Dyes and Pigments 112 (2015) 1–7

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Ionic iridium complexes with conjugated phenyl substituent: Synthesis and DFT calculation on the electrochemical and electrochemiluminescent properties

Tongtong Li, Malin Cui, Guoxia Ran, Qijun Song*

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China

A R T I C L E I N F O

Article history:
Received 9 May 2014
Received in revised form
8 June 2014
Accepted 14 June 2014
Available online 21 June 2014

Keywords:
Iridium complex
Photoluminescence (PL)
Density functional theory (DFT)
Electrochemistry
Electrochemiluminescence (ECL)
Quantum yield

A B S T R A C T

Two ionic iridium complexes, $(bpq)_2Ir(bpy)^+PF_6^-$ (**1**) and $(bpq-OCH_3)_2Ir(bpy)^+PF_6^-$ (**2**), where bpq is 6-methyl-2,4-diphenyl quinolone anion, bpy is 2,2′-bipyridine, were synthesized and structurally characterized. Their photophysical, electrochemical and electrochemiluminescence properties were investigated. With the conjugated phenyl substitution, the $\pi-\pi$ ligand center transitions in the emission process were enhanced, resulting in a broad and strong photoluminescence emission. The photoluminescence quantum yields were measured to be 0.214, 0.209, respectively for complex **1** and **2**. The complex **1** also exhibited greater electrochemiluminescence efficiency than the complex **2**. To further elucidate the influence of different structures on the electrochemical and electrochemiluminescence properties, the density functional theory calculations were performed on the complexes **1**, **2** along with other four well documented bis-cyclometalated iridium complexes. The calculation revealed that about 90% electronic density in the lowest unoccupied molecular orbital were distributed in N^N auxiliary ligand for ionic complexes, whereas most electronic density were distributed in C^N main ligand for neutral complexes.

1. Introduction

Iridium(III) cyclometalated complexes have been the subject of a growing interest to wide scientific community due to their unique photophysical and electrochemical properties [1,2]. The air-stable cyclometalated iridium complexes exhibited long excited-state lifetimes, high emission efficiency and reversible electrochemical properties at room temperature, making them promising materials for electricity-to-light conversion [3–5]. Many applications for which ruthenium(II) α-diimine complexes were used in the past have in the meantime been implemented with cyclometalated iridium(III) species. Examples include iridium-based oxygen sensors [6], luminescent DNA intercalators [7], sensitizers for photocatalytic water splitting [8a,b,c], dye-sensitized solar cells [9], and electroluminescent devices [10]. It is known that the lowest-lying excited state of many cyclometalated iridium(III) complexes is not a pure metal-to-ligand charge-transfer (MLCT) state, as is the case for $[Ru(bpy)_3^{2+}]$ type complexes [11–13], which could result in different photoredox behaviors.

Iridium complexes may be divided into two categories: ionic and neutral complex. Although many neutral Iridium(III) complexes have been demonstrated to display high electrochemiluminescence (ECL) efficiencies in organic solutions usually with a degree of efficiency much higher than $[Ru(bpy)_3^{2+}]$, their applicative field was often restricted by their very poor water-solubility and lack of active groups for biological labeling [14]. More recently, Chen et al. proved that an ionic iridium(III) complex with an appended sugar also displayed a strong ECL signal, which prompted us to design ionic iridium(III) complexes and further apply it to the ECL sensor fabrications [15]. Due to their ionic character, the ionic iridium(III) complexes show good solubility in polar solvent [16]. Recently an ECL reagent with carboxyl substituted ancillary ligand, $[(ppy)_2Ir(dcbpy)]^+PF_6^-$ was prepared. Its UV–vis absorption, photoluminescence (PL), and ECL characteristics were explored and probable mechanisms were speculated [17]. Also, the emission colors of ionic iridium complexes and the ECL efficiencies can be tuned by modulating the ligands [18]. In this context, heteroleptic iridium complexes $[Ir(CN)_2(LX)]$ are very promising luminophors, because in addition to their easy synthetic

---

* Corresponding author. Tel.: +86 510 85700165; fax: +86 510 85917763.
E-mail address: qsong@jiangnan.edu.cn (Q. Song).

