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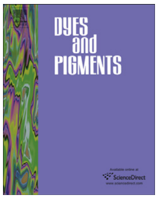

Near-infrared emission of dinuclear iridium complexes with hole/electron transporting bridging and their monomer in solution-processed organic light-emitting diodes

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ABSTRACT

To obtain efficient near-infrared (NIR) emitting materials, a novel iridium (III) complex based on a triphenylamine functionalized pyridylpyrene ligand, namely, Mono-Ir, as well as its two corresonding dinuclear iridium (III) complexes possessing π-conjugated bridging linkages of hole-transporting carbazole (Caz) unit or electron-transporting 2,5-diphenyl-1,3,4-oxadiazole (OXD) unit, namely D-Ir-Caz and D-Ir-OXD, were successfully synthesized and characterized. Under photo-excitation, similar phosphorescence spectrum were obtained for the three complexes with intense NIR emission peak at approximately 698 nm and emission wavelength ranging from 650 to 900 nm. Also, in their single-emissive-layer OLEDs with a device structure of ITO/PEDOT:PSS/TFB/CBP:PBD:complexes/TmPyPB/Liq/Al, similar NIR electroluminescent (EL) emission peaked at 698 nm with a shoulder at 762 nm were obtained. The Mono-Ir-based device showed an external quantum efficiency (EQE) of 1.29% at low current density of 3.5 mA cm^{-2}, while a relatively lower efficiency of 0.27% for the D-Ir-Caz-based device and 0.41% for the D-Ir-OXD-based device, accompanied with negligible efficiencies roll-off at high current densities were achieved, respectively. The better device performance should be achieved when coupled with electron transporting bridging, especially at high currents.

1. Introduction

Since the pioneer work by Tang and Vanslyke in 1980s [1], great progress have been made on developing high-efficiencies visible organic light-emitting diodes (OLEDs), where has potential applications in low cost, efficient, flexible full-color displays and lighting panels, et al. [2–8]. As an extension of visible light, near-infrared (NIR) organic luminescent materials (700–2500 nm) also have emerging applications in night-vision displays, medical diagnosis, sensor, optical communication, et al. [9–11]. However, as for their device performance, NIR materials always suffer low efficiencies and sharp efficiencies roll-off at high currents, which should always be attributed to their decreased energy gap [12,13] and long excited-state lifetimes, and that commonly occurs in square-planar Pt(II)-porphyrin phosphors [14]. Furthermore, in persuit of increasing emission wavelength, many materials are always characterized by their strong donor/acceptor (D/A) or conjugate rigid plane structure, which are easily prone to fluorescence quenching that caused by close molecular packing [15]. Hence, it is still a tough issue for the design of high-efficient NIR emitters for OLEDs application.

Classical phosphorescent transition metal materials are available to exhibit high luminescence quantum efficiencies and narrow energy gap, resulting from their triplet emissive character through strong spin orbit coupling in the presence of heavy metal. Therefore, materials based on the Pt [14,16–20], Ir [21–25], or Os [26] complexes are of particular relevance in NIR applications. Of these, Pt complexes have shown record external quantum

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efficiencies (EQE) up to 8.8–24% with peak emission in the range of 650–800 nm [14,19,20]. However, most of these platinum systems are constructed by square-planar configuration, and the accompanying easy aggregation and relatively long phosphorescence lifetime always generate noticeable efficiency roll-offs at high current density [27].

As another major category in phosphorescent transition metal materials, Ir(III) complexes exhibit typical octahedral configuration and relatively short triplet lifetime, which is favor for their efficiency stabilities in OLEDs [21,24]. Besides, in a C^N bidentate cyclometalated system, spin-orbit coupling (SOC) seems to be more efficient for octahedral d_6 Ir complexes than that for square-planar d_8 Pt complexes [28]. These materials always exhibit slightly reduced device efficiencies at high currents, besides, their EQEs can reach up to as high as 3.4% at 702 nm [21], 3.1% at 714 nm [22], and 4.5% at 760 nm [24], respectively. Qiao etc, reported a cationic iridium emitter based on benzophthalazine in solution-processed NIR OLED, and shows negligible efficiency roll-off even over a wide range of currents of 1–100 mA cm^{-2} [23]. On the basis of the foregoing work, recently, their group designed a neutral homoleptic iridium material, which may has the highest EQEs in the Ir complexes, of that 4.5% at 760 nm with small efficiency roll-off remaining of 3.5% at 100 mA cm^{-2} [24]. Similarly, Kesarkar etc, demonstrated a kind of benzothiophenyl-isoquinolinate-based Ir complexes with different β-diketonate ancillary ligands, and obtained a remarkable EQE of 3.07% in a solution processed OLED with negligible efficiency roll-off [22].

