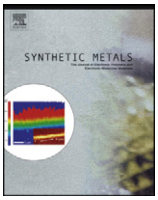
Synthetic Metals 162 (2012) 497–502

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Synthesis and photophysical characterization of orange-emitting iridium(III) complexes containing benzothiazole ligand

Guoyong Xiao[a], Xiao Li[a], Haijun Chi[a], Yunhua Lu[a], Yan Dong[a], Zhizhi Hu[a,*], Jianglong Yu[a,**], Masaru Kimura[a,b]

[a] School of Chemical Engineering, University of Science and Technology Liaoning (USTL), Anshan 114051, China
[b] Chemistry and Biology, Graduate School of Natural Science and Technology, Okayama University, Tsushima-Naka 3-1-1, Okayama 700-8530, Japan

ARTICLE INFO

Article history:
Received 20 November 2011
Received in revised form 10 January 2012
Accepted 19 January 2012
Available online 24 February 2012

Keywords:
Iridium complex
Benzothiazole
Phosphorescence
OLEDs

ABSTRACT

Two novel iridium(III) (Ir(III)) complexes $(dmabt)_2Ir(acac)$ and $(dpabt)_2Ir(acac)$(dmabt, 4-N,N-dimethylbenzenamineyl-2-benzo[d]thiazole; dpabt, 4-N,N-diphenylbenzenamineyl-2-benzo[d]thiazole; acac, acetylacetone) were synthesized and structurally characterized by NMR and mass spectrometry. The organic light-emitting diodes based on these complexes with the structure of ITO/m-MTDATA (10 nm)/NPB (20 nm)/CBP: Ir-complex (X%, 30 nm)/BCP (10 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm) were fabricated. The device based on $(dmabt)_2Ir(acac)$ exhibited a maximum efficiency of 19.5 cd/A, a luminance of 15802 cd/cm^2; and the device based on $(dpabt)_2Ir(acac)$ showed a maximum efficiency of 14.8 cd/A, a luminance of 11334 cd/cm^2. Both devices displayed orange emissions and the corresponding Commission International de L'Eclairage (CIE) coordinates (1931) were (0.517, 0.481) and (0.557, 0.443), respectively.

1. Introduction

Since the organic light-emitting diodes (OLEDs) using green-emitting $Ir(ppy)_3$ fac-tris(2-phenylpridyl)iridium(III) blended with CBP (4,4′-bis(N-carbazolyl)-2,2′-biphenyl) as an emissive layer were reported to have an external quantum efficiency of 19% [1], iridium(III) (Ir(III)) cyclometalated complexes have aroused considerable attention in recent years because of their favorable photochemical and photophysical properties such as good stability, high photoluminescence (PL) quantum yields, ease of spectral tuning, short triplet state lifetimes, and the ability to participate in outer sphere electron-transfer reactions [2]. The strong spin–orbit coupling induced by a heavy-metal ion such as Os, Ir, and Pt can promote an efficient intersystem crossing (ISC) between the singlet and the triplet excited state manifold. Therefore, both singlet and triplet excitons can be harnessed, and then the internal quantum efficiency theoretically approaching to 100% can be achieved [3–7]. To date, various phosphorescent Ir(III) complexes have been synthesized and thoroughly studied [8]. In addition to the three primary color-emitting Ir(III) complexes, the orange-emitting Ir(III) complexes are of great interests as well since they can be used in combination with blue emitters to fabricate two-emitting-component white OLEDs, which has definitely become one of the most important directions of OLEDs study in recent years [9].