http://dx.doi.org/10.1016/j.dyepig.2014.06.018
0143-7208/

accessibility compared with the corresponding homoleptic $[Ir(CN)_3]$ materials, they allow fine-tuning of the emission color by appropriate design of the chemical structure of the neutral cyclometalating ligands CN, the most common one being 2-phenylpyridine (ppy), or by systematic control of the nature and position of substituents on these ligands. The emission energies of the neutral $[Ir(CN)_2(LX)]$ complexes are mainly determined by both CN ligand and metal based orbitals, whereas the nature of the ancillary LX ligand plays, with few exceptions, a secondary role in tuning the photophysical properties [19]. The introduction of electron-donating substituents and π–π conjugation structure to the main ligands represents a convenient structural modification that leads to $[Ir(CN)_2(LX)]$ complexes with red shifted absorption.

To further explore the effect of the increased π-delocalization of phenylquinoline ligand on the ionic iridium, the $(bpq)_2Ir(bpy)^+PF_6^-$ (**1**) and $(bpq-OCH_3)_2Ir(bpy)+PF_6^-$ (**2**) were synthesized and their crystal structure, the electrochemical and ECL properties as well as photophysical properties were investigated. The density functional theory (DFT) studies were also carried out to further elucidate the relationship between the photophysical properties and the structures of the ionic iridium complexes [20–22]. In this respect, six bis-cyclometalated iridium(III) complexes, which are respectively ionic and neutral iridium complexes with different ligands, are selected. It is hoped that a better understanding of the structure–property relationship could facilitate the selection and design of novel cyclometalated iridium^{III} complexes with improved ECL efficiencies.

2. Experimental

2.1. Chemicals

Tris(2,2-bipyridine) ruthenium(II) dichloride hexahydrate was purchased from Sigma. 2-(Dibutylamino) ethanol (DBAE, 99%) was purchased from Aldrich. 2,2′-Bipyridine($C_{10}H_8N_2$, 99%), lithium perchlorate($LiClO_4$, 99%) and ammonium hexafluorophosphate(NH_4PF_6, 99.4%) were purchased from J&K Scientific Ltd. The CH_3CN (99.95%, HPLC grade), CH_3OH (99.5%, AR grade), $CHCl_3$(99.5%, AR grade), nC_6H_{14}(99.5%, AR grade) and the CH_2Cl_2 (99.5%, AR grade) were purchased from Sinopharm Chemical Reagent Co. Ltd. The chloro-bridged dimer $(bpq)_2Ir(\mu\text{-}Cl)_2Ir(bpq)_2$ and $(bpq\text{-}OCH_3)_2Ir(\mu\text{-}Cl)_2Ir(bpq\text{-}OCH_3)_2$ were synthesized previously by our research group [23].

2.2. Instruments

IR spectra were recorded on a FTLA2000 spectrometer by dispersing samples in potassium bromide. NMR spectra were collected on a Bruker ACF-400 spectrometer with deuterated chloroform as solvent and tetramethylsilane as internal standard. Absorption spectra were measured using a UV/Vis spectrophotometer (Model TU-1901). X-ray data for compounds **2** was collected using a Bruker SMART APEX II CCD area detector using monochromated Mo KR radiation ($\lambda = 0.71073$ Å). Crystal data of **2** was measured at 293(2) K. Fluorescence measurements were conducted on a RF-5301PC spectrofluorimeter. The electrochemical study was performed in CH_3CN under N_2 condition with a model CHI 660D electrochemical workstation. A glassy carbon electrode (4 mm in diameter) was used as the working electrode and a platinum wire was used as the counter electrode. The glassy carbon electrode instead of noble metallic electrode was chosen as the working electrode because the growth of anodic oxide films at the platinum or the gold electrode could inhibit the direct oxidation of co-reactant [24]. The electrochemical potentials were referenced to an Ag/Ag^+ electrode (0.01 mol/L $AgNO_3$ and 0.1 mol/L $TBAPF_6$ in CH_3CN). All potential values were calibrated against the saturated calomel electrode (SCE) by measuring the oxidation potential of 5 mmol/L ferrocene (vs. Ag/Ag^+) as a standard ($EFc^+/Fc = 0.424$ V vs. SCE) [25]. The ECL measurements were conducted with a conventional three-electrode setup on the MPI-E ECL analyzer. A voltage of −600 V was supplied to the photomultiplier tube. The ECL experiments were performed at room temperature in CH_3CN by using lithium perchlorate as the supporting electrolyte.

