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Phosphorescence Color Tuning of Ionic Iridium Complexes by Manipulating Excited State Properties

HYUN-SHIN LEE AND YUNKYOUNG HA

Department of Information Display Engineering, Hongik University, Seoul, Korea

*The new ionic iridium complexes, $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$, were prepared and their luminescence properties were investigated, where bpy, dtbbpy and CN represent 2,2′-dipyridyl, 4,4′-di-*tert*-butyl-2,2′-dipyridyl and cyanide, respectively. We expected that introduction of the electron-withdrawing nonchromophoric ligand, -CN, to an Ir complex might effectively lower the HOMO level and lead to the blue-shifted emission compared to $[Ir(bpy)_3]^{3+}$. The main ligand with a sterically bulky group was also considered to orient the binding between the main ligand and iridium center and to improve the solubility. Thus, the new ionic complex, $[Ir(dtbbpy)_2(CN)_2]^+$, was synthesized and its properties was compared with the other complex, $[Ir(bpy)_2(CN)_2]^-$. The maximum PL peak of $[Ir(dtbbpy)_2(CN)_2]^+$ appeared at 491 nm, which was hypsochromically shifted, compared with 528 and 566 nm of $[Ir(bpy)_3]^{3+}$ and $[Ir(bpy)_2(CN)_2]^-$, respectively. Investigation of their electrochemical properties led us to inferring that the cyanide ligand could effectively modulate the HOMO level of its iridium complex for the blue emission. Also, the introduction of the bulky alkyl group in the main ligand might effectively cause direct bindings between both Ns of biphenyl and the iridium center, which also might result in the relative blue-shifted emission in comparison with PL peak of $[Ir(bpy)_2(CN)_2]^-$ in which biphenyl was C- and N-bound to the Ir center.*

Keywords Biphenyl ligand; ionic iridium complex; nonchromophoric ligand; OLED

Introduction

Iridium complexes have being received more attention in the application for the optical devices compared to other metals [1–3]. The iridium itself has a large d-orbital splitting and the strong field ligands such as the ppy ligands can be coordinated in an Ir sphere. Thus, modification of these ligands could easily lead to tuning the emitting color of the complexes from the blue to red [4,5]. Moreover, the emitting color could be determined through the admixture of the MLCT and LC transitions.

Address correspondence to Yunkyoung Ha, Department of Information Display Engineering, Hongik University, Seoul 121-791, Korea. Tel.: (+82)-2-320-1490; Fax: (+82)-2-3142-0335; E-mail: ykha@hongik.ac.kr

Therefore, the mixing degree of these transitions could contribute to the luminescent property as well as the color [6,7].

As previously reported [8–13], the electron-withdrawing nonchromophoric ligands in the iridium complexes could make the highest occupied molecular orbital (HOMO) low, which might lessen the mixing degrees of metal-to-ligand charge transfer (MLCT) transition in the admixture of the MLCT and ligand-centered (LC) states. The strong field ligand, -CN, could also raise the dd states of iridium above the emitting LC state, which could alleviate the MLCT character in the admixture of MLCT/LC during the transition. In addition, it could contribute to enhancement of LC excited state contribution and result in the hypsochromic emission of its iridium complexes.

It was reported that the Ir complexes containing bipyridyl ligands, $[Ir(bpy)_3]^{3+}$ [14], emit from the LC state which is relatively high in energy. In this study, the electron withdrawing group, CN, and the bipyridyl (bpy) ligand are introduced to the iridium sphere to obtain the further higher energy emission for the true blue color. We expect that both CN and bpy ligands can result in increase of the energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) states. Thus, we synthesized a new iridium complex, $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$, and investigated their photophysical, electrochemical and luminescent properties.

Experiments

Materials and Characterization

Iridium trichloride hydrate ($IrCl_3 \cdot H_2O$) was purchased from Strem Co. All other reagents were purchased from Aldrich Co. and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were dried by standard procedures. The complexes were characterized with FAB-mass spectrometer at Seoul National University in Korea.

