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New borylated iridium(III) complexes containing oligothiophene-based cyclometalating ligand were synthesized and characterized. The electron-withdrawing boryl moiety is effective to cause a red-shift of the phosphorescence to the red or even near-infrared. Red to near-infrared emitting organic light-emitting devices were fabricated.

Highlights

> Metallophosphors of iridium with borylated oligothiophene ligands > Red to near-infrared OLEDs were fabricated > Effect of thiophene ring on the emission.

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Metallophosphors of iridium(III) containing borylated oligothiophenes with electroluminescence down to the near-infrared region

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Dedicated to Professor F. G. A. Stone in the special issue of 25th ICOMC

Abstract

The synthesis, structural, electrochemical and photophysical studies of a series of cyclometalated iridium(III) complexes with functionalized borylated oligothiophene ligands are reported. The effect of oligothiophene chain length on the photophysical properties of these metal complexes was examined in detail and their excited state properties can be controlled by increasing the number of thienyl rings in the cyclometalating ligand, thus allowing the emission to be tuned from red to near-infrared. All of the iridium(III) complexes were utilized in the fabrication of phosphorescent organic light-emitting diodes and their device performances were investigated. These electrophosphors emit in the red to near-infrared regions. The present work enables the rational design of new borylated iridium phosphors by synthetically tailoring the structure of oligothiophene-based pyridine ring that can permit color tuning towards near-infrared phosphorescence.

Keywords: Boron \cdot Organic light-emitting diodes \cdot Iridium \cdot Phosphorescence \cdot Near-Infrared emission

1. Introduction

There is a growing interest in the near-infrared (NIR) emission from metal complexes through photoluminescence [1-5] or electroluminescence [6-10]. Sources of near-infrared emission are of interest for a variety of biological and biomedical applications, including glucose monitoring [11] and immunoassay [12,13]. Furthermore, there are also potential uses for NIR light sources in telecommunications [14] and defense applications [15]. The first class of complexes showing notable NIR luminescence have to be credited to the lanthanide complexes [6,16-19] Sharp emission signals for the lanthanide complexes are expected simply because the 4f orbitals of the lanthanide elements are buried deep within the atom. However, these complexes would not be seriously coupled with the ligand vibrational motions, so that their emission properties are not easily tuned by changing the functionality of the attached ligands. Moreover, due to their low optical cross section arising from the forbidden transition, direct emissions from these ions are always weak and inefficient. Other classes of metal complexes exhibiting NIR phosphorescence are Pd porphyrinate or polypyridyl complexes involving the Re(I), Ru(II) and Os(II) metal ions with the d⁶ electronic configuration [20-23]. These complexes absorb appreciably in the low-energy region of the spectra but show very weak luminescence [20-23]. Other attempts to achieve NIR electroluminescence (EL) (such as low band-gap organic chromophores [24-28] and polymers [29,30]) also suffer from the same drawbacks.

Herein, we have designed and synthesized new neutral Ir(III) complexes with very robust

and stable dimesityboryl-oligothiophene groups on the cyclometalated ligands which can extend the emission wavelength to the NIR region. As compared to the structurally analogous Re(I), Ru(II) and Os(II) complexes, Ir(III) complexes usually display longer excited state lifetimes, higher luminescence efficiencies and the strengthened metal-ligand interaction can increase the stability and luminous efficiency of the corresponding Ir(III) complexes [31,32]. Therefore, Ir(III) tris-chelate complexes with extended π -systems have generated much interest recently because of their potential use in a variety of photonic applications, including photocatalysis [33], photoelectrochemistry [34] and electroluminescence [35]. The nature of the cyclometalating ligand was found to affect strongly the energy of the emissive state so that the emission color could be tuned [35]. One of the advantages of using boron center in the cyclometalating ligand is the availability of its empty $p\pi$ orbital which can act as excellent electron acceptors. When we combine the boryl group with thiophene donor, a donor-acceptor (D-A) approach not only enhances the charge transfer properties of the complexes, but also extends the emission of the resulting Ir(III) complexes to the NIR region. Also, the bulky mesityl groups also promote the formation of amorphous films with high glass transition temperatures, which can greatly improve the performance and the long term stability of optoelectronic devices such as OLEDs by removing grain boundaries [36-38]. Four Ir(III) borylated complexes were synthesized here and their application in organic light emitting diodes (OLEDs) will also be investigated and discussed.

2. Experimental

2.1. General information

All reactions were performed under nitrogen. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reagents for the chemical syntheses were purchased from Aldrich or Acros Organics. All reactions were monitored by thin-layer chromatography (TLC) with Merck pre-coated glass plates. Flash column chromatography and preparative TLC were carried out using silica gel from Merck (230–400 mesh). Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. NMR spectra were measured in CDCl₃ on a Varian Inova 400 MHz FT-NMR spectrometer and chemical shifts are quoted relative to tetramethylsilane for ¹H and ¹³C nuclei.

2.2. *Physical measurements*

UV-vis spectra were obtained on a HP-8453 spectrophotometer. The photoluminescent properties and lifetimes of the compounds were probed on the Photon Technology International (PTI) Fluorescence Master Series QM1 system. The quantum yields were determined in CH₂Cl₂ solutions at 293 K against Rhodamine 6G ($\Phi = 0.95$) as a reference [39]. A conventional three-electrode configuration consisting of a glassy carbon working electrode and Pt-wires as the counter and reference electrodes, was used. The solvent in all measurements was THF, and the supporting electrolyte was 0.1 M [Bu₄N]PF₆. Ferrocene was added as a calibrant after each

set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc^+) couple at a scan rate of 100 mV/s. Thermal analyses were performed with Perkin-Elmer TGA6 thermal analyzers.

2.3. Preparation of compounds

2.3.1. Synthesis of L1

A flask containing a mixture of **L1-I** (500 mg, 1.09 mmol) and 2-(tributylstannyl)pyridine (422 mg, 1.31 mmol) and 50 mL toluene was charged with nitrogen, after which a catalytic amount of Pd(PPh₃)₄ (30 mg) was added. The mixture was stirred for two days at 110 °C. The mixture was then allowed to cool to room temperature and water was added. The solution was extracted with ethyl acetate and the organic layer was separated, dried by MgSO₄, filtered and concentrated. After purification by preparative TLC plate (hexane:CH₂Cl₂, 1:1 v/v), the title compound was obtained as a pale yellow oil in 48% yield (214 mg).

L1: Spectral Data: ¹H NMR (CDCl₃): δ = 8.56–8.55 (d, J = 4.8 Hz, 2H, Ar), 7.71–7.66 (m, 2H, Ar), 7.44–7.43 (m, 1H, Ar), 7.17–7.14 (m, 1H, Ar), 6.81 (s, 4H, Ar), 2.25 (s, 6H, mesityl), 2.13 (m, 12H, mesityl). ¹³C NMR (CDCl₃): δ = 156.11, 152.26, 149.73, 140.99, 140.78, 138.54, 136.70, 128.13, 126.64, 122.64, 119.67 (Ar), 23.10, 21.18 (mesityl). FAB-MS: *m/z* = 409 (M⁺).

