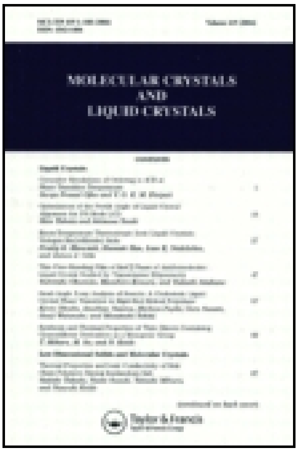

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The Blue Phosphorescent Iridium Complexes Containing the Pyridyltriazole Derivatives as a Main Ligand

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The titled iridium compounds involving the electron-withdrawing pyridyltriazole derivative as a main ligand were synthesized. The main ligand, 2-(5-methoxy-methyl)-2H-1,2,4-triazol-3-yl)pyridine (trzl-CH_2OMe), was designed for development of the blue light-emitting iridium complexes. The ligand involves the electron-withdrawing moiety, N, which may contribute to lowering the HOMO energy level of the complex. In this paper, the new homoleptic complex, tris-(2-(5-(methoxymethyl)-2H-1,2,4-triazol-3-yl)pyridinato)iridium (Ir(trzl-CH_2OMe)$_3$), was synthesized with trzl-CH_2OMe as the main ligand. The heteroleptic complexes containing trzl-CH_2OMe and other ancillary ligands were also prepared, where the ancillary ligands, acac and pic, represent acetylacetonate and picolinate, respectively. The photophysical properties of the iridium complexes prepared herein, Ir(trzl-CH_2OMe)$_3$, Ir(trzl-CH_2OMe)$_2$(acac), Ir(trzl-CH_2OMe)$_2$(pic) were investigated. Their photoluminescence maximum appeared at 445 nm, 460 nm and 472 nm, respectively. We also investigated the electrochemical properties of these iridium complexes for the possible application to organic light-emitting diodes.

Keywords Pyridyltriazole; Organic light-emitting diode; Iridium complex; Blue phosphorescence.

Introduction

A large number of octahedral 5d complexes containing iridium as a metal center and heteroleptic (C^N) cyclometallated ligands, have been extensively studied for multiple emission colors by the group of Thompson [1–5]. The iridium cyclometallated complexes have received the considerable attention because of their favorable photochemical and photophysical properties such as good stability, high photoluminescence (PL) quantum yield, and short triplet lifetimes. Development of blue light-emitting materials is one of the important research subjects. However, blue phosphorescent iridium complexes tend to be less attractive with respect to quantum yields and synthetic efficiency than red phosphorescent emission materials.

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We have been interested in the blue phosphorescent iridium complexes with good color purity. The luminescent properties of iridium(III) complexes are strongly related to the sigma-donating and electron-accepting capabilities of the coordinating ligands, and thus prediction of the properties of the complexes containing the designed ligands is possible to a certain extent [6]. Previously, we reported the synthesis and the luminescence of heteroleptic Ir(F_2-ppy)$_2$(trzl-CH_2OMe) which has the pyridyltriazole derivative, trzl-CH_2OMe, as an ancillary ligand [7]. The iridium complex showed the blue phosphorescence at 462 and 489(sh) nm, hypsochromically shifted from the emission maxima of Ir(F_2-ppy)$_3$ and Ir(F_2-ppy)$_2$(pic) at 470 nm [7]. It was known that N of the pyridyl ligand is more electronegative than C of the unsubstituted phenyl ligand. Thus, replacement of the phenyl ring with a pyridine ring in the C^N ligand of the iridium complex may contribute to lowering the HOMO energy levels of the complex.

In this study, we introduced trzl-CH_2OMe as a new main ligand and reported the synthesis and luminescence of its homoleptic and heteroleptic iridium complexes.

Experimental

All of the chemical reagents were purchased from Aldrich and Strem Co., and used without further purification. The reactions were carried out under an argon atmosphere. The solvents were dried by standard procedures. The column chromatography was performed with the use of silica gel (230-mesh, Merck).

