



Synthesis, characterization, photo- and electro-luminescent properties of blue cationic iridium complexes with nonconjugated bis(pyrazole-1-yl)methane as the ancillary ligand



Fuli Zhang^{a,*}, Weiling Li^b, Donghui Wei^c, Chunyang Li^a, Chen Pan^a, Xiaobin Dong^a, Zhongyi Li^a, Suzhi Li^a, Bin Wei^{b,**}, Fuqiang Zhang^a, Guangxiu Cao^a, Bin Zhai^{a,***}

^a College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, PR China

^b School of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China

^c College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450007, PR China

ARTICLE INFO

Article history:

Received 26 March 2016

Received in revised form

13 June 2016

Accepted 23 June 2016

Available online 24 June 2016

Keywords:

Organic light-emitting diode

Solution-processed

Cationic iridium complex

Blue light emission

Bis(pyrazole-1-yl)methane

ABSTRACT

Two new cationic iridium complexes with nonconjugated bis(pyrazole-1-yl)methane as the ancillary ligand have been prepared, and crystal structure, photophysical and electrochemical properties have been investigated. In degassed acetonitrile solutions, these complexes exhibit blue light emission with peaks at 456 and 453 nm, respectively. Both photophysical properties and quantum chemical calculations indicate that photoluminescence of these complexes are mainly from ligand-centered ${}^3\pi \rightarrow \pi^*$. Solution-processed organic light-emitting diodes based on these complexes exhibit blue light emission with the maximum current efficiencies of 7.34 and 5.36 cd A⁻¹, and maximum external quantum efficiencies of 4.06 and 2.66%, respectively.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Phosphorescent cationic iridium(III) complexes have received significant attention in recent years for their application in light-emitting electrochemical cells (LECs) [1–14] as they offer several advantages for good solubilities, high photoluminescence quantum yields (PLQYs), and tunable light emission color. LECs possess several merits such as very simple device architectures, being independent of the thickness of the active layer and being used with air-stable electrodes. However, LECs suffer from severe excited-state quenching in the active layers and slow response [15–18]. Such drawbacks in LECs can be significantly suppressed by doping the phosphors in polymer host materials as emissive layer as well as using extra functional layer in solution-processed OLEDs. Recently, tremendous progress has been made in the development

of green [19,20] and red [21–23] emitting cationic iridium complexes, but blue emitters are still an ongoing challenge [24]. In general, there are two approaches to obtain blue emission. One is to attach electron-withdrawing substituents to the phenyl groups of the cyclometalated ligands to stabilize the highest occupied molecular orbitals (HOMOs) [21,25,26] and the other is to attach electron-donating substituents to the ancillary ligands to destabilize the lowest unoccupied molecular orbitals (LUMOs) [27,28], thus can lead to a wider HOMO–LUMO gap. During the past few years, some blue-green to blue-emitting cationic iridium(III) complexes have been reported with pyrazole [29,30], imidazole [23], triazole [9,31] and imidazolium carbene [32,33] derivatives as ancillary ligands involving electron-donating atoms, which lead to the destabilized LUMOs and blueshifted emission spectra.

An additional strategy to obtain efficient blue emission is to use nonconjugated ancillary ligand containing high-field-strength moiety, in which the saturated nature of methylene could confine the electronic transition dipole around the dfppy (2-(2,4-difluorophenyl)pyridine), dfpbpy (2-(4,6-difluorophenyl)-4-*tert*-butylpyridine), fppz (5-(2-pyridyl)-3-trifluoromethylpyrazole) and fptz (3-trifluoromethyl-5-(2-pyridyl)-1,2,4-triazole) chromophores

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: zzu_zfl@126.com (F. Zhang), bwei@shu.edu.cn (B. Wei), zhaibin_1978@163.com (B. Zhai).

[34–37]. Adopting this method, De Cola, Ortí and Baranoff reported deep blue-emitting cationic bis-cyclometalated iridium(III) complexes with nonconjugated bis-imidazolium carbene and bis-pyrazole containing methylene as the ancillary ligand [38–40].

Moreover, we recently reported the syntheses, photo- and electro-luminescent properties of new cationic iridium(III) complexes with nonconjugated ancillary ligand 1-[(diphenylphosphino)methyl]-3-methylimidazolin-2-ylidene-C,C2' (dppmmi) [41]. As anticipated, density functional theory calculations based on these complexes show that the electronic transition dipole and emitting triplet state are mainly located on the high-energy cyclometalated chromophores, thus achieved blue to near-UV light emission. Along this line of research, we report here photo-physical and electrochemical properties of two new cationic iridium complexes $[\text{Ir}(\text{dfppy})_2(\text{cdpz})]\text{PF}_6$ (**1**) and $[\text{Ir}(\text{dfpmpy})_2(\text{cdpz})]\text{PF}_6$ (**2**) (Scheme 1), based on nonconjugated bis(pyrazole-1-yl)methane (cdpz) as the ancillary ligand. These complexes exhibit blue light emission with peaks at 456 and 453 nm, respectively, in degassed CH_3CN solutions, which significantly blueshift with respect to previously reported complex based on bis(pyrazole-1-yl)methane (477 nm) [40]. Solution-processed OLEDs were fabricated using these complexes as emitters.

