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A novel deep-red-emitting iridium complex with single-peaked narrow emission band: Synthesis, photophysical properties, and electroluminescence performances

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ABSTRACT

In this paper, we report a novel ligand equipped with both electron-pushing moieties and enlarged conjugation planes, 1-benzo[b]thiophen-2-yl-naphthalene-2-ol (BYNO). Using BYNO as the ancillary ligand, its corresponding Ir(III) complex of $Ir(ppy)_2(BYNO)$ (ppy=2-phenyl pyridine) is also synthesized. An efficient deep-red emission peaking at 620 nm with a narrow emission band (full-width-at-half-maximum=65 nm) was finally observed from $Ir(ppy)_2(BYNO)$. We discuss the photophysical properties, thermal properties, geometric and electronic structures of $Ir(ppy)_2(BYNO)$ in detail. In addition, its electroluminescence performances are investigated and a maximum luminance of 3840 cd/m^2 peaking at 618 nm is achieved. All obtained data suggest that $Ir(ppy)_2(BYNO)$ is a promising candidate for red-emitting dopants in organic light emitting diodes.

1. Introduction

Since the first report of phosphorescent porphyrin platinum as a highly efficient emitter in organic light emitting diodes (OLEDs), the scope and diversity of studies on transition metal complexes have continued to expand at an exponential rate due to the potential advantage of achieving a maximum internal quantum efficiency of 100% [1]. Particularly, the second- and third-row transition metal complexes incorporating chelating ligands, such as 2,2′-bipyridine (bpy) and 2-phenyl pyridine (ppy), have attracted much attention [2–4]. In this series, Ir(III) complexes are particularly promising because of their favorable short excited state lifetimes, well-suited energy levels, thermal stability, and environmental inertness. In exploring high efficiency phosphorescent emitters and moving towards materials with the required color gamut for full color displays, many efforts have been devoted to develop tricolor emitting materials, and a good harvest of Ir(III) complexes covering the whole visible region has been achieved [5–7]. However, efficient deep-red-emitting Ir(III) complexes are still scarce because their photoluminescence (PL) quantum yields tend to be intrinsically low [8]. Moreover, their PL spectra are usually composed of multiple and broad bands with bandwidths of ~100–300 nm, which compromises the color purity and are not suitable for display applications [9,10]. Thus, the exploration for high efficiency deep-red-emitting Ir(III) complexes with single and narrow emission bands is still attractive.

It is reported that the substituent of heteroaromatic cyclometalating ligands can change the emission color of corresponding Ir(III) complexes. Generally, cyclometalating ligands containing electron-withdrawing moieties (fluorine or nitrile substituents) move the emissions of resulting Ir(III) complexes towards higher energies. On the other hand, cyclometalating ligands with electron-pushing moieties (alkyl substituents or aromatic rings) move the emissions towards lower energies [11–14]. Additionally, the enlarged conjugation rings in ligands seem to be effective in narrowing emission bands of their corresponding Ir(III) complexes [15].

Encouraged by the above reports, in this work, we devote our effort to the synthesis of a novel ligand equipped with both electron-pushing moieties and enlarged conjugation planes, hoping to achieve a saturated red emission with narrow a emission band from its corresponding Ir(III) complex. Finally, an efficient emitter (Φ=0.28) peaking at 620 nm with a full-width-at-half-maximum (FWHM) of 65 nm is realized, and its electroluminescence (EL) performances are also investigated.

2. Experimental section

A synthesis route for the ligand of 1-benzo[b]thiophen-2-yl-naphthalene-2-ol (referred as BYNO) and its corresponding Ir(III) complex of $Ir(ppy)_2(BYNO)$ is shown in Scheme 1.

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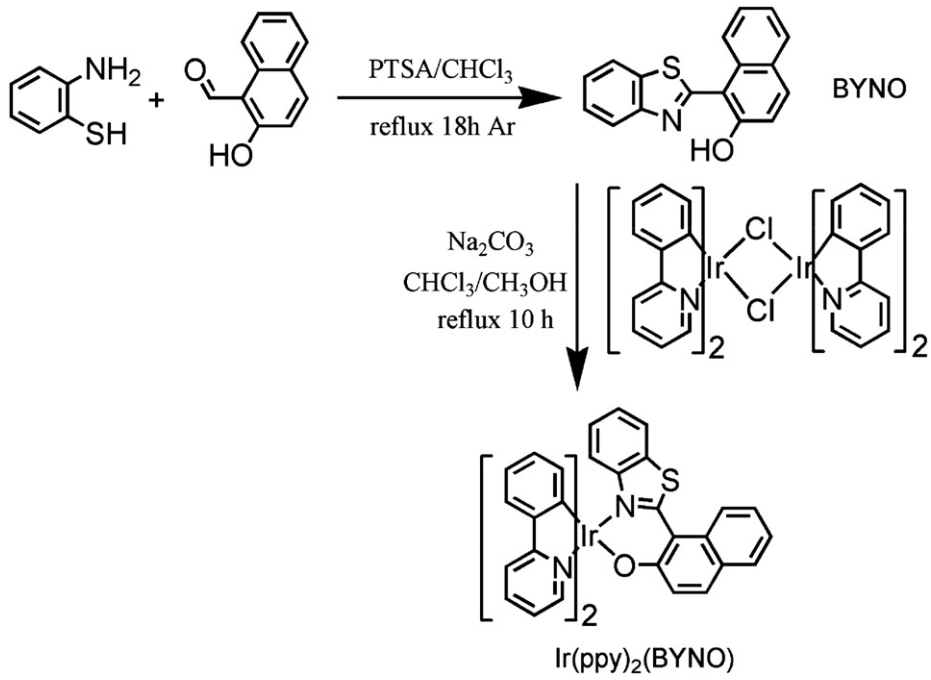

Scheme 1. Synthesis routes for BYNO and Ir(ppy)$_2$(BYNO).

