# Synthesis and Characterization of Green-Emitting Phosphorescent Ir(III) Complexes Based on Phenyl Benzimidazole Ligand<sup>1</sup>

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**Abstract**—Several new Ir(III) complexes with 2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole or 2-(4-bromophenyl)-1-methyl-benzo[*d*]imidazole ligands as cylcometalated ligand and acetylacetonate or picolinate as the ancillary ligand were synthesized and their structures and photophysical properties were characterized. HOMO and LUMO energy levels and the molecular structures of Ir(III) complexes were scrutinized by DFT calculations. The complexes exhibited green luminescence at the maximum emission peaks at ca 495–522 nm. The methyl group substituent and replacing of acetylacetonate with picolinate complex can enhance the complex thermal stability. HOMO energy levels of the complexes vary from -4.99 to -5.44 eV, the LUMO energy levels are between -1.52 and -1.97 eV.

**Keywords:** phenyl benzimidazole, iridium complex, green-emitting phosphorescent, DFT calculation, HOMO and LUMO energy

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Benzimidazole derivatives have recently attracted attention as the ligands of Ir(III) complexes owing to their synthetic availability. Photophysical properties of the cyclometalated iridium complexes can be finely tuned by systematic control of their structure and the corresponding ligands [1–8]. Acetylacetonate (acac) and picolinate (pic) have typically been used as the ancillary ligands of Ir(III) complexes that are excellent green phosphorescent organic light-emitting diodes (OLEDs) [9]. Ir(III) bis(4,6-difluorophenylpyridinato)picolinate (FIrpic) is widely used in blue phosphorescent OLEDs [10].

In this communication 2-(4-bromophenyl)-1Hbenzo[d]imidazole and 2-(4-bromophenyl)-1-methylbenzo[d]imidazole were used as the cyclometalated ligands, acetylacetonate and picolinate as the ancillary ligands in development of four new green phosphorescent heteroleptic iridium complexes. Photophysical properties, HOMO and LUMO energy levels of the complexes were studied. These also can be used as reactive monomers in development of polymer luminescent materials due to bromine atom in the structure.

#### EXPERIMENTAL

*O*-Phenylenediamine (99.5%, Aladdin), 4-bromobenzoic acid (99%, J&K Chemical), acetylacetone (99.5%, Aladdin), picolinic acid (99%, J&K Chemical), iodomethane (99%, J&K Chemical), and other chemicals were analytical reagent grade and used without further purification.

CHN analysis was performed on a Elementar Vario EL-III. Melting points were determined on a Reichert 7905 melting point meter. FT-IR spectra were recorded on a Nicolet 380 FT-IR spectrophotometer (KBr pellets). UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer (in CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR spectra were measured on a Bruker AVIII-400 NMR spectrometer (in DMSO- $d_6$ ). Photoluminescent spectra were measured on an Edinburgh FLS920-stm fluorescent spectrometer at 365 nm excitation wavelength. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA 851e thermogravimetric analyzer under N2 at a heating rate of DFT calculations were performed 10°C/min. employing the Gaussian 03 software package.

Synthetic routes to the monomers and complexes are presented in Fig. 1.

<sup>&</sup>lt;sup>1</sup> The text was submitted by the authors in English.



Fig. 1. Synthetic routes of iridium complexes A–D.

Synthesis of 2-(4-bromophenyl)-1H-benzo[d]imidazole (BrPhBI). O-Phenylenediamine (2.0 g, 18.5 mmol), 4-bromobenzoic acid (4.1g, 20.4 mmol) and polyphosphoric acid (25 g, 85%) were added to a threenecked flask and stirred at 175°C for 10 h. 2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole as a yellow solid was collected by suction filtration, washed with 500 mL of distilled water. The residue was neutralized with 10% aqueous Na<sub>2</sub>CO<sub>3</sub> maintaining pH of 7-8. The crude product was recrystallized from alcohol (yield 78%), mp 292.1–292.2°C. <sup>1</sup>H NMR spectrum, δ, ppm: 13.03 s (1H), 8.13 t (J = 5.4 Hz, 2H), 7.77 t (J = 5.4 Hz, 2H), 7.60 d.d (J = 4.9, 3.3 Hz, 2H), 7.21 d.d (J = 6.0, 3.1 Hz, 2H). <sup>13</sup>C NMR spectrum (101 MHz, DMSO), δ, ppm: 150.69, 132.45, 129.86, 128.83, 123.72, 122.80. IR spectrum, v, cm<sup>-1</sup>: 3430, 3051, 2909, 2875, 1626, 1446, 1428, 709.

