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Synthesis and photophysical characterization of new phosphorescent Ir(III) complexes cyclometallated with imidazole-based ligands

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Abstract

New Ir(III) complexes with a variety of imidazole ligands have been synthesized and fully characterized. The phenylimidazole-based ligands (***L*** = ***dpi***, ***tmspi*** where ***dpi*** = 1,4-diphenylimidazole; ***tmspi*** = 1-trimethylsilyl-4-phenylimidazole) were prepared from copper catalyzed *N*-arylation reaction with 4-phenylimidzole. Ir(III) μ-chloro-bridged dimer, $(\boldsymbol{L})_2\mathrm{Ir}(\mu\text{-Cl})_2\mathrm{Ir}(\boldsymbol{L})_2$, were then prepared according to Nonoyama method [M. Nonoyama, Bull. Chem. Soc. Jpn. 47 (1974) 767]. $(\boldsymbol{L})_2$Ir(acac) and $(\boldsymbol{L})_2$Ir(pic) were finally obtained from the reaction of the dimer with the ancillary ligand, acetylacetonate (acac) or picolinate (pic). The complex coordinated with ***L*** and acac, $(\boldsymbol{L})_2$Ir(acac), does not exhibit emission. On the other hand, the complex coordinated with pic, $(\boldsymbol{L})_2$Ir(pic), showed green luminescence. Between $(\boldsymbol{dpi})_2$Ir(pic) and $(\boldsymbol{tmspi})_2$Ir(pic), $(\boldsymbol{tmspi})_2$Ir(pic) showed stronger emission. Naturally, the phenylimidazole-based ligands are known to have high energy gaps than 2-phenylpyridine. We thus performed the theoretical calculations on these complexes to support their optical properties. The calculation results show that the LUMO energy level of ***dpi*** and ***tmspi*** ligands are similar which that of acac ligand in $(\boldsymbol{L})_2$Ir(acac) complexes, and it leads to the energy transfer from ***dpi*** amd ***tmspi*** ligand, resulting in non-radiative process.

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Keywords: Phosphorescence; Ir complexes; Imidazole ligand; Ancillary ligand; Energy transfer; Non-radiative process

1. Introduction

Numerous d^6 metal complexes of Re(I), Ru(II), Os(II) and Ir(III) have attracted considerable attention due to their intriguing photophysical, photochemical and excited-state redox properties [2,3]. Recently, there also have been growing interests in electroluminescent devices (EL) with phosphorescent dopants for emitting layers [4]. Among these, Ir(III)-based materials are much accounted of promising materials due to their higher stability, larger photoluminescence efficiency and relatively shorter excited-state. In addition, cyclometalated iridium(III) complexes have extensively studied because they can be easily prepared from ligands containing the imine-moiety capable of cyclometalation. Prototype imines used include 2-phenylpyridine, benzoquinoline, and 2-phenylbenzothiazole [5]. However, their utility has been limited due to self-quenching by non-radiative process. To suppress the self-quenching, dendrimers were developed with the branches which keep the distance for the chromophore and make hole or electron transfer more efficiently [6,7]. Herein to suppress the self-quenching, we synthesized the novel imidazole-based ligands and their Ir complexes. Especially,

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trimethylsilyl group was introduced because it was known to be a good electron transporter. In addition, an ancillary ligand (acac or pic) was also adopted. In the present research, introduction of novel imidazole-based ligands along with the ancillary ligand to the Ir complexes may provide stable high luminescence efficiency at a controlled wavelength [8]. The effects of replacement N–H with *N*-phenyl or *N*-trimethylsilylphenyl in the imidazole ligand and the role of ancillary ligands on the luminescent properties of Ir(III) complexes were investigated and accompanied with the theoretical calculation.

2. Experimental

2.1. General method

All reagents were purchased from Aldrich Co. except Ir(III) trichloride hydrate($IrCl_3 \cdot H_2O$) which was purchased from Strem Co. and used without further purification. All reactions were carried out under nitrogen or argon atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel (230–400 Mesh, Merck Co.) Mass spectra were determined on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett–Packard 5890A (capillary column) at Seoul National University, Korea. UV–Vis absorption spectra were measured on Hewlett Packard 8425A spectrometer. The PL spectra were measured on Perkin–Elmer LS 50B spectrometer. Calculations on the ground electronic states of ligands (***ppy***, ***pi-H***, ***dpi***, ***tmspi***, acac and pic) have been carried out using B3LYP density functional theory with Gaussian 98W.

