



# Red-light-emitting electrochemical cells based on cationic iridium complexes with phenanthroimidazole-type ancillary ligand

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## ARTICLE INFO

### Keywords:

Phenanthroimidazole  
Iridium complexes  
Red emission  
Self-quenching  
Electroluminescent properties

## ABSTRACT

Red-emitting cationic iridium complexes, namely,  $[\text{Ir}(\text{ppy})_2(\text{Qtpi})]\text{PF}_6$  (Complex 1) and  $[\text{Ir}(\text{piq})_2(\text{Qtpi})]\text{PF}_6$  (Complex 2) were synthesized using the ancillary ligand 2-(quinolin-2-yl)-1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Qtpi) and 2-phenylpyridine (Hppy) and 1-phenylisoquinoline (Hpiq) as cyclometalating ligands. In acetonitrile solution, Complex 1 emitted orange light, centered at 614 nm, whereas Complex 2 gave rise to orange-red emission centered at 603 and a shoulder peak at 630 nm. Extended  $\pi$ -conjugation on the phenylpyridine ligand in Complex 2 lowered the energy-gap, leading to a red-shift the emission compared to that of Complex 1. A light-emitting electrochemical cell (LEC) fabricated with Complex 1 emitted red light with an emission peak at 618 nm and Commission Internationale de L'Eclairage (CIE) coordinates of (0.59, 0.36), respectively, with corresponding values of 692 nm and (0.56, 0.28) for Complex 2. The LEC based on Complex 1 demonstrated superior performance, with a maximum luminance and current efficiency of 808  $\text{cd m}^{-2}$  and 0.73  $\text{cd A}^{-1}$ , respectively.

## 1. Introduction

Worldwide energy consumption has continued to escalate each year, wherein about 20% of the world's energy is utilized for lighting. To achieve energy-saving in lighting, it is very important to increase the efficiency of lighting devices in a sustainable way. Light-emitting electrochemical cells (LECs) are prominent lighting devices with simple device architecture: a luminescent emitter sandwiched between two metal electrodes (i.e. a reflective cathode and transparent anode) [1–4]. LECs are solution-processed solid-state lighting devices comprising a luminescent material in an ionic environment. The mobile ions in the active layer drift towards the relevant electrodes under an external bias and accumulate at the electrode interfaces, forming electrical double layers (EDLs); these EDLs facilitate the injection of holes and electrons from the anode and cathode, respectively. Since LEC devices are insensitive to the electrode work function, air-stable electrodes such as Au, Ag, or Al are used for their fabrication. This facilitates device fabrication under ambient conditions and precludes the requirements for

rigorous encapsulation. In contrast, multilayered organic light-emitting diodes (OLEDs) rely on air-sensitive charge injection layers and low-work-function electrodes and require device encapsulation, resulting in a high manufacturing cost, which hinders their widespread use in the lighting industry [5]. The above limitations of OLEDs have led to the concept of LECs as next-generation, low-cost, large-area devices for display and lighting applications that should circumvent the prevailing problems of OLEDs.

The luminescent materials used in LECs are based on either polymers (PLECs) [1] or ionic transition metal complexes (iTMCs-LECs) [6–12]. In PLECs, emissive conjugated polymers are mixed with an ion-conducting polymer and an inorganic salt to achieve ionic conductivity [1]. In the case of iTMCs-LECs, the use of an additional ion conducting material to drive the device is not a prerequisite as iTMCs are intrinsically ionic in nature. The first solid-state LECs utilizing iTMCs were reported in 1996, based on a ruthenium polypyridyl complex as the light-emitting material [13]. However, the inadequate color tuning of Ru complexes because of their low ligand-field splitting energies

**Abbreviations:** AFM, Atomic force microscopy; CT, charge transfer; DFT, density functional theory; EDLs, electrical double layers; EL, electroluminescence; Hppy, 2-phenylpyridine; Hpiq, 1-phenylisoquinoline; ITO, indium tin oxide; iTMCs, ionic transition metal complexes; LC, ligand-centered; <sup>1</sup>LLCT, ligand-to-ligand charge transfer; LEC, light-emitting electrochemical cell; LFSEs, ligand-field splitting energies; <sup>1</sup>MLCT, metal-to-ligand charge transfer; OLEDs, organic light-emitting diodes; PL, photoluminescence; PLQYs, photoluminescence quantum yields; PCM, polarizable continuum model; PLEC, polymer light-emitting electrochemical cell; Qtpi, 2-(quinolin-2-yl)-1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole; rms, root-mean-square; TBAPF<sub>6</sub>, tetrabutylammonium hexafluorophosphate; TGA, thermogravimetric analysis; TDDFT, time-dependent density functional theory