All starting materials, including 2-aminothiophenol, 2-hydroxy-naphthalene-1-carbaldehyde, *p*-toluenesulfonic acid monohydrate (PTSA), 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB), tris(8-hydroxy-quinoline)aluminum (Alq_3), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), and 4,4′-dicarbazolyl-1,1′-biphenyl (CBP), were commercially obtained from Aldrich Chemical Co. and used without further purification.

2.1. Synthesis of BYNO

A mixture of 50 mmol of 2-aminothiophenol, 50 mmol of 2-hydroxy-naphthalene-1-carbaldehyde, and 1 mmol of PTSA was dissolved in 50 mL of chloroform. The mixture was stirred at 90 °C under Ar atmosphere for 18 h. After cooling, the mixture was poured into cold water and extracted with chloroform. The solvent was removed by rotary evaporation and the residue was recrystallized from methanol to give light green solid. Yield 61% ^{1}H NMR ($CDCl_3$) δ [ppm]: 6.76 (*d*, 3H), 7.82 (*m*, 5H), and 8.65 (*d*, 2H).

2.2. Synthesis of Ir(III) complexes

To a flask containing 250 mg of $IrCl_3 \cdot 3H_2O$ and 230 mg of ppy was added 30 mL of a mixed solvent of 2-ethoxyethanol and water (3:1). The mixture was refluxed for 2 days and then cooled. Water was added to precipitate an orange solid. After being washed with ethanol and hexane, the precipitate was added into a two-neck flask containing 145 mg of anhydrous sodium carbonate, 25 mL of chloroform/methanol (*V*:*V*=1:1), and 380 mg of BYNO. The mixture was refluxed for 10 h. After cooling, the solvent was evaporated. The crude product was chromatographed using ethyl acetate/petroleum ether (*V*/*V*=0.8:1), resulting in red needle crystals. Yield 54% ^{1}H NMR ($CDCl_3$) δ [ppm]: 6.11 (*d*, 2H), 6.63 (*t*, 2H), 6.88 (*t*, 2H), 6.74 (*d*, 3H), 7.32 (*t*, 2H), 7.48(*d*, 2H), 7.85(*d*, 2H), 7.94(*m*, 5H), and 8.73 (*d*, 2H). Anal. Calcd. for $C_{39}H_{26}IrN_3OS$: C, 60.29; H,3.37 ; N, 5.41. Found: C, 60.17; H, 3.46; and N, 5.44.

2.3. OLED fabrication

EL devices using Ir(ppy)$_2$(BYNO) as the emitter were fabricated by the resistive heating method under a chamber pressure of $\sim 3 \times 10^{-4}$ Pa onto clean glass that was pre-coated with a layer of indium tin oxide (ITO). Prior to use, the ITO surface was cleaned by sonication in detergent solution, water, and ethanol sequentially. After being blown dry with nitrogen, the ITO substrates were treated with oxygen plasma for 1 min before being loaded into the vacuum chamber. LiF and Al were used as the electron injection layer and the cathode, respectively. The thicknesses of the deposited layers and the evaporation speed of individual materials were monitored in vacuum with quartz crystal monitors.

2.4. Measurements

Density functional theory (DFT) calculation was performed on Ir(ppy)$_2$(BYNO), at the RB3LYP/SBKJC level. Singlet excitation calculation on Ir(ppy)$_2$(BYNO) was performed by the time dependent density functional theory (TD-DFT) at the RB3LYP/SBKJC level. The initial geometry was optimized by a semiempirical method of PM6. All computations were finished by GAMESS and MOPAC 2009.

Excited state lifetime was obtained with a 355 nm light generated from the third-harmonic-generator pump, using a pulsed Nd:yttrium aluminum garnet (YAG) laser as excitation source. The Nd:YAG laser possesses a line width of 1.0 cm^{-1}, a pulse duration of 10 ns, and a repetition frequency of 10 Hz. All PL spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. UV-Visible absorption spectra were recorded using an HP 8453 UV–vis-NIR diode array spectrophotometer. Luminescence quantum yield of Ir(ppy)$_2$(BYNO) was determined by the method of Demas and Crosby with quinine sulfate in 1.0 M sulfuric acid (Φ=0.546) as the reference standard [16]. ^{1}H NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Thermogravimetric analysis (TGA) was performed on a thermal analysis instrument (SDT2960, TA Instruments, New Castle, DE) with a heating rate of 10 °C. EL spectra were measured by a PR650 spectrascan spectrometer. The luminance–current–voltage