Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

Intriguing 'Turn-on' phosphorescent response in the near infrared region upon fluoride binding: Dipyrromethene chelating-based Triarylboryl– Iridium(III) conjugates

Ju Hyun Hong¹, Seonah Kim¹, Hyunhee So, Ji Hye Lee, Hyonseok Hwang, Kang Mun Lee

Department of Chemistry and Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon, Gangwon, 24341, Republic of Korea

ARTICLE INFO

Keywords: Iridium Turn-on Near infrared Dipyrromethene Triarylborane

ABSTRACT

Two novel heteroleptic cyclometalated iridium(III) complexes, namely $(C^N)_2 Ir(BL)$ (Ir1 and Ir2) ($C^N = 2-(2,4-1)$) difluorophenyl)pyridine (dfphpy, for Ir1) and 2-phenylpyridine (phpy, for Ir2)), chelated by the triarylboryl dipyrromethene ancillary ligand (BL) were synthesized and characterized. The molecular structures of both complexes in the solid state were fully analyzed by single-crystal X-ray diffraction, and were found to be composed of Ir(III)-centered triarylborane conjugated systems. The UV-vis absorption spectra of both complexes displayed the typical ¹MLCT (metal-to-ligand charge transfer) absorption bands centered at $\lambda_{abs} = 483$ nm, in addition to borane-centered CT absorption bands at \sim 326 nm. The photoluminescence (PL) spectra for these complexes demonstrated phosphorescent emission in the near infrared region ($\lambda_{em} = -690$ nm), which was mainly attributed to the ${}^{3}MLCT$ transition (L = BL). In addition, fluoride titration experiments using these complexes showed gradually quenched absorption bands in the region of 300-350 nm, corresponding to boranecentered CT transitions. Furthermore, ¹H NMR experiments in THF-d₈ for both complexes in the presence of fluoride sources revealed that the fluoride was bound to the dimesitylboryl moieties. Interestingly, upon the addition of fluoride, the PL spectra exhibited a ratiometrically 'turn-on' and gradually blue-shifted emissive response. Computational calculations and cyclic voltammetry measurements using the neutral Ir(III)-conjugates and their fluoride adducts strongly suggested that the intriguing emissive response is the result of fluoride binding interrupting the original ³MLCT transition, reinforcing the dipyrromethene-centered π - π * transition, and further inducing the enhancement of the band-gap.

1. Introduction

Over the past few decades, iridium(III)-based organometallic complexes possessing luminescent characteristics have been extensively investigated as outstanding functional materials in optoelectronic devices, such as photovoltaic cells and organic light-emitting diodes (OLEDs) [1–23], since the heavy atom effect of iridium results in stable intersystem crossing (ISC) and triplet exited states, thereby leading to highly efficient phosphorescence. In particular, the rigid coordination environments of such complexes, which are caused by the Ir-centered octahedral conformation, contribute to their superior properties, such as a high quantum efficiency, a good color purity, and high thermal and electrochemical stabilities [1,2,4–6,8,14,21]. In addition, the intriguing photophysical properties of these Ir(III)-chelating complexes can be finely tuned by systematic formation of the ligand frameworks due to the electronic characteristics for these complexes, which correspond to the emissive lowest-lying triplet excited states, such as metal-to-ligand charge transfer (³MLCT), ligand-centered transitions (³ $\pi\pi^*$ or ³LC), and ligand-to-ligand charge transfer (LL'CT). Such ligand-based electronic transitions are readily influenced by the structural geometries of the chelated ligands and the electronic effects of the functional groups present in the ligands [2,7,14,24–43]. Indeed, the fundamental features of Ir(III)-based phosphors suggest that the observed luminescent properties may be significantly affected by binding external substituents to the ligands, and so such systems could be utilized as luminescent molecular scaffolds for chemosensors that exhibit photophysical changes in the presence of certain target compounds. Indeed, various cyclometalated Ir(III) complexes conjugated with triarylborane derivatives,

* Corresponding author.

https://doi.org/10.1016/j.dyepig.2020.108706

Received 25 May 2020; Received in revised form 4 July 2020; Accepted 9 July 2020 Available online 1 August 2020 0143-7208/© 2020 Elsevier Ltd. All rights reserved.





E-mail address: kangmunlee@kangwon.ac.kr (K.M. Lee).

¹ The first and second authors contributed equally to this work.

which have attracted great attention as receptors for toxic anions such as fluoride and cyanide due to their high Lewis acidities, have recently been reported [44-56]. These conjugated systems clearly exhibit a dramatic phosphorescent response based on the intramolecular electronic transitions controlled by the binding of an anion to the boron center of triarylboranes under ambient conditions, thereby enabling facile detection of the anion. For example, fluoride binding to the dimesitylboryl (Mes₂B) moiety attached on a C^N (donor atoms: carbon and nitrogen) cyclometalating-ligand exhibited high signal-to noise ratios and electrochemical stabilities³³ and also, a fluoride probe based on the (C^N)₂Ir moiety exhibited a strong color-changing emission upon conversion the N^N ancillary ligand after fluoride binding [46,47]. In addition, heteroleptic Ir(III) complexes possessing an LX-type ancillary ligand conjugated with a triarylborane moiety exhibited 'turn-on' phosphorescent signals, since anion binding prevented the photoinduced electron transfer (PET) process [50,54].

Although these Ir(III)-triarylborane conjugated systems have shown intriguing responses toward fluoride, they were mainly composed of common chelating systems, such as 2-phenylpyridyl [44-49,51-53,55, 57], acetylacetonate [50,58], and picolinate [54] triarylborane ligands, and so alteration of their photophysical properties was only possible in the visible energy region centered at ~500–600 nm.

As part of the continuous effort to explore a novel class of Ir(III)based triarylborane conjugates showing a remarkable luminescent response upon the detection of anions, and to further extend their energy ranges to the near infrared (IR) region, we herein focus on a new molecular design for the LX-type chelating system bearing triarylborane units. Thus, the dipyrromethene moiety was utilized as a rigid 6membered N^N chelating backbone for the ancillary ligand linked to the triarylboranes. We therefore report the design and preparation of the triarylborane-based dipyrromethene chelating ligand ((Z)-2-((4-(dimesitylboranyl)phenyl)(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole, BL) and two novel heteroleptic (C^N)₂Ir(BL) complexes bearing different C^N ligands, i.e., $C^N = 2$ -(4,6-difluorophenyl)pyridinato- C^2 ,N (dfphpy, Ir1) and 2-phenylpyridinato-C²,N (phpy, Ir2). Although the structure and simple photophysical characters for Ir2 had been already reported [59], further detailed considerations for the variation of each photophysical feature caused by fluoride binding are demonstrated herein. In particular, it is expected that the electron-abundant character of the dipyrromethene moiety could lead to a shift in the entire emission for the Ir (III) complexes toward the near IR region. Thus, the synthesis, characterization, structural features, photophysical properties, and fluoride binding properties of Ir1 and Ir2, along with theoretical calculation results, are herein presented in detail.

