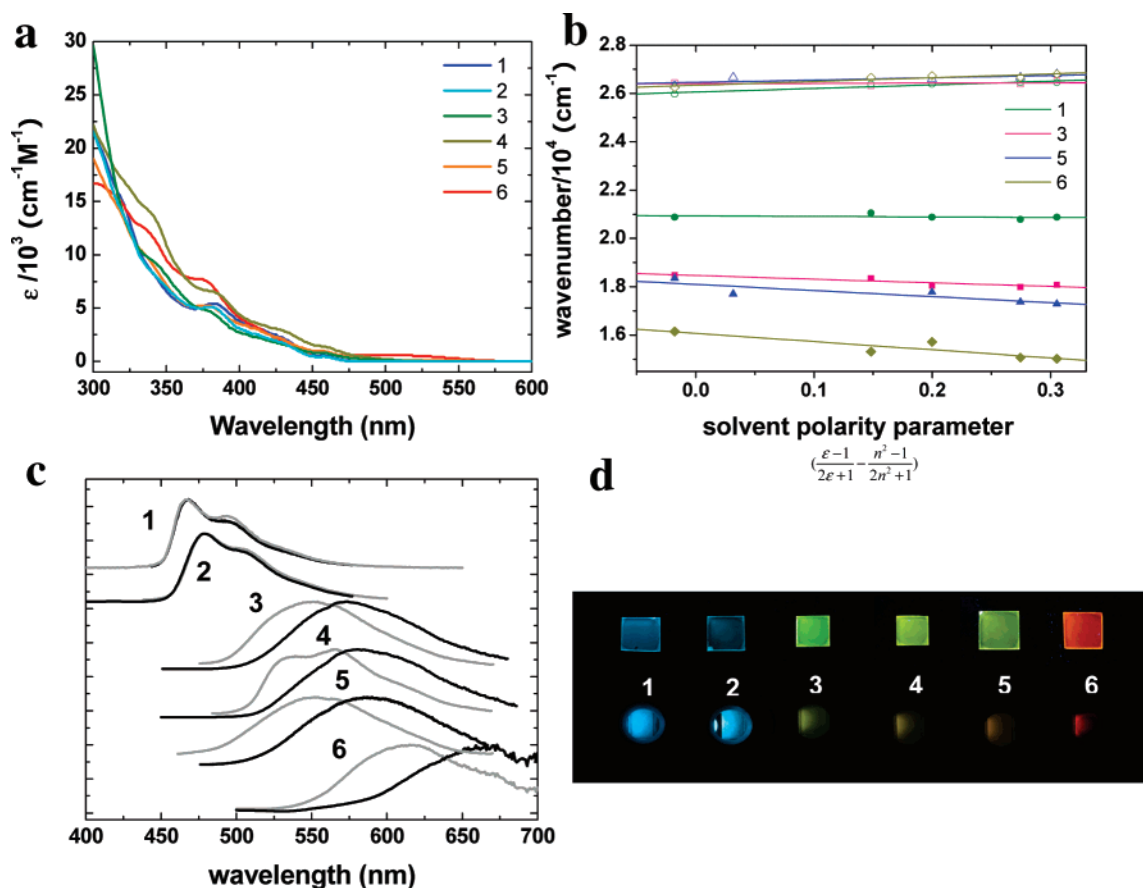


Figure 1. (a) Absorption spectra of Ir(III) complexes in solution (1.0×10^{-5} M in toluene). (b) A plot of the absorption and emission maxima of **1**, **3**, **5**, and **6** as a function of solvent polarity parameter of the Lippert–Mataga model. n and ϵ are the refractive index and dielectric constant of the solvent, respectively. (c) Photoluminescence spectra of cyclometalated heteroleptic Ir(III) complexes: 1.0×10^{-5} M solution in toluene (black) and 5 wt % doped in PMMA film (gray). (d) Photo showing phosphorescent emission of Ir(III) complexes (upper row: doped PMMA films; lower row: solutions in toluene).⁵⁸

centered absorption (¹LC) band at short wavelength (<350 nm).⁵⁸ In addition, spin-allowed metal-to-ligand charge transfer (¹MLCT) absorption is clearly distinguished in the region of 370–400 nm. On the other hand, spin-forbidden triplet ³LC and/or ³MLCT transitions appear as a lower energy absorption shoulder.⁵⁹ All of the Ir(III) complexes exhibit very similar ¹LC, ¹MLCT, and ³LC (or ³MLCT) absorptions, suggesting that the ancillary ligand makes only a small contribution to the absorption process in this system. Overall, as shown in Figure 1a, this system exhibits strong cyclometalating LC and MLCT transitions, but the ancillary ligand-mediated transitions are featureless and relatively weak. (See the Supporting Information for excitation spectra.)

Figure 1c shows the photoluminescence (PL) spectra of **1** to **6**, which exhibit a large bathochromic shift (over 200 nm range) as the band gap of the ancillary ligand is narrowed (see the Supporting Information for calculated band gap energy). The PL spectra of the Ir(III) complexes doped (5 wt %) in poly(methyl methacrylate) (PMMA) films (gray lines in Figure 1c) exhibit a similar trend of bathochromic shifts but with smaller blue shifts compared to the corresponding complexes in solution. The PL spectra of **1** and **2** are similar to that of the homoleptic complex Ir(*dfppy*)₃, suggesting that the PL from **1** and **2** originates from the cyclometalating ligand (see the Supporting Information for the PL spectrum of Ir(*dfppy*)₃, which consists of cyclometalating ligands only). On the other hand, the PL spectra of **3** to **6** exhibit characteristic bathochromic shifts relative to those of **1** and **2**, strongly suggesting the possibility of an ancillary ligand-centered PL emission after ILET. The

PL spectra in Figure 1c can thus be classified into two groups: those of **1** and **2**, which exhibit structured vibronic emission with the same spectral positions in solution and film; and those of **3** to **6**, which show rather broad and differently red-shifted emissions with a discrepancy between the solution and film PL spectra. The characteristic hypsochromic shift of the PL spectra of the film states (rigidochromism) can be thought to be associated with the motional relaxation of the excited-state geometry, which is prone to be affected by the rigidity of the matrix. A similar hypsochromic shift was also observed when the CH₂Cl₂ solution of **3** was frozen (see the Supporting Information). From this observation, it is deduced that the phosphorescent excited states of **3** to **6** are completely different from those of **1** and **2**. Nevertheless, all of the heteroleptic Ir(III) complexes from **1** to **6** are highly phosphorescent, with phosphorescence quantum yields (0.3–0.4, see Table 1) comparable to that of Ir(*ppy*)₃ (0.4).⁶⁰