2.3.2. Synthesis of L2-Br

To a solution of 2,2'-dibromobithiophene (1.0 g, 3.10 mmol) in ether (30 mL) was added

a hexane solution of ⁿBuLi (1.6 M, 2.13 mL, 3.41 mmol) dropwisely at –78 °C. The mixture was stirred at the same temperature for 3 h. A solution of dimesitylboron fluoride (1.11 g, 3.72 mmol) in ether (20 mL) was added to the reaction mixture via syringe. The reaction mixture was gradually warmed to room temperature and stirred overnight. After addition of water (20 mL), the organic layer was separated and the aqueous layer was extracted with diethyl ether for three times. The combined organic layer was dried over MgSO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography with hexane to afford **L2-Br** in 91% yield (1.40 g) as a bright yellow solid.

L2-Br: Spectral Data: ¹H NMR (CDCl₃): δ = 7.34–7.33 (d, J = 4.0 Hz, 1H, Ar), 7.22–7.21 (m, 1H, Ar), 7.00–6.95 (m, 2H, Ar), 6.84 (s, 4H, Ar), 2.31 (s, 6H, mesityl), 2.14 (s, 12H, mesityl). ¹³C NMR (CDCl₃): δ = 148.57, 141.38, 140.79, 138.78, 138.63, 130.87, 128.18, 125.81, 124.89, 112.51 (Ar) 23.45, 21.21 (mesityl). FAB-MS: m/z = 492 (M⁺).

2.3.3. Synthesis of L2

A flask containing a mixture of **L2-Br** (1.36 g, 2.75 mmol) and 2-(tributylstannyl)pyridine (1.07 g, 3.31 mmol) and 50 mL toluene was charged with nitrogen, after which a catalytic amount of $Pd(PPh_3)_4$ (40 mg) was added. The mixture was stirred for two days at 110 °C. The mixture was then allowed to cool to room temperature and water was added. The solution was extracted with ethyl acetate and the organic layer was separated, dried by MgSO₄, filtered and concentrated. After purification by column chromatography (hexane:CH₂Cl₂, 1:1 v/v), the title

compound was obtained as a yellow oil in 59% yield (800 mg).

L2: Spectral Data: ¹H NMR (CDCl₃): $\delta = 8.56$ (d, J = 4.0 Hz, 1H, Ar), 7.64–7.59 (m, 2H, Ar), 7.44 (d, J = 4.0 Hz, 1H, Ar), 7.36 (m, 2H, Ar), 7.23 (m, 1H, Ar), 7.13–7.10 (m, 1H, Ar), 6.84 (s, 4H, Ar), 2.34 (s, 6H, mesityl), 2.16 (s, 12H, mesityl). ¹³C NMR (CDCl₃): $\delta = 151.98$, 149.69, 149.57, 144.71, 141.58, 140.76, 138.97, 138.50, 136.55, 128.98, 128.13, 126.06, 125.79, 125.20, 122.04, 118.51 (Ar) 23.45, 21.18 (mesityl). FAB-MS: m/z = 491 (M⁺).

2.3.4. Synthesis of iridium(III) chloro-bridged dimer

IrCl₃.*n*H₂O and 2.5 molar equivalents of cyclometalating ligand (L1 or L2) were added to a mixture of 2-ethoxyethanol (6 mL) and water (2 mL) and the resulting mixture was heated under a nitrogen atmosphere for 16 h. The reaction mixture was allowed to cool to room temperature and water was added (20 mL). The mixture was filtered and the residue was washed with ethanol, followed by hexane and dried under vacuum completely. The Ir(III) dimers were used without further purification.

2.3.5. Synthesis of homoleptic iridium(III) complex Ir-1

To a solution of **L1** (197 mg, 0.473 mmol) and its corresponding **Ir-1** dimer (232 mg, 0.111 mmol) in 2-ethoxyethanol (8 mL) was added silver trifluoromethane sulfonate (60.5 mg, 0.235 mmol). The mixture was stirred at 110 °C for 3 days in the dark. After that, the reaction mixture was gradually cooled to room temperature and was filtered. After addition of water, the organic

layer was separated and the aqueous layer was extracted with chloroform for three times. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The mixture was purified by silica gel column chromatography (hexane:CH₂Cl₂, 1:4, v/v) of **Ir-1** in 41% yield as a red solid.

Ir-1: Spectral Data: ¹H NMR (CDCl₃): δ = 7.57–7.46 (m, 9H, Ar), 6.76–6.62 (m, 18H, Ar), 2.25 (s, 18H, mesityl), 1.81 (s, 36H, mesityl). ¹³C NMR (CDCl₃): δ = 161.94, 159.52, 153.49, 149.47, 148.46, 148.08, 140.87, 137.75, 136.43, 127.76, 120.55, 118.92 (Ar), 23.07, 21.30 (mesityl). FAB-MS: m/z = 1417 (M⁺). Anal. Calc. for C₈₁H₈₁N₃B₃S₃Ir: C, 68.64; H, 5.76; N, 2.96. Found: C, 68.72; H, 5.79; N, 3.10 %.

2.3.6. Synthesis of heteroleptic iridium(III) complex Ir-2

A mixture of crude iridium chloro-bridged dimer (170 mg, 0.0813 mmol) derived from **L1**, acetylacetone (0.029 mL, 0.244 mmol) and Na₂CO₃ (86 mg, 0.813 mmol) in 2-ethoxyethanol (8 mL) was stirred at 100 °C under nitrogen for 16 h. After the removal of all volatile components, the compound was purified by silica column chromatography using hexane:CH₂Cl₂ (1:5, v:v) as the eluent to afford the target compound as a red solid (28 %, 87 mg).

Ir-2: Spectral Data: ¹H NMR (CDCl₃): δ = 8.32–8.31 (d, J = 5.6 Hz, 2H, Ar), 7.50–7.49 (m, 4H, Ar), 6.88–6.70 (m, 10H, Ar), 6.36 (s, 2H, Ar), 5.28 (s, 1H, acac), 2.24 (s, 12H, Ar), 1.96 (s, 24H, Ar), 1.86 (s, 6H, CH₃). ¹³C NMR (CDCl₃): δ = 184.67 (CO), 164.06, 152.43, 150.94,

148.70, 147.53, 145.49, 141.65, 140.84, 137.95, 137.40, 127.81, 120.41, 118.73 (Ar), 100.73 (acac) 28.66, 23.88 (mesityl), 21.25 (CH₃). FAB-MS: m/z = 1108 (M⁺). Anal. Calc. for $C_{59}H_{61}N_2B_2O_2S_2Ir$: C, 63.95; H, 5.55; N, 2.53. Found: C, 63.86; H, 5.69; N, 2.77%.

2.3.7. Synthesis of homoleptic iridium(III) complex Ir-3

Similar synthetic procedures as complex Ir-1 was adopted but ligand L2 (35 mg, 0.351 mmol) was used instead. The isolated complex was red solid (62 %, 35 mg).

Ir-3: Spectral Data: ¹H NMR (CDCl₃): δ = 7.46–7.44 (d, *J* = 7.6 Hz, 3H, Ar), 7.38–7.37 (m, 6H, Ar), 7.29–7.25 (m, 6H, Ar), 6.79 (s, 12H, Ar), 6.72–6.69 (m, 6H, Ar), 2.28 (s, 18H, mesityl), 2.13 (s, 36H, mesityl). ¹³C NMR (CDCl₃): δ = 161.64, 160.09, 150.90, 148.51, 147.70, 141.57, 141.18, 140.78, 140.13, 138.26, 136.76, 136.62, 133.82, 128.06, 126.14, 119.39, 117.74 (Ar), 23.46, 21.19 (mesityl). FAB-MS: *m*/*z* = 1663 (M⁺). Anal. Calc. for C₉₃H₈₇N₃B₃S₆Ir: C, 67.14; H, 5.27; N, 2.53. Found: C, 67.32; H, 5.32; N, 2.77%.