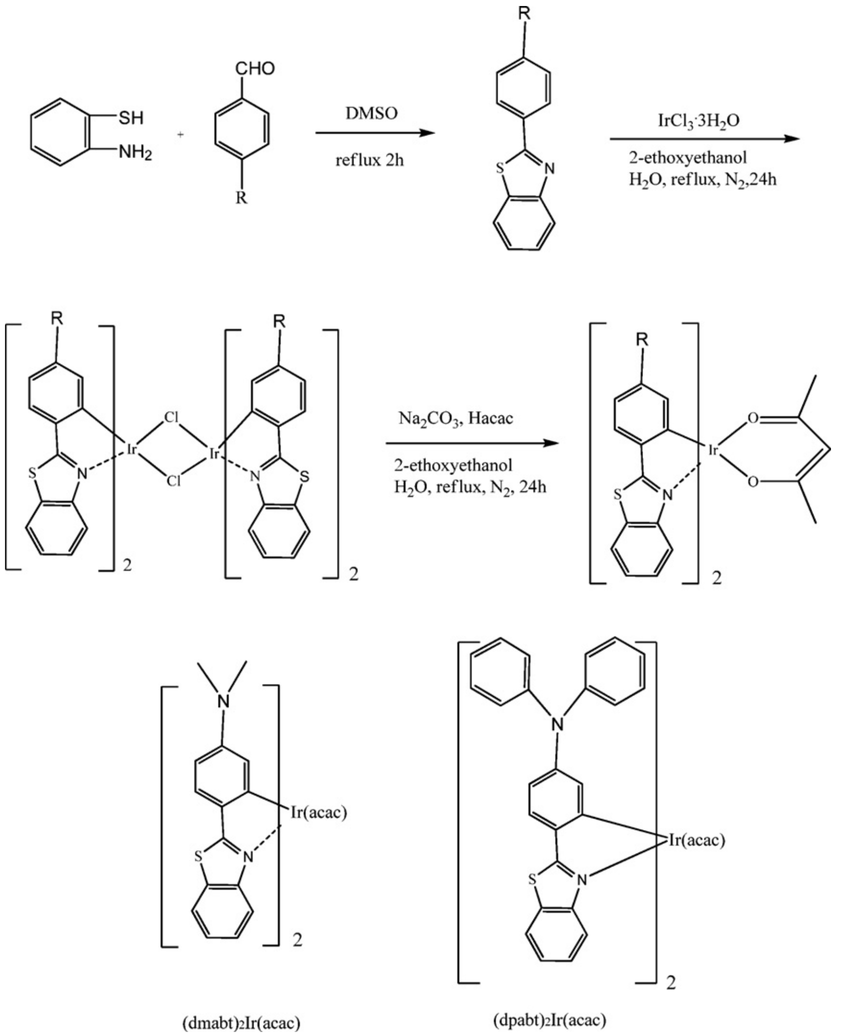
Bis(2-phenylbenzothiozolato-*N*,$C^{2'}$)iridium(acetylacetonate) ($(bt)_2Ir(acac)$) is one typical orange phosphorescent emitter [10]. Although some derivatives of $(bt)_2Ir(acac)$ have been developed for OLEDs [11], the electroluminescent (EL) properties of those complexes used as dopants in OLEDs are still very unsatisfactory. Recently, Li et al. reported a serials of novel Ir(III) complexes based on bt derivatives [11(b), 12], which was found that these phosphors as doped emitter exhibited good EL performances. These results motivated us to design new ligands for Ir(III) complexes based on the bt framework that could lead to enhanced EL performances. What's more, it was well demonstrated that incorporating some groups such as arylamines with hole-transporting function into the ligand frame was beneficial to reducing the barrier for hole injection, decreasing the triplet–triplet annihilation and finally improving the EL performance of the resulting complexes [13].

In this article, two novel Ir(III) complexes $(dmabt)_2Ir(acac)$ and $(dpabt)_2Ir(acac)$ (dmabt, 4-N,N-dimethylbenzenamineyl-2-benzo[d]thiazole; dpabt, 4-N,N-diphenylbenzenamineyl-2-benzo[d]thiazole; acac, acetylacetone) were synthesized and structurally characterized by NMR and mass spectrometry. The results showed that two Ir(III) complexes had strong phosphorescent properties, and the devices based on these complexes exhibited prominent EL performances.

