



Efficient green electrogenerated chemiluminescence from cyclometalated iridium(III) complex



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ABSTRACT

A novel cyclometalated iridium(III) complex, (dfppy)₂Ir(PyBiz), was synthesized by using 2-(2,4-difluorophenyl)pyridine (dfppy) as the C^N main ligand and 2-(2-pyridyl)benzimidazolato-N,N' (PyBiz) as the N^N ancillary ligand. The photophysical, electrochemical and electrogenerated chemiluminescence (ECL) properties of (dfppy)₂Ir(PyBiz) were investigated. (dfppy)₂Ir(PyBiz) shows a green photoluminescence emission with a maximum wavelength at 527 nm and quasi-reversible redox behaviors in acetonitrile solvent. Intense green ECL emissions that could be seen with the naked eyes were observed in annihilation and coreactant processes and the ECL spectra generated from three processes are identical to its photoluminescence spectrum, indicating that the same excited state is formed in these processes. The green ECL emission of (dfppy)₂Ir(PyBiz) can be distinguished from the red emission of Ru(bpy)₃²⁺, which provides the possibility of the identification of (dfppy)₂Ir(PyBiz) and Ru(bpy)₃²⁺ in a single solution containing both compounds. The green ECL emission of (dfppy)₂Ir(PyBiz) with high ECL efficiency makes it promising to develop ECL luminophore for multiple wavelength and potential use in multichannel analytical applications.

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1. Introduction

Electrogenerated chemiluminescence (ECL) is the emission of light from the electron-transfer reaction between electrochemically generated precursors in the vicinity of an electrode [1,2]. Since the first report of ECL from tris-(2,2'-bipyridyl) ruthenium(II), Ru(bpy)₃²⁺, in 1972 by Bard's group [3], Ru(bpy)₃²⁺ derivatives have been studied as the important ECL emitters in immunoassays and DNA bioassays [4,5]. Though Ru(bpy)₃²⁺ derivatives possess great performance in ECL analysis, the search for new ECL emitters with various colors and high ECL efficiency (ECL efficiency of Ru(bpy)₃²⁺ is 0.05 [6,7]) is an important and active area in ECL studies [8,9].

Iridium(III) complexes, which exhibit high photoluminescent efficiencies and stable redox characteristics, have attracted attention as promising materials for organic light emitting diodes, and as ECL emitters for ECL assay [10]. Since the early work of Nishimura [11], Wightman [12], Richter [13], and Kapturkiewicz [14], ECL works on iridium complexes have opened up the possibility in the analytical applications due to their efficient luminescence and tunable emission properties. Many works done by Richter [15,16], Kim [17],

Kapturkiewicz [18,19], Ding [20,21], Hogen [22,23], Marcaccio [24] and Zhou [25] et al. groups have been made in designing or modifying the ligands of the Ir(III) complexes. It was found that iridium(III) complexes have high efficient PL efficiencies because both singlet and triplet excitations are contributed to PL emission [26,27] and the emission color and emission efficiency can be tuned by changing the ligand identity or composition [28,29]. For example, tris(2-phenylpyridine) iridium(III) (Ir(ppy)₃³⁺) shows intense ECL at the maximum wavelength of 512 nm in the annihilation process [30]. Changing the main ligand to dfppy (dfppy = 2-(2,4-difluorophenyl) pyridine, Ir(dfppy)₃³⁺) can result in a blue shift with a maximum wavelength of 495 nm [31,32]. Various ancillary ligands, such as acetylacetonate, avobenzonate (avo) [21], 6-methylpicolinate, picolinamide, quinoxalinate [22], 2-(imidazol-2-yl)pyridine [33] and 2-picolinic acid [34] derivatives, have been synthesized and employed to get blue, yellow, green and red Ir(III) complexes. Although the ECL studies of iridium(III) complexes are currently undergoing a great development, the design and synthesis of new luminophores with distinct ECL emission colors and high efficiency are still needed for the application of iridium (III) ECL complexes in multichannel analytical applications [35].