2.3.8. Synthesis of heteroleptic iridium(III) complex Ir-4

Similar synthetic procedures as complex **Ir-2** was employed and the title complex was isolated as a red solid (70%, 30 mg).

Ir-4: Spectral Data: ¹H NMR (CDCl₃): δ = 8.26–8.24 (d, J = 5.5 Hz, 2H, Ar), 7.63–7.59
(m, 2H, Ar), 7.44–7.43 (m, 2H, Ar), 7.23–7.15 (m, 4H, Ar), 6.94–6.91 (m, 2H, Ar), 6.79–6.77 (s, 8H, Ar), 6.33 (s, 2H, Ar), 5.21 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity), 1.79 (s, 1H, acac), 2.26 (s, 12H, mesity), 2.05 (s, 24H, mesity),

6H, CH₃). ¹³C NMR (CDCl₃): $\delta = 184.56$ (CO), 164.13, 150.68, 149.12, 148.59, 148.36, 141.34, 140.86, 139.94, 138.35, 137.73, 137.60, 130.51, 128.05, 125.82, 118.89, 117.61 (Ar), 100.64 (acac), 28.55, 23.36 (mesity), 21.20 (CH₃). FAB-MS: m/z = 1272 (M⁺). Anal. Calc. for C₆₇H₆₅N₂B₂O₂S₄Ir: C, 63.25; H, 5.15; N, 2.20. Found: C, 63.40; H, 5.34; N, 2.28%.

2.4. X-ray crystallography

X-Ray diffraction data for **Ir-2** were collected at 173 K using graphite-monochromated Mo–K α radiation ($\lambda = 0.71073$ Å) on a Bruker Axs SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT+ [40] and an absorption correction (SADABS) [41] was applied to the collected reflections. The structure was solved by the Direct or Patterson methods (SHELXTL) [42] in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on F^2 . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined anisotropically. Crystal data for **Ir-2**·2CH₂Cl₂: C₆₁H₆₅N₂B₂Cl₄O₂S₂Ir $M_w = 1277.89$, monoclinic, space group $P2_1/n$, a = 14.554(1), b = 24.898(2), c = 16.445(1) Å, $\beta = 90.258(1)^\circ$, V = 5959.0(8) Å³, Z = 4, $\rho_{calcd} = 1.424$ mg m⁻³, $\mu(Mo_{K\alpha}) = 2.533$ mm⁻¹, F(000) = 2592. 28707 reflections measured, of which 10383 were unique ($R_{int} = 0.0434$). Final $R_1 = 0.0416$ and $wR_2 = 0.1022$ for 7905 observed reflections with $I > 2\sigma(I)$.

2.5. OLED fabrication and measurements

Commercial indium tin oxide (ITO) coated glass with sheet resistance of $20-30 \ \Omega/$ was used as the starting substrates. Before device fabrication, the ITO glass substrates were cleaned by ultrasonic baths in organic solvents followed by ozone treatment for 10 min. Each device was assembled in the following sequence: ITO on glass substrate (anode), 50 nm of PEDOT, 80 nm of the emitting layer made of CBP host and phosphorescent dopant (x%), 15 nm of BCP, 30 nm Alq₃, 1 nm of LiF and 100 nm of Al (cathode). The organic layers were evaporated and laminated in the above sequence less than 10^{-6} Torr without breaking vacuum between each vacuum deposition process. The layer thickness was monitored in situ using a quartz crystal oscillator. The EL spectra and CIE coordinates were measured with a PR650 spectra colorimeter. The L–V–J curves of the devices were recorded by a Keithley 2400/2000 source meter and the luminance was measured using a PR650 SpectraScan spectrometer. All the experiments and measurements were carried out at rt under ambient conditions.

2.6. Molecular orbital calculations

Density functional calculations at the B3LYP level were performed based on their experimental geometry obtained from the X-ray data. The basis set used for C, N, B, O, and H atoms was 6-31G while effective core potentials with a LanL2DZ basis set were employed for the Ir atom [43,44]. All the calculations were carried out using the Gaussian 03 program [45]. All the MO plots were made with the use of Molden 3.5 [46].

3. Results and discussion

3.1. Synthetic methodologies and chemical characterization

The chemical structures and synthetic procedures of new dimesityboryl-oligothiophene cyclometalating ligands L1–L2 and their Ir(III) complexes Ir-1–Ir-4 are shown in Schemes 1 and 2. For use as optoelectronic materials and fabrication of their devices, the boron center must be rendered stable to nucleophilic attack and hydrolysis. This can be readily achieved by functionalization of the boron center with bulky aryl substituents, such as mesityl (2,4,6-trimethylphenyl group). The bromo precursor L2-Br can be obtained from selective monolithiation of 2,2'-dibromobithiophene followed by reaction with dimesityboron fluoride. Synthesis of ligands L1–L2 was readily achieved by successive coupling of L1-I or L2-Br with 2-tributylstannylpyridine via Stille-type reaction conditions [47]. L1–L2 were easily converted to the iridium-µ-chloro-bridged dimers by the reaction of iridium trichloride hydrate with ligands [36]. It is worth noting that the homoleptic Ir(III) complexes are typically synthesized by reacting Ir(acac)₃ with cyclometalating ligand at 200°C in glycerol under N₂ [48]. However, our boron based ligands tend to decompose under such high temperature and hence result in very low yields. Prompted by the recent work of Crutchley and coworkers [49] on a lower temperature process for the preparation of new tris(cyclometalated) Ir(III) complexes, we have succeeded in preparing Ir-1 and Ir-3 by reacting the Ir(III) dimer with an excess of the corresponding ligands at 110°C in the dark. Here, the reaction is run with an excess of ligand, which is easily recovered and reused. On the other hand, the diiridium(III) complexes were then

converted to mononuclear iridium(III) complexes Ir-2 and Ir-4 by replacing the two bridging chlorides with bidentate monoanionic acetylacetonate (acac⁻) ligand. All of the Ir(III) complexes with boryl-substituted oligothiophene produced are stable in air and can be purified by column chromatography or preparative TLC plates on silica gel and they are soluble in common chlorinated hydrocarbons and toluene. The structures were unequivocally characterized by elemental analyses, mass spectrometry and NMR spectroscopies (see Experimental section). The facial geometry of homoleptic complexes Ir-1 and Ir-3 is confirmed by the simplicity of 1 H NMR spectral pattern, which indicates that the number of coupled spins is equal to that of the protons on one ligand because the three ligands are magnetically equivalent due to the 3-fold symmetry of the molecule [50]. The molecular structure of Ir-2 was further confirmed by X-ray crystallography (Fig. 1). The molecular structure reveals the central Ir(III) center to be coordinated by two anionic L2 C^N ligands and one chelating acac anion. The Ir(III) atom resides in a distorted octahedral environment, with the cis-O,O, cis-C,C, and trans-N,N chelate disposition. The crystallographic results were tabulated in Table 1. All of the complexes Ir-1 to Ir-4 exhibit high thermal stability with the decomposition temperatures for a 5% weight loss of in the range of 301 to 325 °C.