**2-(4-Bromophenyl)-1-methyl-benzo**[*d*]imidazole (BrPhMBI). 2-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (0.8 g, 2.93 mmol) was dissolved in 25 mL of dimethyl formamide and 1.25 g of anhydrous potassium carbonate and iodomethane (0.25 mL, 4.0 mmol) were added at room temperature. The reaction mixture was stirred for 10 h, then was poured into water (100 mL) and extracted with ethyl acetate ( $3 \times 30$  mL). The combined organic layer was washed with saturated NaCl solution ( $3 \times 100$  mL) and 10% NaOH (aq) ( $3 \times 100$  mL), and dried by anhydrous MgSO<sub>4</sub>. Upon evaporation of the solvent the product was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 2 : 1) to give a yellow powder product (0.656 g, yield 78%).

 $(BrPhBI)_4Ir_2Cl_2 \cdot IrCl_3 \cdot 3H_2O$  (0.56 g, 1.59 mmol), BrPhBI (1.01 g, 3.7 mmol), 2-ethoxyethanol (30 mL), and water (10 mL) were added into a three-neck flask. The mixture was refluxed under the atmosphere of Ar for 24 h and then cooled down to room temperature. A yellow precipitate was filtered off and washed with water and ethanol repeatedly (yield 46.7%).

(**BrPhMBI**)<sub>4</sub>**Ir**<sub>2</sub>**Cl**<sub>2</sub>. The dimeric product was prepared according to the procedure applied to the synthesis of (BrPhBI)<sub>4</sub>**Ir**<sub>2</sub>**Cl**<sub>2</sub> using 1.10 mmol BrPhMBI and 0.448 mmol IrCl<sub>3</sub>·3H<sub>2</sub>O (yield 60%).

Ir(III) bis{2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-C<sup>2</sup>,N}-acetylacetonate [(BrPhBI)<sub>2</sub>Ir(acac)] (complex A). A mixture of 0.12 g (0.078 mmol) (BrPhBI)<sub>4</sub>Ir<sub>2</sub>Cl<sub>2</sub>, 0.02 g (0.2 mmol) acetylacetonate, 0.085g sodium carbonate and 15 mL 2-ethoxyethanol was refluxed under N<sub>2</sub> at 120°C for 24 h. Upon cooling down to room temperature small portion of water was added. A yellow precipitate was filtered off and washed with ethanol, ether and *n*-hexane several times. The yellow solid product was purified by column chromatography (silica gel, dichloromethane), yield 47.8%. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 13.42 d.d (J =32.0, 21.6 Hz, 2H), 8.10–7.39 m (4H), 7.13 d.d (J =16.6, 8.2 Hz, 4H), 6.89–6.58 m (6H), 5.99–5.93 m (1H), 2.60 d (J = 63.4 Hz, 3H), 2.09–1.90 m (3H). IR spectrum, v, cm<sup>-1</sup>: 3445, 3102, 3051, 2962, 2924, 2848, 1727, 1700, 1629, 1589, 1527, 1456, 1412, 738. Found, %: C 44.34, H 2.46, N 6.51. C<sub>31</sub>H<sub>23</sub>Br<sub>2</sub>IrN<sub>4</sub>O<sub>2</sub>. Calculated, %: C 44.56, H 2.77, N 6.71.