Synthesis of Iridium Complexes

$[Ir(dtbbpy)_2(CN)_2]^+$. The intermediate product, $[Ir(dtbbpy)_2(Cl)_2]^+$, was prepared according to Nonoyama method [15] with $IrCl_3 \cdot H_2O$ and 4,4′-di-*tert*-butyl-2,2′-dipyridyl. And then, it was reacted with AgOTf in $MeOH/CH_2Cl_2$ at about 80°C. After 2 hr the AgCl precipitate was removed by filtration. The clear and light yellow filtrate, $[Ir(dtbbpy)_2(H_2O)_2](CF_3SO_3)$, was added to tetra(*tert*-butyl)ammonium cyanide (TBACN) solution in acetonitrile. The mixture was heated to reflux for 2 hr and was then filtrated. The product, $[Ir(dtbbpy)_2(CN)_2]^+PF_6^-$ was obtained by reacting with NH_4PF_6 in methanol and was collected by filtration and washed with methanol. (Yield: 60%) A green powder. MS (FAB): calcd. m/z 781.4; found 781.

$[Ir(bpy)_2(CN)_2]^-$. $[Ir(bpy)_2(CN)_2]^-$ was prepared according to the method as described above. (Yield: 72%) A yellow powder. MS (FAB): calcd. m/z 557.1; found 557.

Results and Discussion

As previously reported [8–13], the electron-withdrawing nonchromophoric ligands could shift the dd states of iridium above the emitting LC state, and thus, it could

lower the HOMO level of their iridium complex. We applied this concept to $[Ir(bpy)_3]^{3+}$ which was reported to have emission maxima at 528 nm [14] for the further blue-shifted emission, and designed the new ionic complexes, $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$. First we tried to prepare $[Ir(bpy)_2(CN)_2]^+$, but the bypyridyl ligand was found to be N, C-bound to Ir center, forming an anion, $[Ir(bpy)_2(CN)_2]^-$. To secure N,N-binding of the bipyridyl ligand, we introduced 4,4′-di-*tert*-butyl-2,2′-dipyridyl (dtbbpy) ligand because its bulky *tert*-butyl groups could lead to N,N-binding of both pyridyl parts to the iridium center and provide the better solubility in organic solvents. With dtbbpy ligands, we were able to synthesize, the N,N-bound iridium bypyridyl cationic complex, $[Ir(dtbbpy)_2(CN)_2]^+$.

The synthesis of the ionic iridium complexes, $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$, involved three steps. These iridium complexes underwent the step of the chloride abstraction with silver trifluoromethane sulfonate [11]. The resulting Ir complex, $[Ir(L)_2(H_2O)_2](CF_3SO_3)$, was reacted with the tetrabutylammonium cyanide (TBACN) in the acetonitrile and then the final salt products were obtained via ion exchange with ammonium hexafluorophosphate [12]. The synthetic method was summarized in Figure 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The strong absorption bands between 200 and 400 nm in the ultraviolet region are assigned to the spin-allowed $^1\pi$-π^* transition of the cyclometallated main ligands, bpy and dtbbpy, in the complexes. The weak bands between 400 and 480 nm in the visible region are assigned to the spin-allowed metal-to-ligand charge transfer band (^{1}MLCT), and the weaker absorption bands at the longer wavelengths can be attributed to the spin-forbidden ^{3}MLCT and spin-orbit coupling enhanced $^3\pi$-π^* transition. The formally spin-forbidden ^{3}MLCT gains the intensity by mixing with the higher-lying ^{1}MLCT transition through the strong spin-orbit coupling on the iridium center. The absorption patterns of the complexes prepared in this study showed different patterns, suggesting that change of the main ligand and thereby