2. Experimental section

2.1. General considerations

All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous solvents (tetrahydrofuran (THF) and 2-ethoxyethanol; Aldrich) were dried by passage through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric-grade solvents (THF, ethyl acetate, dichloromethane (DCM), diethyl ether, dimethyl sulfoxide (DMSO), toluene, and *n*-hexane) were used as received from Alfa Aesar. Commercial reagents were used without any further purification after purchase from Aldrich (1-bromo-4- (diethoxymethyl)benzene, dimesitylboron fluoride (FB(Mes)₂), trifluoroacetic acid, 1H-pyrrole and nbutyllithium (n-BuLi)), TCI (tetrachloro-1,4-benzoquinone (p-chloranil), sodium carbonate, iridium(III) chloride hydrate (IrCl₃·H₂O), 2-phenylpyridine (phpy ligand), 2-(2,4-difluorophenyl)pyridine (dfphpy ligand), magnesium sulfate (MgSO₄), in addition to tetrabutylammonium anion salts (fluoride (TBAF, F⁻), chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), borohydride (BH₄⁻), tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF_6) , nitrate (NO_3) , trifluoromethanesulfonate

 $(CF_{3}SO_{3})$, acetate $(CH_{3}COO^{-})$, hydrogen sulfate (HSO_{4}) , perchlorate (ClO_4^-) , phosphate monobasic $(H_2PO_4^-)$, and cyanide (CN^-)). CDCl₃ and THF-d₈ from Cambridge Isotope Laboratories were used after drying over activated molecular sieves (5 Å). NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ¹H, 100.62 MHz for ¹³C and 376.50 MHz for ¹⁹F) at 25 °C using tetramethylsilane (for ¹H and ¹³C) and trichlorofluoromethane (for ¹⁹F) as internal standards ($\delta = 0$ ppm). The chemical shifts are given in ppm. Elemental analyses were performed on an EA3000 (Eurovector) in the Central Laboratory of Kangwon National University. UV/vis absorption and PL spectra were recorded on a Varian Cary 100 spectrophotometer and a HORIBA FluoroMax-4P spectrophotometer, respectively. Phosphorescent decay lifetimes were measured using a time-correlated single-photon counting (TCSPC) spectrometer (FLS920, EDINBURGH Instruments) equipped with a EPL-375ps pulsed semiconductor diode laser as an excitation source and a microchannel plate photomultiplier tube (MCP-PMT, 200-850 nm) as a detector at 298 K. Dimeric Ir(III) precursors, $[(dfphpy)_2Ir(\mu-Cl)]_2$ and $[(phpy)_2Ir(\mu-Cl)]_2$ were prepared according to literature procedures [60].

2.2. Synthesis of 4-(dimesitylboranyl)benzaldehyde, B2

A solution of 1-bromo-4-(diethoxymethyl)benzene (1.02 mL, 5.0 mmol) in THF (20 mL) was slowly treated with n-BuLi (1.6 M in nhexane, 4.1 mL, 6.5 mmol) at -78 °C. After stirring for 1 h, a solution of FB(Mes)₂ (1.48 g, 5.5 mmol) in THF (10 mL) was added to the mixture and allowed to stir for 1 h. After this time, the reaction mixture was slowly allowed to warm to room temperature and then stirred for a further 12 h. Trifluoroacetic acid (7.7 mL, 100 mmol) was then added to the reaction mixture and stirring continued at room temperature for 6 h. After the subsequent addition of distilled water (30 mL) to the reaction mixture to quench the reaction, the resulting mixture was extracted with DCM (2 \times 30 mL), and the combined organic layer was dried over anhydrous MgSO₄. After filtration, the volatiles were removed under rotary evaporation to afford a yellow residue. The crude product was purified by column chromatography on silica gel (eluent: diethyl ether/ *n*-hexane = 1:5, v/v) to afford **B2** (0.73 g) as a white solid. Yield = 41%. ¹H NMR (CDCl₃): δ 10.07 (s, 1H, HCO), 7.84 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 6.84 (s, 4H, mesityl-H), 2.32 (s, 6H, mesityl-p-CH₃), 1.98 (s, 12H, mesityl-o-CH₃). ¹³C NMR (CDCl₃): δ 192.88 (HCO), 140.98, 139.56, 138.11, 136.09, 129.17, 128.53, 23.58, 21.41. Anal. Calcd for C₂₅H₂₇BO: C, 84.75; H, 7.68. Found: C, 84.66; H, 7.51.

2.3. Synthesis of 2,2'-((4-(dimesitylboranyl)phenyl)methylene)bis(1H-pyrrole), B1

A solution of **B2** (0.73 g, 2.1 mmol) in distilled 1*H*-pyrrole (3.6 mL, 52 mmol) was slowly treated with trifluoroacetic acid (0.02 mL, 0.21 mmol). After stirring at room temperature for 1 h, the volatiles were removed by rotary evaporation to afford a dark brown residue. The crude product was purified by column chromatography on silica gel (eluent: diethyl ether/*n*-hexane = 1:5, v/v) to afford **B1** (0.59 g) as a white solid. Yield = 60%. ¹H NMR (CDCl₃): δ 7.70 (s, 2H, NH), 7.48 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 4H, mesityl-*H*), 6.56 (dd, *J* = 8.0, 2.1 Hz, 2H), 6.12 (dd, *J* = 7.9, 1.6 Hz, 2H), 5.84 (s, 2H), 5.38 (s, 1H, (pyrrole)₂CH), 2.29 (s, 6H, mesityl-*p*-CH₃), 2.03 (s, 12H, mesityl-*o*-CH₃). ¹³C NMR (CDCl₃): δ 146.07, 144.49, 141.79, 140.75, 138.62, 136.80, 132.25, 128.26, 128.08, 117.50, 108.41, 107.53, 44.10 ((pyrrole)₂CH), 2.3.53 (mesityl-*p*-CH₃), 21.28 (mesityl-*o*-CH₃).). Anal. Calcd for C₃₃H₃₅BN₂: C, 84.25; H, 7.50; N, 5.95. Found: C, 84.10; H, 7.49; N, 5.79.

2.4. Synthesis of (Z)-2-((4-(dimesitylboranyl)phenyl)(2H-pyrrol-2-ylidene)methyl)-1H-pyrrole, BL

To a solution of B1 (0.59 g, 1.25 mmol) in DCM (16 mL) was slowly

added *p*-chloranil (0.40 g, 1.63 mmol) at room temperature. After stirring for 1 h, distilled water (20 mL) was poured into the reaction mixture to quench the reaction. The resulting mixture was extracted with DCM (2 × 30 mL), and the combined organic layer was dried over MgSO₄. After filtration, the volatiles were removed by rotary evaporation to afford a dark brown residue. The crude product was purified by column chromatography on silica gel (eluent: DCM) to afford **BL** (0.53 g) as a yellow solid. Yield = 91%. ¹H NMR (CDCl₃): δ 7.76 (s, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 4H, mesityl-*H*), 6.63 (m, 2H), 6.45 (dd, *J* = 4.2, 1.5 Hz, 2H), 2.32 (s, 6H, mesityl-*p*-CH₃), 2.05 (s, 12H, mesityl-*o*-CH₃). ¹³C NMR (CDCl₃): δ 143.96, 140.96, 140.34, 139.22, 135.23, 131.11, 130.66, 128.48, 117.68, 23.63 (mesityl-*p*-CH₃), 21.40 (mesityl-*o*-CH₃). Anal. Calcd for C₃₃H₃₃BN₂: C, 84.61; H, 7.10; N, 5.98. Found: C, 84.45; H, 7.00; N, 5.78.

2.5. General synthesis of iridium(III) complexes (Ir1 and Ir2)

To a mixture of **BL**, the desired dimeric Ir(III) precursor, and sodium carbonate was added 2-ethoxyethanol (10 mL) and the resulting mixture allowed to stir at 130 °C for 20 h. After cooling to 25 °C, distilled water (10 mL) was slowly poured into the reaction mixture to quench the reaction. The resulting mixture was extracted with DCM (2 × 20 mL), and the combined organic layer was dried over anhydrous MgSO₄. The volatiles were then removed by rotary evaporation to afford a dark brown residue. The crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/*n*-hexane = 1:20, v/v) to afford the desired Ir complexes.

2.6. Data for Ir1

BL (0.10 g, 0.21 mmol), [(dfphpy)₂Ir(μ-Cl)]₂ (0.12 g, 0.10 mmol), and sodium carbonate (0.14 g, 1.3 mmol) in 2-ethoxyethanol afforded **Ir1** as an orange solid (91 mg). Yield = 92%. ¹H NMR (CDCl₃): δ 8.24 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 5.6 Hz, 2H), 7.67 (t, J = 7.7 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H), 6.95 (t, J = 6.6 Hz, 2H), 6.85 (s, 4H, mesityl-H), 6.80 (s, 2H), 6.52 (d, J = 4.2 Hz, 2H), 6.44 (t, J = 12.0 Hz, 2H), 6.28 (d, J = 4.2 Hz, 2H), 5.79 (dd, J = 8.5, 2.2 Hz, 2H), 2.33 (s, 6H, mesityl-*p*-CH₃), 2.06 (s, 12H, mesityl-*o*-CH₃). ¹³C NMR (CDCl₃): δ 165.28, 160.67, 152.10, 149.57, 148.49, 142.53, 141.65, 140.86, 138.89, 137.12, 134.73, 133.73, 131.49, 130.14, 128.28, 122.95, 122.75, 122.13, 117.43, 114.03, 113.85, 97.35, 91.41, 23.48 (mesityl-*p*-CH₃), 21.26 (mesityl-*o*-CH₃). ¹⁹F NMR (THF-*d*₈): δ -108.55, 110.71. Anal. Calcd for C₅₅H₄₄BF₄IrN₄: C, 63.52; H, 4.26; N, 5.39. Found: C, 63.44; H, 4.15; N, 5.20.