2.3. Theoretical calculations

The iridium complexes **1**–**6** were optimized by the DFT with Becke's three-parameter functional and the Lee–Yang–Parr functional (B3LYP). A 6-31G* basis set was implemented for C, H, O and N atoms, whereas the LANL2DZ basis set was employed for Ir atom. All of the calculations were performed using the Gaussian 03 software package [26]. The optimized geometries were confirmed to be potential energy minima by vibrational frequency calculation in the presence of only real frequencies [27].

3. Results and discussion

3.1. Synthesis of the ionic iridium complexes with different ligands

The complexes of **1** and **2** were prepared via a procedure similar to that described elsewhere [28a,b]. A typical procedure for the synthesis of complex **2** was depicted in Scheme 1.

2,2′-Bipyridine (24.8 mg) was dissolved in CH_2Cl_2 (4 mL) and added to a suspension of $(bpq\text{-}OCH_3)_2Ir(\mu\text{-}Cl)_2Ir(bpq\text{-}OCH_3)_2$ (122.5 mg) in CH_3OH(5 mL). The solution was refluxed with continuous stirring for 3 h. After completion of the reaction, an excess of NH_4PF_6 was added and the solution was stirred for 2 h. The solution was then evaporated to dryness under reduced pressure, after which the residue was repeatedly washed with pure water. And then the orange precipitation was dried under vacuum to afford the orange crude product, which was further recrystallized in $CHCl_3/nC_6H_{14}$, and the orange crystalline product **2** was obtained in 73% yield (116.6 mg). The structure of **2**, characterized by X-ray diffraction, was shown in Fig. 1.

3.1.1. Synthesis of $(bpq)_2Ir(bpy)^+PF_6^-$

Orange crystal, yield 107.5 mg (71%). The typical procedure for the synthesis of $(bpq)_2Ir(bpy)^+PF_6^-$ along with the NMR spectra (Figs. S1 and S2) were provided in Supporting information. IR (KBr):νbar = 2925, 2375, 2025, 1634, 1536, 1439, 1379, 1124, 1034, 850, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.37$ (d, $J = 8.1$ Hz, 2H), 8.18 (d, $J = 5.3$ Hz, 2H), 8.15–7.93 (m, 6H), 8.00–7.92(d, 2H), 7.70–7.52 (m, $J = 7.6$ Hz, 10H), 7.52–7.49(s, $J = 5.3$ Hz, 2H), 7.48–7.34 (t, 2H), 7.30–7.2 (t, $J = 4.5$ Hz, 6H), 7.18–7.10(t, $J = 7.5$ Hz, 2H), 6.93–6.75 (m, 4H), 6.70–6.60 (d, $J = 7.6$ Hz, 4H), 2.27 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 167.96$, 155.76, 151.28, 150.70, 147.32, 146.34, 145.83, 139.81, 137.35, 136.82, 134.76, 132.96, 130.60, 129.43, 128.94, 127.35, 126.53, 126.28, 124.88, 122.88, 117.6, 77.28, 77.02, 76.71, 21.19 ppm.

3.2. The photophysical properties of ionic iridium complex **1**–**2**

The photophysical properties of ionic complexes **1**–**2** were shown in Fig. 2. The maximum absorption wavelengths of the complexes **1**–**2** were observed at 289 nm and 302 nm, respectively in Fig. 2(a) and (b). The red shift in maximum absorption wavelength of complex **2** could be attributed to the incorporation of the methoxy group to phenyl group of the main ligand. The intense bands from 280 to 320 nm in the ultraviolet part of the absorption spectra can be assigned to the spin-allowed ligand-centered π–π*