To obtain further information on the excited states responsible for the phosphorescence of **3** to **6**, we investigated the solvatochromism of our Ir(III) complexes. We found that **1** and **2** exhibit no apparent dependence of the emission and absorption maxima on the solvent polarity parameter, whereas **3** to **6** show distinct positive solvatochromism of the emission maximum in the Lippert–Mataga plot but little variation in the absorption maximum as a function of the solvent polarity parameter (Figure 1b, data of **2** and **4** are not included for clarity).^{61,62} These findings indicate that there is no significant charge-rearrangement during the emission process of **1** and **2**; thus the dominant emission process in these complexes is most likely from the

TABLE 1: Photophysical^a and Electrochemical^b Properties of Cyclometalated Heteroleptic Ir(III) Complexes

entry	emission λ_{max} (nm)		τ_{ems} (μs)	Φ_{p}^d	E_{ox} (V vs Ag^+/Ag)	E_{red} (V vs Ag^+/Ag)	ΔE (V)	τ_{ILET}^g (ns)
	solution	film ^c						
1	468	474	1.4	0.42	1.57	−1.16	2.73	
2	478	479	0.24	0.31	1.58	−1.17	2.75	
3	573	551	2.5	0.35	1.60	−1.04, −1.54 ^e	2.64	6.5 ± 0.1
4	581	565	1.2	0.27	1.56	−0.98, −1.45 ^e	2.54	5.5 ± 0.1
5	587	554	0.42	0.31	1.62	−0.83, −1.03 ^e	2.45	7.3 ± 0.1
6	666 ^f	615	0.39	0.39	1.65	−0.79, −0.98 ^e	2.44	6.8 ± 0.1

^a Measured in Ar-saturated toluene solution (1.0×10^{-5} M) at room temperature. ^b Measurements were made in 5 mM CH_2Cl_2 solution with Bu_4NBF_4 supporting electrolyte, Pt working and counter electrodes, and a quasi Ag^+/Ag reference electrode. Reduction potentials were irreversible unless otherwise specified. ^c PMMA film doped with 5 wt % of Ir(III) complex. ^d Excitation wavelengths were 400 nm. $\text{Ir}(\text{ppy})_3$ (0.40) was used as an external reference. ^e Reversible reduction potential. ^f Measured in Ar-saturated MeCN solution (1.0×10^{-5} M) at room temperature. ^g See the Supporting Information for the experimental details.

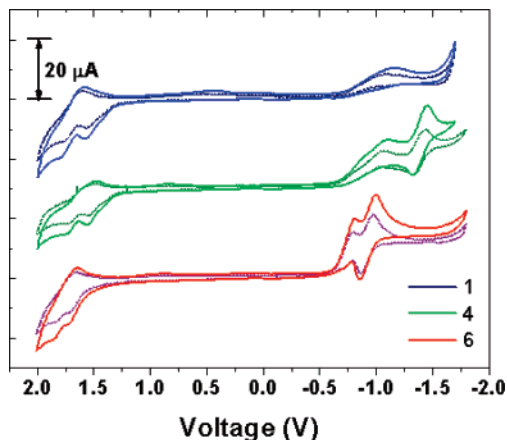


Figure 2. Cyclic voltammograms of **1**, **4**, and **6** (solid line: scan rate 100 mV/s; dotted line: scan rate 50 mV/s).

cyclometalating LC with a small contribution from the MLCT as reported earlier.⁶³ By contrast, the positive solvatochromism observed for **3** to **6** suggests that their emission is related to the charge-redistributed state. This hypothesis is also in accord with the abovementioned rigidochromism, which indicated that the phosphorescent state of **3** to **6** is affected by dipole–dipole relaxation with the assistance of matrix. On the basis of these findings, it is reasonable to conclude that the excited-state population (in **3** to **6**) is largely located over the ancillary ligand. In the PL spectra, therefore, we observe a strong phosphorescent color-tuning toward red in our Ir(III) complexes. Moreover, the characteristic hypsochromic shifts observed in the emission spectra of **3** to **6** in a PMMA film compared to those in solution are attributed to the restricted dipole–dipole relaxation in the rigid matrix.

By cyclic voltammetry, we monitored the positions of the HOMO and the LUMO of the Ir(III) complexes (Figure 2, Table 1). The reduction potentials (LUMO) of the Ir(III) complexes in the voltammograms were lowest for **1** and **2** (−1.16 and −1.17 V vs Ag^+/Ag , respectively), and increased as the band gap of the ancillary ligand decreased from **3** to **6** (−1.04, −0.98, −0.83, −0.79 V vs Ag^+/Ag), which correlates well with the bathochromic shifts observed in the PL spectra (Table 1). While the oxidation potentials (HOMO) showed no distinguishable change across the series of complexes, the ΔE ($E_{\text{ox}} - E_{\text{red}}$) values decreased systematically due to the decrease in the reduction potential.⁶⁴ From the relationship between the steady-state PL spectra and the cyclic voltammograms, we can unambiguously conclude that the bathochromic shift in the PL spectra of the Ir(III) complexes is due to a lowering of the excited states by the ancillary ligands while the ground states remain relatively invariant. These findings are consistent with

existing data showing that the phosphorescent states of Ir(III) complexes are strongly dependent on the characteristics of their ligands.⁶⁵

To obtain further insight into the mechanism underlying the phosphorescence of Ir(III) complexes, we measured time-resolved PL spectra of **1** to **6** after excitation at 355 nm with a nanosecond Nd:YAG laser third-harmonic (TH) pulse. After deconvolution, the phosphorescence decay profiles of the Ir(III) complexes exhibited lifetimes in the range of 0.24–2.5 μs at their PL maxima (see Table 1), which is comparable to that of $\text{Ir}(\text{dfppy})_3$.³²

