Synthesis of heteroleptic iridium complexes with sterically hindered methyl groups on pyrazole ligands for efficient yellow and green light-emitting electrochemical cells

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ARTICLE INFO

ABSTRACT

We report the synthesis of four cationic iridium complexes, $[Ir(ppy)_2(mepzpy)]PF_6$ (**1a**), $[Ir(dfppy)_2(mepzpy)]PF_6$ (**1b**), $[Ir(ppy)_2(dmpzpy)]PF_6$ (**2a**), and $[Ir(dfppy)_2(dmpzpy)]PF_6$ (**2b**), containing the methyl-substituted pyrazole-based ancillary ligand and the phenylpyridine-based cyclometalating ligands. UV−visible, photoluminescence (PL), and voltammetric measurements were made to study the photophysical and electrochemical properties of complexes **1a**−**2b**. Light-emitting electrochemical cells (LECs) were fabricated, which showed yellow emission for complexes **1a** and **2a** and green emission for complexes **1b** and **2b**. The LEC incorporating **2b** exhibited a high luminance of 658 cd m^{-2} and a current efficiency of 0.34 cd A^{-1}. The higher luminance and efficiency of the device based on **2b** were due to the smooth surface morphology and the presence of sterically hindered dimethyl groups on the ancillary ligand (dmpzpy), which causes a more balanced charge carrier injection and recombination.

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1. Introduction

Light-emitting electrochemical cells (LECs) became prominent as a promising alternative to conventional organic light-emitting diodes (OLEDs) because of their simple device architecture, easy fabrication and low-cost production [1−5]. OLEDs are multilayered devices with a neutral emissive active layer and require air-sensitive low-work-function electrodes, in addition to the electron and hole injection layers. The resulting device necessitates rigorous encapsulation, which increases the production cost. Unlike OLEDs, LECs use an ionic active material, which makes them very simple and can be effortlessly processed from solution. Moreover, LECs independent of air-sensitive charge injection layers and metals, allowing nonrigorous encapsulation of the devices. These benefits make LECs a favorable candidate for next-generation display and lighting applications.

The first solid-state LEC device was introduced in 1995 and was based on a polymer blend, specifically, a mixture of an emissive conjugated polymer, an ion-conducting polymer, and an inorganic salt [1]. LECs with ionic transition metal complexes (iTMCs) were introduced there after [6−14]. The first iTMC-LEC, reported in 1996, was based on a ruthenium polypyridyl complex and emitted orange−red light with a maximum luminance of 30−50 cd m^{-2} under a forward bias [6]. Thereafter remarkable efforts have been made on LECs based on iTMCs to enhance the performance of the device. Consequently, iTMC-based LECs have exhibited increasing responsiveness owing to their phosphorescent nature. In comparison with polymer LECs, iTMC-LECs have a simpler device configuration, do not need an ion-conducting polymer or an inorganic salt for charge injection purposes, and possess high ionic conductivity. In addition, iTMCs are easily soluble in benign solvents, so these materials can be prepared by spin-coating on large-area devices. Furthermore, the light emission from iTMCs is from triplet states, so they exhibit higher luminance efficiency and outstanding phosphorescent quantum yields compared to singlet emitters [3,13,15,16]. Moreover, iTMCs display stable oxidation states and possess favorable excited state properties. The existence of these stable multiple redox states suggests that charge carriers can be easily injected and transported in these materials [17]. Under an

applied bias, the mobile ions in the active layer of the LEC move toward the respective electrodes, creating an electrical double layer, which is followed by the injection of holes and electrons from the anode and cathode, respectively. These charge carriers move and combine to form excitons in which a fraction recombines radiatively, resulting the emission of light.

The representative iTMCs used in LEC devices are based on a ruthenium(II)-containing complex as the single active component [6]. The low ligand-field splitting energies (LFSEs) of ruthenium(II) results the emission band of these ruthenium(II) complexes to be centered in the orange–red region of visible spectrum. The limited color tuning capability of these ruthenium complexes has thus restricted their application in lighting technologies [6–8,18,19]. Moreover, these complexes exhibit low stability under device conditions. The use of cyclometalated Ir(III) complexes in lighting devices offers remarkably improved device performance compared to the use of other metal complexes [5,12,20–26]. An LEC based on a cationic iridium complex, $[Ir(ppy)_2(dtb-bpy)]PF_6$ was reported for the first time by Slinker et al. in 2004 [3]. Single-layered LEC devices incorporating $[Ir(ppy)_2(dtb-bpy)]PF_6$ produced yellow light with a peak brightness and power efficiency of 300 cd m^{-2} and 10 lm W^{-1}, respectively under 3 V [3]. Cationic iridium complexes are characterized by high spin–orbit coupling owing to their large size and charge. The high spin–orbit coupling leads to efficient intersystem crossing, resulting in high emission quantum efficiencies. Moreover, iridium complexes hold large LFSEs which leads the color tuning from blue to red through structural modification of cyclometalating and ancillary ligands. In addition to the color tunability, these bis-cyclometalated iridium(III) complexes show excellent thermal and photochemical stability. However, during device operation, LECs based on these complexes experienced severe excited state self-quenching because the complexes in an active layer of LECs are closely packed. By incorporating adequate substituents on ancillary ligands through bulky groups or π–π interaction, it is possible to suppress these nonradiative pathways by creating an enlarged intermolecular distance and thereby to improve both the efficiency and the device lifetime [27–30]. We recently reported the synthesis of a series of cationic iridium complexes containing alkylated-benzimidazole-based ancillary ligands and studied the effect of the chain length on the electroluminescent properties [31]. LECs based on these alkylated-imidazole-based iridium complexes exhibited high efficiencies with increasing chain length from methyl to octyl groups due to the reduced intermolecular interactions and self-quenching [31].