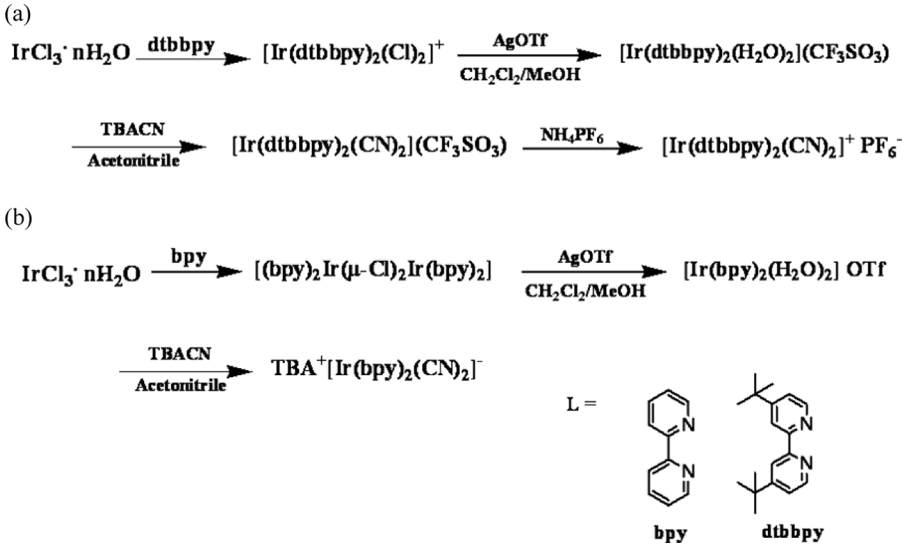

Figure 1. Synthetic scheme of the iridium complexes.

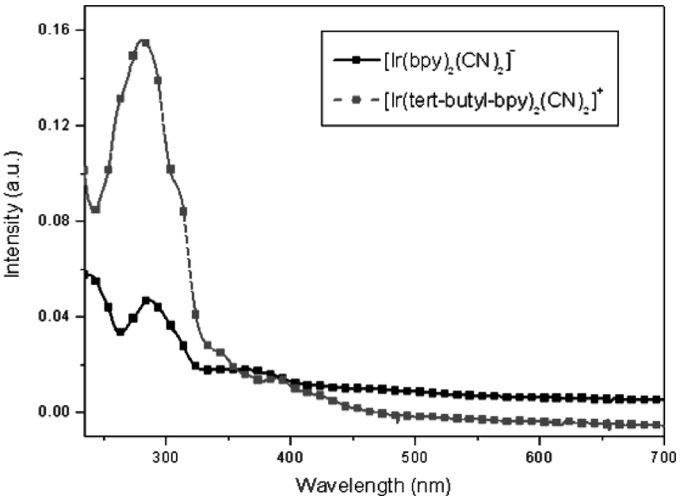

Figure 2. UV-Vis absorption spectra of the iridium complexes in 10^{-5} M CH_2Cl_2.

change of coordination make contribution to the absorption process of their complex.

The PL spectra of the iridium complexes in 10^{-5} M CH_2Cl_2 solution are shown in Figure 3. The emission maxima for $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$ appeared at 566 and 491 nm, respectively. The wavelengths of PL peaks showed significant difference of 75 nm in the presence of the substituent on the bipyridyl main ligand in the complexes. Unexpectedly, $[Ir(bpy)_2(CN)_2]^-$ exhibited significant bathochromic shift in emission compared to $[Ir(bpy)_3]^{3+}$ in spite of introduction of nonchromophoric electron withdrawing ligand, CN. On the other hand, the PL maximum of $[Ir(dtbbpy)_2(CN)_2]^+$ was effectively shifted toward the blue emission as expected, compared to 528 nm of $[Ir(bpy)_3]^{3+}$. We believe that such emission