Parts a and b of Figure 3 show the time-resolved PL spectra of complexes **1** and **3**.⁶⁶ The PL spectrum of **1** exhibits the original vibronic structures with single-exponential decay, which is similar to the steady-state PL spectrum. In the time evolution of the PL spectrum of **3**, on the other hand, we observed an early stage (within several tens of nanoseconds) hypsochromic PL shift (indicated with an arrow in Figure 3b). It is noted that the early stage spectrum of **3** is similar to that of **1**,⁶⁷ which extends over 450–550 nm range, while the later-stage spectrum of **3** is significantly red shifted (spectral range over 500–600 nm) and matches well with the steady-state PL spectrum of this complex (Figure 1c). Considering that all of the absorption spectra of our Ir(III) complexes (**1**–**6**) are largely identical, we can expect that photoexcitation generates the same initial excited states of **1** and **3**. If, in our Ir(III) complexes, energy transfer occurs from the initially populated state to the phosphorescent state, we may observe a shift in the phosphorescence wavelength. Because the ancillary ligands of **1** and **2** have a larger band gap, hence a higher triplet energy, it is considered that the PL spectra of **1** and **2** originate from the cyclometalating ligand (dfppy) centered state. On the other hand, **3** to **6** have ancillary ligands with lower triplet state energies enabling ILET from the cyclometalating ligand to the ancillary ligand, which consequently provides time-dependent bathochromic spectral shifts (Figure 3b).

The transient PL profile of **1** exhibits a single-exponential decay with a time constant of 1.4 μs , without any shorter rise and decay time constants (Figure 3c). In contrast, the transient PL profile of **3** (Figure 3d) is deconvoluted into two components: a fast decay component of 6.5 ns (430 and 510 nm, blue and green lines, respectively) and a rise component of 6.8 ns (600 nm, red line).⁶⁸ The rise time of the fast components at the emission maximum of **3**, whose spectral positions largely coincide with those of the steady-state spectrum (see Figure 1c), is almost identical with the fast decay lifetimes at ~430 nm, which indicates the presence of energy transfer (ILET) processes between the blue (430 nm) and red (600 nm) emitting moieties of the cyclometalating and ancillary ligands, respectively.⁶⁹ The time scales of the energy transfer in the Ir(III)

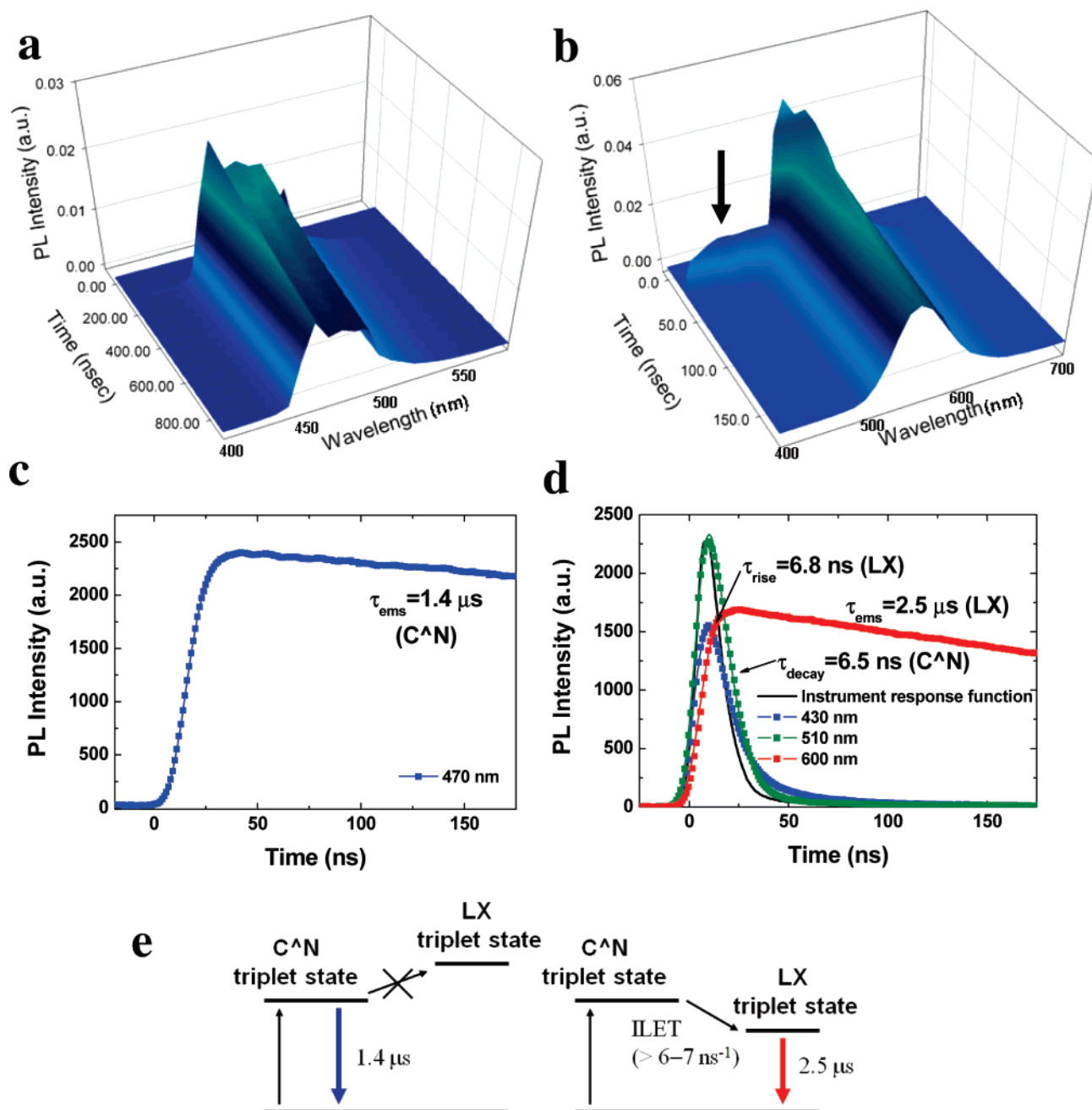


Figure 3. Temporal evolution of the time-resolved photoluminescence spectra of **1** (a) and **3** (b) (1.0×10^{-5} M in toluene). Transient photoluminescence profiles of **1** (c) and **3** (d).⁶⁶ (e) A schematic diagram of the phosphorescence of **1** (left) and **3** (right). Colored arrows indicate phosphorescence.

complexes are summarized in Table 1. Compared to the phosphorescence lifetime (τ_{ems}) of the cyclometalating ligand (*dfppy*) centered triplet emission (1.4 and 0.24 μs for **1** and **2**, respectively), ILET from the cyclometalating ligand (*dfppy*) to the ancillary ligand occurs rapidly (within several nanoseconds), which explains why the steady-state PL measurements did not show dual emission from both the cyclometalating ligand (*dfppy*) and ancillary ligand.

