

Light-emitting properties of cationic iridium complexes containing phenanthroline based ancillary ligand with blue-green and green emission colors



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ARTICLE INFO

Article history:

Received 25 June 2014

Received in revised form 27 October 2014

Accepted 28 October 2014

Available online 15 November 2014

Keywords:

Light-emitting electrochemical cells

Thin films

Photophysical properties

Electrochemical properties

ABSTRACT

We report here two new cationic iridium(III) complexes with phenanthroline-based ancillary ligands, $[\text{Ir}(\text{dfppy})_2(\text{dibutyl-phen})]\text{PF}_6$ (Complex 1) and $[\text{Ir}(\text{ppz})_2(\text{dibutyl-phen})]\text{PF}_6$ (Complex 2) and their uses in light-emitting electrochemical cells (LECs). The design is based on 2-(2,4-difluorophenyl)pyridine (dfppy) and 1-phenylpyrazole (ppz) as the cyclometalating ligands and 2,9-dibutyl-1,10-phenanthroline (dibutyl-phen) as the ancillary ligand. The photophysical and electrochemical properties of the complexes were studied and the results obtained were corroborated with theoretical density functional theory (DFT) calculations. LECs were fabricated incorporating each complexes which resulted in blue-green light emission (502 nm) with Commission Internationale de l'Eclairage (CIE) coordinates of (0.26, 0.49) for Complex 1 and green (530 nm) electroluminescence with CIE coordinates of (0.33, 0.54) for Complex 2. The luminance and the current efficiency of the LECs based on Complex 1 are 947 cd m^{-2} and 0.25 cd A^{-1} , respectively, which are relatively higher than that of Complex 2 with a maximum luminance of 773 cd m^{-2} and an efficiency of 0.16 cd A^{-1} .

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1. Introduction

Recently, light-emitting electrochemical cells (LECs) containing ionic species in their active layer have emerged as promising candidates for next-generation display and solid-state lighting applications [1–4]. Compared to multi-layered organic light-emitting diodes (OLEDs) with neutral molecules, LECs generally consist of a single luminescent material in an ionic environment, which simultaneously satisfies the requirements of charge injection, charge transport and emissive recombination. Moreover, they can be easily processed from solution, do not rely on air-sensitive charge-injection layers and can directly employ air-stable electrodes such as Au, Ag, and Al as cathodes [5–7]. Because of these characteristics, LECs are one of the simplest electroluminescent devices known to date.

LECs can be divided into two main categories: conjugated polymers with an added electrolyte in a blended structure (PLEC), and ionic transition-metal complexes (iTMCs) [5–12]. In the case of iTMC-based LECs, no inorganic salt or ion-conducting polymer is required because of their intrinsic ionic nature. Among the reported phosphorescent iTMCs based on osmium(II), ruthenium(II), and

iridium(III) complexes, cyclometalated iridium(III) complexes are regarded as the best phosphorescent materials due to their high thermal stability, relatively short excited-state lifetime, high photoluminescence efficiency, and excellent color tunability [13–20]. Recently, iridium(III) complexes have been successfully employed in the fabrication of highly efficient LECs owing to their large ligand-field splitting energies (LFSEs) [8,21–23].

To date, the development of green and red emitters in fluorescent and phosphorescent displays has been successful [23–28], whereas blue emitters have poor color quality and low external quantum efficiency. However, because blue light is indispensable for full-color display and solid-state lighting applications, blue-light LECs are highly desired. As LECs are based on only one active material, the most important enhancements to the performance of the device can be obtained by an appropriate tuning of the photophysical and electrochemical properties of the ionic iridium complexes. Previous reports have shown that the highest occupied molecular orbitals (HOMOs) are located on the phenyl groups of the cyclometalating ligands and the 5d orbitals of the Ir(III) ion, whereas the lowest unoccupied molecular orbitals (LUMOs) are located on the ancillary ligands [29–31]. Therefore, the use of fluorine-based substituents to obtain a blue shift of the emission of the complex has become a widely employed strategy.

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We present herein a new way to obtain blue-green and green emitting iridium(III) complexes, based on a butyl substituent attached to a phenanthroline-based ancillary ligand. Two cationic iridium complexes, employing 2-(2,4-difluorophenyl)pyridine (dfppy) or 1-phenylpyrazole (ppz) as the cyclometalating ligands and 2,9-dibutyl-1,10-phenanthroline (butylphen) as an ancillary ligand, namely, $[\text{Ir}(\text{dfppy})_2(\text{butylphen})]^+\text{PF}_6^-$ and $[\text{Ir}(\text{ppz})_2(\text{butylphen})]^+\text{PF}_6^-$ (where PF_6^- is hexafluorophosphate ion), have been synthesized. The effects of the different cyclometalating ligands used in complexes and their photophysical and electrochemical properties have also been investigated. Furthermore, LEC devices based on these complexes have been fabricated, and their device performances have been studied and compared.

