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Orange red iridium complexes with good electron mobility and mild OLED efficiency roll-off

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ABSTRACT

Two iridium(III) complexes with 1-(3,5-*bis*(trifluoromethyl)-pyridin-4-yl)isoquinoline (**tntpiq**) as main ligand, 2-(5-pyridin-4-yl)-1,3,4-oxadiazol-2-yl)phenol (**pop**) and 2-(5-pyridin-4-yl)-1,3,4-thiadiazol-2-yl)phenol (**psp**) as ancillary ligands were investigated. Both complexes emit orange red lights with different photoluminescence efficiencies (**Ir(tntpiq)$_2$(pop)**: $\lambda_{em} = 585$ nm, $\Phi = 0.41$ and **Ir(tntpiq)$_2$(psp)**: $\lambda_{em} = 590$ nm, $\Phi = 0.59$). Moreover, the electron mobility values of the two complexes are higher than that of the electron transport material Alq_3 (tris(8-hydroxyquinoline)aluminium), which are beneficial for their performances in organic light-emitting diodes (OLEDs). The devices with a structure of ITO/MoO_3 (3 nm)/TAPC (1,1-*bis*[4-[*N*,*N*-di(*p*-tolyl)amino]pyridin-4-yl]cyclohexane, 30 nm)/Ir(III) complexes (2 wt%): 26DCzPPy (2,6-*bis*(3-(carbazol-9-yl)pyridin-4-yl)pyridine, 10 nm)/TmPyPB (1,3,5-tri(*m*-pyrid-3-yl-pyridin-4-yl)benzene, 40 nm)/LiF (1 nm)/Al (100 nm) displayed similar performances with a maximum current efficiency of 24.3 cd A^{-1} and a maximum external quantum efficiency of 11.6%, respectively, and the efficiency roll-off is very mild.

1. Introduction

Organic light emitting diodes (OLEDs) have received great attention because of their successful applications in flat-panel displays and solid-state lighting. Cyclometalated iridium(III) complexes are almost the most promising phosphorescent guest materials for highly efficient OLEDs due to their lifetime on the microsecond time-scale, high quantum yields, flexibility in color tuning and excellent thermal stability [1–28]. Furthermore, the phosphorescence of Ir(III) complexes generates by the metal-to-ligand charge transfers (MLCT) and ligand-centered (LC) transition [29], so that it is possible to control the excited state's energy level by adjusting ligands via the substituent effect.

It is well-known that the balance of the electron-hole injection and transport is necessary for high efficient OLEDs using the Ir(III) complexes because both the charge carrier balance deterioration and nonradioactive quenching processes increase will cause a serious efficiency roll-off. Since the majority of hole-transporting materials' hole mobility is much higher than the electron-transporting materials' electron mobility, the OLEDs performances depend on electron transport's capability. Therefore, the use of ambipolar host materials is essential to gain phosphorescent OLEDs with low efficiency roll-off, as well as the synthesis of dopants with excellent electron mobility.

From former work, the bulky trifluoromethyl ($-CF_3$) substituents can affect the molecular packing and the steric protection surrounding the metal would restrain the self-quenching impact, and the C–F bond with low vibrational frequency can reduce radiationless deactivation rate [30–33]. Besides that, nitrogen heterocycle would also enhance the electron affinity and the electron mobility of the Ir(III) complexes. Therefore, the Ir(III) complexes with main ligands containing 2,6-*bis*(trifluoromethyl) pyridin unit always show good device performances [34–37]. Moreover, OLEDs based on Ir(III) complexes with 1,3,4-oxadiazole

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derivatives as ancillary ligands also have good performances due to their high electron mobility, high photoluminescence quantum yield and good thermal, chemical stability [38–40], which would enhance the electron affinity and the electron mobility of the Ir(III) complexes.

On this basis, as shown in Scheme 1, two heteroleptic Ir(III) complexes (**Ir(tntpiq)$_2$(pop)** and **Ir(tntpiq)$_2$(psp)**) were prepared with 1-(3,5-*bis*(trifluoromethyl)pyridin-4-yl)isoquinoline (tntpiq) as main ligand, 2-(5-pyridin-4-yl)-1,3,4-oxadiazol-2-yl)phenol (pop) and 2-(5-pyridin-4-yl)-1,3,4-thiadiazol-2-yl)phenol (psp) as ancillary ligands. These complexes containing 2,6-*bis*(trifluoromethyl)pyridin unit and 1,3,4-oxadiazole/1,3,4-thiadiazole derivatives would have good electron mobility and high photoluminescence quantum yield. Therefore, the devices based on two emitters displayed good performances with a maximum external quantum efficiency up to 11.6% and very low efficiency roll-off.