To explore our hypothesis on ILET between ligands, we additionally performed DFT-based quantum chemical calculations (see Table 2 for the calculation conditions). While the electron density in the HOMOs of **1** to **6** resides significantly on the cyclometalating ligand (*dfppy*) as well as the core Ir(III) atom, the electron density in the LUMOs depends on the ancillary ligand (Figure 4). For example, the LUMO of **3** has a

TABLE 2: Calculated LUMO Energy Difference (ΔE_{LUMO}) of Ir(III) Complexes Relative to LUMO of **1, and Spin Density of Cationic (+1) and Anionic (−1) Cyclometalated Heteroleptic Ir(III) Complexes^a**

entry	ΔE_{LUMO} (eV)	cation			anion		
		Ir	(<i>dfppy</i>) ₂	LX ^b	Ir	(<i>dfppy</i>) ₂	LX
1		0.411	0.415	0.173	−0.002	0.729	0.272
2	0	0.413	0.411	0.176	0.001	0.719	0.28
3	−0.048	0.410	0.416	0.174	0.001	0.437	0.561
4	−0.196	0.392	0.398	0.21	−0.003	0.429	0.574
5	−0.466	0.379	0.385	0.233	−0.002	0.39	0.612
6	−0.801	0.357	0.377	0.265	0.001	0.278	0.721

^a Ground states optimized with the BLYP functional, DNP basis set, and ECP were subject to +1/−1 charged forms, then the spin densities were calculated by using the Mulliken method. ^b Ancillary ligand.

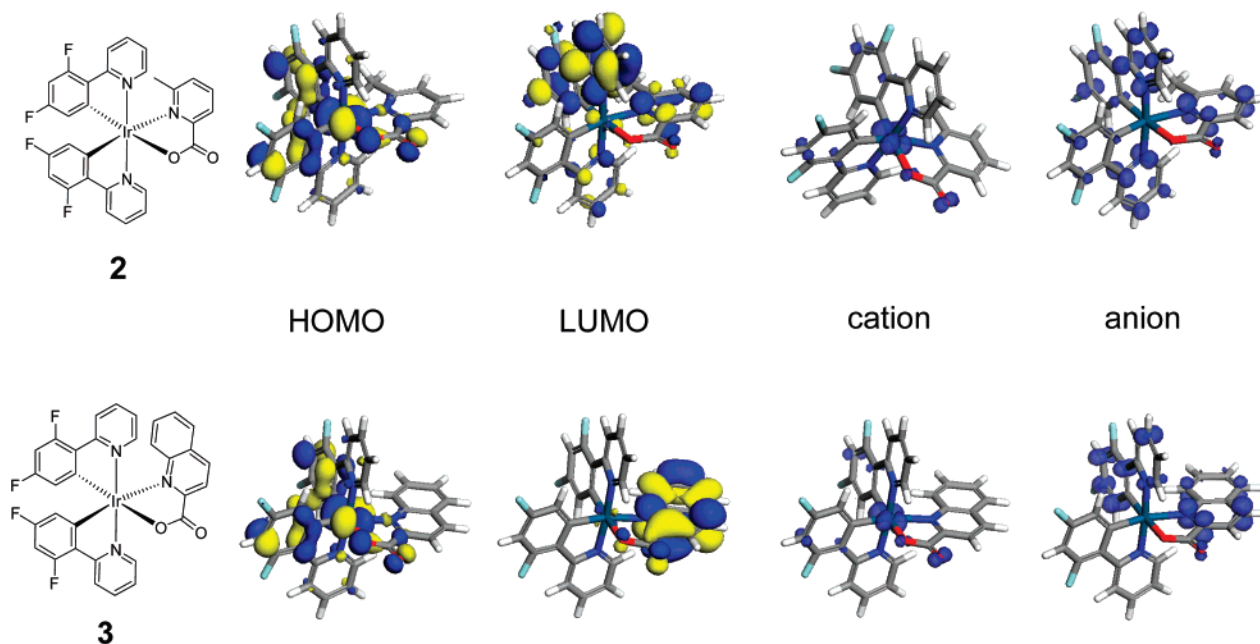


Figure 4. Contour plots of the HOMO and LUMO, and spin density (blue isosurfaces) of cationic and anionic species of **2** (upper row) and **3** (lower row).

large electron density on the ancillary ligand, whereas that of **2** exhibits a large electron density on the cyclometalating ligand (*dfppy*) and only a small electron density on the ancillary ligand. These calculations reveal that the excitations in our Ir(III) complexes mainly involve the cyclometalating ligand (*dfppy*) (i.e., ligand (*dfppy*)-centered (LC) transition as well as the metal-to-ligand (*dfppy*) charge-transfer (MLCT) transition) and, to a small degree, the ancillary ligand mediated transition (observed only in **6**, see Figure 1a). This result is in line with the characteristics of the absorption spectra. The calculated energy differences between the LUMO of each complex and that of **1** are summarized in Table 2; these results correlate well with the ΔE values as well as the wavelengths of the peaks in the PL spectra (Table 1).

The spin density calculations for the cationic species strongly support the calculated HOMOs, in that the unpaired spin resides mostly on the cyclometalating ligand (*dfppy*) and Ir(III) metal. In addition, the spin density on the ancillary ligand clearly increases with decreasing band gap of the ancillary ligand. This theoretical result implies that some degree of ancillary ligand centered excitation exists, thereby explaining the much longer but weak tail in the absorption spectrum of **6**. In addition, the spin density calculations for the anionic species support the calculated LUMO structure. We observe that the location where the unpaired spin resides is strongly dependent on the structure of the ancillary ligand. The spin density on anionic species shows a strong dependence on the ancillary ligand, which supports our explanation where the position of the lowest excited state responsible for the triplet emission is. In addition, the spin density on the ancillary ligand increases as the band gap of the ancillary ligand decreases. Overall, on the basis of the spectroscopic and electrochemical results, as well as those of the quantum chemical calculations, we can safely conclude that efficient energy transfer occurs between the cyclometalating ligand and ancillary ligand, leading to a much broader range of phosphorescence.

