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Pyridyltriazole as a Main Ligand in the Iridium Complexes for Blue Phosphorescence

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New blue-phosphorescent iridium complexes containing pyridyltriazole derivatives (trzl-CH_2OMe) as main ligands and benzyldiphenylphosphines (bdp) as ancillary ligands were synthesized and their photophysical properties were investigated. As a main ligand, 2-(5-(methoxymethyl)-2H-1,2,4-triazol-3-yl) pyridine (trzl-CH_2OMe), which has the strong electron-withdrawing ability was chosen to give the deep blue emission of its iridium complexes. As ancillary ligands, bdp and bdp-F_2, were employed where they represents benzyldiphenylphosphine and (3,5-difluorobenzyl)-diphenylphosphine, respectively. The resulting iridium complexes, Ir(trzl-$CH_2OMe)_2$(bdp) and Ir(trzl-$CH_2OMe)_2$(bdp-F_2), exhibited the blue emission at 484 and 481 nm in CH_2Cl_2 solution, respectively. These emission was blue shifted, compared to that of the previously reported Ir complex containing a fluorinated phenylpyridine and bdp, Ir(4-Me-4′-F-ppy$)_2$(bdp) at 491 nm. We also investigated the solid state luminescence properties of the complexes prepared herein in a polymer film of PMMA (poly (methylmetacrylate)) for their application to the polymeric process.

Keywords Blue phosphorescence; iridium complex; OLED; pyridyltriazole

1. Introduction

The emission colors of iridium complexes, which range from blue to red, are strongly dependent on the choice of the cyclometallated ligands (C^N) [1–4]. Therefore, design of C^N ligand for iridium complexes is great important in order to achieve high efficiency and color purity for OLEDs. To date, most researches were focused on the design and synthesis of the C^N ligand, such as changing π conjugation and introducing electron donating or withdrawing group on the appropriate position of the aromatic ring [5–7]. To achieve full color display applications, red, green and blue emitting materials that have sufficient luminous efficiency and proper chromaticity must be developed. While success has been achieved on the development of red and green phosphorescent materials, development of blue emitting materials showing the pure color purity and high efficiency have lagged behind.

Previously, we reported use of the pyridyltriazole ligands (trzl-CMe_3, $-CH_2OMe$) as ancillary ligands in the iridium complexes [8]. The triazolate moiety of the pyridyltriazole has a strong electron withdrawing ability, which may contribute

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Address correspondence to Yunkyoung Ha, Department of Science, College of Engineering, Hongik University, 72-1 Sangsu-Dong, Mapo-Ku, Seoul 121-791, Korea. Tel.: +82-2-320-1490; Fax: +82-2-3142-0335; E-mail: ykha@hongik.ac.kr to lowering the HOMO energy level of the complex [9]. Using this concept, we designed the new Ir complexes containing pyridyltriazole as a main ligand for the blue emission. In addition, we introduced a non-conjugating benzyldiphenylphosphine (bdp) ancillary ligand to the complexes for true blue emission [10]. We expect that modification of the this strong-field ligand might allow further color purity improvement [11]. Thus, new iridium complexes, Ir(trzl-$CH_2OMe)_2$(bdp) and Ir(trzl-$CH_2OMe)_2$(bdp-F_2), were synthesized and their PL properties were compared in this study. In addition, the PMMA film spin coated with iridium complexes were fabricated and their film PL properties were also studied.

2. Experimental Section

2.1. *Synthesis and Characterization*

All reagents were purchased from Aldrich Co. and Strem Co., and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230-mesh, Merck). Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) at Seoul National University in Korea.

2.2. *Synthesis of Ligands*

Synthesis of Emitting Ligand (trzl-CH_2OMe).

(Pyridine-2-yl)amidrazone (intermediate) [12]. After melting 5.2 g (0.05 mol) of 2-cyanopyridine with gentle heating, 2.65 ml (0.055 mol) of hydrazine monohydrate was added, yielding a cloudy mixture. Ethanol 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, washing with cold petroleum ether. The resulting amidrazone was unstable to air and water and thus used directly for the synthesis and the derivatized ancillary ligand, trzl. Yield: 73%.