Synthesis of Ligands

Synthesis of 2-(5-methoxy-methyl)-2H-1,2,4-triazol-3-yl)pyridine (trzl-CH_2OMe). First, (pyridine-2-yl) amidrazone was prepared from the reaction of the 2-cyanopyridine (10.4 g, 0.10 mol) and hydrazine monohydrate (5.5 g, 0.11 mol), yielding a cloudy mixture. Ethanol (~5 mL) was added until the mixture became clear, and the resulting solution was stirred overnight at room temperature, causing a gel-like product to form. All solvents were removed under reduced pressure, and the solid was suspended in petroleum ether (50 ml), cooled in an ice bath, and filtered. The solid was washed with cold petroleum ether, yielding 9.9 g (73%) of the amidrazone [8]. The amidrazone obtained was unstable to air and water, and thus used immediately for the synthesis of trzl-CH_2OMe.

2-(5-Methoxymethyl-2H-1,2,4-triazol-3-yl)pyridine (trzl-CH_2OMe) was synthesized using (pyridine-2-yl)amidrazone (2.0 g, 15 mmol) and methoxyacetyl chloride. (Pyridine-2-yl) amidrazone and sodium carbonate (1.6 g, 15 mmol) were placed in a dry flask. Dry dimethylacetamide (DMAA) (15 mL) and dry THF (5 mL) were added, yielding a pale yellow suspension that was cooled to 0°C. In another dry flask, methoxyacetyl chloride (1.6g, 15 mmol) was dissolved in 5ml of DMAA. This solution was then added to precooled amidrazone mixture dropwise, which caused it to turn bright yellow. The mixture was slowly warmed to room temperature and stirred for additional 5 h, yielding a thick yellow mixture. The products were filtered, the solid was washed with water and EtOH, and the resulting pale yellow solid was allowed to air dry [8].

Synthesis of Iridium Complexes

Tris-(2-(5-(methoxymethyl)-2H-1,2,4-triazol-3-yl)pyridinato)iridium (Ir(trzl-CH_2 OMe)$_3$). The homoleptic complex was prepared from the reaction of Ir(acac)$_3$ and an excess of trzl-CH_2OMe by a reported procedure[9]. $Ir(acac)_3$ (1.22 g, 2.5 mmol) and trzl-CH_2OMe (2.07 g, 10 mmol) were dissolved in 50 ml of ethylene glycol and the mixture was refluxed for 24 hr. After cooling, 1 N HCl solution was added and the resulting precipitate was filtered off. The residue was purified by silica gel chromatography by using CH_2Cl_2. Yield: 18%.

[Ir(trzl-$CH_2OMe)_3$]: Yield: 29%. FAB-MS: calculated 760; found 382(M-2*trzl-CH_2OMe).

Ir(trzl-$CH_2OMe)_2$(acac) and Ir(trzl-$CH_2OMe)_2$(pic). The heteroleptic iridium complexes with an ancillary ligand, acetylacetonate (acac) or a picolinate (pic) was prepared from the reaction of the cyclometalated Ir(III) μ-chloro-bridged dimer, (trzl-$CH_2OMe)_2Ir(\mu$-$Cl)_2$Ir(trzl-$CH_2OMe)_2$, with the corresponding ancillary ligand, according to the method reported by Nonoyama with slight modification[10]. Yield: 19~27%.

[Ir(trzl-$CH_2OMe)_2$(acac)]: Yield: 25%. FAB-MS: calculated 669; found 669.

Measurements

UV-visible absorption spectra were obtained from Hewlett Packard 8425A spectrometer. Photoluminescence (PL) spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution. Cyclic voltammograms were obtained at scan rate of 100mV/s with Electrochemical Analyzer of CH Instruments, and tetrabutylammonium hexafluorophosphate was added as an electrolyte in CH_2Cl_2 solution.

Results and Discussion

The synthesis of the main ligand, trzl-CH_2OMe, was straightforward. The intermediate and the ligand were subject to immediate use due to its instability in air. Its homoleptic complex, Ir(trzl-$CH_2OMe)_3$, and the heteroleptic iridium complexes, Ir(trzl-$CH_2OMe)_2$(acac) and Ir(trzl-$CH_2OMe)_2$(pic), were prepared according to the reported procedures [1,10]. The reaction schemes are illustrated in Fig. 1. The overall yields of the iridium complexes were rather low presumably due to other possible coordination of the ligand to the iridium center.