From the perspective of practical applications, a very promising aspect of the ILET-mediated phosphorescence observed in our Ir(III) complexes is the generation of white luminescence from a mixture of blue (**1**) and red (**6**) emitting Ir(III) complexes.

Achieving white emission is of practical importance for solid-state illumination and display applications.^{70–73} Previously, white phosphorescence was generated by employing highly sensitive partial resonance energy transfer between the blue-emitting FIrpic (**1**) and the red-emitting iridium(III) bis(2-(2'-benzo[*b*]thienyl)pyridinato-*N,C*^{3'}) (acetylacetonato) ((*Btp*)₂Ir*acac*, see Figure 5a for molecular structure) to produce dual blue and sensitized red emissions.⁷⁰ In this system, however, a tiny change in the doping concentration of (*Btp*)₂Ir*acac* results in a large change in the purity of the white light, as quantized by the Commission Internationale de L'Eclairage (CIE) value. This feature makes controlling the CIE value tedious and difficult. This drawback is due to highly efficient Förster-type (resonance) energy transfer from **1** to (*Btp*)₂Ir*acac* due to the large spectral overlap between the emission spectrum of **1** and the absorption spectrum of (*Btp*)₂Ir*acac* (Figure 5a), yielding red (*Btp*)₂Ir*acac* emission.

Generally, resonance energy transfer from a high-energy donor to a low-energy acceptor is proportional to the spectral overlap between them.⁷⁴ However, the 3-level system (see Figure 3e) of our Ir(III) complexes showing ILET provides a large Stokes shift between absorption and phosphorescent emission (10104 cm⁻¹). Therefore, in the mixture of Ir(III) complexes with different Stokes shifts and negligible cross overlaps, the energy transfer among the complexes is expected to be minimal. This unique characteristic of our Ir(III) complexes stands in contrast to the behavior of previously reported cyclometalated homoleptic and heteroleptic Ir(III) complexes.

As shown in the upper spectra of Figure 5a, the spectral overlap between the emission and absorption bands of **1** and **6**, respectively, is negligible, indicating a possible suppression of Förster-type energy transfer between them. In fact, relatively unperturbed blue emissions could be observed in the mixture of **1** and **6**, which enabled us to obtain white phosphorescence rather easily. Moreover, solutions containing a fixed composition of **1** and **6** (6:4 by mol/mol) exhibited little change in the relative intensity of each PL spectra of **1** and **6** when the total concentration was increased up to 5×10^{-4} mol/L (see the Supporting Information for the spectral changes of solutions containing a mixture of **1** and **6**, and a mixture of **1** and

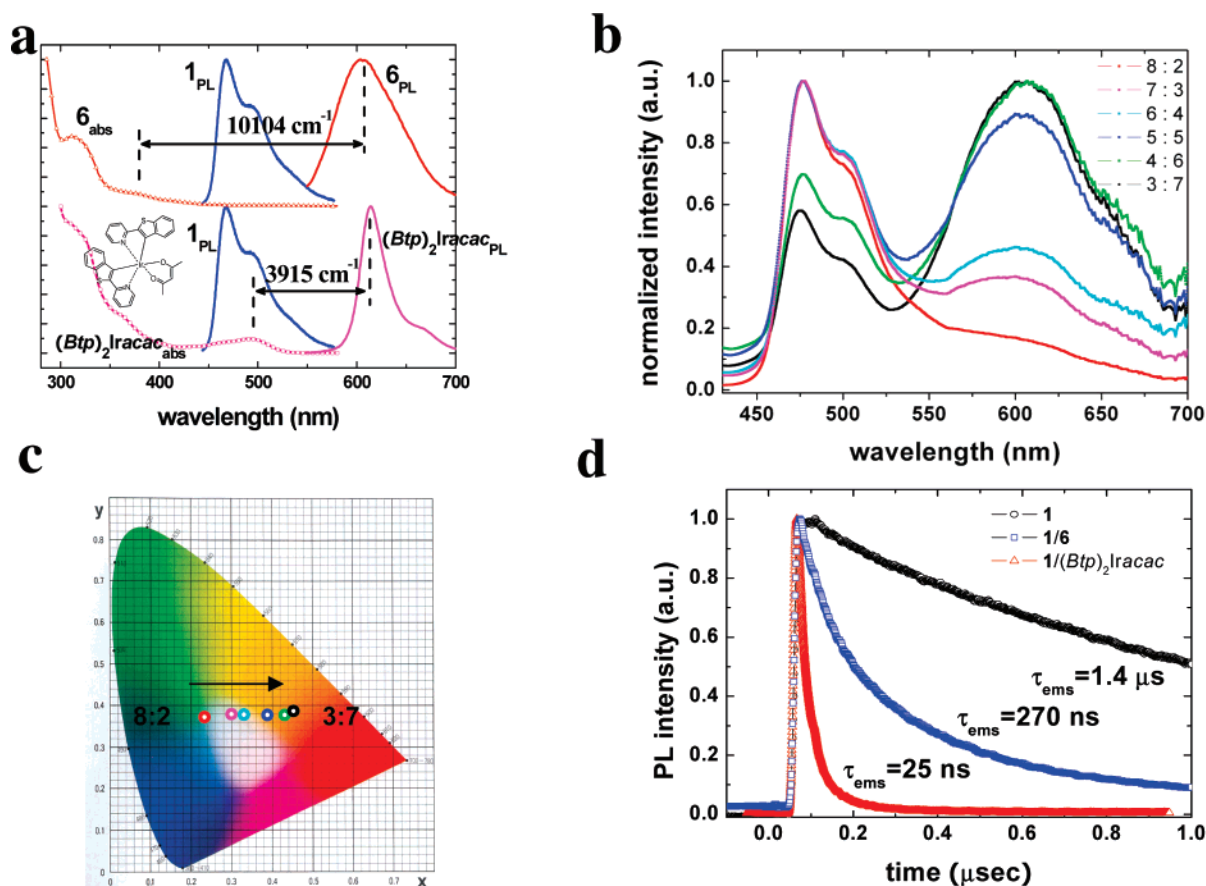


Figure 5. (a) Comparison of the spectral overlap between the PL emission of **1** (blue) and the absorption of **6** (red) (upper part), and **1** and $(Btp)_2Ir(acac)$ (red) (lower part); numbers indicate Stokes shift of red emitters. See the inset structure of $(Btp)_2Ir(acac)$. (b) Photoluminescence spectra of **1** and **6** co-doped (total 5 wt %) PMMA films with different molar ratios, (c) their corresponding Commission Internationale de L'Eclairage coordinate changes, and (d) the PL decay profiles of **1** (black), **1** co-doped with **6** (blue), and **1** co-doped with $(Btp)_2Ir(acac)$ (red) (the total amount of loaded Ir(III) complexes was maintained at 5 wt %) in PMMA films, respectively.