2.7. Data for Ir2

BL (0.06 g, 0.13 mmol), [(phpy)₂Ir(μ-Cl)]₂ (0.06 g, 0.06 mmol), and sodium carbonate (0.12 g, 1.1 mmol) in 2-ethoxyethanol afforded **Ir2** as a deep red solid (90 mg). Yield = 73%. ¹H NMR (CDCl₃): δ 7.83 (dd, *J* = 20,0, 8.4 Hz, 4H), 7.60 (m, 4H), 7.54 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 6.92 (m, 4H), 6.84 (s, 4H, mesityl-*H*), 6.81 (d, *J* = 8.1 Hz, 4H), 6.48 (d, *J* = 4.2 Hz, 2H), 6.38 (d, *J* = 4.2, 2H), 6.23 (d, *J* = 4.2 Hz, 2H), 2.32 (s, 6H, mesityl-*p*-CH₃), 2.05 (s, 12H, mesityl-*o*-CH₃). ¹³C NMR (CDCl₃): *δ* 168.94, 156.63, 152.53, 149.71, 148.40, 144.68, 143.20, 141.01, 138.95, 136.15, 134.84, 134.08, 132.34, 131.11, 130.35, 129.69, 128.39, 123.97, 122.00, 120.88, 118.71, 117.23, 23.61 (mesityl-*o*-CH₃), 21.40 (mesityl-*o*-CH₃). Anal. Calcd for C₅₅H₄₈BIrN₄: C, 68.24; H, 5.00; N, 5.79. Found: C, 68.01; H, 4.89; N, 5.54.

2.8. X-ray crystallography

Single crystals of **Ir1** and **Ir2** suitable for X-ray diffraction were grown from DCM and *n*-hexane mixtures. Single crystals of **Ir1** and **Ir2** were coated with Paratone oil and mounted onto a glass capillary. The crystallographic measurement for **Ir1** was performed on a Bruker SMART Apex II CCD area detector diffractometer with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and synchrotron radiation measurements for **Ir2** were performed at the Pohang Accelerator Laboratory (PAL). All structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by a fullmatrix least-squares method on F^2 using the SHELXTL/PC package, which gave the X-ray crystallographic data of **Ir1** and **Ir2** in CIF format (CCDC 1994590 and 1994589). Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Tables S1 and S2 in Supplementary data.

2.9. Photophysical Measurements

The UV-vis absorption spectra were obtained in degassed THF (3.0 $\times 10^{-5}$ M) under an inert atmosphere on a Varian Cary 100 spectrophotometer. Photoluminescence (PL) spectra were obtained in degassed toluene and THF (3.0×10^{-5} M) under an inert atmosphere using a HORIBA FluoroMax-4P spectrophotometer. The absolute photoluminescence (PL) quantum yields of Ir1 and Ir2 in THF solution (3.0 \times 10^{-5} M) were obtained using a 3.2 inch integrating sphere (FM-sphere, HORIBA) equipped on a Fluoromax-4P spectrophotometer (HORIBA) at 298 K. The THF solutions of Ir1 and Ir2 (3.0 mL, 3.0×10^{-5} M) were titrated with incremental amounts of fluoride anions by adding a TBAF solution (4.4 \times 10⁻⁵ M in THF). The decreasing absorption spectra were monitored at $\lambda_{abs} = 328$ nm for Ir1 and 325 nm for Ir2. The obtained titration results were a good fit to a 1:1 binding isotherm. The limits of detection (C_{LOD}) of Ir1 and Ir2 for the fluoride anions were estimated using the following equation: $C_{LOD} = 3SD/b$, where SD is the residual standard deviation of the linear regression (UV/Vis absorption intensity vs. fluoride anion concentration) and *b* is the slope of the regression line. The absolute PL quantum yields of Ir1 and Ir2 in THF solution (3.0 \times 10^{-5} M) after treatment with TBAF were also measured using the 3.2 inch integrating sphere. PL decay lifetimes for Ir1 and Ir2 in THF solution (3.0 \times 10⁻⁵ M) were measured using a time-correlated singlephoton counting spectrometer (FLS920, EDINBURGH Instruments, used at the Central Laboratory of Kangwon National University) equipped with an EPL-375ps pulsed semiconductor diode laser as an excitation source, and a microchannel plate photomultiplier tube (MCP-PMT, 200-850 nm) as a detector at 298 K.

2.10. Cyclic voltammetry (CV) measurements

The CV plots for **Ir1** and **Ir2** in DMSO (0.5 mM) were obtained using an AUTOLAB/PGSTAT12 system with a three-electrode cell configuration (Pt working and, counter electrodes, and a Ag/AgNO₃ (0.1 M in acetonitrile) reference electrode) at room temperature. Bu₄N·PF₆ in DMSO (0.1 M) was used as a supporting electrolyte. The oxidative and reductive potentials were observed at a scan rate of 100 mV s⁻¹ and measured with reference to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. To compare the potentials of the Ir complexes before and after binding with fluoride anions, the fluoride adducts of the Ir complexes in DMSO (0.5 mM) were prepared via a simple synthetic route. More specifically, TBAF solution (1.2 mM in THF, 5 mL) was added to each Ir complex (1.0 mM in THF, 5 mL), and the volatiles were removed by rotary evaporation to afford a brown residue. Subsequently, DMSO (10 mL) was added to the residue, giving the desired fluoride adducts of the Ir complexes in DMSO (0.5 mM) for CV measurements.

2.11. Theoretical calculations

The geometries of the ground (S₀) and lowest-lying triplet excited (T₁) states of **Ir1** and the T₁ state of [**Ir1**·F]⁻ (fluoride adduct for **Ir1**) were obtained using density functional theory (DFT) calculations with the B3LYP functional. All calculations assumed a THF solution. Solvent

effects were evaluated using the conductor-like polarizable continuum model [61,62]. LANL2DZ basis sets [63] were used for the iridium atom, and 6-31G(d) basis sets [64] were used for all other atoms. TD-DFT [65] measurements based on the hybrid B3LYP functional (TD-B3LYP) were utilized for calculation of the electronic transition energies, which also accounted for electron correlation. All calculations were performed using the GAUSSIAN 09 program [66]. The percentage contribution of a group in a molecule to each molecular orbital was calculated using the GaussSum 3.0 program [67]. Visualizations were carried out using GaussView 6 [68].

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes to the dipyrromethene chelating based triarylboryl-iridium(III) conjugates (Ir1 and Ir2) are outlined in Scheme 1. More specifically, the lithiation reaction of 1-bromo-4-(diethoxymethyl) benzene with dimesitylboron fluoride and treatment with trifluoroacetic acid in situ produced B2 in a moderate yield (41%). Precursor B1 was readily prepared in a high yield (60%) by the simple dehydration of B2 with 2 equivalents of 1H-pyrrole. Dipyrromethene-based bidentate ligand appending triarylborane (BL) was obtained by an aromatization reaction via dihydrogen elimination with p-chloranil. Finally, the subsequent reactions of the 2-(2,4-difluorophenyl)pyridine (dfphpy)- and 2phenylpyridine (phpy)-containing chloride-bridged iridium(III) dimer, i.e., [(dfphpy)₂Ir(µ-Cl)]₂, and [(phpy)₂Ir(µ-Cl)]₂, with the BL ligand in the presence of a weak base (Na₂CO₃) in 2-ethoxyethanol afforded the desired Ir-complexes, Ir1 (based on dfphpy) and Ir2 (based on phpy), in high yields (i.e., 92% for Ir1 and 73% for Ir2). Both Ir1 and Ir2 were highly air- and moisture-stable and showed good solubility in common organic solvents.