3.2. Photophysical and electrochemical characterization

The photophysical properties of **Ir-1–Ir-4** in CH₂Cl₂ solution were investigated (Table 2). The absorption and photoluminescence (PL) spectra of all complexes at 293 K are shown in Fig.

2. In common with most Ir(III) complexes, the absorption spectra exhibited two major bands. The intense absorption bands with distinct vibronic features in the UV region are assigned to the spin-allowed ${}^{1}\pi{-}\pi^{*}$ transitions of C^N ligands. The next weaker, low-energy features with peak wavelengths in the region of 400–600 nm which appear as humps can be ascribed to an admixture of ${}^{1}MLCT$, ${}^{3}MLCT$ and ${}^{3}\pi{-}\pi^{*}$ excitations [51]. However, these absorption bands cannot be distinctly resolved mainly owing to their hidding inside the UV region of the strong singlet transitions which are of much lower but non-negligible absorptivities. Relatively higher absorption coefficients for the complexes with L2 than those with L1 in both regions were observed as the number of thiophene rings increases [52].

Upon photoexcitation, each of **Ir-1** and **Ir-2** emits an intense red light in CH₂Cl₂. Both of them show a strong room-temperature phosphorescence band at 643 and 661 nm, respectively. It is believed that their emissions arise predominantly from the ligand-centered ${}^{3}\pi-\pi^{*}$ excited state since they display a large Stokes shift (> 100 nm) from the lowest energy absorption peak and vibronic progressions. Also, there is only a small dependence of the PL on solvent polarity and temperature. The full width at half maximum (FWHM) of the PL is only 52 and 56 nm for **Ir-1** and **Ir-2**, respectively, which precludes the possibility of their emissions to be contributed by the charge transfer characters since the emissions from CT states are often broad, featureless and sensitive to solvent polarity and temperature [53]. The vibronic progression of ca. 1267 and 1240 cm⁻¹ (v₀₋₁) in the emission profile of **Ir-1** and **Ir-2** corresponds to the aromatic stretching of the cyclometalated ligands which is diagnostic of the substantial involvement of the

ligand-centered π - π * transitions in the emission. On the other hand, as compared to the Ir(III) complexes with $B(Mes)_2$ -ppy (Hppy = 2-phenylpyridine) reported previously by us [54], a large red-shift was observed upon replacement of phenyl ring ($\lambda_{PL} = 605$ nm) by the electron-donating thiophene group in Ir-2. This is in agreement with the observable bathochromic shift in the emission wavelength from $[Ir(ppy)_3]$ ($\lambda_{PL} = 514$ nm) to $[Ir(thpy)_3]$ ($\lambda_{PL} = 550$ nm) [55] due to the fact that this kind of ligands having intramolecular donor-acceptor (D-A) systems would exhibit bathochromic shifts in both absorption emission and spectra. Generally, 2-thiophenylpyridine (thpy) itself has a D-A character resulting from the interaction between an electron-rich group, thiophene, and an electron-deficient group, pyridine. Through the introduction of B(Mes)₂ group, a powerful π -electron acceptor (with vacant p_{π} orbital on boron) and an inductive σ -donor (related to the electropositive nature of the boron atom), the D-A character of the resulting complex is enhanced. Therefore, a further red shift in the emission wavelength was observed in Ir-1 as compared to [Ir(thpy)₃]. Interestingly, the emission profiles of Ir-3 and Ir-4 are very different from that of Ir-1 and Ir-2, further extending the π -conjugation to the C^N ligand that results in dual emission. For Ir-3, one emission appears as a band at around 530 nm and another NIR band at > 750 nm with some evidence of vibrational structure. The former band corresponds to fluorescence with a small Stokes shift while the latter one to phosphorescence on the basis of the much larger Stokes shift and long emission lifetime. This phenomenon was commonly observed in many heavy-metal complexes [56]. Therefore, we believe that the $S_1 \rightarrow T_1$ intersystem crossing is not fast enough to completely eliminate the

fluorescence. For Ir-1 and Ir-2, population of the triplet state from the singlet is favored that fluorescence cannot compete with ISC and no fluorescence can be observed. We anticipate that there is a weakening of the spin-orbit coupling as the size of the cyclometalating organic group increases which is consistent with some previously reported data [57,58]. The phosphorescence of Ir-3 and Ir-4 are red-shifted relative to those of Ir-1 and Ir-2 because of the more extended π -conjugated structure in the former cases. Their phosphorescence intensities are also weaker than those of Ir-1 and Ir-2. These results also indicate that the triplet state energy drops more rapidly than the singlet state upon introduction of a second thiophene ring onto the ligand and this is well reflected by the larger influence on the phosphorescence energy than on the energy of the lowest-energy absorption band. On the other hand, the relative ratios of fluorescence to phosphorescence emission intensities of Ir-3 and Ir-4 are different. Here, the intensity of fluorescence relative to that of phosphorescence in the homoleptic compound Ir-3 is almost the same, whereas the emission of the heteroleptic congener Ir-4 is mainly caused by fluorescence with very weak phosphorescence only. This implies that the nonradiative decay is expected to increase since the emission energy of the latter is substantially lower than that in the former, in line with the energy gap law [35]. The lower emission energy also reveals a larger energy gap between the S_1 and T_1 states which will also lead to a reduction in the $S_1 \rightarrow T_1$ rate due to the poorer overlap integral, hence multiplying the above effect. Moreover, the inefficient intersystem crossing indicates that the rate of the formally forbidden radiative $T_1 \rightarrow S_0$ process would not be facilitated to the same extent as it was for Ir-1 and Ir-2. The higher ligand-field

strength of acetylacetonate anion also leads to the bathochromic shifts in λ_{em} for **Ir-2** and **Ir-4** relative to **Ir-1** and **Ir-3**, respectively. The lifetimes of the lower energy peaks of all the Ir(III) complexes fall in the range of microseconds, suggesting that this band is due to spin-forbidden triplet excited states. The PL quantum efficiencies of **Ir-1–Ir-4** were measured against Rhodamine 6G standard. Clearly, we can observe that complexes with **L1** show much higher quantum yields than those with **L2**. This is a manifestation of the fact that decreasing the energy gap toward NIR may trigger a much faster radiationless decay channel because of the interaction between ground and emitting states (c.f. energy gap law), giving rise to poorer quantum efficiencies in **Ir-2** and **Ir-4**.

Cyclic voltammetry was used to investigate the electrochemical behavior of these Ir(III) complexes. The redox potentials, measured relative to an internal ferrocenium/ferrocene reference (Fc⁺/Fc), are listed in Table 3. On the basis of the peak potentials of oxidation and reduction, the HOMO and LUMO energy levels of these Ir(III) complexes, relative to the energy levels of ferrocene (4.80 eV under vacuum) were estimated [59]. Upon the anodic sweep in THF at 298 K, each of these complexes undergoes a reversible one-electron oxidation with the oxidative potential falling within the range 0.21–0.51 V, mainly involving the Ir-aryl center according to the previously reports [60]. It is believed that the oxidation potential is strongly dependent on the electronic environment of the Ir(III) cations, i.e. a better electron donor would shift the oxidation potential to a less positive value [61]. Herein, with the extension of π -conjugated aromatic motif by thiophene in the ligand frame, the HOMO levels systematically

increase from -5.31 to -5.16 V in **Ir-1** and **Ir-3** and from -5.22 to -5.01 V in **Ir-2** and **Ir-4** [44]. During the cathodic scan, all complexes undergo reversible reduction processes on the cyclometalated C^N ligand. This may be attributed to the sequential reduction of thiophene and boron center, which was commonly observed in other boron-containing compounds [62].