Ir(III) bis{2-(4-bromophenyl)-1-methyl-benzo[*d*]imidazole-C<sup>2</sup>,N}-acetylacetonate [(BrPhMBI)<sub>2</sub>Ir(acac)] (complex B). The complex was prepared following the procedure as above (yield 46%). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 7.88–7.64 m (6H), 7.46–7.32 m (4H), 7.04 d (*J* = 8.1 Hz, 4H), 6.23 s (1H), 4.37 t (*J* = 21.0 Hz, 6H), 1.24 s (6H). IR spectrum, v, cm<sup>-1</sup>: C 44.34, H 2.46, N 6.51.:3047, 2920, 1718, 1613, 1577, 1527, 1504, 1461. Found, %: C 46.03, H 3.28, N 6.21. C<sub>33</sub>H<sub>27</sub>Br<sub>2</sub>IrN<sub>4</sub>O<sub>2</sub>. Calculated, %: C 45.89, H 3.15, N 6.49.

Ir(III) bis{2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-C<sup>2</sup>,N}-picolinate [(BrPhBI)<sub>2</sub>Ir(pic)] (complex C). The complex was prepared following the similar procedure as above (yield 63%). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 8.10 s (1H), 8.02 s (1H), 7.80–7.60 m (8H), 7.36– 7.24 m (4H), 7.20 m (4H), 5.52 d (2H). IR spectrum, v, cm<sup>-1</sup>: 3438, 3089, 2968, 2923, 2854, 1727, 1629, 1590, 1532, 1453, 1301, 1004, 808, 697 cm<sup>-1</sup>. Found, %: C 45.02, H 2.53, N 8.21. C<sub>32</sub>H<sub>20</sub>Br<sub>2</sub>IrN<sub>5</sub>O<sub>2</sub>. Calculated, %: C 44.77, H 2.35, N 8.16.

Ir(III) bis{2-(4-bromophenyl)-1-methyl-benzo[*d*]imidazole-C<sup>2</sup>,N}-picolinate [(BrPhMBI)<sub>2</sub>Ir(pic)] (complex D). The complex was prepared following the similar procedure as above (yield 61%). <sup>1</sup>H NMR spectrum, δ, ppm: 7.98 d (J = 8.7 Hz, 4H), 7.88 m (6H), 7.70 m (4H), 7.21 m (4H), 4.38 d (J = 7.0 Hz, 6H). IR spectrum, v, cm<sup>-1</sup>: 3062, 2970, 2922, 1726, 1654, 1601, 1462, 1358, 1307, 1026, 802, 697 cm<sup>-1</sup>. Found, %: C 46.28, H 2.64, N 7.69. C<sub>34</sub>H<sub>24</sub>Br<sub>2</sub>IrN<sub>5</sub>O<sub>2</sub>. Calculated, %: C 46.06, H 2.73, N 7.90.

### **RESULTS AND DISCUSSION**

**Photophysical properties.** UV-Vis absorption and photoluminescence (PL) spectra of complexes A-D in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature are presented in Fig. 2. The complexes possess similar absorption



Fig. 2. UV absorption and photoluminescence spectra of complexes (a) A, (b) B, (c) C, and (d) D in  $CH_2Cl_2$  solutions at room temperature.

bands in the spectral region of 230–320 nm, that are mainly assigned to the spin-allowed  $\pi \rightarrow \pi^*$  transition characteristic of the C<sup>A</sup>N ligands. The broad absorption peaks around 320–400 nm are metal-to-ligand charge-transfer (MLCT) and ligand-to-ligand charge-transfer transitions [11]. The long tail absorption from 400 to 500 nm were assigned to the mix states containing spin-orbit coupling enhanced  ${}^3\pi \rightarrow \pi^*$  and  ${}^3MLCT$  transitions [12].

As for PL emission spectra, complexes A–D exhibited intense greenish emission at 505, 508, 522, and 495 nm, respectively. Variation of the ligands, such as substitution of methyl group in the benzimidazole in complexes B and D (cf. complex A and C), the replacement of acetylacetonate with picolinate in complexes C and D (cf. complex A and B), resulted in a shift of the emission peak wavelengths as well as a slight boost of the intensity of the bands. The data indicated that the ancillary ligand and modification of the cyclometalated ligand by adding methyl group to the benzimidazole have influenced on the emission of the iridium complexes.