Through the introduction of triphenylamine appendices at the peripheral side of the pyridylpyrene (PyPyr) ligand [29] to extend the π-conjugation, an effectively narrow energy gap with longer emission wavelength was achieved in a new complex Mono-Ir. This material exhibit an efficient NIR emission peaked at 698 nm with a vibronic shoulder, while the spin-coated OLEDs achieved a maximum external quantum efficiency of 1.29%. Besides, carbazole and oxadiazole derivatives usually exhibit high hole-transporting and electron-injecting abilities, and are ideal component in constructing OLEDs materials [30]. To gain an insight into the performance change of materials that have these functional group act as bridging linkages, two dinuclear iridium (III) complexes incorporating a hole-transporting carbazole (Caz) or an electron-transporting oxadiazole (OXD) bridging unit were also designed and synthesized, namely D-Ir-Caz and D-Ir-OXD, respectively. The synthetic routes of the three complexes are shown in Scheme 1. Their thermal, electrochemical, and optophysical properties were also investigated. The strategy is focused on the introduction of the bulky structure to suppress molecular aggregation and provide with efficient hole/electron transporting abilities in device. It is interesting that the similar PL spectra were obtained in the three iridium (III) complexes. However, much lower luminescence quantum yields were detected in the dinuclear iridium (III) complexes. We think that it should be caused by a lower degree of spin-orbit coupling (SOC) in a system with centrosymmetric environment at the ancillary ligand. Therefore, the D-Ir-Caz- and D-Ir-OXD-based devices suffer relatively lower efficiencies of 0.27% and 0.41%, along with negligible efficiency roll-off values.

2. Experimental section

2.1. Materials and synthesis

All reagents were purchased from Aldrich and Acros Inc. Tetrahydrofuran (THF) was distilled over sodium before used. The other reagents were directly used without further purification. All reactions were performed under nitrogen atmosphere and were monitored by thin-layer chromatography. As shown in Scheme 1, both dinuclear iridium (III) complexes D-Ir-Caz and D-Ir-OXD with hole-transporting carbazole- or electron-transporting oxadiazole bridging, as well as their corresponding monomer complex Mono-Ir were designed and synthesized, respectively. Both the ligand *t*-BuTPAPyPyr and the target dinuclear iridium (III) complexes were obtained simply through Suzuki coupling reactions which are similarly to the previous reports [16,18]. The yields of dinuclear iridium (III) complexes are low due to steric hindrance, and the reaction environment was carried out in two kinds of large polarity solvents. The target iridium (III) complexes were synthesized according to the literature procedures [21–24]. *t*-BuPyr-B was prepared followed by the literature reported [31].

2.2. Apparatus and procedures

^1H and ^{13}C NMR spectra were measured with a Bruker Dex-400 NMR instrument using $CDCl_3$ as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix. The thermogravimetric analysis (TGA) was undertaken using a NETZSCH STA449 measurement under nitrogen atmosphere at a heating rate of 20 °C min^{-1}. The ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) spectra of the compound were recorded on a Varian Cray 50 and Perkin-Elmer LS50B luminescence spectrometer, respectively. The optical band gap (E_g) energy level was estimated from the onset of the absorption edge. Excited-state lifetimes were recorded at excitation wavelengths of 440 nm for three complexes on FLS920 with time-corrected single-photon-counting (TCSPC) measurement, while the low temperature phosphorescence spectra were obtained on an Edinburgh FLS920 Spectrometer at 77 K in DCM solution. The Φ_p values of complexes in degassed DCM solutions were measured with tris(2,2′-bipyridine) ruthenium(II) ($\Phi_p = 0.062$ in acetonitrile solution at 298 K) as the standard. The equation of $\Phi_s = \Phi_r(\eta_s^2 A_r I_s / \eta_r^2 A_s I_r)$ was used to calculate the fluorescence quantum yields where Φ_s is the quantum yield of the sample, Φ_r is the quantum yield of the reference, η is the refractive index of the solvent, A_s and A_r are the absorbance of the sample and the reference at the wavelength of excitation, and I_s and I_r are the integrated areas of emission bands [32]. Cyclic voltammetry (CV) measurements were performed on a CHI600E electrochemical workstation with platinum as the working electrode, platinum wire as the counter electrode, and KCl saturated Ag/AgCl as the reference electrode at a 100 mV s^{-1} scanning rate. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.10 M) was used as the supporting electrolyte in acetonitrile solvent. Standard ferrocenium/ferrocene (Fc^+/Fc) system was used to calibrate the experiment data.

2.3. Device fabrication

The OLEDs structure employed in this study is ITO/PEDOT:PSS (30 nm)/TFB (10 nm)/CBP:PBD:complexes (60:30:10, 40 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), where PEDOT is poly(3,4-ethylenedionythiophene) and PSS is poly(styrenesulfonic acid) (Batron-P 4083, purchased from Bayer AG). The ITO surface was pre-cleaned in an ultrasonic solvent bath, and dried in an oven at 120 °C for more than 3 h, then treated with UV ozone for 15 min. After that, the substrates were transferred to the spin-coating process, and then different functional layers (PEDOT: PSS layer and transporting layer and emissive layer) were sequentially spin-coated onto the substrates and were dried in vacuum. Then the samples were transferred to the deposition system, and TmPyPB and Liq/Al layers were sequentially deposited onto the substrate by thermal deposition in the vacuum of 10^{-6} Torr. The emitting layer consisted of the host of CBP:PBD and dopant of the complex. The dopant concentration was 10 wt %. The electroluminescent (EL)