3.3. DFT Calculations

We have examined the electronic structure of **Ir-2** by computational methods based on the experimental geometry obtained from the X-ray crystal data. The time-dependent density functional theory (TD-DFT) calculations show that the $S_0 \rightarrow S_1$ transitions correspond to the HOMO \rightarrow LUMO transitions with non-zero oscillator strengths (Table 4). The results of DFT calculations show that **Ir-2** and the one with B(Mes)₂-ppy as previously reported [54] have similar HOMOs and LUMOs in terms of their orbital character (Fig. 3). The coutour plots show that the HOMOs mainly consist of the t_{2g} d orbitals from the metal center that mix with the π orbitals of the thiophene rings that are directly bonded to the metal center. The LUMOs correspond to the lowest π orbital of the conjugated organic ligands, to which pyridyl ring as well as electron deficient boron atom contribute more.

3.4. Electroluminescence behavior

To date, there are only limited examples on electrophosphorescent devices based on Ir(III) complexes functionalized with organoboron-type ligand [54,63,64]. To investigate the

electroluminescence characteristics of these complexes, multilayer devices with configuration ITO/PEDOT:PSS (50 nm)/CBP:x% Ir (80 nm)/BCP (15 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 fabricated (Fig. following layers nm) were 4). The were used: а layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) for hole transport and smoothing the ITO surface [65], a layer of 4.4'-dicarbazolebiphenyl (CBP) doped with different concentrations (1 to 20 wt.-%) of Ir(III) complexes as the emitter to optimize the device efficiency, a thin layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) for hole and exciton blocking to confine the recombination zone inside the doped CBP layer; a layer of tris(8-hydroxyquinolinato)aluminum (Alq₃) for electron transport [66] and LiF as an electron injection layer. Fig. 5 shows the normalized EL spectra with various concentration of Ir(III) dopant. The EL color of these complexes varies from single red emission of Ir-1 and Ir-2 to dual emission bands consisting of both visible and NIR peaks of Ir-3 and Ir-4. The EL emission peaks are centered at ~650 and 667 nm for Ir-1 and Ir-2-doped devices with low-intensity shoulders on the red side of the peak near over 715 and 730 nm, respectively. Their EL spectra are voltage independent and nearly coincident with the PL spectra of the corresponding complexes in the polymer matrix at room temperature, indicating an effective energy transfer from the host exciton to the phosphor upon electrical excitation and the effective hole-blocking effect of BCP. The corresponding Commission Internationale de L'Eclairage (CIE) coordinates were calculated to be (0.66, 0.31) for Ir-1 and (0.63, 0.32) for Ir-2 at 1 wt.-% doping level. However, there are some differences between the PL and EL patterns of each of the Ir-3 and

Ir-4-doped devices, in which two distinct peaks were observed and the relative ratio of the peak height varied with the doping concentration. The relative intensities for their NIR emissions in the EL spectra are dramatically higher than those in their PL spectra and increase as the doping concentration increases. It can be shown that the devices displayed the strong visible and NIR emissions simultaneously (especially at low dopant concentrations), and the visible green emission peak can be attributed to either the Alq₃ emission or the singlet emission from the metal complexes. The energy transfer from the host exciton to the phosphor becomes more significant as the doping concentration increases for **Ir-3** and **Ir-4**, although the degree of such energy transfer is still much lower than that of **Ir-1** and **Ir-2**.

The performance data for the devices are summarized in Table 5. Fig. 6 shows the current density and brightness as a function of applied voltage for the devices. The corresponding current efficiency (η_L), power efficiency (η_P) and external quantum efficiency (η_{ext}) as a function of current density for the devices are displayed in Fig. 7. As usual, the current density and brightness increase with the driving potential. The overall efficiencies of the **Ir-1**-doped devices (device **A1**) are the highest among the four metallophosphors. It has a turn-on voltage of 5.9 V, maximum luminance of 451 cd/m² at 14.6 V, external quantum efficiency (η_{ext}) of 0.58%, power efficiency (η_P) of 0.82 lm/W and current efficiency (η_L) of 1.90 cd/A. On the contrary, for complex **Ir-2** at the same doping concentration (device **B1**), it shows a poorer performance with η_{ext} of 0.23%, η_P of 0.25 lm/W and η_L of 0.67 cd/A. All the devices show a gradual decrease of the luminance and external quantum efficiency with an increase of doping

concentration, an effect that is likely due to self molecular quenching at high concentrations. The devices with **Ir-3** and **Ir-4** show an overall poorer performance. Their lower PL quantum efficiencies are probably the reason why the devices have such low efficiencies. We believe through further material development and device optimization, such as by using different host materials and assistant dopants, these kind of NIR emissive phosphors would show better potential in night-vision displays or sensors operating in the NIR spectral regime [67,68].

4. Conclusions

In conclusion, a new family of borylated Ir(III) cyclometalated complexes with oligothiophene-based ligands were prepared and characterized. These complexes represent the first example of this kind of iridium(III)-based NIR-emitting OLEDs using boron directly bound to the cyclometalating ligand. Ir-1 and Ir-2 display strong red emission at around 650 nm, while the emission is red-shifted to the NIR region for Ir-3 and Ir-4 after inserting an extra thiophene unit in the ligand. This approach opens up a new avenue to develop NIR materials by using simple ligand modification of Ir(III) cyclometalates with electron-withdrawing borylated substituent.

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Appendix. Supplementary material

CCDC 911166 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at xxxxx.

References

- [1] M.H.V. Werts, J.W. Hofstraat, F.A.J. Geurts, J.W. Verhoeven, Chem. Phys. Lett. 276 (1997) 196–201.
- [2] M.P.O. Wolbers, F.C.J.M. van Veggel, B.H.M. Snellink-Ruel, J.W. Hofstraat, F.A.J. Geurts, D.N. Reinhoudt, J. Chem. Soc., Perkin Trans. 2 (1998) 2141–2150.
- [3] S.I. Klink, L. Grave, D.N. Reinhoudt, F.C.J.M. van Veggel, M.H.V. Werts, F.A.J. Geurts, J.W. Hofstraat, J. Phys. Chem. A 104 (2000) 5457–5468.
- [4] M.H.V. Werts, J.W. Verhoeven, J.W. Hofstraat, J. Chem. Soc., Perkin Trans. 2 (2000)433–439.