Our research group has recently synthesized five iridium(III) complexes with green, orange and red efficient ECL emissions by changing the main and ancillary ligands [36]. Compared to the ECL efficiency of iridium(III) complexes with orange and red emissions, the ECL efficiency from iridium(III) complex with green emission is relatively low.

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With our interest in developing ECL multiple emitter in multichannel analytical applications, herein, a new green heteroleptic iridium(III) complex, $(dfppy)_2Ir(PyBiz)$, in which common cyclometalating ligand 2-(2,4-difluorophenyl)pyridine (*dfppy*) is used as the C^N main ligand while a novel ligand 2-(2-pyridyl)benzimidazolato-N,N' (*PyBiz*) is used as the N^N ancillary ligand, is synthesized and characterized. Its photophysical, electrochemical and ECL characteristics were evaluated. The possibility of the identification of $(dfppy)_2Ir(PyBiz)$ and typical $Ru(bpy)_3^{2+}$ in a single solution containing both compounds was also examined.

2. Experimental

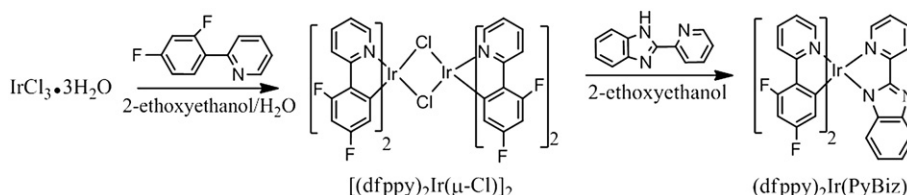
2.1. Chemicals

$IrCl_3 \cdot 3H_2O$, 2-(2-pyridyl)benzimidazolato-N,N' (*PyBiz*) and 2-(2,4-difluorophenyl)pyridine (*dfppy*) were purchased from J&K Chemical Ltd (China). 2-Ethoxyethanol, methanol, dichloromethane, ethyl acetate, and *tri-n*-propylamine (TPA) were obtained from Sinopharm Chemical Reagent Co., Ltd (China). Tris(2,2'-bipyridine) dichlororuthenium(II) hexahydrate ($Ru(bpy)_3^{2+}$), benzoyl peroxide (BPO), *tetra-n*-butylammonium hexafluorophosphate ($TBAPF_6$) and anhydrous acetonitrile (MeCN, 99.8%) were obtained from Sigma-Aldrich (St. Louis, MO).

2.2. Synthesis and characterization

The synthetic route of $(dfppy)_2Ir(PyBiz)$ is shown in Scheme 1. Typically two steps were employed for the synthesis of $(dfppy)_2Ir(PyBiz)$. Firstly, the chloride-bridged dimer $[(dfppy)_2Ir(\mu-Cl)]_2$ was synthesized according to reported procedures [37]. Secondly, the $(dfppy)_2Ir(PyBiz)$ was synthesized as follows. $[(dfppy)_2Ir(\mu-Cl)]_2$ (0.3063 g, 0.25 mmol), sodium carbonate (0.2125 g, 2.0 mmol) and 2.2 equivalent ancillary ligand were dissolved in 30 mL of 2-ethoxyethanol. After degassed, the reaction mixture was stirred for 15 h at 140 °C under nitrogen. The cooled crude mixture was then poured into 100 mL ethyl acetate and extracted with 50 mL water for three times to remove 2-ethoxyethanol. The product in organic phase was dried over anhydrous sodium sulfate. Silica column purification with a methanol:dichloromethane (v:v = 1:1) eluent was employed to obtain the pure product with a yield of 59% for $(dfppy)_2Ir(PyBiz)$.