---

[*] Corresponding author. Tel.: +86 412 5929881; fax: +86 412 5216902.
[**] Corresponding author. Tel.: +86 412 5929638.
E-mail address: guoyong_xiao@yahoo.com.cn (G. Xiao).

0379-6779/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2012.01.014



Scheme 1. Synthetic routes of iridium complexes in this study.

2. Experimental details

$IrCl_3 \cdot 3H_2O$ and other reagents were obtained from commercial purchase, used without further purification. All procedures were carried out in inert gas atmosphere despite the air stability of the compounds. NMR and Mass spectroscopy (MS) were in agreement with the structure and were obtained on a Bruker AVANCE 500 MHz (TMS as internal reference) and Agilent 1100, respectively. Elemental analysis was performed on Vario EL III CHNS instrument. UV–vis absorption spectra were recorded using a Perkin-Elmer Lambda-900 spectrophotometer. PL spectra were measured on a Perkin-Elmer LS-55 luminescence spectrophotometer.

2.1. Synthesis of Ir-complexes

2.1.1. Synthesis of dmabt [14]

The mixture of 4-dimethylaminobenzaldehyde 1.49 g (10 mmol), 2-aminobenzenethiol 1.38 g (11 mmol), 10 mL DMSO was heated to reflux for 2 h. After cooling to room temperature, treated with water, the resultant yellow green precipitate was filtered off. The crude product was obtained. After recrystallized from methanol, the product was given with the yield of 88.9%. Mp 175–176 °C. MS (APCI): *m*/*z* 255.1 [M+H$^+$]. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ(ppm): 3.05 (s, 6H), 6.74 (dd, *J* = 1.5 Hz, *J* = 7.5 Hz, 2H), 7.30 (ddd, *J* = 1.0 Hz, *J* = 7.5 Hz, 1H), 7.43 (ddd, *J* = 1.0 Hz, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.95–7.99 (m, 3H); ^{13}C NMR: ($CDCl_3$, 125 MHz) δ (ppm): 168.80, 154.50, 152.23, 134.62, 128.90, 125.99, 124.20, 122.33, 121.50, 121.36, 111.74, 40.19.

2.1.2. Synthesis of dpabt

This compound was prepared similarly from the reaction of 4-(dimethylamino)benzaldehyde with 2-aminobenzenethiol. Yield: 98.7%. Mp 178–179 °C. MS (APCI): *m*/*z* 379.2 [M+H$^+$]. ^{1}H NMR: ($CDCl_3$, 500 MHz) δ(ppm): 7.07–7.12(m, 4H), 7.16(d, *J* = 8.0 Hz, 4H), 7.29–7.36(m, 5H), 7.46(t, *J* = 7.5 Hz, 1H), 7.86(d, *J* = 8.0 Hz, 1H), 7.92(d, *J* = 8.5 Hz, 2H), 8.01(d, *J* = 8.0 Hz, 1H); ^{13}C NMR: ($CDCl_3$, 125 MHz) δ(ppm): 167.84, 154.37, 150.48, 146.98, 134.88, 129.54, 128.58, 126.20, 125.45, 124.74, 124.07, 122.83, 12 1.79, 121.51.

2.1.3. Synthesis of (dmabt)$_2$Ir(acac) [10]

The dmabt 0.561 g (2.2 mmol) was dissolved in 2-ethoxyethaol (10 mL) in 100 mL round-bottom flask. Iridium trichloride hydrate (1.0 mmol) and 3.0 mL of water were then added to the flask. The mixture was refluxed at 100 °C under nitrogen atmosphere for 24 h. After cooling to room temperature, the precipitate was collected and dried in vacuum to give the corresponding chloro-bridged dimmer. Then in a 50 mL flask, the dimmer complex, acetylacetone (5.0 mmol) and Na_2CO_3 (10.0 mmol) were mixed with 2-ethoxyethanol (15 mL) and the mixture was refluxed at 100 °C under a nitrogen atmosphere for 24 h. After cooling to room temperature, the precipitate was filtered off and washed with water and methanol. The crude product was purified on a silica