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Efficient greenish-blue phosphorescent iridium(III) complexes containing carbene and triazole chromophores for organic light-emitting diodes

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ABSTRACT

Two heteroleptic iridium(III) complexes using carbene as cyclometalated ligands and pyridine-triazole as ancillary ligand, namely **(fpmi)$_2$Ir(mtzpy)** (**1**) and **(fpmi)$_2$Ir(phtzpy)** (**2**) [**fpmi** = 1-(4-fluorophenyl)-3-methylimdazolin-2-ylidene-C,C$^{2'}$, **mtzpy** = 2-(5-methyl-2*H*-1,2,4-triazol-3-yl)pyridine, **phtzpy** = 2-(5-phenyl-2*H*-1,2,4-triazol-3-yl)pyridine], were synthesized and their structural, photophysical and electrochemical properties investigated systematically. Both complexes exhibit bright greenish-blue phosphorescence (λ_{max} ~490 nm) with quantum yields of about 0.50. Comprehensive density functional theory (DFT) approach was then performed to gain insights into their photophysical and electrochemical characters. The fabrication of organic light-emitting diodes (OLEDs), employing complexes **1** and **2** as phosphorescent dopants, was successfully achieved. Among them, the device based on **1** exhibited considerable power efficiency (η_p) of 11.43 lm W^{-1} and current efficiency (η_c) of 11.78 cd A^{-1}. With the merit of intrinsic characteristic of complex **1**, a white OLED comprised of **1** and one orange phosphor **(pbi)$_2$Ir(biq)** achieved a peak η_p of 9.95 lm W^{-1} and η_c of 10.81 cd A^{-1}, together with Commission Internationale de l'Eclairage (CIE) coordinates of (0.34, 0.40). The results indicate that two iridium(III) complexes reported here are promising phosphorescent dyes for OLEDs.

1. Introduction

Solid-state luminescent materials have attracted great attention due to their enormous potential applications in organic light-emitting diodes (OLEDs) and other optoelectronic material technology [1–7]. In OLEDs, recombination of electrons and holes in emitting layer gives rise to the formation of 25% singlet excitons and 75% triplet ones. For conventional fluorescent OLEDs, however, the 75% triplet excitons are usually lost due to the forbidden transition from the triplet to the ground state during electroluminescence process. To achieve high electroluminescence efficiency, efficient luminescent materials that can harness both singlet excitons and the spin-forbidden triplet excitons are highly desired. Since the pioneering electrophosphorescence works of Forrest and Ma et al. in 1998 [8,9], intensive efforts have been carried out to design and synthesize phosphorescent materials for highly efficient OLEDs. The readily available, Ru(II)- [10–13], Os(II)- [14,15], Cu(I)- [16–19], Pt(II)- [18,20–27] and Ir(III)- [28–40] based phosphorescent complexes can give effective harvesting of both singlet and triplet excitons endowed by heavy-atom spin-orbit coupling (SOC), achieving nearly 100% internal quantum efficiencies in theory [1,8,41]. In particular, iridium(III) complexes displaying high quantum yields, broad range of emission colors, excellent optical- and thermal-stabilities, as well as short excited-state lifetimes have been regarded as appealing phosphors for optical devices [4,34]. To date, efficient red- and green-emitting iridium(III) complexes have been well developed through ingenious ligands modification [18,42–44]. Despite these advances in display technology, the development of stable phosphorescent materials with wide band gap, which is essential for solid-state lighting and flat panel displays, remains elusive and still challenge [45–50].

The above urgency prompts scientific researchers to develop appropriate design strategy for iridium(III) complexes with wide band gaps. In this respect, a number of intensive studies [4,51] have

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been performed to obtain blue or greenish-blue materials by structural modification. The general approaches [18] to achieving such phosphorescent iridium(III) complexes can be mainly divided into following sections: i) introduction of electron-withdrawing groups on the phenyl rings of 2-phenylpyridine (ppy) type ligand such as fluorine, trifluoromethyl and cyanide, to stabilize the HOMO energy level of the complexes [52–54]; ii) addition of electron-donating groups to pyridine ring of ppy ligand, for instance methoxy and methylamine, to increase the LUMO energy level [55,56]; iii) using *N*-heterocyclic ligand to replace pyridine ring to a higher LUMO, such as five membered heterocycle pyrazole or triazole [57,58]. Although widened energy gap E_g can be obtained using the methods mentioned above, a mixture of the ligand centered $\pi-\pi^*$ and metal-to-ligand change transfer (MLCT) transitions may be found to gradually reduce, leading to a relatively low quantum yield.