We attempted to control the band gap by lowering HOMO energy levels of the main ligand through the change of π conjugation length and introduction of an electron withdrawing nitrogen atom on the appropriate position of the aromatic ring. In addition, picolinate (pic) which was known to be an ancillary ligand for the blue emission as well as acetylacetonate (acac), a typical chelating ancillary ligand, was introduced to the synthesis of the heteroleptic iridium complexes.

The UV-Vis absorption spectra of the homoleptic and heteroleptic complexes were compared, as shown in Fig. 2. The absorption spectra of these complexes have intense bands appearing in the ultraviolet part of the spectrum between 230 and 300 nm. These bands have been assigned to the spin-allowed $^1(\pi \rightarrow \pi^*)$ transitions of the ligands. The $^1(\pi \rightarrow \pi^*)$ bands are accompanied by weaker and lower energy features extending from 300 to 400 nm that have been assigned to both allowed and spin-forbidden MLCT transitions[11]. The absorption patterns of Ir(trzl-$CH_2OMe)_3$ and Ir(trzl-$CH_2OMe)_2$(pic) are similar in the MLCT region with weak absorption intensities, but that of Ir(trzl-$CH_2OMe)_2$(acac) does not show distinguishable absorption in the MLCT region.

The photoluminescence (PL) spectra of the iridium complexes prepared in this study were shown in Fig. 3. The photoluminescence spectra of the complexes have very similar