2. Experimental

2.1. Materials and methods

All starting materials and solvents were purchased from Aldrich and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 500 MHz FT-NMR spectrometer and the chemical shifts were measured relative to residual CD_2Cl_2 solvent with tetramethylsilane as the internal standard. Elemental analyses were performed on an Elementar Vario EL CHN elemental analyzer. Absorption spectra were acquired in a 1-cm path length quartz cell using a 8453 UV-visible Agilent spectrophotometer. Photoluminescence (PL) emission spectra were recorded with an F-7000 FL spectrophotometer. PL quantum yields (PLQYs) were measured in acetonitrile solutions at an excitation wavelength of 390 nm with quinine sulfate ($\Phi_p = 0.545$ in 1 M H_2SO_4) as the reference substance. Electrochemical measurements were performed using a potentiostat/galvanostat (Iviumstat) voltammetric analyzer by employing a 10^{-3} M solution of CH_3CN at a scan rate of 100 mV s^{-1} . The electrolytic cell consisted of glassy carbon as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in CH_3CN . The redox potentials of each

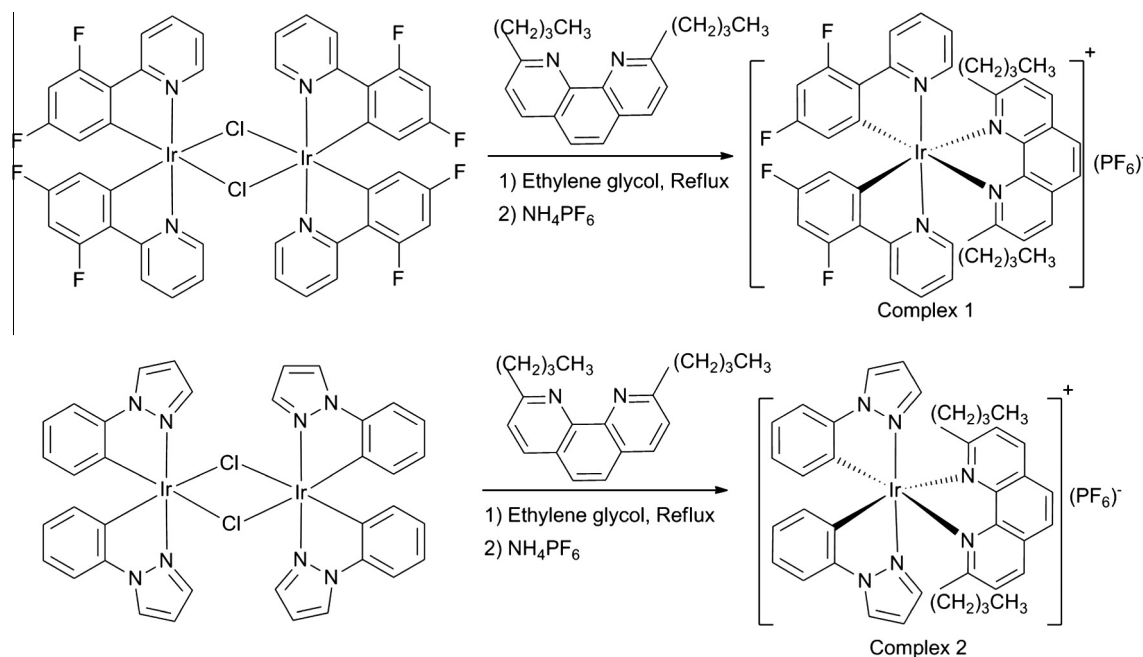
measurement were recorded against ferrocenium/ferrocene (Fc^+/Fc) couple and used as an internal standard.

2.2. Synthesis of luminous materials

Two cationic iridium complexes, $[\text{Ir}(\text{dfppy})_2(\text{dibutyl-phen})]\text{PF}_6^-$ (Complex 1) and $[\text{Ir}(\text{ppz})_2(\text{dibutyl-phen})]\text{PF}_6^-$ (Complex 2), were synthesized according to previously reported procedures [32,33]. The synthetic routes, including the structures of both complexes, are shown in Scheme 1. The first step, in which cyclometalated iridium(III) chloro-bridged dimers (generally having the formula, $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\mu\text{-Cl})_2]$) were synthesized by the Nonoyama reaction of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ with 2.2 equivalents of the respective cyclometalating ligands ((dfppy) or (ppz)) in a mixture of 2-ethoxyethanol and water (3:1 v/v) for 24 h [33]. The dimeric iridium (III) intermediates then underwent a facile reaction with neutral 2,9-dibutyl-1,10-phenanthroline, followed by an ion exchange reaction with ammonium hexafluorophosphate (NH_4PF_6) to afford the luminescent iridium complexes in high yields. The resulting complexes were characterized by various spectroscopic, photophysical, and electrochemical methods.

2.2.1. Synthesis of $[\text{Ir}(\text{dfppy})_2(\text{butylphen})]^+\text{PF}_6^-$ (Complex 1)

Tetrakis(2-(2,4-difluorophenyl)pyridine- C_2, N') (μ -dichloro)diiridium(III) (0.079 g, 0.065 mmol) and 2,9-dibutyl-1,10-phenanthroline (0.04 g, 0.137 mmol) were heated to reflux in ethylene glycol (20 mL) for 16 h. The mixture was transferred into a separation funnel and extracted three times with water (90 mL) and diethyl ether (60 mL). A concentrated solution of ammonium hexafluorophosphate in water was slowly added to the aqueous layer, affording a colored suspension. The precipitate was collected by filtration and dried in an oven for 24 h (see Scheme 1). Yield: 0.1143 g (82%). ^1H NMR (500 MHz, CD_2Cl_2): 8.56 (d, $J = 8.39 \text{ Hz}$, 2H), 8.08 (s, 4H), 7.82 (t, $J = 15.7 \text{ Hz}$, 2H), 7.74 (d, $J = 8.38 \text{ Hz}$, 2H), 7.42 (d, $J = 5.42 \text{ Hz}$, 4H), 6.91 (t, $J = 12.48 \text{ Hz}$, 2H), 2.74–2.68 (m, 4H), 1.77–1.60 (m, 4H), 1.34–1.26 (m, 4H), 1.0–0.91 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): 169.8, 165.0, 163.0, 151.6, 150.3, 148.3, 140.4, 139.9, 130.7, 128.2, 126.7, 124.5, 124.3, 123.7, 118.4, 114.4, 99.4, 39.9, 32.8, 23.2, 14.0.



Scheme 1. Synthetic routes and structures of cationic iridium complexes.

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