$(Btp)_2Ir(acac)$. These findings thus indicate that a mixture of **1** and **6** is a highly efficient system for generating white emission due to the limited energy transfer between these complexes. Figure 5b shows dual emission by mixtures of **1** and **6** in a doped film state (5 wt % to PMMA). Importantly, for the system with a molar ratio of the blue emitter **1** to the red emitter **6** (3:7), the emission of **1** is still observed (Figure 5b). As the molar ratio between **1** and **6** was changed from 8:2 to 3:7, the corresponding CIE coordinates were shifted from (0.23, 0.37) to (0.45, 0.39), which is quite a small change compared to the case of the mixture of **1** and $(Btp)_2Ir(acac)$. Importantly, the film doped with **1** and **6** at a molar ratio of 6:4 gave nearly white emission (0.33, 0.38).

The suppression of energy transfer between **1** and **6** is evident in the transient PL profiles of the co-doped PMMA film. For the PMMA film doped with a mixture of **1** and $(Btp)_2Ir(acac)$ (6:4 molar ratio), we observe almost complete quenching of the phosphorescence of **1**, and a phosphorescence lifetime of only 25 ns (Figure 5d). When we consider that the inherent phosphorescence lifetime of **1** is 1.4 μs , this corresponds to almost 100% of energy transfer from **1** to $(Btp)_2Ir(acac)$.^{75,76} For the film co-doped with **1** and **6**, by contrast, the phosphorescent lifetime of **1** was reduced from 1.4 μs to 270 ns (less than 80% energy transfer⁷⁷) due to their physical proximity. As a result, the large portions of the blue emission of **1** were not quenched, and white emission was achieved.

3. Summary

Herein we have established an efficient color-tuning methodology for cyclometalated heteroleptic Ir(III) complexes. We demonstrated that by varying the ancillary ligand, the phosphorescence of Ir(III) complexes could be modulated across the entire visible range. This modulation of the phosphorescence was attributed to ILET processes between the cyclometalating and ancillary ligands. In addition, through a series of ILET-related photophysical and electrochemical measurements, as well as DFT-based quantum chemical calculations, we revealed the presence of a triplet emitting ancillary ligand. Finally, from transient PL measurements, we observed a spectral shift with an energy transfer rate of ca. 6–7 ns⁻¹. Finally, facile and efficient white light generation was demonstrated by using a mixture of a blue-emitting Ir(III) complex and red-emitting Ir(III) complex exhibiting ILET. The initial excited states in the cyclometalating ligand of red-emitting complex increase the population of the triplet emitting excited state of the ancillary ligand by ILET, so that the relatively unperturbed dual blue and red dual emission is produced.

4. Experimental Section

Materials. Synthesis of all Ir(III) complexes has already been reported in the previous communication.⁴³ Other materials supplied from commercial suppliers were used without further purification.

Characterization. Absorption spectra of a solution (1×10^{-5} M in toluene) and a doped poly(methylmethacrylate) (PMMA) film (a spin-coated film on a precleaned glass substrate under 2000 rpm with 5 wt % solution of 1,2-dichloroethane) were recorded with SHIMAZU UV-1650PC from 280 to 700 nm. Photoluminescence spectra were obtained with a SHIMAZU RF 5301 PC spectrophotometer in the range of 400–700 nm. Absorption and PL spectra of Ir(III) complexes in solutions were measured after Ar saturation. Cyclovoltametric experiments were carried out with a model 273A (Princeton Applied Research), using three electrode cell assemblies. Pt wires were used for counter and working electrodes, and a quasi Ag/Ag⁺ wire was used for a reference electrode. Measurements were carried out in a dichloromethane solution with tetrabutylammonium tetrafluoroborate as supporting electrolyte at a scan rate of 50 or 100 mV/s under nitrogen condition. Concentrations of Ir(III) complexes and supporting electrolyte were 5×10^{-3} and 0.1 M, respectively. Each oxidation potential was calibrated with use of ferrocene as a reference. A Dmol³ module installed within the Accelrys Materials Studio was used for DFT calculation. Ground state geometry optimization and single point calculation were performed with BLYP functional and DNP basis set under effective core potential. SCF tolerance was maintained within 10^{-6} . For the time-resolved PL measurement, an excitation pulse of 355 nm was generated from the third harmonic output of a Q-switched Nd:YAG laser (Continuum, Surelite). The time duration of the excitation pulse was ca. 6 ns. However, the instrument response function with a half-life of 3 ns was deconvoluted to ensure the accuracy of the measurement. The emission light was collimated before entering the monochromator slit and then spectrally resolved by using a 15 cm monochromator (Acton Research, SP150) equipped with a 600 grooves/mm grating after passing the sample. Spectral resolution was about 3 nm for the transient photoluminescence experiment. The light signal was detected via a photomultiplier tube (Hamamatsu, R928). The output signal from the PMT was recorded with a 500 MHz digital storage oscilloscope (Tektronix, TDS3052) for the temporal profile measurement.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the National Research Lab. Program funded by the Ministry of Science and Technology (No.2006-03246). We are grateful for financial support provided by Dongwoo FineChem Co., Ltd. K.S.K. acknowledges the financial support through the BK21 program and the Star Faculty program from the Ministry of Education and Human Resources Development.

