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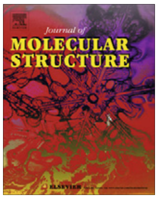

Enhanced quantum efficiency of cationic iridium(III) complexes with carbazole moiety as a steric hindrance unit

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HIGHLIGHTS

- ▶ Designed and synthesized two cationic iridium(III) complexes with different degrees of steric hindrance.
- ▶ The electronic natures of excited state have not been changed compared with those of model complex.
- ▶ Carbazole moieties as steric hindrance units effectively reduce the intermolecular interaction.
- ▶ These two complexes have potential applications in electroluminescent devices.

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ABSTRACT

Two cationic iridium(III) complexes with different degrees of steric hindrance, namely, $[Ir(L1)_2(bpy)]PF_6$ (**1**) and $[Ir(L2)_2(bpy)]PF_6$ (**2**) (where HL1, HL2 and bpy ligands are 1,2-diphenylbenzo[d]imidazole, 9-(4-(2-phenylbenzo[d]imidazol-1-yl)phenyl)-9H-carbazole and 2,2′-bipyridine, respectively), have been designed and synthesized. Photoluminescence measurements show that the photoluminescence quantum yield of complex **2** with the introduction of carbazole moieties as steric hindrance units is up to 36% in the neat film, which is obviously higher than that (27%) of the model complex **1**. On basis of the quantum calculations and photophysical data, we conclude that the carbazole moieties effectively reduce the intermolecular interaction by enhancing the steric hindrance of the complex, which inhibits the quenching process without altering the nature of the excited-state. In addition, the results of thermogravimetric analysis (TGA) and cyclic voltammetry (CV) measurements reveal that complexes **1** and **2** have potential applications in electroluminescent devices.

1. Introduction

Phosphorescent transition-metal complexes are under intense investigation due to their potential applications, such as reagents for biological labeling [1–3], oxygen sensing, photocatalytic hydrogen production, chemosensors for inorganic ions [4–6], and so on. Of those, phosphorescent iridium(III) complexes are particularly important and often used to fabricate organic light-emitting diodes (OLEDs) [7] and light-emitting electrochemical cells (LECs) [8–10] as they exhibit high luminescence efficiency, relatively long excited-state lifetimes and tunable light emission color [8–10]. Typically, the iridium(III) complexes can be divided into neutral iridium(III) complexes and cationic iridium(III) complexes. The neutral complexes containing cyclometalated ligands and anionic ligands [11] have been extensively studied until now [8–10]. At the same time, the number of researchers relying on cationic iridium(III) complexes containing bidentate ligands (e.g., bipyridine and phenanthroline derivatives) is constantly increasing because of their rich photophysical properties, ionic character, good solubility in polar solvents and even in aqueous media [8,12–14]. Moreover, the cationic iridium(III) complexes could be synthesized under mild conditions compared with the neutral ones. The electroluminescence devices based on cationic iridium(III) complexes, namely, LECs, possess several advantages over conventional OLEDs, such as the simple device architecture, low turn-on voltage and independence of the work function. Up to now, Ir(III)-based LECs with different emission colors, including red–, yellow–, green–, blue–green as well as white emitting, have been developed since one LEC based on cationic iridium(III) complex was reported [15].

However, the excited-state self-quenching associated with triplet–triplet annihilation always happens due to the strong interactions between closely packed molecules, which hinders the development of the widespread applications of iridium(III) complexes in the high-efficient and stable devices. Many efforts have been devoted to overcome the issue in neutral iridium(III) complexes via attaching enhanced steric hindrance or bulky side groups

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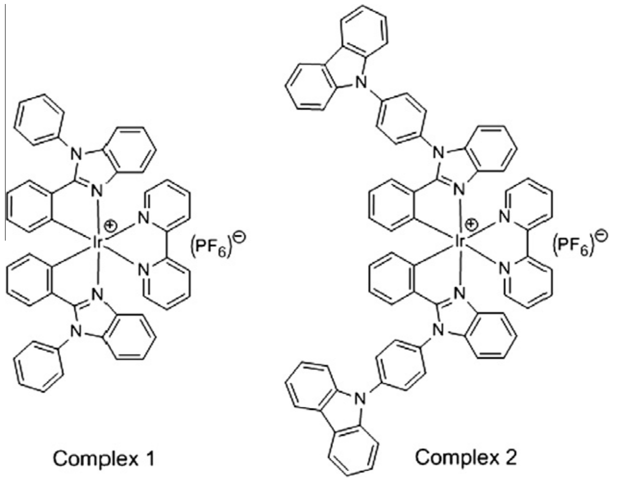

Scheme 1. Chemical structures of complexes **1** and **2**.

into the complexes to separate the emissive cores [16–19]. However, there are only a limited number of approaches to developing highly efficient cationic iridium(III) complexes using steric hindrance ligands [20–25]. It can be seen that attention is mainly paid to improvement of the efficiency of cationic iridium(III) complexes through the introduction of steric hindrance units to ancillary ligands of the complexes. Nevertheless, the reports concerning the design and preparation of highly efficient cationic iridium(III) complexes with a certain degree of steric hindrance of cyclometalated ligands are rare [22,23,26].