- [5] S.I. Klink, P.O. Alink, L. Grave, F.G.A. Peters, J.W. Hofstraat, F. Geurts, F.C.J.M. van Veggel, J. Chem. Soc., Perkin Trans. 2 (2000) 363–366.
- [6] R.G. Sun, Y.Z. Wang, Q.B. Zheng, H.J. Zhang, A.J. Epstein, J. Appl. Phys. 87 (2000) 7589–7591.
- [7] L.H. Slooff, A. Polman, F. Cacialli, R.H. Friend, G.A. Hebbink, F.C.J.M. van Veggel,D.N. Reinhoudt, Appl. Phys. Lett. 78 (2001) 2122–2124.
- [8] Y. Kawamura, Y. Wada, S. Yanagida, Jpn. J. Appl. Phys., Part 1 40 (2001) 350–356.
- [9] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357–2368.
- [10] B.S. Harrison, T.J. Foley, M. Bouguettaya, J.M. Boncella, J.R. Reynolds, K.S. Schanze, J. Shim, P.H. Holloway, G. Padmanaban, S. Ramakrishnan, Appl. Phys. Lett. 79 (2001) 3770–3773.
- [11] M.R. Robinson, R.P. Eaton, D.M. Haaland, G.W. Koepp, E.V. Thomas, B.R. Stallard, P.L. Robinson, Clin. Chem. 38 (1992) 1618–1622.
- [12] A.E. Boyer, M. Lipowska, J.M. Zen, G. Patonay, V.C.W. Tsang, Anal. Lett. 25 (1992)415–428.
- [13] M.I. Daneshvar, J.M. Peralta, G.A. Casay, N. Narayanan, L. Evans, G.L. Patonay, Strekowski, J. Immunol. Methods 226 (1999) 119–128.
- [14] J.-C. G. Bünzli, S. V. Eliseeva, J. Rare Earths 28 (2010) 824–842.
- [15] A. Rogalski, K. Chrzanowski, Opto-Electron. Rev. 10 (2002) 111–136.
- [16] R.J. Curry, W.P. Gillin, Appl. Phys. Lett. 75 (1999) 1380–1382.

- [17] Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, S. Yanagida, Appl. Phys. Lett. 74 (1999) 3245–3247.
- [18] Z.R. Hong, C.J. Liang, R.G. Li, F.X. Zang, D. Fan, W.L. Li, L.S. Hung, S.T. Lee, Appl. Phys. Lett. 79 (2001) 1942–1944.
- [19] Z.R. Hong, C.J. Liang, R.G. Li, D. Zhao, D. Fan, W.L. Li, Thin Solid Films 391 (2001) 122–125.
- [20] C.H. Cheng, Z.Q. Fan, S.K. Yu, W.H. Jiang, X. Wang, G.T. Du, Y.C. Chang, C.Y. Ma, Appl. Phys. Lett. 88 (2006) 213505-1–213505-3.
- [21] C.J. Yang, C. Yi, M. Xu, J.H. Wang, Y.Z. Liu, X.C. Gao, J.W. Fu, Appl. Phys. Lett. 89 (2006) 233506-1–233506-3.
- [22] C. Borek, K. Hanson, P.I. Djurovich, M.E. Thompson, K. Aznavour, R. Bau, Y.R. Sun, S.R. Forrest, J. Brooks, L. Michalski, J. Brown, Angew. Chem. Int. Ed. 46 (2007) 1109–1112.
- [23] T.C. Rosenow, K. Walzer, K. Leo, J. Appl. Phys. 103 (2008) 043105-1-043105-3.
- [24] M. Casalboni, F. De Matteis, P. Prosposito, R. Pizzoferrato, Appl. Phys. Lett. 75 (1999) 2172–2174.
- [25] H. Suzuki, Appl. Phys. Lett. 80 (2002) 3256–3258.
- [26] G. Qian, Z. Zhong, M. Luo, D.B. Yu, Z.Q. Zhang, Z.Y. Wang, D.G. Ma, Adv. Mater. 21 (2009) 111–116.

- [27] Y.X. Yang, R.T. Farley, T.T. Steckler, S.H. Eom, J.R. Reynolds, K.S. Schanze, J.G. Xue, Appl. Phys. Lett. 93 (2008) 163305-1–163305-3.
- [28] G. Qian, B. Dai, M. Luo, D.B. Yu, J. Zhan, Z.Q. Zhang, D.G. Ma, Z.Y. Wang, Chem. Mater. 20 (2008) 6208–6216.
- [29] M. Berggren, G. Gustafsson, O. Inganas, M.R. Andersson, O. Wennerstrom, T. Hjertberg, Appl. Phys. Lett. 65 (1994) 1489–1491.
- [30] M.R. Andersson, M. Berggren, O. Inganas, G. Gustafsson, J.C. Gustafssoncarlberg, D. Selse, T. Hjertberg, O. Wennerstrom, Macromolecules 28 (1995) 7525–7529.
- [31] S. Stagni, S. Colella, A. Palazzi, G. Valenti, S. Zacchini, F. Paolucci, M. Marcaccio, R.Q. Albuquerque, L.D. Cola, Inorg. Chem., 47 (2008) 10509–10521.
- [32] R. Tao, J.Qiao, G. Zhang, L. Duan, L. Wang, Y. Qiu, J. Phys. Chem. C, 2012, 116 (21), pp 11658–11664.
- [33] K.A. Belmore, R.A. Vanderpool, J.C. Tsai, M.A. Khan, K.M. Nicholas, J. Am. Chem. Soc. 110 (1988) 2004–2005.
- [34] T.J. Meyer, Acc. Chem. Res. 11 (1978) 94–100.
- [35] W.-Y. Wong, C.-L. Ho, Coord. Chem. Rev. 253 (2009) 1709–1758.
- [36] T. Noda, Y. Shirota, J. Am. Chem. Soc. 120 (1998) 9714–9715.
- [37] Y. Shirota, M. Kinoshita, T. Noda, K. Okumoto and T. Ohara, J. Am. Chem. Soc. 122 (2000) 11021–11022.
- [38] T. Noda, H. Ogawa, Y. Shirota, Adv. Mater. 11 (1999) 283–285.

- [39] SAINT+, ver. 6.02a, Bruker, Analytical X-ray System, Inc., Madison, WI, 1998.
- [40] G.M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Germany, 1997.
- [41] G.M. Sheldrick, SHELXTLTM, Reference Manual, ver. 5.1, Madison, WI, 1997.
- [42] R.F. Kubin, A.N. Fletcher, J. Luminescence 27 (1982) 455-462.
- [43] W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284–298.
- [44] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299-310.
- [45] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J. A. Montgomery, T. Vreven, Jr, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03, revision B05, Gaussian, Inc., Pittsburgh, PA 2003.

- [46] G. Schaftenaar, Molden v3.5, CAOS/CAMM Center Nijmegen, Toernooiveld, Nijmegen, The Netherlands 1999.
- [47] W.-Y. Wong, C.-L. Ho, Z.Q. Gao, B.X. Mi, C.-H. Chen, K.-W. Cheah, Z. Lin, Angew. Chem. Int. Ed. 45 (2006) 7800–7803.
- [48] X.-M. Yu, H.-S. Kwok, W.-Y. Wong, G.-J. Zhou, Chem. Mater. 18 (2006) 5097–5103.
- [49] M.C. DeRosa, D.J. Hodgson, G.D. Enright, B. Dawson, C.E.B. Evans, R.J. Crutchley, J. Am. Chem. Soc. 126 (2004) 7619–7626.
- [50] M.G. Colombo, T.C. Brunold, T. Riedener, H.U. Güdel, M. Förtsch, H. Bürgi, Inorg. Chem. 33 (1994) 545–550.
- [51] Y. You, S.Y. Park, J. Am. Chem. Soc. 127 (2005) 12438–12439.
- [52] A. Adronov, P.R.L. Malenfant, J.M.J. Fréchet, Chem. Mater. 12 (2000) 1463–1472.
- [53] W.-J. Xu, S.-J. Liu, X.-Y. Zhao, S. Sun, S. Cheng, T.-C. Ma, H.-B. Sun, Q. Zhao, W. Huang, Chem. Eur. J. 16 (2010) 7125–7133.
- [54] G.-J. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T.B. Marder, A. Beeby, Adv. Funct. Mater. 18 (2008) 499–511.
- [55] A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, J. Am. Chem. Soc. 125 (2003) 12971–12979.
- [56] W.-Y. Wong, C.-L. Ho, Coord. Chem. Rev. 250 (2006) 2627–2690.