The CIE values of complexes A-D were calculated to be (0.301, 0.591), (0.286, 0.544), (0.343, 0.544) and (0.258, 0.573), respectively. As shown in Fig. 3, the CIE chromaticity coordinate of the complex C is located in green-yellow light region, and complex A, B, and D all located in the green region.

**Thermostability.** Thermal durability of complexes is important for OLED devices performance. Complexes A-D were analyzed by thermogravimetric data under an N<sub>2</sub> atmosphere and the 10% weight loss temperature are 343°, 352°, 422°, and 441°, respectively. In general, the results indicated that complexes had an excellent thermal stability even at ca 300°. Compound **B** was stable up to 352°. The observations indicated that the Ir(III) complexes thermal stability has been enhanced by introducing methyl group substituents and the replace ligand of acetyl-acetonate with picolinate.



Fig. 3. CIE1931 chromaticity coordinates for complexes A–D.

**Theoretical calculations.** Calculations of complexes A-D were performed employing the Gaussian 03 software package. HOMOs of complexes were assigned to an admixture of the *d*-orbital of metal and cyclometalated phenyl ligands, while the LUMOs of complexes **A** and **B** were located on the cyclometalated ligands, complexes **C** and **D** were contributed by the  $\pi$ -orbitals of picolinic acid ancillary ligands, respectively.

HOMO levels of organic compounds play an important role in hole-injection/transporting, while LUMO levels influence the capability of electron-injection/transporting. In the complexes **A**–**D**, electron-donating/withdrawing were introduced on the phenyl ring of the phenyl benzimidazole ligand regulating the

The HOMO and LUMO values for complexes **A–D** according to DFT calculations

Complex	HOMO, eV	LUMO, eV	$E_g$ , eV
Α	-5.09	-1.61	3.48
В	-4.99	-1.52	3.47
С	-5.44	-1.97	3.47
D	-5.36	-1.90	3.46

HOMO energy, meanwhile the LUMO energy could be readily tuned by modification of the ancillary ligands. So, we could change the ligands to construct different energy-gap new Ir(III) complex, design and synthesize phosphorescent materials for highly efficient OLEDs. DFT calculation data indicated that the HOMO and LUMO distributions were mainly focused on cyclometalated ligands that contributed to the appropriate selection of ligands and the electrondonating or -withdrawing groups introduced to the proper position of ligands thus geting new phosphorescent materials with excellent electronic and luminescent properties.

Table summarized the HOMO and LUMO data of complexes A–D. The HOMO energy levels were in the range of -4.99 to -5.44 eV. The LUMO energy levels were between -1.52 and -1.97 eV, while the energy gap  $E_g$  were very close. The target Ir(III) complexes **B** and **D** containing methyl group substituents on the benzimidazole main ligand promoted both HOMO and LUMO energies, while the HOMO and LUMO levels of the complexes that used picolinic acid as the ancillary ligand.

#### CONCLUSIONS

We report the synthesis and characterization of four Ir(III) complexes based on 2-(4-bromophenyl)-1Hbenzo[d]imidazole or 2-(4-bromophenyl)-1-methylbenzo[d]imidazole as main ligand and the acetylacetone or picolinic acid as ancillary ligand. The complexes possess similar absorption bands in the spectral region of 230-320 nm and PL emission spectra demonstrated maximum peaks of 505, 508, 522, and 495 nm, respectively. DFT calculation results indicated that Ir(III) complexes containing methyl group substituents on the benzimidazole main ligand promoted an increase in both HOMO and LUMO energies and the HOMO and LUMO levels of the complexes containing acetylacetone were higher than those of using picolinic acid as the ancillary ligand. For the complexes A and B the benzimidazole may possess hole injection and electronic transmission bipolar capabilities.

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