Guided by above situations, in this paper, we report a systematic design and synthesis of two cationic iridium(III) complexes with different degrees of steric hindrance, namely, $[Ir(L1)_2(bpy)]PF_6$ (**1**) and $[Ir(L2)_2(bpy)]PF_6$ (**2**). Herein, the HL1, HL2 and bpy ligands are 1,2-diphenylbenzo[d]imidazole, 9-(4-(2-phenylbenzo[d]imidazol-1-yl)phenyl)-9H-carbazole and 2,2′-bipyridine, respectively. The chemical structures of complexes **1** and **2** are shown in Scheme 1. The photophysical results indicate that the photoluminescence quantum yield (PLQY) of complex **2** in the neat film can be improved to some extent by introducing carbazole moieties as steric hindrance units into complex **1**. The excited-state properties of **1** and **2** were also investigated by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Meanwhile, the results of thermogravimetric analysis (TGA) and cyclic voltammetry (CV) measurements reveal that **1** and **2** show good thermal stability properties and excellent stability against electrochemical oxidation and reduction, which is important for their applications in electroluminescent devices.

2. Experimental section

2.1. Materials and physical measurements

All experiments were performed under a nitrogen atmosphere by using commercially available anhydrous solvents or solvents that were well treated with an appropriate drying reagent. ^1H NMR spectra were measured on Bruker Avance 500 MHz spectrometer with tetramethylsilane as the internal standard. The thermogravimetric analyses were performed on a Perkin–Elmer TG-7 analyzer heated from 30 to 800 °C in flowing nitrogen. Complexes **1** and **2** were verified through using matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry. UV–vis absorption spectra were recorded on U3010 spectrometer (Hitachi, Japan). The emission spectra of these two complexes were recorded on a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. The photoluminescence quantum yields (PLQYs) in neat film were measured with an integrating sphere in a fluorospectrophotometer. The excited-state lifetimes of the complexes were measured on a transient spectrofluorimeter (Edinburgh FLSP920) using time-correlated single-photon counting technique.

2.2. Synthesis

2.2.1. $[Ir(L1)_2(bpy)]PF_6$ (**1**)

A solution of ligand bpy (0.16 g, 1.03 mmol) and the dichloro-bridged diiridium complex $[Ir(L1)_2Cl]_2$ (0.74 g, 0.48 mmol) in dichloromethane (10 mL) and methanol (5 mL) was refluxed for 24 h in the dark. After cooling to room temperature, the mixture was filtrated, and then an excess of solid KPF_6 was added and stirred for another 0.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using dichloromethane and ethyl acetate (5:1) as eluent to yield complex **1** as an orange powder (70%). ^1H NMR (500 MHz, d_6–DMSO, δ [ppm]): 8.92 (d, *J* = 8 Hz, 2H), 8.35 (t, *J* = 7.5 Hz, 2H), 8.21 (d, *J* = 5 Hz, 2H), 7.80–7.85 (m, 10H), 7.67–7.68 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8 Hz, 2H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.84 (t, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.5 Hz, 2H), 6.58 (d, *J* = 8 Hz, 2H), 6.43 (d, *J* = 7.5 Hz, 2H), 5.69 (d, *J* = 8.5 Hz, 2H). MS (MALDI-TOF): *m*/*z* 887.2 ($M–PF_6$).

2.2.2. $[Ir(L2)_2(bpy)]PF_6$ (**2**)

The synthesis of complex **2** was similar to that of complex **1** except that the cyclometalated ligand L1 was replaced by L2. The crude product was also purified by silica gel column chromatography using dichloromethane and ethyl acetate (5:1) as eluent to yield complex **2** as an orange powder (61%). ^1H NMR (500 MHz, d_6–DMSO, δ [ppm]): 8.96 (d, *J* = 8 Hz, 2H), 8.40 (t, *J* = 7.8 Hz, 2H), 8.28–8.33 (m, 6H), 8.08–8.10 (m, 6H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.87 (t, *J* = 6.8 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 4H), 7.54 (t, *J* = 7.5 Hz, 4H), 7.32–7.40 (m, 8H), 7.09 (t, *J* = 7.8 Hz, 2H), 6.89–6.92 (m, 6H), 6.54–6.55 (m, 2H), 5.75 (d, *J* = 8 Hz, 2H). MS (MALDI-TOF): *m*/*z* 1217.3 ($M–PF_6$).

2.3. X-ray crystallography

The single-crystal X-ray diffraction data for complexes **1** and **2** were collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 293(2) K. Absorption correction was applied by using multi-scan technique. The structures of **1** and **2** were solved by Direct Method of SHELXS-97 and refined by full-matrix least-square techniques using the SHELXL-97 program [27]. Metal atoms in **1** and **2** were located from the E-maps and non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms were calculated in ideal geometries. The detailed crystallographic data and structure refinement parameters are summarized in Table S1. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 871256 (**1**) and 871257 (**2**) contain the supplementary crystallographic data for this paper.

2.4. Electrochemical measurements

Cyclic voltammetry was performed on a BAS 100 W instrument with a scan rate of 100 mV s^{-1} in CH_3CN (10^{-3} M) with the three-electrode configuration: a glassy carbon electrode as the working electrode, an aqueous saturated calomel electrode as the operating reference electrode and a platinum wire as the counter electrode. A