- [57] D.N. Kozhevnikov, V.N. Kozhevnikov, M.Z. Shafikov, A.M. Prokhorov, D.W. Bruce, J.A. G. Williams, Inorg. Chem. 50 (2011) 3804–3815.
- [58] P.-T. Chou, Y. Chi, M.-W. Chung, C.-C. Lin, Coord. Chem. Rev. 255 (2011) 2653–2665.
- [59] J. Pommerehne, H. Vestweber, W. Guss, R.F. Mahrt, H. Bässler, M. Porsch, J. Daub, Adv. Mater. 7 (1995) 551–554.
- [60] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, Inorg. Chem. 41 (2002) 3055–3066.
- [61] P. J. Hay, J. Phys. Chem. A 106 (2002) 1634–1641.
- [62] H.-Y. Chen, C.-H. Yang, Y. Chi, Y.-M. Cheng, Y.-S. Yeh, P.-T.Chou, H.-Y. Hsieh, C.-S. Liu, S.-M. Peng, G.-H. Lee, Can. J. Chem. 84 (2006) 309–318.
- [63] G.-J. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder, A. Beeby Adv. Funct. Mater. 18 (2008) 499–511.
- [64] G.-J. Zhou, C.-L. Ho, W.-Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T.B. Marder, A. Beeby, Adv. Funct. Mater. 18 (2008) 499–511.
- [65] T.M. Brown, J.S. Kim, R.H. Friend, F. Cacialli, R. Daik, W.J. Feast, Appl. Phys. Lett. 75 (1999) 1679–1681.
- [66] M.A. Baldo, S. Lamansky, P.E. Burrows, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 75 (1999) 4–7.
- [67] K.S. Schanze, J.R. Reynolds, J.M. Boncella, B.S. Harrison, T.J. Foley, M. Bouguettaya, T.-S. Kang, Synth. Met. 137 (2003) 1013–1014.

[68] E.L. Williams, J. Li, G.E. Jabboura, Appl. Phys. Lett. 89 (2006) 083506-1-083506-3.

Captions for Figures and Schemes

Fig. 1. ORTEP drawing of **Ir-2** with thermal ellipsoids shown at 25% probability level. Labels on carbon atoms (except for those bonded to Ir) and hydrogen atoms are omitted for clarity.

Fig. 2. Absorption and emission spectra of Ir(III) phosphors (a) Ir-1; (b) Ir-2; (c) Ir-3 and (d)

Ir-4 in CH₂Cl₂ at 293 K.

Fig. 3. Coutour plats of the frontier molecular orbitals for Ir-2 (1 au = 27.2114 eV).

Fig. 4. The general structure for OLED devices and the molecular structures of the relevant

compounds used in these devices

Fig. 5. The normalized EL spectra of the OLEDs with various concentration of Ir(III) complexes (a) **Ir-1**, (b) **Ir-2**, (c) **Ir-3** and (d) **Ir-4**.

Fig. 6. Current density and brightness versus voltage curves of the devices with (a) Ir-1; (b)

Ir-2; (c) Ir-3 and (d) Ir-4 at different doping concentrations.

Fig. 7. Luminance, power and external efficiencies versus current density curves of the devices with (a) **Ir-1**; (b) **Ir-2**; (c) **Ir-3** and (d) **Ir-4** at different doping concentrations.

Scheme 1. Synthesis of boron-thiophene ligands.

Scheme 2. Synthesis of new Ir(III) homoleptic and heteroleptic cyclometalated complexes containing borylated oligothiophenes.

Table 1

Structural bond lengths (Å) and angles (°) for complex Ir-2

	Bond lengths		Bond angles		Bond angles
	(Å)		(°)		(°)
Ir(1) - N(1)	2.048(4)	C7-Ir(1)-C(34)	87.1(2)	C(34)- $Ir(1)$ - $O(2)$	93.2(2)
Ir(1) - N(2)	2.039(5)	C7-Ir(1)-N(2)	95.4(2)	N(2)- $Ir(1)$ - $O(2)$	89.4(2)
Ir(1)-O(1)	2.134(4)	C34-Ir(1)-N(2)	81.2(2)	N(1)-Ir(1)-O(2)	94.7(2)
Ir(1)-O(2)	2.128(4)	C(7)– $Ir(1)$ – $N(1)$	80.6(2)	C(7)– $Ir(1)$ – $O(1)$	91.2(2)
Ir(1)-C(7)	1.983(5)	C(34)- $Ir(1)$ - $N(1)$	97.2(2)	C(34)– $Ir(1)$ – $O(1)$	174.3(2)
Ir(1)-C(34)	1.986(6)	N(2)-Ir(1)-N(1)	175.7(2)	N(2)-Ir(1)-O(1)	93.6(2)
		C7-Ir(1)-O(2)	175.2(2)	N(1)-Ir(1)-O(1)	87.9(2)
				O(2)-Ir(1)-O(1)	89.2(2)

	Absorption (293 K)		Emission (293	$T_{\rm dec}$	
	$\lambda_{abs} [nm] CH_2Cl_2 [a]$	$\lambda_{\rm em} [\rm nm] \ CH_2Cl_2$	Φ _P [%] [b]	$ au_{ m P}$ [µs]	[°C]
Ir-1	348 (12.37)	643*	0.396	6.9	315
	364 (11.10)	700sh			
	423 (4.38)				
	438 (4.32)				
	520 (0.76)				
Ir-2	327 (15.86)	661*	0.312	2.3	301
	365 (17.55)	720sh			
	498 (2.76)				
	524 (2.80)				
Ir-3	375 (24.80)	492	0.057	6.2	325
	405 (21.38)	540			
	443 (24.56)	741*			
	469 (19.74)	800sh			
	514 (9.13)				
Ir-4	342 (13.27)	470*	[c]	6.0	311
	423 (20.85)	499sh			
	439 (20.18)	548sh			
	498 (8.03)	747			
	518 (7.91)		× Y		

Table 2

Photophysical and thermal data for Ir-1–Ir-4

[a] ε values (10⁴ M⁻¹ cm⁻¹) are shown in parentheses.

[b] Measured in degassed CH₂Cl₂ relative to Rhodamine 6G ($\Phi = 0.95$), $\lambda_{ex} = 435$ nm. [c] Too weak to be determined accurately.

* Peak maximum

sh = shoulder

Electrochemical properties and frontier orbital energy levels of 1–4.								
Complex	$E_{1/2}^{\text{ox}}$ [V] [a]	HOMO [eV]	$E_{1/2}^{\text{red}}$ [V] [a]	LUMO [eV]	$E_{\rm g}[{\rm eV}]$	_		
1	0.51	-5.31	2.31	-2.49	2.82			
2	0.42	-5.22	2.22	-2.58	2.63			
3	0.36	-5.16	2.15	-2.65	2.51			
4	0.21	-5.01	2.08	-2.72	2.29			

Tal	ble 3
Ele	ctrochemical properties and frontier orbital energy levels of 1–4

[a] 0.1 M [Bu₄N]PF₆ in THF, scan rate 100 mV s⁻¹, versus Fc/Fc⁺ couple.

