A novel blue-emitting Ir(III) complex with short excited state lifetime: Synthesis, structure, photophysical property, and electrophosphorescence performance

Yangqing Zhang [a,b,*], Mingjing Song [c], Laiqiang Huang [a,b,**]

[a] School of Life Sciences, Tsinghua University, Beijing 100084, PR China
[b] Graduate School at Shenzhen, Tsinghua University, Shenzhen, Guangdong 518055, PR China
[c] Institute of Laboratory Animal Science, Peking Union Medical College, Beijing 100021, PR China

ARTICLE INFO

ABSTRACT

In this paper, we synthesize a triphenylamine-derived cyclometalating ligand of (4-benzothiazol-2-yl-phenyl)-diphenyl-amine (referred as BPDA) and its corresponding Ir(III) complex of $(BPDA)_2Ir(acac)$ (acac=acetylacetone). The photophysical property, molecular structure, thermal property and electro-luminescence performance of $(BPDA)_2Ir(acac)$ are investigated in detail. It is found that $(BPDA)_2Ir(acac)$ is an efficient emitter with high thermal stability and short excited state lifetime. The emission of $(BPDA)_2Ir(acac)$ changes from deep blue (417 nm) to bluish green (500 nm) upon addition of different solvents. We also investigate its electrophosphorescence performance. A maximum electroluminance of 8820 cd/m^2 peaking at 494 nm is achieved, with the highest device efficiency of 1.72 cd/A.

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 study on transition metal complexes have continued to expand at an exponential rate due to the potential advantage of achieving maximum internal quantum efficiency of 100% [1]. Particularly, the second-row and the third-row transition metal complexes incorporating chelating ligands, such as 2,2′-bipyridine (bpy) and 2-phenyl pyridine (ppy), have attracted a great deal of research interest [2–4]. In this series, Ir(III) complexes are particularly promising because of their favorable short-excited-state-lifetime, well-suited energy level, high thermal stability and environmental inertness. In exploring efficient phosphorescent emitters for full color display, many efforts have been devoted to develop tricolor emitting materials [5–7]. However, both design and preparation of practicable blue-emitting Ir(III) complexes have been experiencing considerable challenges. This task is far more difficult than those for preparing green- and red-emitting ones [8]. Thanks for the

efforts from Adachi and Chou et al., blue emitters based on Ir(III) complexes have been developed, and then proved to be excellent candidates for OLED applications [9,10]. Nevertheless, it is still an important consideration to develop highly efficient and blue-emitting phosphorescent emitters for the realization of full color display.

Literature reports have demonstrated that the luminescence of cyclometalated Ir(III) complexes originates from the lowest ligand-centered triplet excited state (^{3}LC), admixed with contributions from singlet metal-to-ligand-charge-transfer excited state (^{1}MLCT) [11,12]. The electronic nature of cyclometalating ligand thus exerts obvious effect on the emissive state of their corresponding Ir(III) complex. Triphenylamine (TPA) and its derivatives have been proved to be efficient emitting systems [13]. Given proper conjugation length, both emissive energy and quantum yield can be controlled, suggesting that triphenylamine and its derivatives own a favorable electronic nature for efficient emissions. In addition, benzothiophene moiety has been proved to own high ^{3}LC energy level due to the electro-donor of S atom, which may be helpful to move the emission towards high energy region [14].

Guided by above considerations, in this paper, we synthesize a triphenylamine derived cyclometalating ligand of (4-benzothiazol-2-yl-phenyl)-diphenyl-amine (referred as BPDA) and its corresponding Ir(III) complex of $(BPDA)_2Ir(acac)$ (acac=acetylacetone), hoping to realize a high-energy-emitting Ir(III) complex with high luminescence