2.2. Synthesis of imidazole ligands

Phenylimidazole-based ligands (***L*** = ***dpi***·***tmspi***) were prepared from the reaction of 4-phenylimidazole and the corresponding phenylhalide by slight modification of reported procedure.

2.2.1. ***dpi*** *(1.4-diphenylimidazole)*

$(CuOTf)_2$, benzene (0.1 mmol), phen (2.0 mmol), dba (0.1 mmol), and Cs_2Co_3 (2.2 mmol) were charged in 10 ml round bottom flask under Ar atmosphere. 4-phenylimidazole (3 mmol), iodobenzene (2 mmol) and xylenes (0.8 ml) were placed in the flask. The mixture was stirred at 110 °C for 36 h. The crude product was purified by flash chromatography on silica gel with1:4 hexanes-ethyl acetate eluent to afford the product as yellow oil. Further purification using sublimation was performed on vacuum (50×10^3 Torr) at 80 °C to obtain white powder product. (475.2 mg, 72%) MS calced for $C_{15}H_{12}N_2$ *m/e* 220.1, found *m/e* 220.

2.2.2. ***tmspi*** *(1-trimethylsilylphenyl-4-phenylimidazol)*

tmspi were prepared from the reaction of 4-phenylimidazole with 1-bromo-4(trimethylsilyl)-benzene by similar method described above. The reaction at 115 °C and for 40 h led to the quantitative conversion. The resulting product was obtained as white powder after purification with column chromatography and sublimation. (604.4 g, 69%) MS calced for $C_{18}H_{17}N_2Si$ *m/e* 292.14, found *m/e* 292.

2.3. Synthesis of Ir(III) complexes [(***dpi***)$_2$Ir(acac), (***dpi***)$_2$Ir(pic), (mspi)$_2$Ir(acac), (***mspi***)$_2$Ir(pic)]

Cyclometalated Ir(III) μ-chloro-bridged dimers of general formula, $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$, where ***L*** represents the cyclometalated imidazole derivatives, were synthesized by the method reported by Nonoyama [1]. The synthesis of $(\boldsymbol{L})_2$Ir(acac) (acac = acetylacetonate) and $(\boldsymbol{L})_2$Ir(pic) (pic = picolinate) were described in detail as follows.

2.3.1. (***L***)$_2$Ir(acac), (***L***)$_2$Ir(pic)

To a flask containing $IrCl_3 \cdot H_2O$ (203 mg, 0.68 mmol) and ***L*** (***dpi*** or ***tmspi*** = 1.36 mmol) was added a 3:1 mixture of 2-ethoxyethanol and water (25 mL). The mixture was refluxed for 12 h and cooled to room temperature. The mixture solution was evaporated under vacuum slowly to obtain crude product $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$. The brownish yellow solid was filtered and washed with ethanol. Crude $(\boldsymbol{L})_2Ir(\mu\text{-}Cl)_2Ir(\boldsymbol{L})_2$ (104 mg, 0.078 mmol) was then mixed with Na_2CO_3 (85 mg) in a two-neck flask. 2,4-pentanedione (0.0.2 ml, d = 0.975, 2.00 mmol) or picolinic acid (24.6 mg, 0.2 mmol) in 2-ethoxyethanol (10 mL) were added and the mixture was refluxed for 2 h. The solution was cooled to room temperature and a small quantity of water was added. The solid was filtered and extracted with CH_2Cl_2. $(\boldsymbol{L})_2$Ir(acac) was chromatographed using CH_2Cl_2 while $(\boldsymbol{L})_2$Ir(pic) was chromatographed using 1% methanol/CH_2Cl_2 to afford bright yellow powder.

(***dpi***)$_2$Ir(acac) in 35% yield (173 mg), (***dpi***)$_2$Ir(pic) in 65% yield (332 mg), (***tmspi***)$_2$Ir(acac) in 30% yield (178 mg), (***tmspi***)$_2$Ir(pic) in 55% yield (335 mg).

2.4. Photoluminescence properties measurement

UV–Vis and PL spectra of the free ligands, 2-phenylpyridine(***ppy***), 4-phenylimidazole(***pi***), 1.4-diphenylimidazole(***dpi***) and 1-trimethylsilyl phenyl-4-phenylimidazol(***tmspi***) were measured in 10^{-5} M dilute solution. UV–Vis and PL spectra of the iridium complexes, $(\boldsymbol{L})_2$Ir(acac) and $(\boldsymbol{L})_2$Ir(pic), were obtained both in the solution(10^{-6} M) and in the solid state. In addition, UV–Vis and PL data were measured for the complexes (6 wt%) in CBP (4,4′-*N*,*N*′-dicarbazole-biphenyl) in the solid state.