2. Experimental

2.1. General experiments

All solvents and materials were used as received from commercial suppliers without further purification. Synthetic route of the two complexes are outlined in Scheme 1. Complexes $[\text{Ir}(\text{dfppy})_2(\text{cdpz})]\text{PF}_6$ (**1**) and $[\text{Ir}(\text{dfpmpy})_2(\text{cdpz})]\text{PF}_6$ (**2**) were prepared according to the literature [40]. All reactions were monitored using precoated thin-layer-chromatography plates (0.20 mm with fluorescent indicator UV254). ^1H NMR spectra were recorded on a Bruker DPX 400 NMR spectrometer with tetramethylsilane $[\text{Si}(\text{CH}_3)_4]$ as the internal standard. Mass spectrometry (MS) was performed with an Esquire-LC_00136 mass spectrometer. Elemental analysis for carbon, hydrogen, and nitrogen was determined on an Exeter Analytical CE-440 elemental analyzer. Absorption spectra were recorded with a UV–Vis spectrometer (Agilent Cary 60) and photoluminescent (PL) spectra were recorded with a fluoro spectrophotometer (Hitachi F-7000). PLQYs were

measured in CH_3CN solutions with quinine sulfate ($\phi = 0.545$ in 1 M H_2SO_4) [42] as the standards. The excited state lifetimes of the complexes were measured on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920) with a time-correlated single-photon counting technique. Cyclic voltammetry was performed on a CHI 820C electrochemical station (Shanghai Chenhua Co., China) in CH_3CN solutions (1×10^{-3} M) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with argon for 15 min before measurements.

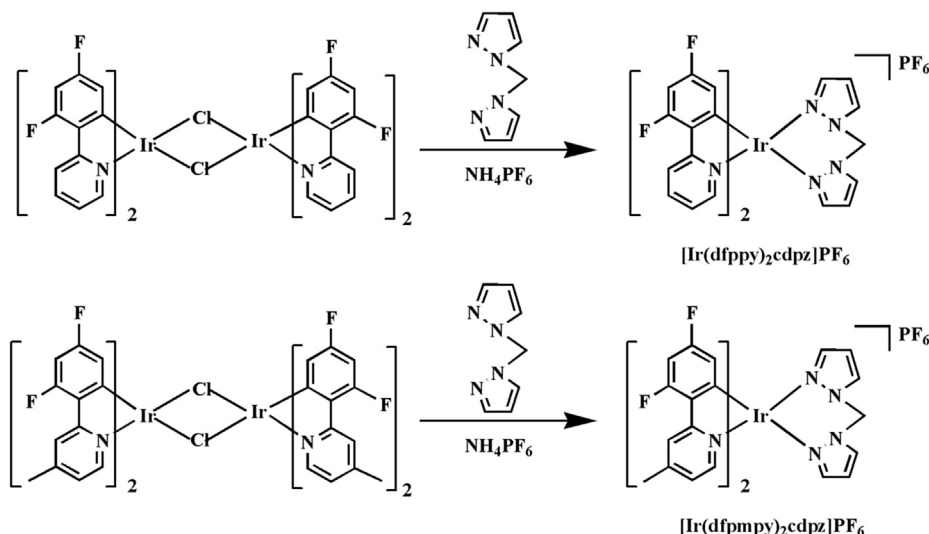
2.2. Syntheses

The ancillary ligand bis(pyrazole-1-yl)methane (cdpz) [43], complexes **1** and **2** [29] were synthesized from reported procedures. All reactions were performed under argon.

2.2.1. Synthesis and Structural Characterization of

$[\text{Ir}(\text{dfppy})_2(\text{cdpz})]\text{PF}_6$ (**1**)

The dichloro-bridged diiridium complex $[(\text{dfppy})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(\text{dfppy})_2]$ (0.35 g, 0.29 mmol) and cdpz ancillary ligand (0.09 g, 0.62 mmol) were dissolved in 2-methoxyethanol (10 mL). The mixture was then refluxed at 130°C for 12 h under an argon atmosphere. After cooling to room temperature, an aqueous solution of NH_4PF_6 (1.80 g in 20 mL deionized water) was slowly added into the reaction mixture under stirring, resulting in a yellow suspension. The suspension was then filtrated and the resulting precipitate was washed with deionized water and dried under vacuum at 70°C for 12 h. The crude product was purified by column chromatography on silica gel (200–300 mesh) with $\text{CH}_2\text{Cl}_2/\text{acetone}$ (20:1) as the eluent, yielding a yellow powder (0.34 g, 0.39 mmol). Yield: 67%. ^1H NMR (400 MHz, DMSO-*d*₆, δ): 8.32 (s, 4H), 8.11 (t, $J = 8.0$ Hz, 2H), 7.97 (s, 2H), 7.38 (dd, $J = 8.0$ Hz and 4.0 Hz, 2H), 7.04 (s, 2H), 6.94 (dd, $J = 8.0$ Hz and 12.0 Hz, 2H), 6.69 (s, 2H), 6.54 (s, 2H), 5.63 (d, $J = 8.0$ Hz, 2H). MS (MALDI-TOF) $[m/z]$: 721.4 ($\text{M} - \text{PF}_6$)⁺. Anal. found: C 40.28, H 2.35, N 9.68. Anal. Calcd for $\text{C}_{29}\text{H}_{20}\text{N}_6\text{PF}_{10}\text{Ir}$: C 40.24, H 2.33, N 9.71.



Scheme 1. The synthetic route of iridium complexes **1** and **2**.

Download English Version:

<https://daneshyari.com/en/article/175228>

Download Persian Version:

<https://daneshyari.com/article/175228>

[Daneshyari.com](https://daneshyari.com)