---

* Corresponding author at: School of Life Sciences, Tsinghua University, Beijing 100084, PR China. Tel.: +86 013718440582.
** Corresponding author at: School of Life Sciences, Tsinghua University, Beijing 100084, PR China.
E-mail address: zhangyangqing01@163.com (Y. Zhang).
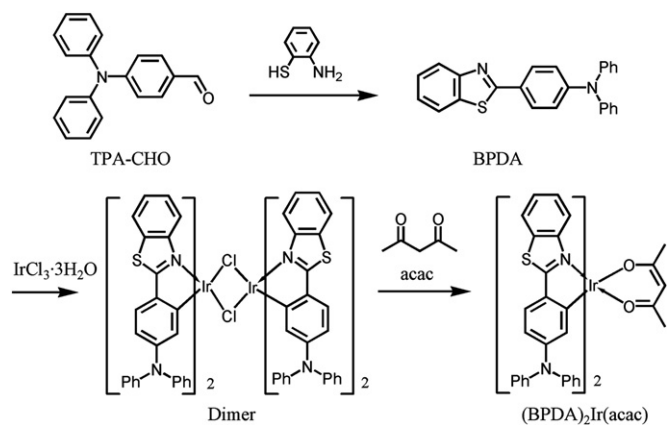
Scheme 1. A synthetic procedure for BPDA ligand and (BPDA)$_2$Ir(acac).

efficiency. The photophysical property, molecular structure, thermal property and electroluminescence (EL) performance of (BPDA)$_2$Ir (acac) are also investigated.

2. Experimental section

The synthetic procedure for BPDA ligand and its corresponding Ir(III) complex of (BPDA)$_2$Ir(acac) is shown in Scheme 1.

4-diphenylamino-benzaldehyde (TPA-CHO) was synthesized according to the literature procedure reported by Zhang et al. [13]. All starting materials, including triphenylamine, 2-amino-thiophenol, *p*-toluenesulfonic acid monohydrate, IrCl$_3 \cdot$3H$_2$O, 4,4′-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB), tris (8-hydroxy-quinoline)aluminum (Alq$_3$), 2,9-dimethyl4,7-diphenyl-1,10-phenanthroline (BCP) and 4,4′-dicarbazolyl-1,1′-biphenyl (CBP) were purchased from Aldrich Chemical Co. and used without further purifications unless otherwise stated. Organic solvents were carefully dried and distilled prior to use.

2.1. Synthesis of BPDA

BPDA was synthesized according to a literature procedure with minor modifications described as follows [15]. The mixture of 16 mmol of 2-aminothiophenol, 16 mmol of TPA-CHO, 1.6 mmol of *p*-toluenesulfonic acid monohydrate and 20 mL of CHCl$_3$ was refluxed under N$_2$ atmosphere for 24 h. After cooling, the mixture was poured into cold water and extracted with CH$_2$Cl$_2$. The organic phase was washed with water and dried over anhydrous sodium sulfate. After the evaporation of solvent, the residue was recrystallized from hot methanol to give the desired product as white solid. ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 6.94–6.98 (*d*, 2H), 7.17–7.23 (*t*, 6H), 7.39–7.46 (*t*, 4H), 7.74 (*d*, 2H), 7.87–7.88 (*t*, 2H) and 8.01–8.03 (*d*, 2H). Anal. Calcd for C$_{25}$H$_{18}$N$_2$S: C 79.33, H 4.79 and N 7.40. Found: C 79.21, H 4.86 and N 7.31.

2.2. Synthesis of (BPDA)$_2$Ir(acac)

The synthetic procedure for (BPDA)$_2$Ir(acac) is described as follows [16]. The mixture of 0.68 mmol of IrCl$_3 \cdot$3H$_2$O, 1.37 mmol of BPDA and 25 mL of 2-ethoxyethanol/water mixed solvent (*V:V*=3:1) was refluxed for 48 h. After cooling, a small quantity of water was added to precipitate solid product. The dried chloro-bridged dimmer was then mixed with 2.1 mmol of anhydrous sodium carbonate, 25 mL of 2-ethoxyethanol and 2.1 mmol of acac. The mixture was refluxed for 16 h. After cooling, a small quantity of cold water was added to precipitate solid product. The crude product was chromatographed on a silica gel column to