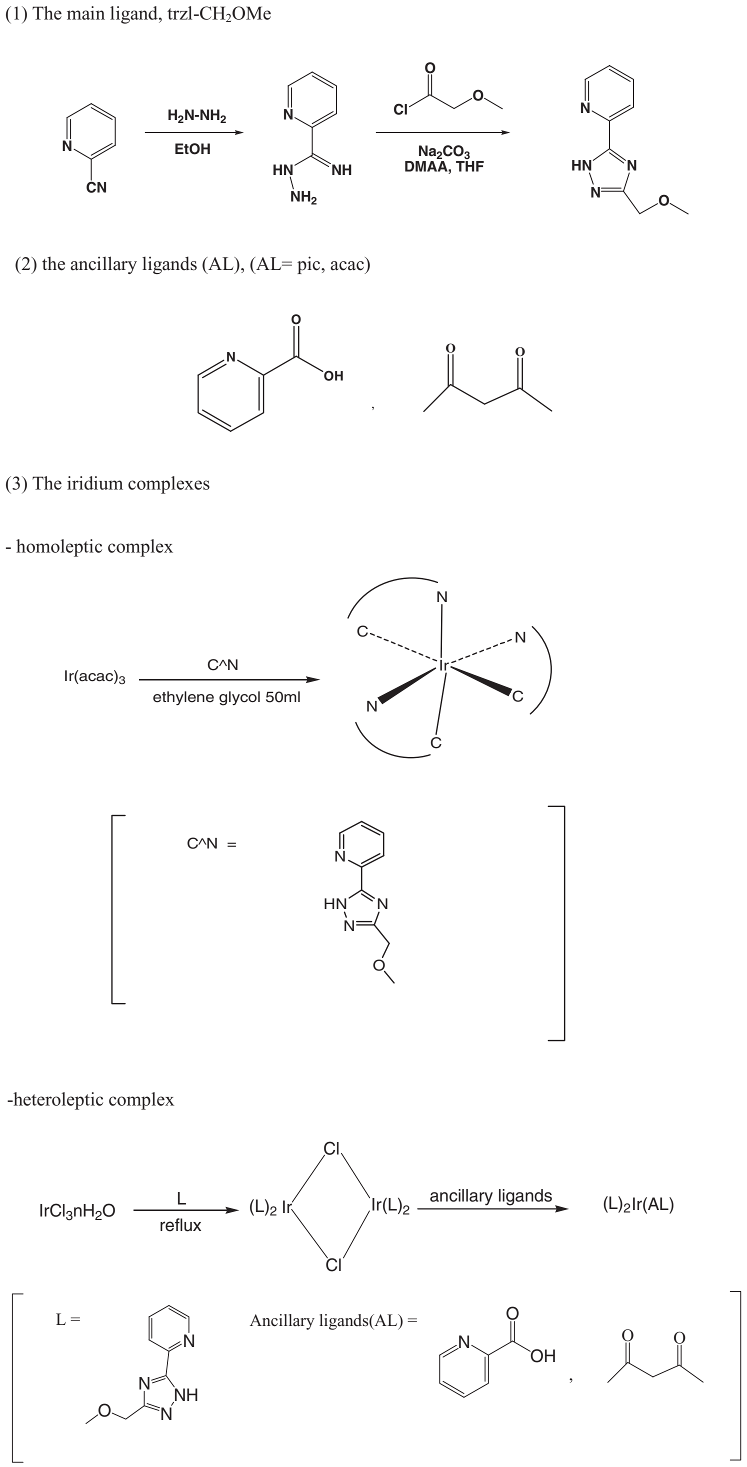

Figure 1. The synthesis of trzl-CH$_2$OMe, and its iridium complexes.

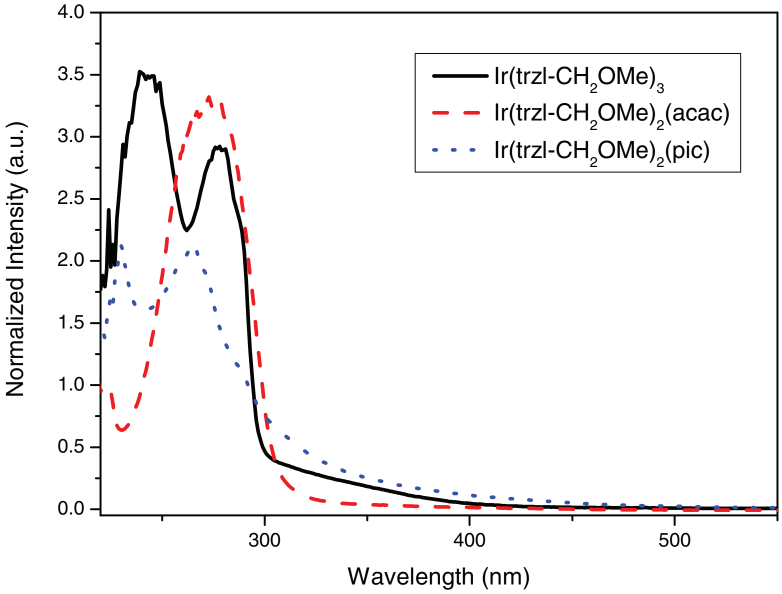

Figure 2. UV-Vis absorption spectra of the homoleptic and heteroleptic iridium complexes of trzl-CH_2OMe.

patterns with 80–100 nm of full-width at half maxima (FWHM) which is related to color purity. Ir(trzl-$CH_2OMe)_3$, Ir(trzl-$CH_2OMe)_2$(acac) and Ir(trzl-$CH_2OMe)_2$(pic) exhibited the blue PL with the emission peaks at 445, 460 and 472 nm, respectively. The luminescence maxima of homoleptic Ir(trzl-$CH_2OMe)_3$ underwent the most blue-shift among the