All compounds were fully characterized by multinuclear NMR spectroscopy (Fig. S1-S6 in Supplementary data) and elemental analyses. In particular, the ¹H and ¹³C NMR spectra of **Ir1** and **Ir2** revealed the predicted resonances and integrals corresponding to the dimesityl groups of the triarylborane moieties. Furthermore, two characteristic signals assignable to phenyl-F groups were clearly detected at approximately -110 ppm in the ¹⁹F NMR spectrum of Ir1 (Fig. S5 in Supplementary data). The solid-state molecular structures of Ir1 and Ir2 were then determined by single-crystal X-ray diffraction measurements, as shown in the insets of Scheme 1, and the corresponding structural parameters are listed in Table S1 of Supplementary data. Both crystal structures exhibited reasonable bond lengths and angles (Table S2 in Supplementary data) and showed the bidentate chelation behavior of the BL ligands. Investigations into their structural features showed that the Ir(III) centers are present in a distorted octahedral environment, with each C atom (i.e., C1 and C12, see insets, in Scheme 1) of the dfphpy (for Ir1) and phpy (for Ir2) ligands and the two N atoms (N3 and N4) of the pyrrole moieties of **BL** ligands in the equatorial position. As a result, the N atoms (N1 and N2) of the 2-phenylpyridine ligands adopt the axial position. Furthermore, the boron atoms in the Ir(III) complexes were observed to adopt a perfectly trigonal planar geometry, as evidenced by the sum of the three C–B–C angles (i.e., $\Sigma_{C-B-C} = 360^{\circ}$, Ir1: 118.4°, 116.0°, and 125.7°, and Ir2: 120.9°, 121.2°, and 117.9°, Table S2 in Supplementary data). Importantly, X-ray analysis revealed that the phenyl ring bridging the dimesitylboryl and dipyrromethene moieties in the Ir(III) complexes is significantly distorted with respect to the dipyrromethene plane, with torsional angles of 73.8° (in Ir1) and 69.6° (in Ir2) being determined. Although the features of the solid state structure of each complex suggest that electron delocalization between the bridging phenyl group and the dipyrromethene moieties is unfavorable, both moieties are electronically connected through the free rotation of the bridging phenyl group in solution, which is clearly supported by intramolecular charge-transfer (ICT) transition bands between the triarylboryl units and dipyrromethene or Ir(III) metal moieties (see photophysical properties and theoretical calculation results below).

3.2. UV-vis absorption and emission properties

To investigate the photophysical properties of both Ir complexes, UV–Vis absorption and photoluminescence (PL) measurements were performed in degassed THF at 298 K (blue solid lines in Fig. 2 (left) and Table 1). As shown in the figure, in THF, both complexes exhibited distinct low-energy absorption bands centered at $\lambda_{abs} = 483$ nm, which tailed off to 600 nm. These were attributed to ¹MLCT (metal to ligand charge transfer) transitions ($\varepsilon \approx 31000 \text{ M}^{-1} \text{ cm}^{-1}$ for Ir1 and 36000 $\text{M}^{-1} \text{ cm}^{-1}$ for Ir2) (see the theoretical calculation results below). The spectra also showed shoulder absorption traces ~326 nm, which correspond to the π (Mes)–p $_{\pi}$ (B) charge transfer (CT) transition in the borane moiety (as is typically observed for other triaylborane groups). The fact that both complexes exhibited significantly similar absorption features indicates that the origin of the electronical transitions is the same in both the cases.

The emissive characteristics of the complexes were then examined using PL measurements (blue solid lines in Fig. 2 (right) and Table 1). In degassed THF, the PL spectra of both complexes recorded at 298 K exhibited an intense emission in the near infrared (IR) energy region, i. e., at $\lambda_{em} = 687$ nm for Ir1 and 696 nm for Ir2, (excitation points, $\lambda_{ex} = 465$ nm for Ir1 and 467 nm for Ir2, Fig. S7 in Supplementary data). The emission decay lifetimes (τ_{obs}) of Ir1 and Ir2 were measured as 0.22 and 0.12 µs, respectively, indicating that the emissions are apparently phosphorescence (Table 1 and Fig. S8 in Supplementary data). In addition, the fact that such emissions were not significantly blue-shifted in a non-protic solvent (i.e., toluene, $\lambda_{em} = 686$ nm for Ir1 and 694 nm for Ir2, Fig. S9 in Supplementary data) tentatively implies that the



Scheme 1. Synthetic routes toward dipyrromethene-based bidentate ligand (**BL**) and the Ir(III) complexes, **Ir1** and **Ir2**. Reaction conditions: (i) *n*-BuLi, FB(Mes)₂, THF, -78 °C, 12 h. (ii) CF₃COOH, THF, 25 °C, 6 h (iii) 1*H*-pyrrole, CF₃COOH, THF, 25 °C, 1 h. (iv) Tetrachloro-1,4-benzoquinone (*p*-chloranil), DCM, 25 °C, 1 h. (v) **B1**, Na₂CO₃, 2-ethoxyetahnol, 130 °C, 20 h. The inset shows the X-ray crystal structures of **Ir1** and **Ir2** (50% thermal ellipsoids, H atoms in the unit cell are omitted for clarity).

Table 1

Photophysical properties of Ir1 and Ir2.

	λ_{abs}^{a}/nm in THF	λ_{ex}/nm	λ_{em}^{b}/nm		$\Phi_{em}{}^{c}$		$\tau_{obs}{}^a/\mu s$		$K_{\rm F}/{ m M}^{-1}$	$K_{\rm F}/{\rm M}^{-1}$ $C_{\rm LOD}/{\rm M}$		Eox, onset ^e /V		E _{red, onset} ^f /V	
	$(\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1})$		THF	$+[F]^d$	THF	$+[F]^{d}$	THF	$+[F]^d$			THF	+[F] ^g	THF	+[F] ^g	
Ir1 Ir2	483 (3.1), 328 (2.7) 483 (3.6), 325 (2.5)	465 467	687 696	660 662	0.012 0.020	0.027 0.041	0.22 0.12	0.09 0.07	$\begin{array}{c} \textbf{7.1}\times \textbf{10}^{4} \\ \textbf{7.6}\times \textbf{10}^{4} \end{array}$	$\begin{array}{c} 2.1\times10^{-6}\\ 2.0\times10^{-6} \end{array}$	0.62 0.54	0.58 0.52	$-1.28 \\ -1.10$	$\begin{array}{c} -1.60 \\ -1.48 \end{array}$	

 $^a~c=3.0\times 10^{-5}$ M in THF.

 $^{b}~c=3.0\times10^{-5}$ M.

^c Absolute PL quantum yield.

 d After addition of TBAF (4.4 \times 10^{-5} M) in THF.

^e Oxidative.

 $^{\rm f}$ Reductive onset potential in DMSO (c = 5.0 × 10⁻⁴ M, scan rate = 100 mV s⁻¹) with reference to a ferrocene/ferrocenium (Fc/Fc⁺) redox couple.

 g Fluoride adduct of each Ir complex (c = 5.0 \times 10 $^{-4}$ M in DMSO).

phosphorescence is not only due to typical ³MLCT transitions between the Ir(III) center and the ligands, but also could be attributed to a spinallowed π - π * transition on the ligand moieties (see the DFT results below).