Supporting Information Available: Quantum chemical calculation results of ancillary ligands, photoluminescence spectrum of Ir(*dfppy*)₃, photoluminescence spectral shifts of both solvatochromism and rigidochromism, comparison between excitation and absorption spectra of **1** to **6**, fluorescence spectrum of free ancillary ligand of **3**, transient PL spectra and decay profiles of **1**–**6**, evolution of photoluminescence spectra of a mixture of **1** and **6**, and the comparative mixture of **1** and (*Btp*)₂Iracac. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Baldo, M. A.; O'Brian, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151–154.
- Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 4–6.
- Ikai, M.; Tokito, S.; Sakamoto, Y.; Suzuki, T.; Taga, Y. *Appl. Phys. Lett.* **2001**, *79*, 156–158.
- Chen, F. C.; Yang, Y.; Thompson, M. E.; Kido, J. *Appl. Phys. Lett.* **2002**, *80*, 2308–2310.
- Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Nature* **2000**, *403*, 750–753.
- Tung, Y.-L.; Lee, S.-W.; Chi, Y.; Chen, L.-S.; Shu, C.-F.; Wu, F.-I.; Carthy, A. J.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Adv. Mater.* **2005**, *17*, 1059–1064.
- Liu, C.-Y.; Bard, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 4190–4191.
- Barron, J. A.; Bernhard, S.; Houston, P. L.; Abruna, H. D.; Ruglovsky, J. L.; Malliaras, G. G. *J. Phys. Chem. A* **2003**, *107*, 8130–8133.
- Rudmann, H.; Shimada, S.; Rubner, M. F. *J. Am. Chem. Soc.* **2002**, *124*, 4918–4921.
- Tung, Y.-L.; Wu, P.-C.; Liu, C.-S.; Chi, Y.; Yu, J.-K.; Hu, Y.-H.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H.; Tao, Y.; Carthy, A. J.; Shu, C.-F.; Wu, F.-I. *Organometallics* **2004**, *23*, 3745–3748.
- Cunningham, G. B.; Li, Y.; Liu, S.; Schanze, K. S. *J. Phys. Chem. B* **2003**, *107*, 12569–12572.
- Gao, F. G.; Bard, A. J. *Chem. Mater.* **2002**, *14*, 3465–3470.
- Lamansky, S.; Djurovich, P. I.; Abdel-Razzaq, F.; Garon, S.; Murphy, D. L.; Thompson, M. E. *J. Appl. Phys.* **2002**, *92*, 1570–1575.
- Markham, J. P.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2645–2647.
- Adachi, C.; Lamansky, S.; Baldo, M. A.; Kwong, R. C.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *78*, 1622–1624.
- Lo, S.-C.; Anthopoulos, T. D.; Nandas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2005**, *17*, 1945–1948.
- Chen, L.; Yang, C.; Qin, J.; Gao, J.; Ma, D. *Synth. Met.* **2005**, *152*, 225–228.
- Yang, C.-H.; Li, S.-W.; Chi, Y.; Cheng, Y.-M.; Yeh, Y.-S.; Chou, P.-T.; Lee, G.-H.; Wang, C.-H.; Shu, C.-F. *Inorg. Chem.* **2005**, *44*, 7770–7780.
- Coppo, P.; Plummer, E. A.; De Cola, L. *Chem. Commun.* **2004**, 1774–1775.
- Stylianides, N.; Danopoulos, A. A.; Tsoureas, N. *J. Organomet. Chem.* **2005**, *690*, 5948–5958.
- Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979.
- Xie, H. Z.; Liu, M. W.; Wang, O. Y.; Zhang, X. H.; Lee, C. S.; Hung, L. S.; Lee, S. T.; Teng, P. F.; Kwong, H. L.; Zheng, H.; Che, C. M. *Adv. Mater.* **2001**, *13*, 1245–1248.
- Lo, S.-C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater.* **2002**, *14*, 975–979.
- Lo, S.-C.; Nandas, E. B.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **2003**, *36*, 9721–9730.
- Ragni, R.; Plummer, E. A.; Brunner, K.; Hofstra, J. W.; Babudri, F.; Farinola, G. M.; Naso, F.; De Cola, L. *J. Mater. Chem.* **2006**, *16*, 1161–1170.
- Moon, D. G.; Podo, R. B.; Lee, C. J.; Han, J. I. *Mater. Sci. Eng. B* **2005**, *121*, 232–237.
- Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2001**, *40*, 1704–1711.
- Anthopoulos, T. D.; Frampton, M. J.; Nandas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2004**, *16*, 557–560.
- Yeh, S.-J.; Wu, M.-F.; Chen, C.-T.; Song, Y.-H.; Chi, Y.; Ho, M.-H.; Hsu, S.-F.; Chen, C. H. *Adv. Mater.* **2005**, *17*, 285–289.
- Li, J.; Djurovich, P. I.; Alleyne, B. D.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *Polyhedron* **2004**, *23*, 419–428.
- Nazeeruddin, M. K.; Humphry-Baker, R.; Berner, D.; Rivier, S.; Zuppiroli, L.; Graetzel, M. *J. Am. Chem. Soc.* **2003**, *125*, 8790–8797.
- Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377–7387.
- Duan, J.-P.; Sun, P.-P.; Cheng, C.-H. *Adv. Mater.* **2003**, *15*, 224–228.
- Huang, W.-S.; Lin, J.-T.; Chien, C.-H.; Tao, Y.-T.; Sun, S.-S.; Wen, Y.-S. *Chem. Mater.* **2004**, *16*, 2480–2488.
- Hwang, F.-M.; Chen, H.-Y.; Chen, P.-S.; Liu, C.-S.; Chi, Y.; Shu, C.-F.; Wu, F.-I.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **2005**, *44*, 1344–1353.
- Yang, C.-H.; Tai, C.-C.; Sun, I.-W. *J. Mater. Chem.* **2004**, *14*, 947–950.
- Tsuzuki, T.; Shirakawa, N.; Suzuki, T.; Tokito, S. *Adv. Mater.* **2003**, *15*, 1455–1458.
- Song, Y.-H.; Yeh, S.-J.; Chen, C.-T.; Chi, Y.; Liu, C.-S.; Yu, J.-K.; Hu, Y.-H.; Chou, P.-T.; Peng, S.-M.; Lee, G.-H. *Adv. Funct. Mater.* **2004**, *14*, 1221–1226.