give the desired product as white needles. ^{1}H NMR (CDCl$_3$, 500 MHz) δ (ppm): 1.81 (*s*, 6H), 5.16 (*s*, 1H), 6.93–6.98 (*d*, 4H), 7.17–7.23 (*t*, 12H), 7.39–7.46 (*t*, 8H), 7.75 (*d*, 2H), 7.87–7.88 (*t*, 4H) and 8.01–8.03 (*d*, 4H). Anal. Calcd for C$_{55}$H$_{41}$N$_4$S$_2$O$_2$Ir: C 63.14, H 3.95 and N 5.35. Found: C 63.06, H 4.02 and N 5.27.

2.3. Methods and measurements

^{1}H NMR spectra were recorded with a Bruker AVANVE 500 MHz spectrometer. Element analyses were performed using a Vario Element Analyzer. UV–visible absorption spectra were obtained with a Shimadzu UV-3101PC spectrophotometer. Steady state photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. PL decay data were measured by a quanta ray DCR-3 pulsed Nd:YAG laser system in solution excited by a laser pulse at wavelength of 355 nm. Thermal gravimetric analysis (TGA) data were obtained using a SDT 2960 Simultaneous DSC–TGA of TA instruments with the heating rate of 10 °C/min under N$_2$.

Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations were performed on (BPDA)$_2$Ir(acac) by GAMESS at RB3PW91/SBKJC level. The initial structure was first optimized with MOPAC 2009 with PM6 Hamilton.

3. Results and discussion

3.1. Photophysical property of (BPDA)$_2$Ir(acac)

Fig. 1 shows the absorption spectrum of (BPDA)$_2$Ir(acac) in CHCl$_3$ with a concentration of 1×10^{-5} mol/L. Clearly, the absorption spectrum is composed of two absorption peaks. Compared with literature reports, we assign the intense absorption peak centering at ~380 nm to the spin-allowed $\pi \rightarrow \pi^*$ absorption of triphenylamine moiety, while, the weak peak around ~300 nm is attributed to the spin-allowed $\pi \rightarrow \pi^*$ absorption of benzothiophene moiety [13,17]. It is worth notable that no newly generated absorption bands for ^{1}MLCT or ^{3}MLCT transitions are detected in low energy region, suggesting that the participation of Ir(III) electrons in frontier molecular orbitals of (BPDA)$_2$Ir(acac) may be both slim and ineffective. Nevertheless, the absorption spectrum ends at ~440 nm, providing a wide band gap favoring high energy emitting.

The emission spectra of (BPDA)$_2$Ir(acac) upon different solvents, including *n*-hexane (polarity=0.06), toluene (polarity=2.4), chloroform (polarity=4.4), acetonitrile (polarity=6.2) and methanol
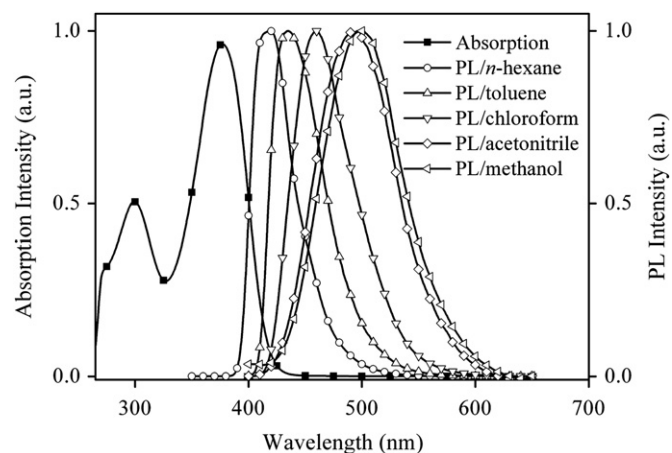

Fig. 1. Absorption spectrum of (BPDA)$_2$Ir(acac) in chloroform (1×10^{-5} mol/L), and PL spectra of (BPDA)$_2$Ir(acac) in various solvents (1×10^{-5} mol/L).