2. Experimental section

2.1. General information

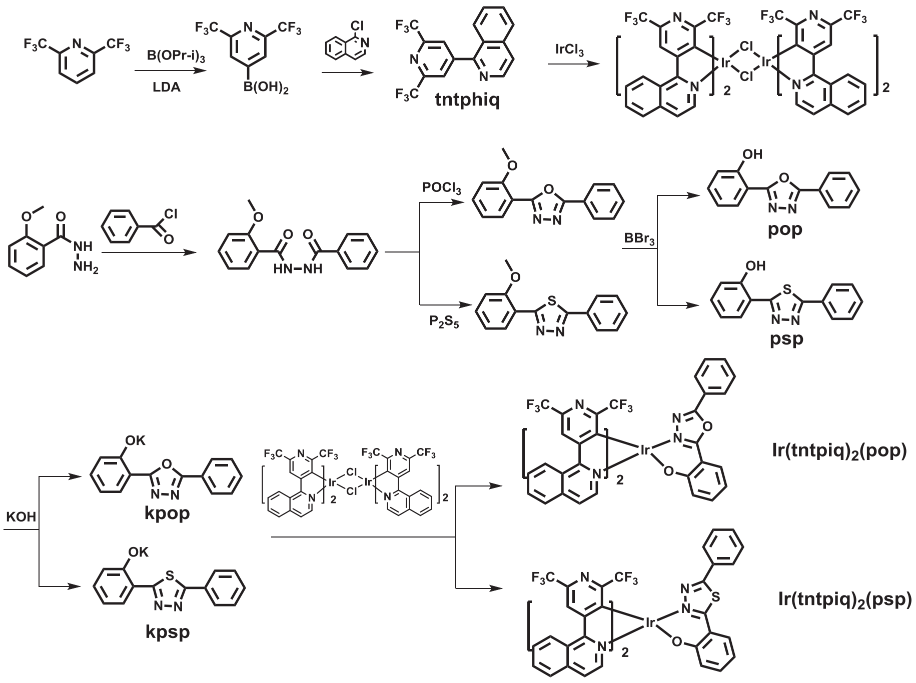
^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer. Electrospray ionization mass spectra (ESI-MS) were obtained with ESI-MS (LCQ Fleet, Thermo Fisher Scientific) and Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (autoflex TOF/TOF, Bruker Daltonics). Elemental analyses for C, H and N were performed on an Elementar Vario MICRO analyzer. TGA measurements were carried out on a DSC 823e analyzer (METTLER). UV–vis absorption and photoluminescence spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 spectrophotometer at room temperature, respectively. A conventional three-electrode configuration, consisting of Glassy Carbon Electrode (GCE) as working electrode, a Pt wire counter electrode, and a reference electrode of Ag/AgNO$_3$ (0.1 M), was used to record cyclic voltammetry data in nitrogen-deaerated CH$_3$CN solution with 0.1 M [Bu$_4$N]ClO$_4$ as the supporting electrolyte and ferrocene as internal standard at a scan rate of 50 mV/s.

2.2. X-ray crystallography

X-ray crystallographic measurements of the single crystals were carried out on a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.) using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Cell parameters were retrieved using SMART software and refined using *SAINT* [41] program in order to reduce the highly redundant data sets. Data were collected using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s per frame. Absorption corrections were applied using *SADABS* [42] supplied by Bruker. The structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 using the program *SHELXS-2014* [43]. The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps, other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and during the final cycles refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso}.

2.3. OLEDs fabrication and measurement

All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω sq^{-1}. The deposition rate for organic compounds is 1–2 Å s^{-1}. The phosphor and host were co-evaporated from two separate sources. The cathode consisting of LiF/Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å s^{-1} and then by evaporation of Al metal with a rate of 3 Å s^{-1}. The effective area of the emitting diode is 0.1 cm^2. The characteristics of the devices were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the CIE coordinates were calculated using a test program of the spectra scan PR650 spectrophotometer.



Scheme 1. Synthetic routes of the ligand and the complexes.