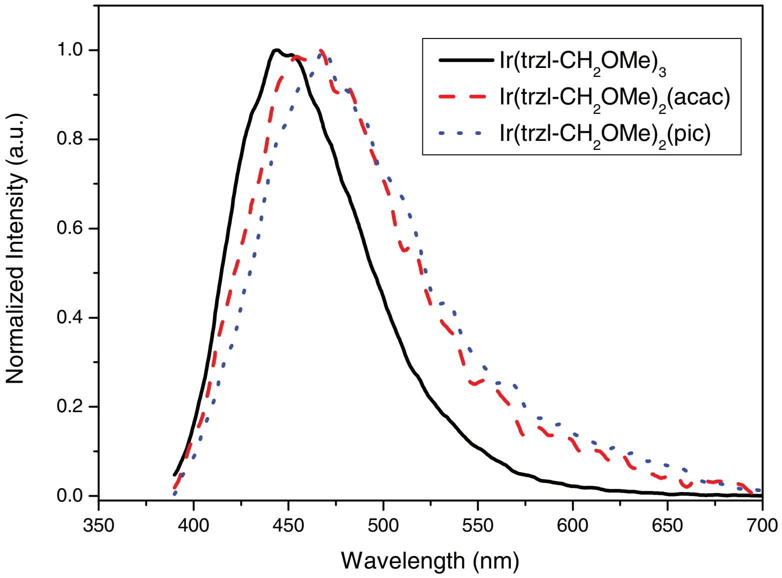

Figure 3. PL spectra of the homoleptic and heteroleptic iridium complexes of trzl-CH_2OMe.

Table 1. Physical parameters for the iridium complexes

Sample	E_{ox}/V[a]	HOMO/eV[b]	LUMO/eV[c]	ΔE/eV[d]
Ir(trzl-CH_2OMe)$_3$	0.696	−5.496	−2.371	3.125

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

iridium complexes of trzl-CH_2OMe prepared herein. Thus, the iridium complex containing trzl-CH_2OMe as both a main ligand and an ancillary ligand showed the deepest blue phosphorescence with high color purity.

We also investigated electrochemical properties of the iridium complexes with the cyclic voltammetry(CV) which could reveal their positions of the HOMOs and LUMOs [12,13]. The oxidation potential which indicates the HOMO of Ir(trzl-CH_2OMe)$_3$ was irreversible at 0.69 V relative to an internal ferrocenium/ferrocene reference (Fc^+/Fc). The LUMOs of the complexes were estimated from their respective absorption spectra and electrochemical data, using the optical edge and band gap equation ($\Delta E = E_{ox} - E_{red}$). The band gap of Ir(trzl-CH_2OMe)$_3$ was estimated to be 3.13 eV, and its reduction potential was calculated to be −2.37 eV. The detailed CV data of the homoleptic iridium complex was summarized in Table 1.

According to our previous study [7], the iridium complex of F_2-ppy main ligand in which trzl-CH_2OMe was introduced as an ancillary ligand showed the blue-shifted emission, compared to the complexes containing pic or acac as an ancillary ligand. In this study, we also observed the hypsochromic shift in the luminescence of the homoleptic complex containing trzl-CH_2OMe ligands. The ancillary ligands, acac and pic, are not luminescent ligands while trzl-CH_2OMe can be luminescent itself. Thus, the complexes containing acac and pic ligands cannot significantly influence luminescence color, just leading to the minor tuning in the blue emission of their complexes. On the other hand, trzl-CH_2OMe is a blue-luminescent ligand and trzl-CH_2OMe could cause relative blue-shift in the luminescence of its complex.

In fact, we were able to demonstrate the most blue-shifted luminescence spectra of the homoleptic complex, Ir(trzl-CH_2OMe)$_3$, as expected. Therefore, we have shown that the luminescence properties of the iridium complexes can be tuned to achieve deep blue emission with high color purity by employing the pyridyltriazole derivative not only as a main ligand but also as an ancillary ligand.

Conclusions

We reported the synthesis of the new homoleptic and heteroleptic iridium(III) complexes coordinated with an electron withdrawing pyridyltriazole derivative, trzl-CH_2OMe, as a main ligand. The iridium complexes, Ir(trzl-CH_2OMe)$_3$, Ir(trzl-CH_2OMe)$_2$(acac) and Ir(trzl-CH_2OMe)$_2$(pic), prepared in this study exhibited the blue emission at 445, 460 and 472 nm, respectively. We found that the homoleptic iridium complex containing the trzl-CH_2OMe exhibited the more hypsochromic shift than the heteroleptic complexes of trzl-CH_2OMe containing acac or pic ligand, displaying deep blue phosphorescence with narrow color range. Though the other ancillary ligands, pic and acac, did not show a significant effect on the modulating the emission wavelengths of their iridium complexes, they could also influence the minor tuning in the blue photoluminescence of their complexes. The photophysical and electrochemical properties of the complexes supported that deep blue phosphorescence could be exhibited by the Ir complexes chelated with trzl-CH_2OMe.

Acknowledgment

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