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# Heteroleptic iridium(III) complex with *N*-heterocyclic carbene ligand: Synthesis, photophysics, theoretical calculations and electrochemiluminescence

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## ABSTRACT

A novel $\mathrm{C}_{(\mathrm{carbene})}\hat{}\mathrm{O}$ bidentate ancillary ligand has been designed and synthesized through an imidazolium bromide with carboxylic acid as a *N*-heterocyclic carbene (NHC) precursor, and further successfully been coordinated to iridium center for the first time in this work. Accordingly, a NHC-based iridium(III) complex has been synthesized and characterized by chemical structural (NMR, mass, UPLC purity, single crystal structure), photophysical, theoretical calculation, electrochemical and electrochemiluminescent (ECL) properties. Most importantly, five alkyl amines have been selected as co-reactants for ECL generation of this novel ECL luminophores and the relationships between ECL intensity and the co-reactant have been investigate by experimental results and theoretical calculations, which would be very important to exploit novel excellent co-reactants for the emerging iridium-based ECL luminophores in the future.

## 1. Introduction

Since the detailed ECL mechanism of tri-2,2’-bipyridylruthenium(II) [abbreviated as Ru(bpy)$_3^{2+}$] revealed by Bard and co-workers in the early 1970s [1,2], electrochemiluminescence (ECL), also named electrogenerated chemiluminescene, has been developed to be an powerful analytical technique in terms of sensitivity, dynamic concentration response range [3,4]. Due to the importance of luminophores in the luminescence-based analytical techniques, exploiting novel excellent ECL dyes is always the research hotspot in the ECL-related technologies [5–7].

Currently, except ruthenium(II) complexes, there has been a large number of non-ruthenium ECL dyes reported so far, such as europium [8], rhenium [9], copper [10], osmium [11], aluminum [12,13], terbium [14], platinum [15] and iridium [15–24]. In the non-ruthenium system, iridium(III) complexes received much attention [25–30] and are identified as the most competent candidates of the alternatives of Ru(bpy)$_3^{2+}$ due to their high quantum efficiencies, tunable emission colors. Our goup [23,24,31] and others [32–38] have focused on exploiting novel excellent ECL dyes comprising iridium(III) complexes.

After the successful isolation of a crystalline and stable carbene by Arduengo and co-workers in 1991 [39], *N*-heterocyclic carbene (NHC) derived from the deprotonation of imidazolium salts has attracted much attentions as coordination ligands in organometallic chemistry [40]. Due to NHC's strong coordination abilities to transition metals, a large number of NHC-based transition-metal complexes, such as ruthenium [41], gold [42,43], silver [44], rhenium [45], platinum [46,47], copper [48] etc., have been designed and synthesized. Beyond their traditional applications in catalytic chemistry, luminescence and related functional materials have also become emerging research focuses for NHC-based organometallic complexes [49]. Since the pioneering work about NHC-based iridium(III) complexes as dopants of organic light emitting diodes (OLEDs) reported by Sajoto et al., [50] the synthetic methods [51] and novel applications [52] about luminescent iridium(III) complexes containing NHC ligands have been gradually revealed. From then on, more and more kinds of NHC ligands have been designed and incorporated into iridium complexes, which have displayed excellent properties in related areas, such as OLEDs [53–55] and bio-imaging [52]. However, as a family of relatively new luminescent complexes with increasing importance, the studies about ECL properties of the NHC-based iridium complexes

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are still very rare until now [56].

Herein, *N*-methyl-N'-(acetic acid)imidazolium bromide as a novel NHC precursor has been designed and successfully synthesized. Furthermore, one NHC-based iridium(III) complexes with $C_{(carbene)}$ˆO bidentate ancillary ligand has also been synthesized through metal transfer reaction between silver and iridium(III) in this work (as shown in Scheme 1). Beside the characterization of chemical structure, the photoluminescent and electrochemiluminescent properties of this novel NHC-based iridium(III) complex have been comprehensively investigated in this work. Most importantly, the relationship between ECL performance and co-reactant are also thoroughly investigated based on experimental results and theoretical calculations in this study, which would be very helpful to develop efficient coreactant assisted ECL system for the emerging iridium-based ECL luminophores in the future.

## 2. Results and discussions

### 2.1. Synthesis and characterization

Due to the unique nature of carbene, including electronic effect and steric effect [57], it's usually hard to find a general method to synthesize the NHC-based iridium complexes after reviewing the literature reported so far [50,51,53,56,58,59]. In this work, CˆO bidentate ligand as a novel NHC-based ancillary ligand is coordinated to iridium(III) center and the corresponding NHC-based iridium(III) complex (abbreviated as **Irppyimac** in this work) has been successfully synthesized through two major steps as shown in Scheme 1. The first step mainly involved the synthesis of two critical intermediates, i.e. iridium(III) dichlorobridged dimer and silver carbene. For the intermediate of iridium(III) dichlorobridged dimer, the synthetic method is well-established [60,61] and there is no need to discuss further. However, it should be noted the synthesis of Ag carbene. According to Scheme 1, the quaternary ammonium reaction between 1-methyl-1H-imidazole and 2-bromoacetic acid was employed to synthesize the imidazolium bromide as NHC precursor. Subsequently, Ag carbene was formed by the reaction between this precursor with silver oxide in dichloromethane solution with nitrogen atmosphere protecting from light [62]. Without purification, Ag carbene was directly used to react with iridium(III) dichlorobridged dimer and the final NHC-based iridium(III) complex was generated through metal transfer reaction in base condition as shown in Scheme 1. The chemical structure of this novel NHC-based iridium complex is characterized by NMR and mass spectra, the purity is up to 99% according to UPLC spectra (Figure S3 in supplementary material). Furthermore, the single crystal structure of this complex has also been obtained from the mixture solution of methanol and dichloromethane and shown in Fig. 1.