3.3. Spectral changes upon fluoride anion binding

The fluoride anion binding properties and affinities of **Ir1** and **Ir2** were investigated using both UV–vis absorption and PL titration experiments with THF as the solvent (Fig. 1). Upon the addition of an increasing concentration of tetrabutylammonium fluoride (TBAF) between 0 and 4.4×10^{-5} M (in THF), both **Ir1** and **Ir2** (3.0×10^{-5} M in THF) exhibited gradual quenching phenomena of the absorption band

between 300 and 350 nm, corresponding to the CT transition in the borane moiety. ¹H NMR experiments in THF- d_8 for Ir1 (Fig. S10 in Supplementary data) and Ir2 (Fig. S11) in the presence of excess amounts of TBAF revealed that the mesitylene-aryl (~6.8 ppm) and alkyl (~2.3 and 2.0 ppm) peaks had been shifted to the up-field region (~6.4 ppm for aryl peaks and 2.1–1.9 ppm for alkyl peaks), indicating that fluoride was bound to the dimesitylboryl moieties. The anionic character of fluoride also provoked the broadening and up-shift of the aryl peaks for the bridged phenyl borane moieties from ~7.5 to ~7.0 ppm. The sharp peaks observed at approximately –173 ppm in the ¹⁹F NMR spectra of Ir1 and Ir2 also verified fluoride binding to the boron centers (Fig. S12 for Ir1 and S13 for Ir2). Consequently, these spectral changes suggest that the binding of a fluoride anion to the boron atom of



Fig. 1. Changes in the UV–vis absorption (left) and PL spectra (right) of (a) **Ir1** and (b) **Ir2** solutions $(3.0 \times 10^{-5} \text{ M})$ in THF upon the addition of TBAF (0 (blue solid line) to 4.4×10^{-5} M (violet solid line)). The insets show the absorbances at 328 nm (**Ir1**) and 325 nm (**Ir2**) as functions of [F⁻]. The lines correspond to binding isotherms calculated using $K_F = 7.1 \times 10^4$ M⁻¹ (**Ir1**) and 7.6 $\times 10^4$ M⁻¹ (**Ir2**). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. Oxidative (right) and reductive (left) cyclic voltammetry curves for (a) **Ir1** (orange line) and (b) **Ir2** with each fluoride adduct (blue lines) (0.5 mM in DMSO, scan rate = 100 mV s^{-1}). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Ir1 or Ir2 results in the disruption of the CT transition centered at the triarylborane moiety.

The linear decrease (see insets, Fig. 1) in the absorption bands of both complexes is indicative of a 1:1 binding between the triarylborane and the fluoride anion. The binding constants ($K_{\rm F}$) for Ir1 and Ir2 were estimated as 7.1×10^4 and $7.6\times10^4\,M^{-1},$ respectively. These values are four times lower than that of trimesitylborane (Mes₃B, $3.3 \times 10^5 \text{ M}^{-1}$) [69,70], likely due to the sufficient electron density of the dipyrromethene moiety appended to the triarylborane segment. The C_{LOD} values of Ir1 and Ir2 for the fluoride anions were calculated to be 2.1 and 2.0 \times 10^{-6} M (Table 1) based on the UV/Vis absorption intensity data vs. the fluoride anion concentration (see the Photophysical Measurements subsection in the Experimental section). Interestingly, the PL titration experiments for the Ir complexes in THF solution showed significant changes in the PL spectra following the addition of fluoride (Fig. 1, right). Upon the addition of incremental amounts of fluoride, significantly enhanced emissions were observed for both complexes, resulting in absolute quantum yields (Φ_{em}) that were >2 times higher compared to those prior to fluorine binding (1.2% \rightarrow 2.7% for Ir1 and 2.0% \rightarrow 4.1% for Ir2, Table 1). In addition, spontaneous but slight blue-shifts were also observed (i.e., $\Delta \lambda_{em} = 27$ nm for Ir1 and 34 nm for Ir2, Table 1) and the emission decay lifetimes (τ_{obs}) of Ir1 and Ir2 after the addition of excess TBAF (4.4 \times 10⁻⁵ M in THF) became significantly shorter (τ_{obs} = 0.09 μs for Ir1 + TBAF and 0.07 μs for Ir2 + TBAF, respectively, Table 1 and Fig. S14 in Supplementary data) than those of neutral Ir1 and Ir2, respectively. These findings imply that the intramolecular electronic transitions of the complexes were significantly altered by fluoride binding, and furthermore, such binding appeared to

evoke extension of the band gaps in the complexes, thereby leading to blue-shifted emission patterns. Indeed, the cyclic voltammetry (CV) results obtained for Ir1, Ir2, and their fluoride adducts confirmed such blue-shifted emissive features (Fig. 2 and Table 1). For comparison, the fluoride adducts of the Ir complexes were prepared via a simple synthetic route using each Ir complex and TBAF (see the CV Measurements subsection in the Experimental section). Importantly, the reductive onset potentials (Ered, onset) for the neutral Ir complexes were greatly shifted by fluoride binding (-1.28 V for Ir1 \rightarrow -1.60 V for [Ir1·F]⁻, $\Delta E_{red} = 0.32$ V; -1.10 V for Ir2 \rightarrow -1.48 V for [Ir2·F]⁻, $\Delta E_{red, onset} =$ 0.38 V, Table 1), while the oxidative onset potentials ($E_{ox, onset}$) were relatively similar both before and after fluoride binding (0.62 V for Ir1 \rightarrow 0.58 V for [Ir1·F]⁻, $\Delta E_{ox,\mbox{ onset}}=0.04$ V; 0.54 V for Ir2 \rightarrow 0.52 V for $[\text{Ir2}{\cdot}\text{F}]^-,~\Delta E_{red,~onset}$ = 0.04 V). These findings indicate that fluoride anion binding to the borane units elevated the LUMO levels, which are partially localized on the triarylborane moieties, to a greater extent than the HOMO levels, thereby expanding the band-gap and blue-shifting the emission patterns. These experimental results correspond well with the computational calculations outlined below. Moreover, both Ir complexes underwent consistent oxidation and reduction processes during consecutive cycles, implying a strong electrochemical stability (Fig. S15 in Supplementary data).

The dimesitylboryl moiety is well-known to be selective for cyanide anions as well as fluoride ions over other anions [71-73]. The UV–vis absorption and PL spectra of the **Ir1** and **Ir2** solutions $(3.0 \times 10^{-5} \text{ M})$ in THF after the addition of excess cyanide $(4.4 \times 10^{-5} \text{ M} \text{ in THF})$ were similar to those observed in the presence of fluoride (Fig. S16 in Supplementary data), indicating that both iridium complexes can also capture the cyanide anion. The absorption and emission spectra of both complexes showed little variation upon the addition of a range of anions (i.e., Cl⁻, Br⁻, I⁻, BH⁻₄, BF⁻₄, PF⁻₆, NO⁻₃, CF₃SO⁻₃, CH₃COO⁻, HSO⁻₄, ClO⁻₄, and H₂PO⁻₄, 4.4 × 10⁻⁵ M in THF, Fig. S16), indicating their good selectivity toward the fluoride and cyanide anions.

3.4. Computational calculations and molecular orbital analyses

To gain further insight into the origin of the electronic transitions and the emission behaviors of Ir1 and Ir2, time-dependent density functional theory (TD-DFT) calculations on the ground state (S_0) and the first triplet excited state (T₁) were carried out on Ir1 as a representative complex using the B3LYP functional and the 6-31G(d) basis sets (Table 2, Fig. 3a, Table S3-S4 and Fig. S17 in Supplementary data). The molecular geometries used for the calculations were optimized from the obtained X-ray structures. To include the solvent effects of THF, the conductor-like polarizable continuum model (CPCM) was used [61,62]. The results of the calculated transition in the S₀ optimized geometries show that the major low-energy absorption ($f_{calc} > 0.1$, Table S3) mainly involves HOMO \rightarrow LUMO (>94%, Table 2) and HOMO-3 \rightarrow LUMO+1 (>86%) transitions. While the HOMO level of Ir1 is mainly delocalized over the Ir center (~66%, Table S4), the dipyrromethene + bridged phenyl moieties are the major contributors to the LUMO (~88%). These orbital distribution results suggest that the lowest absorption spectra of

Table 2

Major low-energy electronic transitions in THF for Ir1 and its fluoride adduct $[Ir1 \cdot F]^-$ in the ground (S₀) and the first triplet excited states (T₁) calculated using the TD-B3LYP method with the 6-31G(d) basis set.^a.

	state	λ_{calc}/nm	$f_{ m calc}$	$assignment^{b}$
Ir1	S ₀	458.93	0.1096	H → L (94.3%)
		337.29	0.2401	$H{-}3 \rightarrow L{+}1$ (86.9%)
	T_1	698.73	0	$\mathrm{H} \rightarrow \mathrm{L} \ (90.5\%)$
		675.78	0	$\mathrm{H} \rightarrow \mathrm{L} + 1 \ \textbf{(81.5\%)}$
[Ir1·F] ⁻	T_1	646.02	0	$\mathrm{H} \rightarrow \mathrm{L} \; (81.5\%)$

 $^{\rm a}$ Singlet energies for the vertical transition calculated for the optimized ${\rm S}_0$ geometries.

