

Synthesis and characterization of cationic iridium complexes for the fabrication of green and yellow light-emitting devices



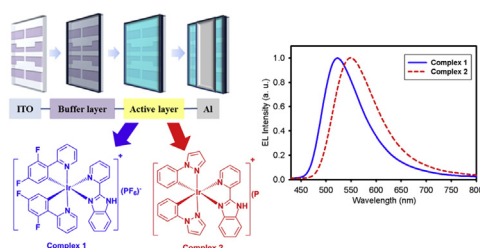
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HIGHLIGHTS

- Green and yellow emitting cationic iridium complexes were synthesized.
- Photophysical and electrochemical properties of the complexes were studied.
- LECs were fabricated using both complexes and studied their electrical properties.
- The highest luminance of 1492 cd m^{-2} has achieved for the LEC utilizing Complex 2.

GRAPHICAL ABSTRACT



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ABSTRACT

Green- and yellow-emitting cationic iridium complexes, $[\text{Ir}(\text{dfppy})_2(\text{pybi})]\text{PF}_6$ (Complex 1) and $[\text{Ir}(\text{ppz})_2(\text{pybi})]\text{PF}_6$ (Complex 2), were synthesized using 2-(2,4-difluorophenyl)pyridine (Hdfppy) and 1-phenylpyrazole (Hppz) as the cyclometalating ligands and 2-(2-pyridyl)benzimidazole (pybi) as the ancillary ligand. In order to gain insight into the photophysical and electrochemical behavior, density functional theory (DFT) calculations were simulated on the above complexes, which showed consistency in energy gaps obtained from both experimental and theoretical results. Light-emitting electrochemical cells (LECs) based on Complex 1 were obtained by solution-processed fabrication, and they showed green (523 nm) electroluminescence with Commission Internationale de L'Eclairage (CIE) coordinates of (0.33, 0.58); on the other hand, the LEC utilizing Complex 2 showed yellow electroluminescence with CIE coordinates of (0.41, 0.56). The highest luminance of 1492 cd m^{-2} and current density of 83.13 mA cm^{-2} were achieved for the LEC utilizing Complex 2, owing to the more balanced carrier injection and recombination as compared to those for Complex 1. The negative role of the free –NH group in the electroluminescent properties of LECs is confirmed by comparing the current results with those previously reported for N-alkylated benzimidazole moieties.

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Abbreviations: DFT, density functional theory; LEC, light-emitting electrochemical cell; CIE, Commission Internationale de L'Eclairage; OLED, organic light-emitting diode; iTMC, ionic transition metal complex; LFSE, ligand-field splitting energy; Hppy, 2-phenylpyridine; Hdfppy, 2-(2,4-difluorophenyl)pyridine; pybi, 2-(2-pyridyl)benzimidazole; PL, photoluminescence; FL, fluorescence; PLQY, PL quantum yield; NMR, nuclear magnetic resonance; FT, Fourier transform; TBAPF₆, tetrabutylammonium hexafluorophosphate; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate; ITO, indium tin oxide; MLCT, metal-to-ligand charge transfer; LLCT, ligand-to-ligand charge transfer; DMF, dimethylformamide; DCM, dichloromethane; THF, tetrahydrofuran; CV, cyclic voltammetry; EL, electroluminescent.

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1. Introduction

Over the past few decades, light-emitting electrochemical cells (LECs) have received considerable attention owing to their potential applications in display and lighting devices [1–4]. LECs represent a class of new-generation technology consisting of ionic luminescent species spin coated between two metal electrodes. The simple device architecture and solution-processed fabrication make LECs promising candidates over conventional multilayered organic light-emitting diodes (OLEDs). Moreover, LECs do not require charge injection layers or metals for electron injection. Mobile ions in the active layer of LECs, which move toward the respective electrodes under an external bias, promote electroluminescence. These accumulated ions generate a strong interfacial electric field at the electrode surfaces, which facilitates the injection of charge carriers [1,5]. These characteristics enable the use of inert metals such as Al, Au, or Ag as cathodes since LECs are insensitive to the electrode work function [6].

Commonly used luminescent materials for the fabrication of LECs are ionic transition metal complexes (iTMCs) and conjugated polymers. The concept of LECs was first put forward by Hegger et al., who used a blend of a conjugated polymer, an ion-conducting polymer, and an inorganic salt as the light emitter [1]. Soon after this, Lee et al. reported the first iTMC-based LEC in 1996 using a ruthenium polypyridyl complex [2]. Since then, many studies have focused on the use of ionic ruthenium complexes and other iTMCs with d^6 and d^{10} electronic configurations for LEC applications in order to improve the device performance [7–14]. LECs based on such iTMCs have exhibited high efficiency and luminescence, in addition to good thermal and photophysical stability owing to their phosphorescent nature. The intrinsic ionic nature of iTMCs enables them to dissolve in organic polar solvents, which allows easy processability of LEC devices. Moreover, iTMCs can be synthesized and purified very easily as compared to polymer materials. All these characteristics make iTMCs superior light emitters in solid-state LEC devices over polymer materials.