It is well known that *N*-heterocyclic carbenes (NHCs) have been widely used in transition metal catalysts [59,60]. Recently, the transition metal complexes containing NHCs moieties have been proved to be promising luminescent materials for OLEDs. Since they possess sufficiently large covalent metal-carbene bonds that are beneficial to stabilize the complexes [22,61–70]. Furthermore, the strong ligand field of the carbene can effectively further push up the energy of nonradiative d–d excited states on the metal center, resulting in stable phosphors with wide band gap and high quantum yields [65]. On the basis of these principles, Forrest and co-workers [63] reported homoleptic iridium(III) carbene phosphorescent complex showing luminescence in the near-UV region with a relatively high quantum efficiency at room temperature. In addition, Cheng et al. [44] have recently reported iridium(III) carbene complexes that show wide-range color tuning from blue to red emitting. Using functional carbene groups as cyclometalated ligands brings a new and feasible way to construct wide energy-gap iridium(III) complex [46]. To date, however, iridium(III) complexes with carbene ligands showing blue or blue-green phosphorescence are rarely reported. Thus, further design and synthesis of novel carbene-based iridium(III) complexes will be helpful to investigate their structure–property relationship and develop more promising phosphorescent iridium(III) complexes for full-color display. Moreover, in numerous nitrogen heterocyclic ligands, 2-pyridylazole composed of the strong σ-donor property azole fragment together with the π-accepting ability pyridyl fragment, can enhance the chelate interaction and possess a very large intraligand $\pi-\pi^*$ energy gap. Furthermore, such ligands exhibit fascinating photoelectronic properties and can induce a blue-shifted emission, thereby they are regarded as the alternative chromophore for obtaining short-wavelength luminescent materials [4,71,72].

With the aim of obtaining efficient, stable and wide band gap phosphors, we herein designed and synthesized carbene-triazole based iridium(III) complexes **(fpmi)$_2$Ir(mtzpy)** (**1**) and **(fpmi)$_2$ Ir(phtzpy)** (**2**) (**fpmi**: 1-(4-fluorophenyl)-3-methylimdazolin-2-ylidene-C,C$^{2'}$; **mtzpy**: 2-(5-methyl-2*H*-1,2,4-triazol-3-yl)pyridine; **phtzpy**: 2-(5-phenyl-2*H*-1,2,4-triazol-3-yl)pyridine; shown in Scheme 1). Their photophysical results indicate that both complexes exhibit strong greenish-blue emissions with quantum efficiencies of about 0.50 in CH_2Cl_2 solution. They also enjoy excellent electrochemical properties and thermal stabilities. Moreover, the theoretical calculations have been performed to gain insight into their photophysical and electrochemical properties. The vapor-deposited electroluminescence (EL) devices using complexes **1** and **2** as dopants have been fabricated successfully. The constructed greenish-blue and white OLEDs both exhibit good efficiencies. This result reveals that these two complexes offer an opportunity for constructing high performance OLEDs towards full-color displays.

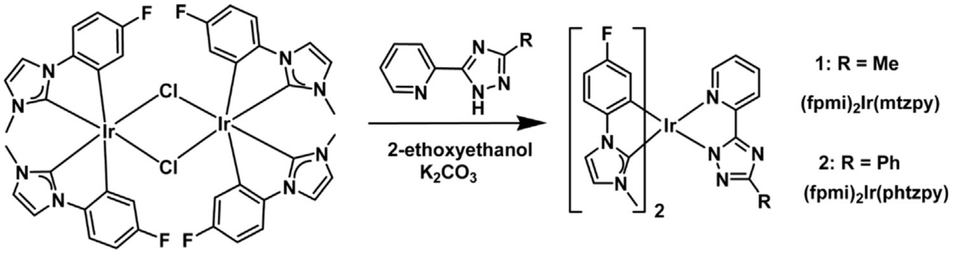
2. Experimental

2.1. Materials and general information

All reactants and solvents employed in synthesis were commercially available without further purification. The solvents for characterization were purified or dried by standard methods. All of the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques in oil baths. ^{1}H NMR spectra were recorded at 25 °C in dry $CDCl_3$ or DMSO-d_6 on Bruker Avance 500 MHz with tetramethylsilane (TMS) as the internal standard. The molecular weights of complexes **1** and **2** were recorded on Agilient 1100 LCMsD mass spectrometer. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C elemental analyzer. UV–vis absorption spectra were recorded on a Hitachi U3030 spectrometer, and photoluminescence spectra were recorded using a F-7000 FL spectrophotometer. The excited-state lifetimes were measured on a transient spectrofluorimeter (Edinburgh FLS920) with a time-correlated single-photo-counting technique. The photoluminescence quantum yields (Φ_{PL}) in the degassed solution were determined by an integrating sphere (Edinburgh FLS920). Cyclic voltammetry (CV) was performed on a BAS 100 W instrument electrochemical analyzer at a scan rate of 100 mV s^{-1} in CH_2Cl_2 solutions of supporting electrolyte tetrabutylammonium hexafluorophosphate ((TBA)PF_6, 0.1 M). Glassy carbon electrode was used as the working electrode, an aqueous saturated calomel electrode as the reference electrode and a platinum wire as the counter electrode. Potentials were obtained using ferrocene-ferrocenium (Fc/Fc$^+$) couple as the internal standard. The solutions were deoxygenated with argon. Thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA-2 thermogravimetric analyzer, with temperature gradient set at 10 °C min^{-1} from 55 °C to 800 °C under a flowing nitrogen atmosphere.

2.2. Synthesis

The carbene precursor 1-(4-fluorophenyl)-3-methyl-imidazolium iodide (**H$_2$fpmiI**) was prepared by reacting imidazole with 1-fluoro-4-iodobenzene using a modified Ullmann coupling reaction,



Scheme 1. Synthetic routes and structures of complexes **1** and **2**.