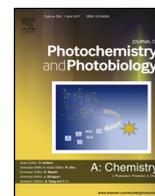




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Invited feature article

Synthesis and properties of novel blue light-emitting iridium complexes containing 2',6'-difluoro-2,3'-bipyridine ligands

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ABSTRACT

Two novel tricyclic metalated heteroleptic iridium complexes, namely Ir(dfppy)₂(pt) and Ir(dfppy)₂(dfppy), were designed and synthesized for application as blue phosphors in optoelectronic devices. 2',6'-difluoro-2,3'-bipyridine (dfppy) was used as the cyclometalating ligand. In comparison with the parent homoleptic Ir(dfppy)₃, the newly developed 3-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (pt) with higher triplet energy than dfppy or 2-(2,4-difluorophenyl)pyridine (dfppy) was used as the ancillary ligands to tune the electronic properties of these heteroleptic complexes. Both complexes emit strong blue phosphorescence with high quantum yields. The incorporation of high-energy ancillary ligand pt in Ir(dfppy)₂(pt) makes the highest-energy sub-band intensity in the phosphorescence spectrum increase relative to those of the parent Ir(dfppy)₃, and leads to narrower phosphorescence spectrum than the analogue Ir(dfppy)₂(dfppy) as well, which may provide a practical method to adjust the phosphorescence spectra and color purity of the complexes.

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1. Introduction

Light-emitting complexes containing third-row transition metals have attracted much attention owing to their applications in photonics and electronics [1–3], especially in organic light-emitting diodes (OLEDs). In particular, cyclometalated iridium(III) complexes are regarded as most successful phosphorescent materials due to their ability to achieve maximum internal quantum efficiency of nearly 100%, flexible color tenability, and relatively short lifetimes in OLEDs [4–6]. To achieve full color display, three primary colors RGB are necessary. However, iridium complexes with deep blue emission at room temperature are hard to obtain due to the large energy gaps of blue phosphorescent emitters [7]. Phenylpyridine (ppy) derivatives are typical cyclometalating ligand frameworks for iridium phosphors. In order to obtain deep blue iridium complexes, electron withdrawing group is usually attached to the phenyl group of the ppy ligand to shift the HOMO of the emitter downwards, while electron donating group is introduced onto the pyridine unit to shift the LUMO upwards [8–11]. Additionally, the incorporation of five-member heterocycle in ligands is helpful for obtaining deep blue phosphorescent emitter by destabilizing the LUMO level of the complexes [12–14].

When used as the main cyclometalating ligand of iridium phosphors, 2',6'-difluoro-2,3'-bipyridine (dfppy) [15] was proved to be a powerful ligand that can further shift the emission wavelength to blue region in comparison with the 2-(2,4-difluorophenyl)pyridine (dfppy) (corresponding to the famous phosphor Flrpic). The phosphorescence spectrum of the dfppy based homoleptic iridium complex Ir(dfppy)₃ are well-resolved with two major vibrational bands at 438 nm and 463 nm [15], which correspond to the (0,0) and (0,1) vibrational transitions, respectively. Furthermore, the emission intensity of the (0,1) transition band at 463 nm is comparable with or higher than that of (0,0) band at 438 nm. This can be attributed to enhanced coupling of the excited state to vibrational modes [16]. The increase in the intensity of the longer-wavelength band may result in large nonradiative decay rates in the complex and unsatisfied color saturation of the OLED incorporating the complex as the emitter.

The excited states of iridium complexes are typically composed of metal-to-ligand charge-transfer triplet state and ligand centered $\pi-\pi^*$ triplet state. It is reasonable to select cyclometalating ligand with high triplet energy to obtain short wavelength emission. The introduction of five-membered heterocycle, which is characterized with high triplet energy, is helpful for the widening of energy bandgap. For the purpose of enhancing the (0,0) transition band intensity and a narrow emission spectrum of the dfppy based iridium phosphors, a new ancillary ligand with high triplet energy, namely 3-(1-benzyl-1H-1,2,3-triazol-4-yl)pyridine (pt), was

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developed in present work and novel iridium complex Ir(dfppy)₂(pt) (M₁) was prepared. For comparison, dfppy with lower triplet energy than dfbpy was also employed as ancillary ligand to prepare the complex (M₂). The properties of these two new complexes M₁ and M₂ were investigated in details.

2. Experimental

2.1. Materials and methods

The ¹H NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. The mass spectra were taken on HP1100LC/MSD MS spectrometer. The fluorescence and UV–vis absorption spectra measurements were performed on a Perkin-Elmer LS55 spectrometer and a Perkin-Elmer Lambda 35 spectrophotometer, respectively. The phosphorescence spectra were measured on an Edinburgh FLS920 Spectrometer at 77 K in 2-MeTHF. Thermogravimetry analyses (TGA) were carried out using a Perkin-Elmer thermogravimeter (Model TGA7) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. The electrochemical measurements were carried out by using a conventional three electrode configuration and an electrochemical workstation (BAS100B, USA) at a scan rate of 100 mV s⁻¹. A glass carbon working electrode, a Pt-wire counter electrode, and a saturated calomel electrode (SCE) reference electrode were used. All the measurements were made at room temperature on samples dissolved in dichloromethane (positive mode) and in DMF (negative mode), deoxygenated with argon, and with 0.1 M Bu₄NPF₆ as the electrolyte. Density functional theory (DFT) calculations using B3LYP functional were performed using Gaussian 09 package. The basis set used for C, H, N and F atoms was 6–31G while the LanL2DZ basis set were employed for Ir atoms. There are no imaginary frequencies for both optimized structures.