2-(5-(Methoxymethyl)-2H-1,2,4-triazol-3-yl)pyridine (trzl-CH_2OMe) [12]. The intermediate, (pyridine-2-yl)amidrazone (2.0 g, 15 mmol), and $NaCO_3$ (1.6 g, 15 mmol) were placed 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 a separate, dry flask, methoxyacetyl chloride (1.6 g, 15 mmol) was dissolved in 5 ml of DMAA. This solution was then added dropwise to precooled amidrazone mixture, which caused it to turn bright yellow. The mixture was slowly warmed to room temperature and stirred for additional 5 hr, yielding a thick yellow mixture. The contents were filtered and the solid was washed with water and EtOH. The resulting white solid was dried under vacuum. Yield: 61%. ^1H NMR (DMSO-d6, 300 MHz): δ 8.56, 8.05, 7.85, 7.43 (m, 1H each, aromatic Hs'); 3.32 (overlapped s, 5H, $C\underline{H_2}O\underline{CH_3}$).

Synthesis of Ancillary Ligand (bdp-F_2).

(3,5-Difluorobenzyl)diphenylphosphine (bdp-f_2) [13]. Diphenylphosphine (0.88 ml, 5 mmol) and cesium hydroxide monohydrate (0.84 g, 5 mmol) were placed in

anhydrous N,N-dimethylformamide (20 ml), the reaction mixture was stirred for 1 hr resulting in a dark red-orange solution. 3,5-Difluorobenzyl bromide (0.77 ml, 6 mmol) was added in one portion, at which point, the mixture turned immediately to white. The reaction mixture was stirred for 26 hr under a dry argon atmosphere at room temperature. Degassed basic water (30 ml) was added and the mixture was subsequently extracted with CH_2Cl_2 (3 × 30 ml). The combined organic layers were then washed with degassed basic water (3 × 30 ml), dried using anhydrous sodium sulfate, decanted and the solvent was removed in vacuum. Purification via recrystallization from benzene afforded bdp-F_2 as an air-sensitive white powder. Yield: 21%.

2.3. *Synthesis of Ir(III;) Complexes*

Ir(trzl-CH_2OMe)$_2$(bdp) [10]. Ir(tht)$_3$Cl$_3$ [14] (1.12 g, 2 mmol) and bdp (0.55 g, 2 mmol) were combined in degassed decahydronaphthalene (30 mL), and the mixture was refluxed for 1 hr. Upon cooling to room temperature, Na_2CO_3 (2.12 g, 20 mmol) and trzl-CH_2OMe (0.8 g, 4.2 mmol) were added, and the mixture was again refluxed for another 3 hr. After cooling to room temperature and removal of solvent, the solid was chromatographed on a silica gel column with dichloromethane (CH_2Cl_2) to give Ir(trzl-CH_2OMe)$_2$(bdp). Yield: 19%. FAB-MS: calculated 846.22; found 847.

Ir(trzl-CH_2OMe)$_2$(bdp-F_2). This compound was prepared from the reaction of trzl-CH_2OMe with Ir(tht)$_3$Cl$_3$ and bdp-F_2, according to the similar procedure described for Ir(trzl-CH_2OMe)$_2$(bdp). Yield: 17%. FAB-MS: calculated 882.2; found 883.

2.4. *Optical Measurements*

UV-Vis absorption spectra were measured on a Hewlett Packard 8425A spectrometer. PL spectra were measured on a Perkin Elmer LS 50B spectrometer. UV-Vis and PL spectra of the iridium complexes were measured in 10^{-5} M dilute CH_2Cl_2 solution and in the PMMA film. The PMMA film was fabricated by the spin-coating onto the glass substrate with 10 wt% Ir complexes of PMMA in 1,2-dichloroetane solution and following solvent evaporation.

3. Results and Discussion

The synthesis of the main ligand, the ancillary ligand and their iridium complexes was straightforward. Synthesis of the main ligand, 2-(5-(methoxymethyl)-2H-1,2,4-triazol-3-yl)pyridine (trzl-CH_2OMe), was prepared from the reaction of amidrazone precursor with methoxyacetyl chloride, according to the reported procedure [12]. The ancillary ligand, (3,5-difluorobenzyl)diphenylphosphine (bdp-F_2) was synthesized according to the procedure reported previously [13]. Their iridium complexes were obtained from the reaction of Ir(tht)$_3$Cl$_3$ [14] with bdp followed by addition of trzl-CH_2OMe. The overall synthetic schemes are illustrated in Figure 1.