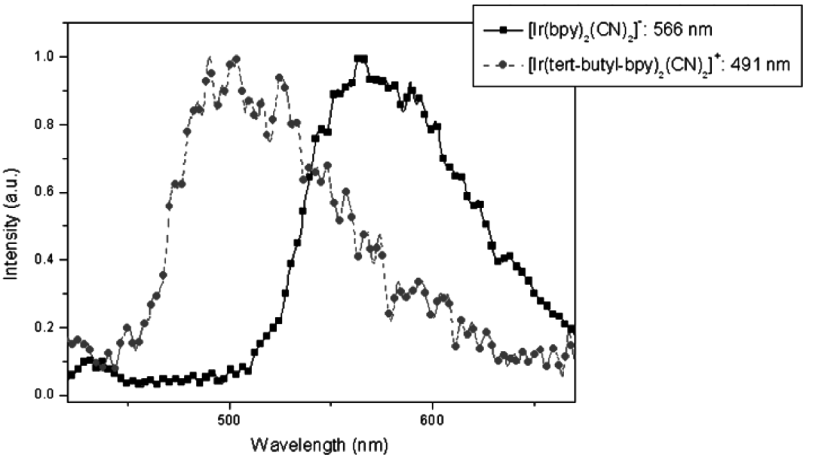

Figure 3. PL spectra of the iridium complexes in 10^{-5} M CH_2Cl_2.

Table 1. Physical parameters for the iridium complexes

Ir complex	λ_{abs}/ nm[a]	λ_{em}/ nm[a]	E_{ox}/V[b]	HOMO/ eV[c]	LUMO/ eV[d]	$\triangle E$/ eV[e]
$[Ir(bpy)_2(CN)_2]^-$	240, 287, 340	566	0.35	−5.15	−2.89	2.26
[Ir(tert-butyl-bpy)$_2$(CN)$_2$]$^+$	253, 280, 350	491	0.35	−5.15	−2.60	2.55

[a]Measured in CH_2Cl_2 solution.
[b]scan rate: 100 mV/s, Electrolyte: tetrabutylammonium hexafluorophosphate. The potentials are quoted against the internal ferrocene standard.
[c]Deduced from the equation HOMO = $-4.8 - E_{ox}$, LUMO = $-4.8 - E_{red}$.
[d,e]Calculated from the optical edge and the relation $\triangle E$ = HOMO - LUMO.

difference between $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$ was attributed to the coordination change in bipyridyl ligands. Addition of the bulky alkyl group on the bipyridyl ligand might cause the steric hindrance of the Ir complex, and thus, it could contribute to the direct binding between the Ns of the bipyridyl and the Ir center. In contrast, the metal center of $[Ir(bpy)_2(CN)_2]^-$ was easily to coordinate with the C of the other pyridyl ring on the bipyridyl ligand instead of the N, resulting in the substantial PL peak shift to the orange-red emission region.

We investigated the electrochemical properties of the complexes, using cyclic voltammetry (CV). The HOMO and the LUMO energies of $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$ were estimated. The oxidation potentials of $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$ were almost same with the value of −5.15 eV. The reduction curves of all complexes were not clearly observed up to −2.5 V. Therefore, the LUMOs of the complexes were estimated from their respective absorption spectra, using the optical edge and band gap equation ($\Delta E = E_{ox} - E_{red}$) [16]. Their calculated reduction potentials were −2.89 and −2.55 eV for $[Ir(bpy)_2(CN)_2]^-$ and $[Ir(dtbbpy)_2(CN)_2]^+$, respectively. The further detailed CV data were summarized in Table 1.

Conclusions

The effects of the electron-withdrawing nonchromophoric ligand, CN, in the ionic iridium complexes on the luminescence and electrochemical properties of its iridium complexes were studied. The PL emission of the cationic iridium complexes were substantially blue-shifted about 40–80 nm, from $[Ir(bpy)_2(CN)_2]^-$ to $[Ir(bpy)_3]^{3+}$ and $[Ir(dtbbpy)_2(CN)_2]^+$. It could be thought that addition of the bulky *tert*-butyl group might effectively prohibit the rotation of each of the pyridyl rings in the bipyridyl ligand, resulting in the expected N,N-binding to the iridium center and thus, the shorter emission wavelength of the iridium complex. In addition, we could infer that CN ligand made a significant contribution to lower the HOMO level of the complexes, based on their cyclic voltammetry results. Thus, it was concluded that the sterically bulky substituent on the bipyridyl ligand could enhance the direct N,N-binding to the iridium sphere, and thus, the cyanide ligand could effectively lower the HOMO level for the further blue-shifted emission.

Acknowledgments

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