^b H = HOMO, L = LUMO.



Fig. 3. Frontier molecular orbitals for (a) **Ir1** in the ground state (S_0) and the first triplet excited state (T_1), and (b) [**Ir1**·F]⁻ in the T_1 state, with their relative energies determined by DFT calculation (isovalue 0.04). The transition energy (in nm) was calculated using the TD-B3LYP method with the 6-31G(d) basis set.

both Ir complexes could be primarily attributed to the ¹MLCT transition from the metal center to the dipyrromethene ligands. In addition, HOMO–3 and LUMO levels are predominantly occupied on the dimesityl borane segment (~95%) or on both the dimesityl borane (~57%) and the dipyrromethene + bridged phenyl moiety (43%), respectively. These results are indicative of a π (mesityl)– p_{π} (B) ICT transition, and the computational results are consistent with the experimentally-observed absorption features, thereby suggesting that significant absorptions take place independently of the ¹MLCT and borane-centered ICT transitions.

Conversely, the major transitions for the T₁-optimized geometries of Ir1 are HOMO \rightarrow LUMO and LUMO+1 transitions ($\lambda_{calc} = 699$ and 676 nm, Table 2). The calculated electronic transitions of the T₁ states for Ir1 are in good agreement with the experimentally observed phosphorescent emissions of both complexes. While the LUMO levels are mainly localized on the entire dipyrromethene + triarylborane ligand (LUMO = 98.4% and LUMO+1 = 99.2%, Table S4), the contribution of the HOMO is not only over the dipyrromethene segment (~52%) but also on the Ir center (~44%). These results strongly support that the phosphorescence observed at ~690 nm for both Ir complexes is due to ³MLCT transitions between the metal center and the dipyrromethene ligand.

Furthermore, TD-DFT calculation results for the fluoride adduct of Ir1, i.e., [Ir1·F]⁻, in the T₁-state appear to demonstrate changes in the intramolecular electronic transitions after fluoride binding to the boron centers of Ir1 and Ir2 (Table 2, Fig. 3b, Table S5–S6 and Fig. S18 in Supplementary data). More specifically, the lowest-energy transition in [Ir1·F]⁻ could be assigned entirely to the HOMO \rightarrow LUMO transition ($\lambda_{calc} = 646$ nm, Table 2). The LUMO is located fully on the dipyrromethene + bridged phenyl moiety (92.4%, Table S6), whereas the HOMO level involves both the dipyrromethene (~71%) and triarylborane units (~36%). These results strongly suggest that the experimentally observed emission, which is turned-on upon fluoride binding, originates from the dipyrromethene moiety-centered π - π^* ($^3\pi\pi^*$) transition with a partial ICT transition between the dipyrromethene and triarylborane units.

Interestingly, the calculated HOMO and LUMO levels for $[Ir1 \cdot F]^-$ in the T₁-state were higher compared to the frontier levels for Ir1 in the T₁-state (Fig. 3). In particular, the energy gap between the LUMO levels (0.67 eV) of Ir1 and $[Ir1 \cdot F]^-$ is significantly larger than that (0.32 eV) between the HOMO levels. These findings are in good agreement with the experimentally observed frontier levels for Ir1 and $[Ir1 \cdot F]^-$, as determined by cyclic voltammetry analysis. Such an enhanced band gap

of the fluoride adduct $[Ir1\cdot F]^-$ resulting from the elevation of the LUMO level supports the blue-shifted emission maxima after fluoride binding to the Ir complexes.

Consequently, fluoride binding to the borane moieties of the Ir complexes interrupts the ³MLCT transition corresponding to the Ir center, simultaneously reinforcing the dipyrromethene-based ligand centered π - π * transitions, and evoking the elevation of the LUMO energy levels, thereby leading to the 'turn-on' response and blue-shifted emissive patterns upon the addition of fluoride anions.

4. Conclusions

We herein reported the preparation and characterization of two novel Ir(III)-borane conjugated complexes (Ir1 and Ir2) chelated by a dipyrromethene based ancillary ligand (BL). The solid-state structures of the two complexes were fully analyzed by single-crystal X-ray diffraction measurements, and their UV-vis absorption spectra exhibited typical metal-to-ligand charge transfer (¹MLCT) absorption bands at 483 nm in addition to borane-centered charge transfer (CT) absorption bands at ~326 nm. The photoluminescence (PL) spectra for these complexes demonstrate phosphorescent emission in the near IR region $(\lambda_{em} = \sim 690 \text{ nm})$, which can be attributed to the ³MLCT transition. In addition, fluoride titration experiments for both complexes exhibited a ratiometrically 'turn-on' emissive response and gradual blue-shifted patterns ($\Delta \lambda = 27$ nm for Ir1 and 34 nm for Ir2, respectively). Furthermore, the results of computational calculations for the fluoride adduct of Ir1, [Ir1·F]⁻, verify that the intriguing emissive features could be attributed to fluoride binding to the boron center, which interrupts the ³MLCT transition, reinforces the dipyrromethene-based ligand centered π - π * transition, and induces an enhancement in the band-gap. Consequently, intramolecular electronic transitions on the Ir(III)-borane conjugated complexes could be fine-tuned via fluoride anion binding. suggesting that the described complexes are good candidates for iridium-based phosphorescent sensory materials to detect fluoride anions through 'turn-on' emission in the near IR region.

Author statement

Ju Hyun Hong: Methodology, Investigation, Data Curation, Writing - Review & Editing.

Seonah Kim: Methodology, Investigation, Data Curation, Writing - Review & Editing.

Hyunhee So: Methodology, Investigation, Data Curation.

Ji Hye Lee: Investigation, Data Curation, Software, Resources.

Hyonseok Hwang: Investigation, Data Curation, Software, Resources.

Kang Mun Lee: Visualization, Supervision, Writing - Original Draft, Writing - Review & Editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant (NRF-2016M3A7B4909246, 2020R111A1A01073381 and NRF-2020R1A2C1006400) funded by the Ministry of Science and ICT and the Ministry of Education. We thank Dongwook Kim (Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS)) for assistance with X-ray diffraction experiments involving **Ir1** and **Ir2**.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108706.