The UV-Vis absorption spectra of the complexes in CH_2Cl_2 are shown in Figure 2. The absorption spectra of these compounds have strong absorption bands appearing at the ultraviolet region of the spectrum between 230 and 330 nm. These bands were 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

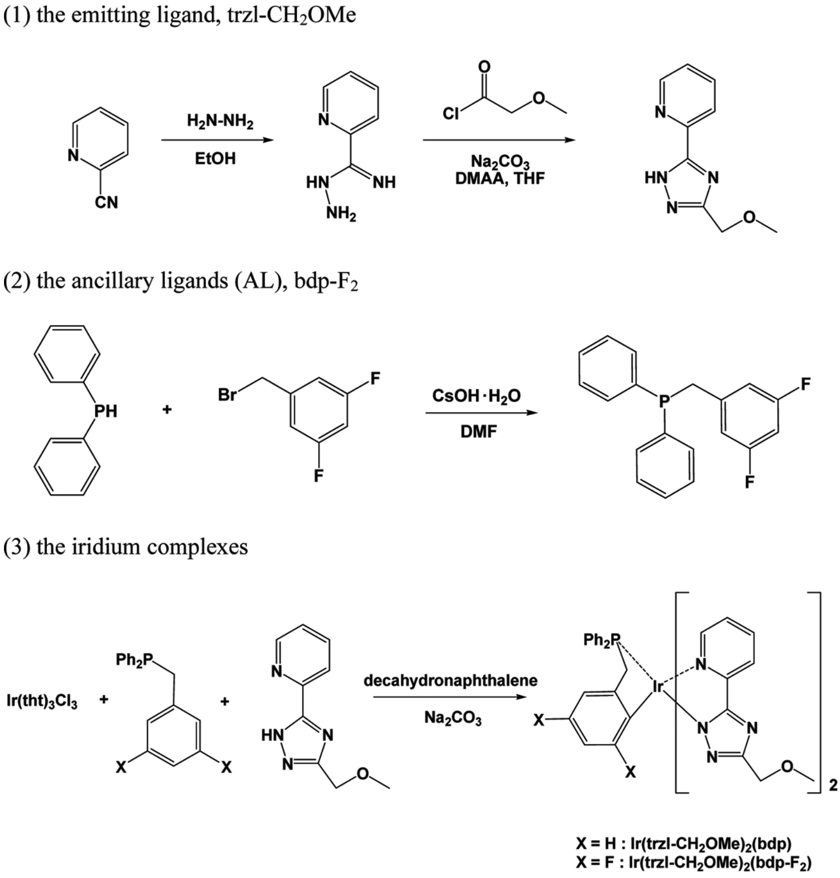

Figure 1. The synthesis of trzl-CH_2OMe, bdp-F_2 and their iridium complexes.

into the visible region from 330 to 400 nm. These absorption bands have been assigned to both allowed and spin-forbidden metal-to-ligand charge transfer (MLCT) transitions. The high intensity of the MLCT bands has been attributed to effective mixing of these charge-transfer transitions with higher lying spin-allowed transitions on the cyclometallating ligand [15]. MLCT is important with respect to the emission efficiency of the complexes. The absorption patterns of Ir(trzl-CH_2-OMe)$_2$(bdp) and Ir(trzl-CH_2OMe)$_2$(bdp-F_2) are almost identical in the MLCT region, suggesting that substituent change of its ancillary ligands does not make significant contribution to the absorption process.

The photoluminescence (PL) spectra of the Ir complexes in 10^{-5} M CH_2Cl_2 solution are shown in Figure 2. Ir(trzl-CH_2OMe)$_2$(bdp) and Ir(trzl-CH_2OMe)$_2$(bdp-F_2) exhibited the emission maxima at 484 and 481 nm, respectively. The PL spectra of two complexes have similar emitting pattern, which are consistent with their UV-vis absorption results. These results also support that the substituent effect at the 3 and 5-position of the benzyldiphenylphosphine (bdp) is negligible in PL color of their complexes. For comparison, the iridium complex containing 2-phenylpyridine(ppy)-based ligands, Ir(4-Me-4′-F-ppy)$_2$(bdp), was reported to exhibit emission at 491 nm [16]. Thus, we were able to show further blue shift of the Ir complexes by employment of pyridyltriazole instead of the fluorinated phenylpyridine as a main ligand.