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<https://doi.org/10.1016/j.orgel.2017.12.035>

Received 21 October 2017; Received in revised form 14 December 2017; Accepted 22 December 2017

Available online 27 December 2017

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(LFSEs) limits their utility in display and lighting technologies that demand wider color tunability. In order to tune the emission colors, LECs based on the cationic iridium complex,  $[\text{Ir}(\text{ppy})_2(\text{dtb-bpy})]\text{PF}_6$  were first fabricated by Slinker et al. in 2004; these LECs emit in the yellow region of the visible spectrum with a peak brightness and power efficiency of  $300 \text{ cdm}^{-2}$  and  $10 \text{ lm W}^{-1}$ , respectively at 3 V [2]. Compared to other reported iTMCs, the cyclometalated Ir(III) complexes show outstanding properties due to their high metal oxidation states and the presence of strong-field anionic cyclometalating ligands (C'N) producing large LFSEs [14–16]. In addition, the strong spin–orbit coupling of iridium complexes enables efficient intersystem crossing between the triplet and singlet states, resulting in theoretical efficiencies of 100%. Moreover, color tuning of iridium complexes from blue to red can be achieved via chemical modification of the organic ligands. The aforementioned characteristics of iridium complexes can lead to high emission quantum yields, short excited-state lifetimes, and remarkable color tunability with excellent thermal and photochemical stabilities.

A large number of iridium complexes have been reported for LEC applications; however, red-emitting devices are scarce because most of the developed devices emit in the orange or orange-red spectral region [17,18]. However, red-emitting devices are crucial for the fabrication of white-light devices through additive color mixing, as well as for signaling applications [19–21]. Red-emitting iridium complexes are obtained via structural modification of both cyclometalating (C'N) and ancillary (N'N) ligands of the archetypal iridium complex,  $[\text{Ir}(\text{C}'\text{N})_2(\text{N}'\text{N})]\text{PF}_6$ . The addition of electron-donating groups to the phenyl ring of the C'N ligand or incorporation of electron-withdrawing substituents on the N'N ligand are potential strategies for shifting the emission to the red region [22,23]. The former causes destabilization of the highest occupied molecular orbital (HOMO) and the latter leads to stabilization of the lowest unoccupied molecular orbital (LUMO), thereby resulting in a narrow HOMO–LUMO energy gap. Increasing the delocalization of the  $\pi$  system of the C'N and N'N ligands also results in tuning of the iridium complex emission to the red spectral region [24,25]. In addition to the color tunability, stability of the iridium complex is also crucial for practical application. During device operation, the iridium complexes may experience severe excited-state self-quenching because the complexes are closely packed in the device architecture. The stability of iridium complexes can be enhanced by incorporating bulky substituents on ancillary ligands or by introducing  $\pi$ – $\pi$  interactions, thereby reducing both water-induced substitution reactions and non-radiative pathways, and hence can augment both the efficiency and lifetime of the devices [6,18,26,27].

Herein, we present an account of the synthesis and characterization of two new cationic iridium complexes, namely,  $[\text{Ir}(\text{ppy})_2(\text{Qtpi})]\text{PF}_6$  (Complex 1) and  $[\text{Ir}(\text{piq})_2(\text{Qtpi})]\text{PF}_6$  (Complex 2) using 2-(quinolin-2-yl)-1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Qtpi) as an ancillary ligand and 2-phenylpyridine (Hppy) and 1-phenylisoquinoline (Hpiq) as cyclometalating ligands for the fabrication of efficient red-emitting devices. The ancillary ligand Qtpi was chosen due to its remarkable photophysical properties, thermal stability, and balanced charge transport ability. The cationic iridium complexes (Complexes 1 and 2), synthesized using Qtpi, show orange emission (614 nm) and orange-red emission (603 and 630 nm), respectively, in acetonitrile solution. Cyclic voltammetric measurements were performed on both complexes and the results are supported by density functional theory (DFT) calculations. Complexes 1 and 2 were incorporated into LECs; these devices display red-shifted electroluminescence (EL) spectra compared to the PL spectra in solution. The red-emitting LECs based on Complex 1 and Complex 2 show peak current efficiencies of 0.73 and  $0.20 \text{ cd A}^{-1}$ , respectively. Moreover, the complexes show high stability with increasing voltage, which may be attributed to decreased intermolecular interaction and luminescence self-quenching due to the presence of the *N*-aryl group attached to the imidazole moiety of Qtpi. Based on the results, the use of phenanthroimidazole in iridium complexes is

anticipated to significantly contribute to the advancement of display and lighting technologies.