References

- Baldo MA, O'Brien DF, You Y, Shoustikov A, Sibley S, Thompson ME, Forrest SR. Highly efficient phosphorescent emission from organic electroluminescent devices. Nature 1998;395. 151–4.
- [2] Lamansky S, Djurovich P, Murphy D, Abdel-Razzaq F, Lee H-E, Adachi C, Burrows PE, Forrest SR, Thompson ME. Highly phosphorescent bis-cyclometalated iridium Complexes: Synthesis, photophysical characterization, and use in organic light emitting diodes. J Am Chem Soc 2001;123. 4304–12.
- [3] Wong W-Y, Ho C-L. Functional metallophosphors for effective charge carrier injection/transport: new robust OLED materials with emerging applications. J Mater Chem 2009;19. 4457–82.
- [4] Wong W-Y, Ho C-L. Heavy metal organometallic electrophosphors derived from multi-component chromophores. Coord Chem Rev 2009;253. 1709–58.
- [5] Zhou G, Wong W-Y, Suo S. Recent progress and current challenges in phosphorescent white organic light-emitting diodes (WOLEDs). J Photochem Photobiol C 2010;11. 133–56.
- [6] Sasabe H, Takamatsu J-I, Motoyama T, Watanabe S, Wagenblast G, Langer N, Molt O, Fuchs E, Lennartz C, Kido J. High-efficiency blue and white organic lightemitting devices incorporating a blue iridium carbene complex. Adv Mater 2010; 22. 5003–7.
- [7] Chi Y, Chou P-T. Transition-metal phosphors with cyclometalating ligands: fundamentals and applications. Chem Soc Rev 2010;39. 638–55.
- [8] Zhou G, Wong W-Y, Yang X. New design tactics in OLEDs using functionalized 2phenylpyridine-type cyclometalates of iridium(III) and platinum(II). Chem Asian J 2011;6. 1706–27.
- [9] Wróbel D, Graja A. Photoinduced electron transfer processes in fullerene–organic chromophore systems. Coord Chem Rev 2011;255. 2555–77.
- [10] Yersin H, Rausch AF, Czerwieniec R, Hofbeck T, Fischer T. The triplet state of organo-transition metal compounds. Triplet harvesting and singlet harvesting for efficient OLEDs. Coord Chem Rev 2011;255. 2622–52.
- [11] Yam VW-W, Wong KM-C. Luminescent metal complexes of d⁶, d⁸ and d¹⁰ transition metal centres. Chem Commun 2011;47. 11579–92.
- [12] Ho C-L, Wong W-Y. Small-molecular blue phosphorescent dyes for organic lightemitting devices. New J Chem 2013;37. 1665–83.
- [13] Ho C-L, Wong W-Y. Charge and energy transfers in functional metallophosphors and metallopolyynes. Coord Chem Rev 2013;257. 1614–49.
- [14] Lee CW, Lee JY. Above 30% external quantum efficiency in blue phosphorescent organic light-emitting diodes using pyrido[2,3-b]indole derivatives as host materials. Adv Mater 2013;25. 5450–4.
- [15] Ying L, Ho C-L, Wu H, Cao Y, Wong W-Y. White polymer light-emitting devices for solid-state lighting: materials, devices, and recent progress. Adv Mater 2014;26. 2459–73.
- [16] Yang X, Zhou G, Wong W-Y. Recent design tactics for high performance white polymer light-emitting diodes. J Mater Chem C 2014;2. 1760–78.
- [17] Visbal R, Gimeno MC. N-heterocyclic carbene metal complexes: photoluminescence and applications. Chem Soc Rev 2014;43. 3551–74.

- [18] Xu X, Yang X, Zhao J, Zhou G, Wong W-Y. Recent advances in solution-processable dendrimers for highly efficient phosphorescent organic light-emitting diodes (PHOLEDs). Asian J Org Chem 2015;4. 394–429.
- [19] Yang X, Zhou G, Wong W-Y. Functionalization of phosphorescent emitters and their host materials by main-group elements for phosphorescent organic lightemitting devices. Chem Soc Rev 2015;44. 8484–575.
- [20] Jou J-H, Kumar S, Agrawal A, Li T-H, Sahoo S. Approaches for fabricating high efficiency organic light emitting diodes. J Mater Chem C 2015;3:2974–3002.
- [21] Longhi E, De Cola L. Chapter 6. Iridium(III) complexes for OLED application. Iridium(III) in optoelectronic and photonics applications. John Wiley & Sons Ltd; 2017. p. 205–74. and references cited therein.
- [22] Lee J.H, Chen C-H, Lee P-H, Lin H-Y, M-k Leung, Chiu T-L, Lin C-F. Blue organic light-emitting diodes: current status, challenges, and future outlook. J Mater Chem C 2019;7. 5874–88.
- [23] Wang S, Zhang H, Zhang B, Xie Z, Wong W-Y. Towards high-power-efficiency solution-processed OLEDs: material and device perspectives. Mater Sci Eng R Rep 2020;140:100547.
- [24] Grushin VV, Herron N, LeCloux DD, Marshall WJ, Petrov VA, Wang Y. New, efficient electroluminescent materials based on organometallic Ir complexes. Chem Commun 2001. 1494–5.
- [25] Lamansky S, Djurovich P, Murphy D, Abdel-Razzaq F, Kwong R, Tsyba I, Bortz M, Mui B, Bau R, Thompson ME. Synthesis and characterization of phosphorescent cyclometalated iridium complexes. Inorg Chem 2001;40. 1704–11.
- [26] Tsuboyama A, Iwawaki H, Furugori M, Mukaide T, Kamatani J, Igawa S, Moriyama T, Miura S, Takiguchi T, Okada S, Hoshino M, Ueno K. Homoleptic cyclometalated iridium complexes with highly efficient red phosphorescence and application to organic light-emitting diode. J Am Chem Soc 2003;125. 12971–9.
- [27] Tamayo AB, Alleyne BD, Djurovich PI, Lamansky S, Tsyba I, Ho NN, Bau R, Thompson ME. Synthesis and characterization of facial and meridional triscyclometalated iridium(III) complexes. J Am Chem Soc 2003;125. 7377–87.
- [28] Yersin H. Triplet emitters for OLED applications. Mechanisms of exciton trapping and control of emission properties. Top Curr Chem 2004;241:1–26.
- [29] Ma B, Djurovich PI, Thompson ME. Excimer and electron transfer quenching studies of a cyclometalated platinum complex. Coord Chem Rev 2005;249. 1501– 10.
- [30] Flamigni L, Barbieri A, Sabatini C, Ventura B, Barigelletti F. Photochemistry and photophysics of coordination compounds: iridium. Top Curr Chem 2007;281: 143–203.
- [31] Chou P-T, Chi Y. Phosphorescent dyes for organic light-emitting diodes. Chem Eur J 2007;13. 380–95.
- [32] You Y, Park SY. Phosphorescent iridium(iii) complexes: toward high phosphorescence quantum efficiency through ligand control. Dalton Trans 2009. 1267–82.
- [33] Wiegmann B, Jones PG, Wagenblast G, Lennartz C, Munster I, Metz S, Kowalsky W, Johannes H-H. A new framework of a heteroleptic iridium(III)–Carbene complex as a triplet emitting material. Organometallics 2012;31. 5223–6.
- [34] Baranoff E, Curchod BFE, Frey J, Scopelliti R, Kessler F, Tavernelli I, Rothlisberger U, Grätzel M. Nazeeruddin MdK. Acid-induced degradation of phosphorescent dopants for OLEDs and its application to the synthesis of trisheteroleptic iridium(III) bis-cyclometalated complexes. Inorg Chem 2012;51. 215– 24.
- [35] Karatsu T, Takahashi M, Yagai S, Kitamura A. Photophysical properties of substituted homoleptic and heteroleptic phenylimidazolinato Ir(III) complexes as a blue phosphorescent material. Inorg Chem 2013;52. 12338–50.
- [36] Beydoun K, Zaarour M, Williams JÄG, Roisnel T, Dorcet V, Planchat A, Boucekkine A, Jacquemin D, Doucet H, Guerchais V. Palladium-catalyzed direct arylation of luminescent bis-cyclometalated iridium(III) complexes incorporating C^{*}N- or O^{*}O-coordinating thiophene-based ligands: an efficient method for color tuning. Inorg Chem 2013;52.12416–28.
- [37] Lee S, Kim S-O, Shin H, Yun H-J, Yang K, Kwon S-K, Kim J-J, Kim Y-H. Deep-blue phosphorescence from perfluoro carbonyl-substituted iridium complexes. J Am Chem Soc 2013;135. 14321–8.
- [38] Edkins RM, Fucke K, Peach MJG, Crawford AG, Marder TB, Beeby A. Syntheses, structures, and comparison of the photophysical properties of cyclometalated iridium complexes containing the isomeric 1- and 2-(2'-pyridyl)pyrene ligands. Inorg Chem 2013;52. 9842–60.
- [39] Monti F, Kessler F, Delgado M, Frey J, Bazzanini F, Accorsi G, Armaroli N, Bolink HJ, Ortí E, Scopelliti R. Nazeeruddin MdK, baranoff E. Charged biscyclometalated iridium(III) complexes with carbene-based ancillary ligands. Inorg Chem 2013;52. 10292–305.
- [40] Xu Q-L, Wang C-C, Li T-Y, Teng M-Y, Zhang S, Jing Y-M, Yang X, Li W-N, Lin C, Zheng Y-X, Zuo J-L, You X-Z. Syntheses, photoluminescence, and electroluminescence of a series of iridium complexes with trifluoromethylsubstituted 2-phenylpyridine as the main ligands and tetraphenylimidodiphosphinate as the ancillary ligand. Inorg Chem 2013;52. 4916–25.
- [41] Kuo H-H, Chen Y-T, Devereux LR, Wu C-C, Fox MA, Kuei C-Y, Chi Y, Lee G-H. Bistridentate Ir(III) metal phosphors for efficient deep-blue organic light-emitting diodes. Adv Mater 2017;29:1702464.
- [42] Li X, Zhang J, Zhao Z, Wang L, Yang H, Chang Q, Jiang N, Liu Z, Bian Z, Liu W, Lu Z, Huang C. Deep blue phosphorescent organic light-emitting diodes with CIEy value of 0.11 and external quantum efficiency up to 22.5%. Adv Mater 2018;30: 1705005.
- [43] Sun Y, Yang X, Feng Z, Liu B, Zhong D, Zhang J, Zhou G, Wu Z. Highly efficient deep-red organic light-emitting devices based on asymmetric iridium(III)

J.H. Hong et al.