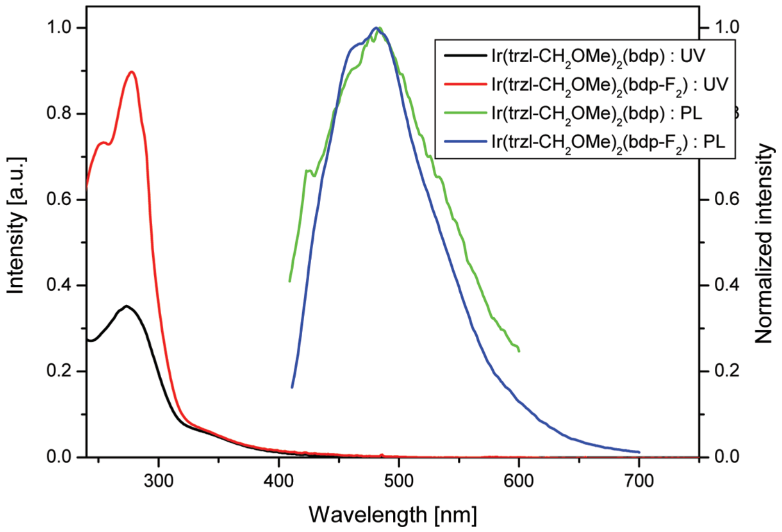

Figure 2. UV-Vis absorption and PL spectra of Ir(trzl-CH$_2$OMe)$_2$(AL) in a 10^{-5} M CH$_2$Cl$_2$ solution (AL = bdp, bdp-F$_2$).

Additionally, we attempted to investigate the UV absorption and PL emission of new Ir complexes in PMMA (poly(methylmethacrylate)) film for the polymer light-emitting device (PLED) application. PMMA was chosen as a host because its non-emitting property within the visible range could provide the PL of the iridium complexes only [17]. The UV absorption pattern of Ir(trzl-CH$_2$OMe)$_2$(bdp-F$_2$) in solution and film are somewhat different. The UV spectra of film has weak band at the visible region from 400 to 500 nm may be originated from the formation of

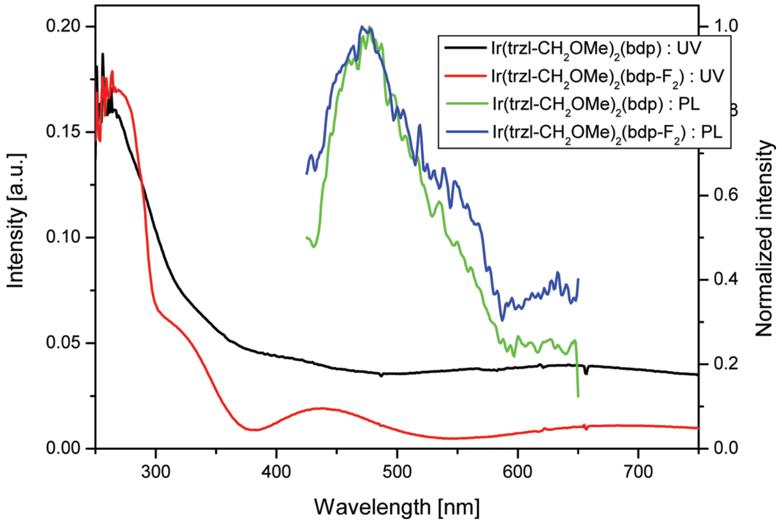

Figure 3. UV-Vis absorption and PL spectra of Ir(trzl-CH$_2$OMe)$_2$(AL) on the PMMA film.

the aggregation. The solid PL peak of the Ir(trzl-CH_2OMe)$_2$(bdp) and Ir(trzl-CH_2 OMe)$_2$(bdp-F_2) in the PMMA had emission maxima at 477 and 474 nm, respectively, as shown in Figure 3. The solid PL spectra of the films underwent hypsochromic shift with respect to its solution PL maxima. However, such shift is not conclusive due to the low intensity of PL in the film state. We presume that the energy transfer did not seem to be efficient from the host, PMMA, to the dopant, the iridium complex because energy levels are not well matched between PMMA and Ir complexes studied herein. Further investigation of the complexes in other host materials such as UGH2 is in progress for its PLED application having high efficiency.

4. Conclusion

The pyridyltriazole ligand having strong electron withdrawing character was introduced as main ligands in the iridium complexes, and the photoabsorption and photoluminescence properties of its iridium complexes were studied. The iridium complexes prepared in this study, Ir(trzl-CH_2OMe)$_2$(bdp) and Ir(trzl-CH_2OMe)$_2$ (bdp-F_2), exhibited blue emission at 484 and 481 nm, respectively in its solution PL. The hypsochromic shifts were observed in the PL spectra of Ir(trzl-CH_2OMe)$_2$ (bdp) and Ir(trzl-CH_2OMe)$_2$(bdp-F_2), compared with that of Ir(4-Me-4′-F-ppy)$_2$ (bdp) containing fluorinated phenylphyridine main ligands. On the other hand, the substituent in the bdp-based ancillary ligand did not show a significant effect on the modulating the emission wavelength of the iridium complexes. The PL spectra in the solution and the film states had similar patterns, but the emission maxima of the complexes in the PMMA film were somewhat blue-shifted and had low intensities. Further studies are in progress on the film fabrication with other host materials.

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