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Synthesis and characterization of blue-to-green electrophosphorescence emitter based on pyrazole iridium complexes

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ABSTRACT

To overcome the roll-off efficiency of electrophosphorescent organic light-emitting devices, Ir(III) complexes of $(ppz)_2Ir(NN)$ were synthesized and named for $(ppz)_2$Ir(tfmpptz), $(ppz)_2$Ir(fpptz), $(ppz)_2$Ir(tfmptz) and $(ppz)_2$Ir(pybi) (ppz: 1-phenylpyrazolato; *NN*: *N*, *N*′-heteroaromatic). Their molecular structures, photophysical properties and cyclic voltammetric data were reported. The crystals of $(ppz)_2$Ir(tfmpptz), $(ppz)_2$Ir(fpptz) are monoclinic, space group P2(1)/n, and $(ppz)_2$Ir(tfmptz) is triclinic, space group P-1. The emission maximum peaks of $(ppz)_2$Ir(tfmpptz), $(ppz)_2$Ir(fpptz), $(ppz)_2$Ir(tfmptz) and $(ppz)_2$Ir(pybi) at room temperature appear at 486, 497, 473 and 530 nm, respectively. The devices with architecture of ITO/NPB (30 nm)/CBP: $(ppz)_2Ir(NN)$ (6%, 30 nm)/BAlq(10 nm)/Alq_3(30 nm)/LiF(1 nm)/Al (100 nm) were fabricated by thermal evaporation. The results indicate that the larger steric hindrance of ancillary ligands efficiently suppressed the roll-off of efficiency at high current density.

1. Introduction

Phosphorescent organic light-emitting devices (PhOLEDs) have shown great potential in digital terminal displays and planar solid-state lighting. However, it is difficult to develop high-efficiency blue PhOLEDs because of the roll-off in efficiency at high current density [1–3]. The primary importance in achieving high-efficiency PhOLED is that the density of triplet excitons should be right low for the purpose of minimizing triplet–triplet (T–T) exciton annihilation. This intention can be realized by synthesizing Ir(III) complex with larger steric hindrance to distribute the triplet excitons in the bulk emission layer [4,5]. The well-known blue-light Ir(III) complex, FIrpic (iridium(III) bis(4,6-difluorophenylpyridinato-N, C2′) picolinate) was designed based on the green emission $(ppy)_2$Ir(acac) (bis(2-phenylpyridine) (acetylacetonate)-iridium(III)) by the introduction of electron-withdrawing fluoro groups to the phenyl ring and the use of pic ligand as the ancillary ligand [4]. The efficiencies of FIrpic-based OLEDs have been improved over the years, but a few critical problems need to be resolved, such as inferior color purity [6,7]. The true-blue *fac*-$Ir(ppz)_3$ (*fac*-tris(1-phenylpyrazolato)iridium(III)) was reported with a λ_{max}414 nm at 77 K, while it is non-emissive at room temperature as a result of the small activation energy to a non-emissive dd excited state [8]. To obtain room-temperature blue-light phosphorescent emitter, FIrtaz and $FIrN_4$ were reported by substituting pic with triazolate or tetrazolate ligand [9]. However, the efficiency decrease sharply from 7.2 to 1.7 lm/W of device based-on $FIrN_4$ at 100 mA/cm^2 of current density. Thus, it is a desirable approach to realize room-temperature blue phosphorescent emitter and avoid the efficiency roll-off by inserting larger steric hindrance *N*, *N*′-heteroaromatic (*NN*) ligands [3,10].

Therefore, in this manuscript, the design and synthesis of a series of $(ppz)_2Ir(NN)$ phosphorescent heteroleptic iridium complexes were described. Their chemical structure and synthetic routs are displayed in Scheme 1.

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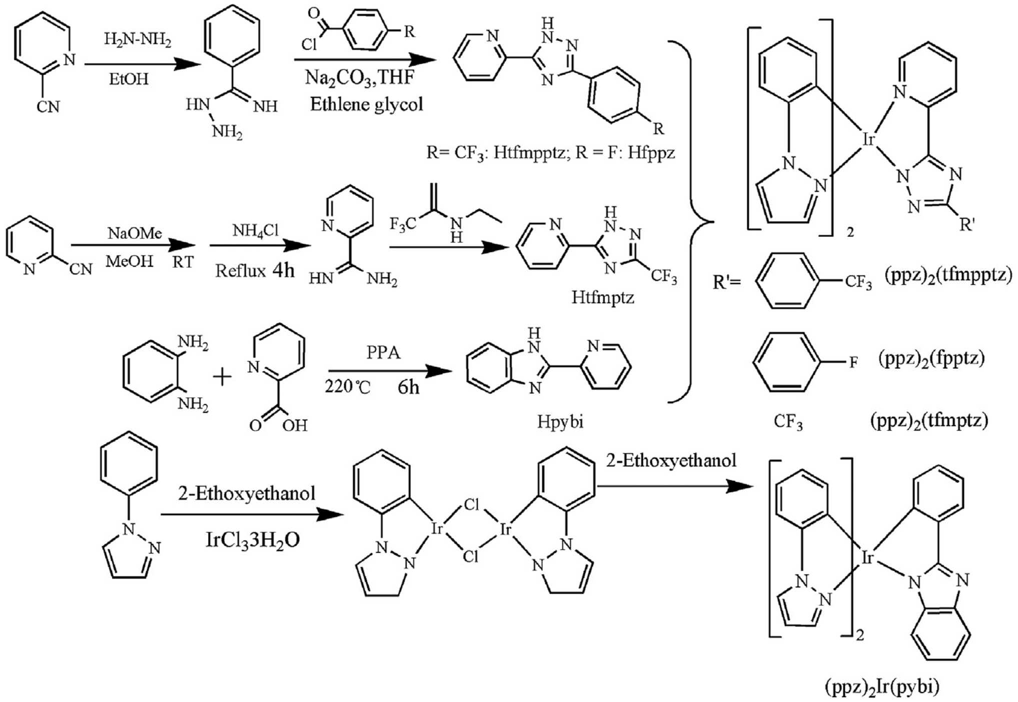