Dyes and Pigments 183 (2020) 108706

complexes with the thianthrene 5,5,10,10-tetraoxide moiety. ACS Appl Mater Interfaces 2019;11. 26152–64.

- [44] You Y, Park SY. A phosphorescent Ir(III) complex for selective fluoride ion sensing with a high signal-to-noise ratio. Adv Mater 2008;20. 3820–6.
- [45] Zhao Q, Li F, Liu S, Yu M, Liu Z, Yi T, Huang C. Highly selective phosphorescent chemosensor for fluoride based on an iridium(III) complex containing arylborane units. Inorg Chem 2008;47. 9256–64.
- [46] Xu W-J, Liu S-J, Zhao X-Y, Sun S, Cheng S, Ma T-C, Sun H-B, Zhao Q, Huang W. Cationic iridium(III) complex containing both triarylboron and carbazole moieties as a ratiometric fluoride probe that utilizes a switchable triplet-singlet emission. Chem Eur J 2010;16. 7125–33.
- [47] Xu W, Liu S, Sun H, Zhao X, Zhao Q, Sun S, Cheng S, Ma T, Zhou L, Huang W. FRET-based probe for fluoride based on a phosphorescent iridium(iii) complex containing triarylboron groups. J Mater Chem 2011;21. 7572–81.
- [48] Ito A, Hiokawa T, Sakuda E, Kitamura N. Bright green-phosphorescence from metal-to-boron charge-transfer excited state of a novel cyclometalated iridium(III) complex. Chem Lett 2011;40. 34–6.
- [49] Xu W, Liu S, Zhao Q, Ma T, Sun S, Zhao X, Huang W. A near-infrared phosphorescent probe for F⁻ based on a cationic iridium(III) complex with triarylboron moieties. Sci China Chem 2011;54. 1750–8.
- [50] Vadavi RS, Kim H, Lee KM, Kim T, Lee J, Lee YS, Lee MH. Turning on MLCT phosphorescence of iridium(III)–Borane conjugates upon fluoride binding. Organometallics 2012;31. 31–4.
- [51] Ho C-L, Wong K-L, Kong H-K, Ho Y-M, Chan CT-L, Kwok W-M, Leung KS-Y, Tam H-L, Lam MH-W, Ren X-F, Ren A-M, Feng J-K, Wong W-Y. A strong two-photon induced phosphorescent golgi-specific *in vitro* marker based on a heteroleptic iridium complex. Chem Commun 2012;48. 2525–7.
- [52] Yang X, Huang Z, Ho C-L, Zhou G, Whang DR, Yao C, Xu X, Park SY, Chui C-H, Wong W-Y. Dynamic dual stage phosphorescence chromatic change in a diborylated iridium phosphor for fluoride ion sensing with concentration discriminating capability. RSC Adv 2013;3. 6553–63.
- [53] Xu W-J, Liu S-J, Zhao X, Zhao N, Liu Z-Q, Xu H, Liang H, Zhao Q, Yu X-Q, Huang W. Synthesis, one- and two-photon photophysical and excited-state properties, and sensing application of a new phosphorescent dinuclear cationic iridium(III) complex. Chem Eur J 2013;19. 621–9.
- [54] Sharma S, Kim H, Lee YH, Kim T, Lee YS, Lee MH. Heteroleptic cyclometalated iridium(III) complexes supported by triarylborylpicolinate ligand: ratiometric turnon phosphorescence response upon fluoride binding. Inorg Chem 2014;53. 8672– 80.
- [55] Lin W, Tan Q, Liang H, Zhang KY, Liu S, Jiang R, Hu R, Xu W, Zhao Q, Huang W. Phosphorescence switch and logic gate of iridium(iii) complexes containing a triarylboron moiety triggered by fluoride and an electric field. J Mater Chem C 2015;3. 1883–7.
- [56] Xu W-J, Qin Y-Y, Wei L-W, Zhang KY, Liu S-J, Zhao Q. Boron-functionalized phosphorescent iridium(III) complexes. Eur J Inorg Chem 2017. 4393–405.
- [57] Zhou G, Ho C-L, Wong W-Y, Wang Q, Ma D, Wang L, Lin Z, Marder TB, Beeby A. Manipulating charge-transfer character with electron-withdrawing main-group moieties for the color tuning of iridium electrophosphors. Adv Funct Mater 2008; 18:499–511.

- [58] Kumar GR, Behera SK, Thilagar P. Room temperature phosphorescent triarylborane functionalized iridium complexes. Dalton Trans 2019;48. 6817–23.
- [59] Takaki K, Sakuda E, Ito A, Horiuchi S, Arikawa Y, Umakoshi K. Controlling the electronic structures and excited-state characteristics of dipyrrinatoiridium(III) complexes by an arylborane or an arylamino unit. Inorg Chem 2019;58. 14542–50.
- [60] You Y, Park SY. Inter-ligand energy transfer and related emission change in the cyclometalated heteroleptic iridium Complex: facile and efficient color tuning over the whole visible range by the ancillary ligand structure. J Am Chem Soc 2005;127. 12438–9.
- [61] Barone V, Cossi M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. J Phys Chem A 1998;102: 1995–2001.
- [62] Cossi M, Rega N, Scalmani G, Barone V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. J Comput Chem 2003;24. 669–81.
- [63] Binkley JS, Pople JA, Hehre WJ. Self-consistent molecular orbital methods. 21. Small split-valence basis sets for first-row elements. J Am Chem Soc 1980;102. 939–47.
- [64] Hay PJ, Wadt WR. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J Chem Phys 1985;82. 270–83.
- [65] Runge E, Gross EKU. Density-functional theory for time-dependent systems. Phys Rev Lett 1984;52. 997–1000.
- [66] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09 revision D.01. Wallingford CT: Gaussian. Inc.; 2013.
- [67] O'Boyle NM, Tenderholt AL, Langner KM. A library for package-independent computational chemistry algorithms. J Comput Chem 2008;29. 839–45.
- [68] Dennington R, Keith TA, Millam JM. GaussView 6. KS: Semichem Inc.;Shawnee Mission; 2016.
- [69] Huh JO, Kim H, Lee KM, Lee YS, Do Y, Lee MH. o-Carborane-Assisted Lewis acidity enhancement of triarylboranes. Chem Commun 2010;46. 1138–40.
- [70] Sole S, Gabbaï FP. A bidentate borane as colorimetric fluoride ion sensor. Chem Commun 2004. 1284–5.
- [71] Wade CR, Gabbaï FP. Cyanide anion binding by a triarylborane at the outer rim of a cyclometalated ruthenium(II) cationic complex. Inorg Chem 2010;49. 714–20.
- [72] Chiu C-W, Gabbaï FP. Cyanide ion complexation by a cationic borane. Dalton Trans 2008. 814–17.
- [73] Hudnall TW, Gabbaï FP. Ammonium boranes for the selective complexation of cyanide or fluoride ions in water. J Am Chem Soc 2007;129. 11978–86.