Herein, we report the synthesis and characterization of four cationic iridium complexes with methyl-substituted pyrazole ligands, namely, $[Ir(ppy)_2(mepzpy)]PF_6$ (**1a**), $[Ir(dfppy)_2(mepzpy)]PF_6$ (**1b**), $[Ir(ppy)_2(dmpzpy)]PF_6$ (**2a**) and $[Ir(dfppy)_2(dmpzpy)]PF_6$ (**2b**), where mepzpy is 2-(3-methyl-1H-pyrazol-1-yl)pyridine, dmpzpy is 2-(3,5-dimethyl-1H-pyrazol-1-yl)pyridine, Hppy is 2-phenylpyridine, and Hdfppy is 2-(2,4-difluorophenyl)pyridine. The photoluminescence (PL) spectra of complexes **1a** and **2a** in acetonitrile solution show blue–green emission, whereas complexes **1b** and **2b** emit in the blue region of the visible spectrum. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations were performed for complexes **1a**–**2b**, and the obtained results are consistent with the experimental photophysical and electrochemical data. LECs were fabricated that produced yellow emission when complexes **1a** and **2a** were used and green emission when complexes **1b** and **2b** were used. Among the complexes, LECs based on **2b** resulted the highest luminance, 658 cd m^{-2} and current efficiency, 0.34 cd A^{-1}, due to the reduced intermolecular interaction and self-quenching, which resulted in inhibition of the nonradiative pathways. In addition, complex **2b** showed smooth surface morphology, which again enhance the

device performance by decreasing the charge transfer resistance at the interface of electrode.

2. Results and discussion

2.1. Synthesis and characterization of heteroleptic iridium complexes (*1a*–*2b*)

The ancillary ligands (mepzpy and dmpzpy) were synthesized by a noncatalyzed C—N coupling reaction of 2-bromopyridine with 3-methyl-1H-pyrazole/3,5-dimethyl-1H-pyrazole in presence of potassium tert-butoxide [32]. The cationic iridium complexes were synthesized according to the previously reported procedures [33,34]. First, commercially available $IrCl_3 \cdot xH_2O$ (1 equiv.) was treated with 2.2 equiv. of the corresponding cyclometalating ligands (C$^\wedge$N), namely, 2-phenylpyridine (Hppy) or 2-(2,4-difluorophenyl)pyridine (Hdfppy) in 2-ethoxyethanol and water (3:1, 40 mL) mixture to give a cyclometalated Ir^{III} μ-dichloro-bridged dimer, $[Ir(C^\wedge N)_2(\mu-Cl)]_2$. Next, heteroleptic cationic iridium complexes (**1a**, **1b**, **2a**, and **2b**) were synthesized by reacting the desired dimeric complex with the preferred neutral ancillary ligands. The iridium complexes were formed as chloride salts and underwent anion metathesis reaction with solid NH_4PF_6 to replace Cl$^-$. The complexes obtained in high yields were characterized by elemental analysis, NMR and mass spectroscopic methods. The synthetic routes with the structures of ancillary ligands and cationic iridium complexes are shown in Fig. 1.

2.2. Photophysical properties

Fig. 2 shows the room temperature UV–visible absorption spectra of the complexes in acetonitrile solution. All the complexes (**1a**, **1b**, **2a**, and **2b**) show intense absorption bands ($\varepsilon > 2.5 \times 10^4$ M^{-1} cm^{-1}) between 200 and 300 nm in the ultraviolet region. These high-energy bands are attributed to ligand-centered (LC) singlet $^1\pi$–π^* transitions in both the coordinated cyclometalating and ancillary ligands. Following the LC bands, broad and less intense absorption bands are observed from 330 nm extending toward the visible region. These lower-energy bands are related to both spin-allowed and forbidden metal-to-ligand charge transfer (^{1}MLCT and ^{3}MLCT), ligand-to-ligand charge transfer (^{3}LLCT and ^{1}LLCT), and LC $^3\pi$–π^* transitions of the complexes [35]. The considerable intensity of the spin-forbidden transitions (^{3}MLCT, ^{3}LLCT, and ^{3}LC) is the result of strong spin–orbit coupling of the heavy iridium center, which facilitates the mixing of these states with higher-lying ^{1}MLCT transitions [34,36]. The main absorption bands and molar extinction coefficients of all the complexes are given in Table 1. The absorption spectra in the lower-energy region of complexes **1b** and **2b** are significantly blue-shifted by 20 nm compared to those of complexes **1a** and **2a**. The hypsochromic shift in the absorption spectra is ascribed to the presence of electron-withdrawing fluorine atoms on the cyclometalated ligands of the complexes **1b** and **2b**. It is clear from Fig. 2 that alkyl substitution on ancillary ligands does not significantly affect the absorption spectra of the complexes, unlike the change in cyclometalating ligands.

Fig. 3 shows the PL emission spectra of the complexes in acetonitrile solution, which were taken at room temperature. The complexes in solution show vibronically structured emission spectra for all the complexes **1a**–**2b**, indicating that the emissive excited states have a mainly LC $^3\pi$–π^* character and less of a ^{3}MLCT character [34,36,37]. In acetonitrile solution, complexes **1a** and **2a** show similar emission properties; complex **1a** has an emission peak at 478 nm and a shoulder peak at 505 nm, whereas those of complex **2a** appear at 476 and 504 nm, respectively. Note that the