## 2. Materials and methods

### 2.1. Materials

All chemicals and reagents from commercial suppliers were used without further purification, including iridium(III) chloride hydrate (99.9%, Alfa Aesar), quinoline-2-carboxaldehyde (97%, Alfa Aesar), *p*-toluidine (> 99%, TCI), 9,10-phenanthrenequinone (95%, Sigma Aldrich), and ammonium acetate ( $\geq 98\%$ , Sigma Aldrich).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes in  $\text{CD}_2\text{Cl}_2$  were acquired on a Unity-Inova 500 MHz FT-NMR spectrometer with tetramethylsilane (TMS) as an internal standard (the *J* values are given in Hz). Elemental analyses were performed on an Elementar Vario EL CHN elemental analyzer. Electrospray ionization mass spectrometric (ESI-MS) analyses were conducted with an Agilent Q-TOF 6530 MS/MS system. The UV–visible absorption spectra of the complexes in acetonitrile solutions ( $10^{-5} \text{ M}$ ) were recorded at room temperature using an Agilent 8453 spectrophotometer. Photoluminescence (PL) emission spectra were recorded for both complexes in acetonitrile solutions ( $10^{-5} \text{ M}$ ) with an F-7000 FL spectrophotometer. The photoluminescence quantum yields (PLQYs) of the complexes in solution were measured with  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in water ( $\Phi_r = 0.04$ ) as the reference substance. Electrochemical measurements were performed in acetonitrile solution ( $10^{-3} \text{ M}$ ) using a potentiostat/galvanostat (Iviumstat) voltammetric analyzer at a scan rate of  $100 \text{ m V s}^{-1}$ . The electrolytic cell consisted of a glassy carbon electrode, platinum wire, and Ag/AgCl as the working, counter, and reference electrodes, respectively. Ferrocene was added as an internal standard and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile solution (0.1 M) served as the supporting electrolyte. The energy values of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), and the electrochemical bandgaps ( $E_g$ ) of the complexes were calculated using the empirical relation [28,29]:  $E_{\text{HOMO}} = [-e(E_{\text{ox}}(\text{vs. Ag/AgCl}) - E_{1/2}(\text{Fc}^+/\text{Fc vs. Ag/AgCl}))] - 4.8 \text{ eV}$ ,  $E_{\text{LUMO}} = [-e(E_{\text{red}} - E_{1/2})] - 4.8 \text{ eV}$  and  $E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$ . Here,  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the oxidation and reduction potentials respectively, whereas  $E_{1/2}(\text{Fc}^+/\text{Fc vs. Ag/AgCl})$  is the redox potential of ferrocene, which was found to be 0.43 V. The surface morphology of the films and their root-mean-square (rms) roughness were measured by atomic force microscopy (AFM; Hitachi High Tech Science NanoNavi/L-trace II). The films were prepared on an ITO/PEDOT:PSS surface by spin-coating the complexes from acetonitrile solution. The film formation process is explained in detail in Section 2.6. “LEC Device Fabrication and Characterization”.

### 2.2. Synthesis of 2-(quinolin-2-yl)-1-(*p*-tolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Qtpi)

The ancillary ligand Qtpi was synthesized according to the literature procedure [30–32]. Quinoline-2-carboxaldehyde (1.10 g, 7 mmol) and *p*-toluidine (0.75 g, 7 mmol) were dissolved in 15 mL of glacial acetic acid and stirred for 20 min at room temperature. 9,10-Phenanthrenequinone (1.46 g, 7 mmol) and ammonium acetate (539 g, 70 mmol) were added to the reaction mixture and refluxed under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was extracted with water and dichloromethane. The organic layer was then dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated under vacuum. The crude product was loaded onto a silica gel column and eluted with hexane/ethylacetate (9:1) to give the product as a yellow solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm): 8.92 (d, *J* = 7.91 Hz, 1H), 8.77 (d, *J* = 8.17 Hz, 1H), 8.71 (d, *J* = 8.15 Hz, 1H), 8.44 (d, *J* = 8.59 Hz, 1H), 8.18 (d, *J* = 8.61 Hz, 1H), 7.79–7.73 (m, 2H), 7.70–7.64 (m, 1H), 7.62–7.59 (m, 1H), 7.56–7.52 (m, 2H), 7.50–7.46 (m, 3H), 7.40 (d, *J* = 7.89 Hz, 2H), 7.35–7.27 (m, 2H), 2.59 (m, 3H).

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