2.2. Synthesis

2.2.1. Synthesis of the ligand pt

To a 250 mL two-necked bottle was added 3-ethynylpyridine (5.0 g, 48.5 mmol), benzyl bromide (5.0 mL, 44.0 mmol), sodium

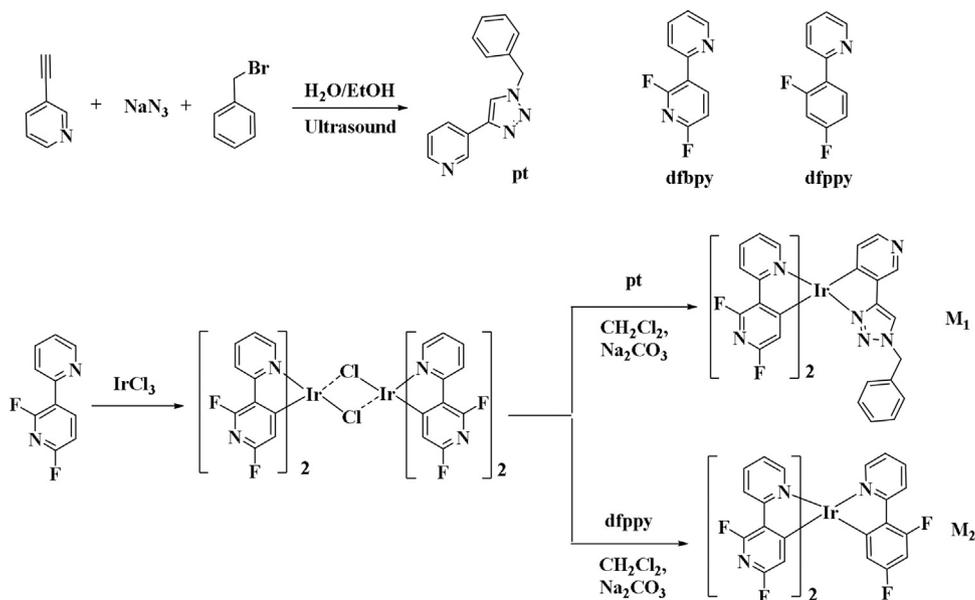
azide (2.8 g, 44.0 mmol) and CuI (0.42 g, 2.2 mmol) successively. Then water (75 mL) and ethanol (25 mL) was added as solvent. The mixture was sonicated for 30 min in a laboratory ultrasonic cleaning bath. The reaction mixture was diluted with water and extracted with dichloromethane (100 mL × 3). The aqueous phase was treated with sodium hypochlorite to remove excessive sodium azide, while the organic phase was evaporated to produce the crude product, which was then separated by column chromatography over silica gel with ethyl acetate as the eluent to give ligand pt as a white solid (3.2 g, 32.5% yield). ESI–MS (*m/z*): calcd. for C₁₄H₁₂N₄ 236.1062, found 236.1058 [M]⁺. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.96 (s, 1H), 8.58 (s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.76 (s, 1H), 7.40 (m, 4H), 7.33 (m, 2H), 5.61 (s, 2H).

2.2.2. General procedure for synthesis of the iridium complexes M₁ and M₂

To a 50 mL two-neck bottle was added IrCl₃·3H₂O (440 mg, 1.26 mmol), 2,6-difluoro-2,3'-bipyridine (dfbpy, 600 mg, 3.12 mmol), 2-ethoxyethanol (12 mL) and water (4 mL). The mixture was refluxed under nitrogen for 24 h. Upon cooling to room temperature, water (30 mL) was added into the reaction mixture. The precipitate was collected by filtration and washed with water. The wet solid was completely dried to give the yellow green dichloro-bridged dimer complex (580 mg). Without further purification, this dimer (200 mg, 0.24 mmol) was added to a mixture of K₂CO₃ (130 mg, 2.4 mmol), dfppy or pt (0.55 mmol), and dichloromethane (10 mL). The mixture was allowed to react at 15–20 °C for 20 h. Then the solvent was evaporated to obtain the crude product, which was separated by column chromatography over silica gel to produce the final complexes.

M₁: Yellow green powder, yield 55%. MALDI-TOF-MS (*m/z*): calcd. for C₃₄H₂₁F₄IrN₈ 810.15, found 811.10 [M+H]⁺. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.84 (d, *J* = 5.2 Hz, 1H), 8.40 (m, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 5.2 Hz, 1H), 7.89 (m, 3H), 7.40–7.34 (m, 10H), 7.18 (m, 1H), 5.58 (s, 2H).

M₂: Yellow green powder, yield 40%. MALDI-TOF-MS (*m/z*): calcd. for C₃₁H₁₆F₆-IrN₅ 765.09, found 765.20 [M]⁺. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.12 (d, *J* = 5.6 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.22 (m, 1H), 8.06 (m, 1H), 7.99 (m, 2H), 7.75 (m, 4H), 7.67 (m, 1H), 7.53 (m, 1H), 7.47 (m, 1H), 6.99 (m, 1H), 6.94 (m, 2H).



Scheme 1. Chemical structures and synthetic routes of ligand pt and iridium complexes M₁ and M₂.

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