- (39) Garces, F. O.; King, F. A.; Watts, R. J. *Inorg. Chem.* **1988**, *27*, 3464–3471.
- (40) Carlson, G. A.; Djurovich, P. I.; Watts, R. J. *Inorg. Chem.* **1993**, *32*, 4483–4484.
- (41) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. *Inorg. Chem.* **2005**, *44*, 7992–8003.
- (42) Li, J.; Djurovich, P. I.; Alleyne, B. D.; Yousufuddin, M.; Ho, N. N.; Thomas, J. C.; Peters, J. C.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 1713–1727.
- (43) You, Y.; Park, S. Y. *J. Am. Chem. Soc.* **2005**, *127*, 12438–12439.
- (44) Laine, P. P.; Bedioui, F.; Loiseau, F.; Chiorboli, C.; Campagna, S. *J. Am. Chem. Soc.* **2006**, *128*, 7510–7521.
- (45) Wilson, G. J.; Launikonis, A.; Sasse, W. H. F.; Mau, A. W.-H. *J. Phys. Chem. A* **1997**, *101*, 4860–4866.
- (46) Amouyal, E.; Homs, A.; Chambron, J.-C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, *6*, 1841–1845.
- (47) Gehlen, M. H.; de Carvalho, I. M. M.; de Sousa Moreira, I. *Inorg. Chem.* **2003**, *42*, 1525–1531.
- (48) Hissler, M.; Harriman, A.; Khatyr, A.; Ziesler, R. *Chem. Eur. J.* **1999**, *5*, 3366–3381.
- (49) Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.
- (50) Morales, A. F.; Accorsi, G.; Armaroli, N.; Barigelletti, F.; Pope, S. J. A.; Ward, M. D. *Inorg. Chem.* **2002**, *41*, 6711–6719.
- (51) Abrahamsson, M.; Hammerström, L.; Tocher, D. A.; Nag, S.; Datta, D. *Inorg. Chem.* **2006**, *45*, 9580–9586.
- (52) Jukes, R. T. F.; Bozic, B.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2006**, *45*, 8326–8341.
- (53) Belser, P.; Dux, R.; Baak, M.; De Cola, L.; Balzani, V. *Angew. Chem., Int. Ed.* **1995**, *34*, 595–598.
- (54) Chiorboli, C.; Fracasso, S.; Ravaglia, M.; Scandola, F.; Compagna, S.; Wouters, K. L.; Konduri, R.; MacDonnell, F. M. *Inorg. Chem.* **2005**, *44*, 8368–8378.
- (55) Adachi, C.; Kwong, R. C.; Djurovich, P. I.; Adamovich, V.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 2082–2084.
- (56) Holmes, R. J.; Forrest, S. R.; Tung, Y.-J.; Kwong, R. C.; Brwon, J. J.; Garon, S.; Thompson, M. E. *Appl. Phys. Lett.* **2003**, *82*, 2422–2424.
- (57) Tokito, S.; Iijima, T.; Suzuri, Y.; Kita, H.; Tsuzuki, T.; Sato, F. *Appl. Phys. Lett.* **2003**, *83*, 569–571.
- (58) For the sake of complete explanation, some of the steady state absorption and photoluminescence data in Figure 1 and Table 1 were reproduced from our previous communication.⁴³
- (59) Wilde, A. P.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1991**, *95*, 629–634.
- (60) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647–6653.
- (61) Chou, P.-T.; Liu, Y.-I.; Liu, H.-W.; Yu, W.-S. *J. Am. Chem. Soc.* **2001**, *123*, 12119–12120.
- (62) Seo, J. W.; Kim, S.; Park, S. Y. *J. Am. Chem. Soc.* **2004**, *126*, 11154–11155.
- (63) Lamansky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.-E.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4304–4312.
- (64) Although the $\Delta E (E_{\text{ox}} - E_{\text{red}})$ value does not exactly match phosphorescence energy of the corresponding Ir(III) complex, LUMO tuning with ancillary ligands can be evidenced by a linear proportionality between them.
- (65) Kwon, T.-H.; Cho, H. S.; Kim, M. K.; Kim, J.-H.; Kim, J.-J.; Lee, K. H.; Park, S. J.; Shin, I.-S.; Kim, H.; Shin, D. M.; Chung, Y. K.; Hong, J.-I. *Organometallics* **2005**, *24*, 1578–1585.
- (66) See the Supporting Information for data of other Ir(III) complexes.
- (67) The early stage spectrum of **3** can be safely assigned as cyclometalating ligand-centered phosphorescence from the facts that (1) fluorescence from the free ancillary ligand (quinaldic acid) was observed at 374 nm, thus eliminating contamination by fluorescence from the residual ancillary ligand (see the Supporting Information), and (2) all of **3** to **6**, whose LUMOs exist in the ancillary ligands, showed early stage spectra with identical spectral position, excluding a possibility of singlet emission from Ir(III) complexes.
- (68) Instrument response function (IRF) was determined to be a Gaussian curve with a time constant of 13.04 ns. The decay fittings were made by using a least-squares deconvolution fitting process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania), which ensures a temporal resolution of one third of IRF time constant. Practically, a time constant different from IRF time can be determined. In addition, our transient curves were averaged after accumulating thousands of times. We can find the difference in the initial rise of the prompt emission (C[∞]N) and the delayed emission (LX) of **3** in Figure 3d.
- (69) ILET time scale of the ns regime can be rationalized by the fact that energy transfer takes place between spatially separated ligands (cyclometalating *dfppy* and ancillary ligand).
- (70) Tanaka, I.; Suzuki, M.; Tokito, S. *Jpn. J. Appl. Phys.* **2003**, *42*, 2737–2740.
- (71) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585–1595.
- (72) Gong, X.; Ma, W.; Ostrowski, J. C.; Bazan, G. C.; Moses, D.; Heeger, A. J. *Adv. Mater.* **2004**, *16*, 615–619.
- (73) Qin, D.; Tai, Y. *Appl. Phys. Lett.* **2005**, *86*, 113507–113509.
- (74) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; Chapter 9.
- (75) Justin Thomas, K. R.; Thompson, A. L.; Sivakumar, A. V.; Bardeen, C. J.; Thayumanavan, S. *J. Am. Chem. Soc.* **2005**, *127*, 373–383.
- (76) Palilis, L. C.; Melinger, J. S.; Wolak, M. A.; Kafafi, Z. H. *J. Phys. Chem. B* **2005**, *109*, 5456–5463.
- (77) Shi, M.; Li, F.; Yi, T.; Zhang, D.; Hu, H.; Huang, C. *Inorg. Chem.* **2005**, *44*, 8929–8936.
- (78) The efficiency of energy transfer (Φ_{ET}) was calculated by using the relationship $\Phi_{\text{ET}} = (\tau - \tau')/\tau$, where τ and τ' denote the phosphorescence lifetime of **1** in the absence and presence of energy accepting red emitters, respectively.