1H NMR and ^{13}C NMR spectra were acquired on a Bruker Avance 400 MHz NMR spectrometer and a Bruker Avance 300 MHz NMR spectrometer. $\delta(CDCl_3) = 7.26$ ppm and $\delta(CDCl_3) = 77.0$ ppm were used as the internal standard solvent signals for 1H NMR and ^{13}C NMR, respectively. Mass spectra (MS) were acquired in ESI positive mode using a Bruker Maxis UHR-TOF Mass Spectrometer using methanol as mobile phase. Elemental analyses were performed on VarioEL III CHNS instrument. The final product was satisfactorily characterized by 1H , ^{13}C NMR spectroscopy (Figs. S-1 and S-2), mass spectrometry (Fig. S-3) and elemental analysis. Elemental analysis calculated (%) for $C_{34}H_{20}F_4IrN_5$: C 53.26, H 2.63, N 9.13; Found: C 52.57, H 3.15, N 8.81.



Scheme 1. The chemical structure and synthesis process of iridium complex $(dfppy)_2Ir(PyBiz)$. *dfppy* = 2-(4,6-difluorophenyl)pyridine; *PyBiz* = 2-(2-pyridyl)benzimidazolato-N,N'.

2.3. Apparatus

The absorbance and photoluminescence (PL) spectra were recorded on a UV-Vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan) and a Cary Eclipse fluorescence spectrophotometer (Varian, USA), respectively. All electrochemical experiments were carried out with a CHI 660 electrochemical workstation (Chenhua Instruments Co., Shanghai, China) and done under anhydrous conditions in an argon atmosphere glove box (MIKROUNA, China). The electrochemical investigations were similar with that in Ref. [38]. A typical three-electrode setup with a platinum disk working electrode (2.0 mm diameter), a Pt auxiliary electrode, and a quasi-reference silver wire electrode was used for electrochemical experiment. The area of the Pt disk electrode was 0.029 cm². Cyclic voltammetry (CV) potentials were calibrated with ferrocene as a standard, taking $E^0 = 0.342$ V vs. SCE.

2.4. ECL detection

The ECL transients and simultaneous CV and ECL measurements were recorded using a MPI-E ECL detector (Xi'an Remax Electronics, China). ECL spectra were recorded with a Princeton Instruments PyLon100BX CCD camera (Trenton, NJ) coupled with an Acton SP2300 monochromator cooled with liquid nitrogen to -120 °C. ECL images were obtained under dark room conditions using a Canon camera 770D EOS.

ECL quantum efficiencies were calculated according to the previous report: [39,40]

$$\varphi_{ECL} = \phi_{ECL}^s \left(\frac{I_x Q_s}{I_s Q_x} \right)$$

where Φ_{ECL}^s is the ECL efficiency of the standard; Q_s and Q_x are the faradaic charges (in Coulombs) measured during chronoamperometric experiments with the standard species and the investigated species; I_s and I_x are the integrated ECL intensity of the standard species and the investigated species, respectively.

3. Results and discussion

3.1. Photophysical and electrochemical properties of $(dfppy)_2Ir(PyBiz)$

Fig. 1 shows the UV-Vis absorption and PL spectra of $(dfppy)_2Ir(PyBiz)$ in MeCN solvent under air-saturated conditions with the corresponding pictures. The correspondingly spectroscopic data of $(dfppy)_2Ir(PyBiz)$ were summarized in Table S-1. It can be seen that $(dfppy)_2Ir(PyBiz)$ has strong intra-ligand absorption bands ($\pi-\pi^*$) in the UV region (212 nm, 242 nm, Fig. 1a), as typically observed for iridium complex [41]. The absorption wavelength at 347 nm with an extinction coefficient of 11.3×10^3 L·mol⁻¹·cm⁻¹ is assigned to the metal-to-ligand charge transfer transitions (MLCT).

$(dfppy)_2Ir(PyBiz)$ displays structureless green emission band with a maximum wavelength at 527 nm (Fig. 1b). The green photoluminescence is readily visible to the naked eyes using a UV light in solution. The emission spectrum of $(dfppy)_2Ir(PyBiz)$ was broad, evidence of the substantial MLCT character of the emitting

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