In early studies, large numbers of iTMCs based on ionic Ru(II) [2,3,13,15–17] and Os(II) [12,15] complexes were synthesized for the fabrication of LEC devices. However, the low ligand-field splitting energies (LFSEs) of these complexes resulted in yellow, orange, or red light emission, which reduced their application in LEC devices. LECs utilizing non-toxic and inexpensive Cu(I) complexes were also reported [11,18,19]. However, the inability to tune the emission color to shorter wavelength regions of the visible spectra again limited the application of these complexes in LECs. The development of a color-tunable material was finally accomplished with the synthesis of iridium complexes owing to their larger LFSEs. Slinker et al., who fabricated the first iridium complex-based LEC, incorporated bis(2-phenylpyridine) (4,4'-di-tert-butyl-2,2'-dipyridyl)iridium(III) hexafluorophosphate as a light-emitting material, which gave yellow light (560 nm) with a maximum brightness of 300 cd m^{-2} at 3 V [4].

Since 2004, iridium complexes have received much more attention than other metal complexes in LEC research owing to the large LFSE of heavy iridium atom [7–10,20–33]. The higher oxidation state and large size of iridium(III) ions are the main factors for the large LFSE of iridium complexes. The larger LFSE of central Ir(III) ions makes e_g orbitals less accessible, which leads to higher photoluminescent quantum yields and better photostability as compared to other metal complexes used for LEC applications. The most outstanding feature of iridium complexes is tunable emission colors attained by the chemical modification of organic ligands around the iridium center. LECs based on iridium complexes have been reported recently with various emission colors, and they have exhibited high luminance and efficiency [34,35]. For

lighting purposes, the generation of primary colors is very important, in addition to high luminance. Since LECs are composed of neat films of luminescent materials, the closely packed molecules in the active layer exert strong intermolecular interactions that lead to the quenching of excited states, which is detrimental to device performance. These interactions are minimized by the meticulous design of organic ligands that provide steric hindrance, thereby suppressing excited-state self-quenching. In our previous study [34], we reported a series of cationic iridium complexes containing alkylated benzimidazole ancillary ligands (alkylation on the NH group of the benzimidazole moiety with methyl, ethyl, and octyl groups), and we studied the effect of chain length on the electroluminescent properties of LEC devices. LECs incorporating cationic iridium complexes having 2-phenylpyridine (Hppy) and 2-(2,4-difluorophenyl)pyridine (Hdfppy) as the cyclometalating ligands exhibited yellow and green emission colors, respectively, irrespective of the chain length on the benzimidazole-based ancillary ligands [34]. The introduction of an octyl chain to the NH group of the benzimidazole ancillary ligand more effectively suppressed the intermolecular interaction and self-quenching than methyl- and ethyl-substituted complexes, achieving a high current efficiency of 3.85 cd A^{-1} .

Herein, we report the synthesis and characterization of two cationic iridium complexes, $[\text{Ir}(\text{dfppy})_2(\text{pybi})]\text{PF}_6$ (Complex 1) and $[\text{Ir}(\text{ppz})_2(\text{pybi})]\text{PF}_6$ (Complex 2), employing 2-(2-pyridyl)benzimidazole (pybi) ancillary ligand-bearing free NH group and the effect of these group on self-quenching. The complexes were synthesized utilizing 1-phenylpyrazole (Hppz) and Hdfppy as the cyclometalating ligands, and we studied the effect of these ligands on the photophysical properties of both Complex 1 and Complex 2. The photophysical and electrochemical properties of these complexes were investigated, and the results were corroborated with theoretical DFT calculations. LECs were fabricated using the phosphorescent iridium complexes as the light emitter, and we studied their electroluminescent properties, which resulted in green (523 nm) and yellow (549 nm) electroluminescence for Complexes 1 and 2, respectively. LECs incorporating Complex 1 and Complex 2 exhibited high luminance values of 656 and 1492 cd m^{-2} , respectively. The luminance values of these complexes are comparatively low as compared to those reported for N-alkyl-substituted iridium complexes owing to increased intermolecular interactions, which confirms the significance of inducing steric hindrance to suppress self-quenching for the fabrication of highly efficient LEC devices.

2. Experimental

2.1. Materials and methods

Iridium(III) chloride hydrate (99.9%, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) was purchased from Alfa Aesar, South Korea and used without further purification. All other starting materials and solvents were supplied by Sigma Aldrich and used as received. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 500 MHz Fourier transform (FT)-NMR spectrometer. Chemical shifts, δ (in ppm), were measured relative to a residual CD_2Cl_2 solvent with tetramethylsilane as the internal standard. Elemental analyses were performed on an Elementar Vario EL CHN elemental analyzer. Mass spectra were recorded on an Agilent Q-TOF 6530 MS/MS system. The UV–visible absorption and photoluminescence (PL) emission spectra of the complexes in acetonitrile solutions were recorded on an Agilent 8453 spectrophotometer and F-7000 fluorescence (FL) spectrophotometer, respectively. PL quantum yields (PLQYs) were measured in acetonitrile solutions (excited at 425 nm) with quinine bisulfate ($\Phi_p = 0.545$ in 1 M H_2SO_4) as the standard. Electrochemical measurements of the complexes

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