Scheme 1. The synthetic routs of (ppz)$_2$Ir(*NN*) complexes.

2. Experimental section

2.1. General information

^{1}H NMR data were recorded with Switzerland Bruker DR × 600 NMR spectrometers. FT-IR spectra were measured with a Nicolet 7199B spectrometer in KBr pellets in the range of 4000–400 cm^{-1}. UV–vis absorption spectra were recorded by Lambda Bio 40, American PE Co. The electroluminescent (EL) spectra were measured by PR-655 spectrophotometer. Photoluminescent (PL) spectra were examined by Cary Eclipse fluorescence spectrophotometer in CH_2Cl_2 solution. Phosphorescent spectra at 77 K in 2-methyltetrahydrofuran were measured on Hitachi Model F-7000 spectrophotometer upon excitating at the absorption maxima. Cyclic voltammetry was performed with Autolab/PG STAT302 in a one-compartment electrolysis cell using two platinum wires as working electrode and counter, a calomel electrode as reference. $TBAPF_6$ was used as supporting electrolyte (0.1 M). Cyclic voltammetric behaviors were monitored at scan rate 50 mV/s.

To evaluate the electroluminescent properties of these complexes, several electroluminescent devices were fabricated by using (ppz)$_2$Ir(*NN*) complexes as dopant emitters. Organic layers were fabricated by high-vacuum (3×10^{-4} Pa) thermal evaporation onto a glass substrate precoated with an indium tin oxide (ITO) layer. The device structure was ITO/NPB (30 nm)/CBP: (ppz)$_2$Ir(*NN*) complexes (6%, 30 nm)/BAlq(10 nm)/Alq$_3$(30 m)/LiF(1 nm)/Al (100 nm). Materials used for the device were NPB (N, *N'*-Bis (naphthalen)-N, *N'*-bis (phenyl)-benzidine) for hole-transport layer, (ppz)$_2$Ir(*NN*) (6%) in CBP (4,4'-*N*,*N'*-dicarbazolebiphenyl) for light-emitting layer, BAlq (aluminum (III) bis (2-methyl-8-quninolinato)-4-phenylphenolate) for hole-blocking layer, and Alq$_3$ (tris(8-hydroxyquinoline) aluminum) for electron-transport layer. The voltage–current density (V-J) characteristics of PhOLEDs were recorded on Keithley 2400 Source Meter and L-2188 Spot Brightness Meter.

X-ray single-crystal diffractions of all complexes were performed on Bruker SMART APEX II diffractometer with Mo Ka radiation ($\lambda = 0.710\ 73$ Å). The structures were solved with direct methods (SHELX-97) and refined with full-matrix least-squares technique. All non-hydrogen atoms were refined anistropically and hydrogen atoms of organic ligands were geometrically placed.

2.2. Theoretical methodology

All calculations were performed using Gaussian 03 package by employing experimental parameters determined by X-ray single-crystal diffraction as input file. The geometry optimization of ground state were carried out using B3LYP functional with 6-31G(d) basis sets [11,12], except for LANL2DZ basis sets for Ir atom. The theoretical absorption spectra were calculated by time-dependent density functional theory (TD-DFT) method [13,14] based on the optimized ground-state structures with solvent effects take into account by the polarizable continuum model (PCM) [15]. Dichloromethane (CH_2Cl_2) was chosen as to be consistent with experimental conditions.

3. Synthesis of ligand

Procedure for the synthesis of 2-(5-(4-(trifluoromethyl)phenyl)-2H-1,2,4-triazol-3-yl)pyridine (Htfmpptz): A mixture of picolinonitrile (50 mmol), hydrazine hydrate (50 mmol) and ethanol (25 ml) was reacted for 8 h under nitrogen air. The redundant ethanol was removed at room temperature by vacuum. The residue was washed using ether. A white crystal of (2-pyridine) amidrazone was filtered and dried. Then, (2-pyridine)amidrazone (30 mmol), Na_2CO_3 (30 mmol) and 4-(trifluoromethyl)benzoyl chloride (30 mmol) in THF solution were reacted for 6 h at room temperature under nitrogen air. The resulting residue was recrystallized in ethanol. The needle-like crystal of 2-(5-(4-