Table 4

Contribution of the metal d_{π} orbitals to HOMO and LUMO together with the TDDFT calculation results for Ir-2 and the analogous Ir complex with B(Mes)₂-ppy ligand.

compound	contribution of <i>d</i> orbitals to HOMO	contribution of <i>d</i> orbitals to LUMO	the largest coefficient in the CI expansion of the S_1 state ^{<i>a</i>}	the oscillator strength (f) of the $S_0 \rightarrow S_1$ transition
Ir-2	41.0%	1.1%	$H \rightarrow L: 0.67$	0.054
Ir-B(Mes) ₂ -ppy [48]	49.7%	1.4%	$H \rightarrow L: 0.68$	0.026

 a H \rightarrow L represents the HOMO to LUMO transition. CI stands for configuration interaction.

Device	Phosphor	V _{turn-on}	Luminance	$n_{\rm r}$	$\eta_{\rm avt}$	n	$\lambda_{\rm FL}$	CIE
	Dopant	[V]	$[cd/m^2]$	[cd/A]	[%]	[lm/W]	[nm]	(\mathbf{x}, \mathbf{y})
	(wt%)							
A1	Ir-1	5.9	451 (14.6)	0.89 [a]	0.29 [a]	0.25 [a]	649,	0.661, 0.314
	(1%)			1.90 (6) [b]	0.58 (7) [b]	0.82 (6) [b]	715sh	
A2	Ir-1	6.19	620 (15.2)	0.94 [a]	0.30 [a]	0.28 [a]	649,	0.685, 0.302
	(2%)			1.65 (7.4) [b]	0.53 (7.4) [b]	0.71 (7) [b]	713sh	
A3	Ir-1	6.28	1103 (17.2)	1.12 [a]	0.37 [a]	0.31 [a]	650,	0.694, 0.299
	(5%)			1.65 (7.8) [b]	0.54 (7.8) [b]	0.75 (6.8) [b]	715sh	
A4	Ir-1	6.36	803 (17.8)	0.86 [a]	0.28 [a]	0.23 [a]	654.	0.700, 0.295
	(10%)			1.27 (6.8) [b]	0.41 (6.8) [b]	0.59 (6.8) [b]	715sh	
B1	Ir-2	8.54	520 (17.8)	0.51 [a]	0.18 [a]	0.14 [a]	667,	0.626, 0.318
	(1%)			0.67 (8.4) [b]	0.23 (8.42) [b]	0.25 (8.4) [b]	730sh	
B2	Ir-2	9.02	571 (17.2)	0.46 [a]	0.25 [a]	0.12 [a]	665,	0.655, 0.305
	(2%)			0.517 (10.4) [b]	0.278 (10.4) [b]	0.16 (9.6) [b]	718sh	
B3	Ir-2	9.45	459 (21.2)	0.34 [a]	0.20 [a]	0.08 [a]	669,	0.692, 0.297
	(5%)			0.414 (10) [b]	0.242 (10) [b]	0.130 (10) [b]	730sh	
B4	Ir-2	8.94	454 (21.2)	0.32 [a]	0.19 [a]	0.07 [a]	672,	0.695, 0.296
	(10%)			0.354 (10.6) [b]	0.208 (10.6) [b]	0.111 (9.6) [b]	730sh	
C1	Ir-3	8.83	364 (17.8)	0.21 [a]	0.13 [a]	0.06 [a]	531, 746,	[c]
	(1%)			0.214 (13.2) [b]	0.137(13) [b]	0.072 (8.4) [b]	823sh	
C2	Ir-3	9.39	283 (17.8)	0.14 [a]	0.17 [a]	0.04 [a]	533, 746,	[c]
	(2%)			0.156 (13.8) [b]	0.189 (13.8) [b]	0.0376 (12) [b]	825sh	
C3	Ir-3	10.82	131 (19.4)	0.07 [a]	0.12 [a]	0.02 [a]	536, 747,	[c]
	(5%)			0.081 (15.2) [b]	0.137 (15.2) [b]	0.0175 (14) [b]	825sh	
C4	Ir-3	10.74	90 (19.6)	0.06 [a]	0.12 [a]	0.01 [a]	538, 749,	[c]
	(10%)			0.060 (15.4) [b]	0.129 (15.4) [b]	0.0157 (10.2) [b]	825sh	
D1	Ir-4	8.57	179 (18)	0.10 [a]	0.07 [a]	0.03 [a]	538, 776,	[c]
	(2%)			0.183 (8.6) [b]	0.127 (8.6) [b]	0.0669 (8.6) [b]	836sh	
D2	Ir-4	9.36	111 (20.4)	0.04 [a]	0.05 [a]	0.01 [a]	536, 756,	[c]
	(5%)			0.10 (9.6) [b]	0.06 (10.6) [b]	0.03 (9.6) [b]	836sh	
D3	Ir-4	12.72	103 (22)	0.03 [a]	0.05 [a]	0.006 [a]	552, 756,	[c]
	(10%)			0.05 (18.6) [b]	0.07 (18.8) [b]	0.009 (18) [b]	842sh	
D4	Ir-4	11.31	21.4 (18.2)	0.006 [a]	0.018 [a]	0.0016 [a]	555, 760,	[c]
	(20%)			0.011 (16) [b]	0.034 (15.2) [b]	0.0023 (15.2) [b]	842sh	

 Table 5

 Performance of Ir-doped electrophosphorescent OLEDs

[a] Values collected at 20 mA/cm^2 .

[b] Maximum values of the devices. Values in parentheses are the voltages at which they were obtained.

[c] Cannot be determined accurately because the program for CIE calculation cannot read data beyond

850 nm.



Fig. 1. ORTEP drawing of **Ir-2** with thermal ellipsoids shown at 25% probability level. Labels on carbon atoms (except for those bonded to Ir) and hydrogen atoms are omitted for clarity.



Fig. 2. Absorption and emission spectra of Ir(III) phosphors (a) Ir-1; (b) Ir-2; (c) Ir-3 and (d) Ir-4 in CH₂Cl₂ at 293 K.



(-0.06445 au) **LUMO+1**





(-0.06828 au) LUMO





(-0.19753 au) **HOMO-1**

(-0.20304 au) **HOMO-2**

(-0.20921 au) **HOMO-3**

Fig. 3. Coutour plats of the frontier molecular orbitals for Ir-2 (1 au = 27.2114 eV).

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Fig. 4. The general structure for OLED devices and the molecular structures of the relevant compounds used in these devices.



Fig. 5. The normalized EL spectra of the OLEDs with various concentration of Ir(III) complexes (a) **Ir-1**, (b) **Ir-2**, (c) **Ir-3** and (d) **Ir-4**.



(b) Ir-2; (c) Ir-3 and (d) Ir-4 at different doping concentrations.



Fig. 7. Luminance, power and external efficiencies versus current density curves of the devices with (a) **Ir-1**; (b) **Ir-2**; (c) **Ir-3** and (d) **Ir-4** at different doping concentrations.





Scheme 2. Synthesis of new Ir(III) homoleptic and heteroleptic cyclometalated complexes containing borylated oligothiophenes.