The critical bond lengths and angles of **Irppyimac** have also been listed in Table 1. Notably, the bond length between carbene carbon and iridium atom (Ir(1)-C(3) in Table 1 and Fig. 1) is a little longer than that between general carbon (non-carbene) and iridium atom (such as Ir(1)-C(18) and Ir(1)-C(7) in Table 1 and Fig. 1). According to Fig. 1 and Table 1, two coordinated nitrogen atoms in the main ligands (N(4) and N(3)) are in the *trans* position and the bond angle of N(4)-Ir(1)-N(3) are nearly to 180°, while the coordinated carbon atoms in the main ligand (C(18) and C(7)) are in the *cis* position and the bond angle of C(18)-Ir(1)-C(7) is close to 90°. Furthermore, two bond angles between main ligand and central iridium atom (C(18)-Ir(1)-N(4) and C(7)-Ir(1)-N(3) in Table 1 and Fig. 1) are nearly identical to each other, while they are

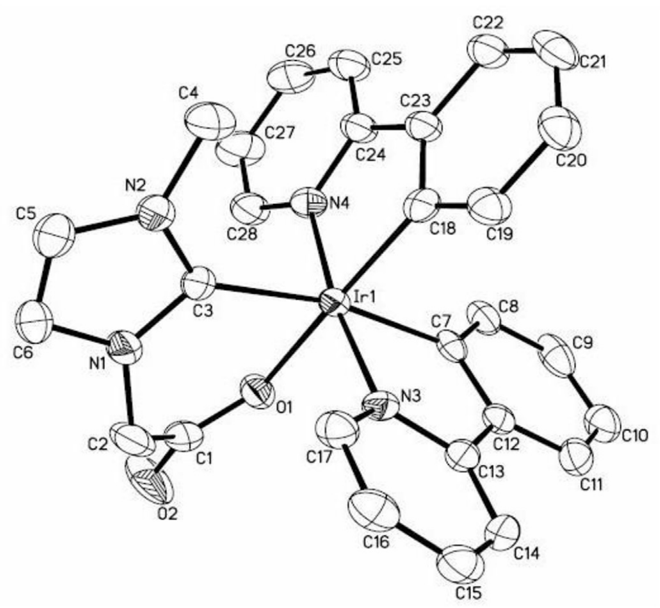
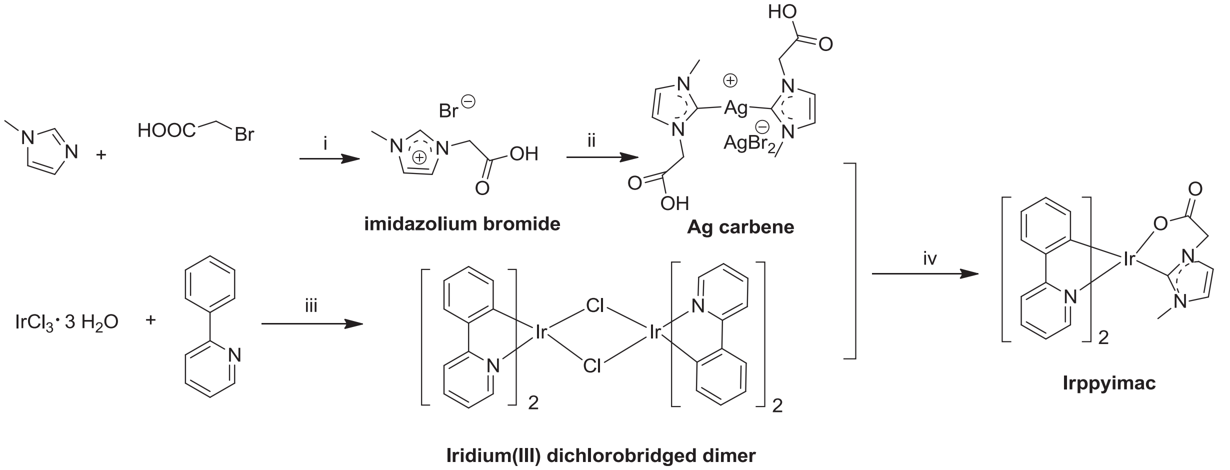


**Fig. 1.** Crystal structure of **Irppyimac**. The hydrogen atoms are omitted for clarity.



**Scheme 1.** The synthetic routes of iridium(III) complex used in this work. i: $CH_3CN$, reflux, 24 h, $N_2$; ii: $Ag_2O$, $CH_2Cl_2$, reflux, 12 h, $N_2$, in dark; iii, 2-ethoxyethanol/$H_2O$(v:v = 3:1), reflux, 24 h, $N_2$; iv: xylenes, $K_2CO_3$, 24 h, $N_2$, in dark.