View Article Online

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Niu, J. Chen, P. Tan, W. Sun, Y. Zheng, G. Li and J. Zuo, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT01479E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/dalton

Dalton Transactions

RSCPublishing

ARTICLE

			LIIIUU	
Cite 10.1039/x02	this: xx00000x	DOI:	comp	
			Zhi-Gan Jing-lin Z	
Received 00 Accepted 00)th April 2018,)th April 2018		Four bis- (dfbt)₂Ir (1	
DOI: 10.103	39/x0xx00000x		phenyl-6-	
www.rsc.or	·g/		tetrapheny lights peal	

Efficient yellow electroluminescence of four iridium(III) complexes with benzo[d]thiazole derivatives as main ligands

Zhi-Gang Niu^{1,2}, Jun Chen¹, Peng Tan², Wei Sun², You-Xuan Zheng^{*,1}, Gao-Nan Li^{*,2}, Jing-lin Zuo^{*,1}

Four bis-cyclometalated iridium(III) complexes, (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) (bt = 2-phenylbenzo[*d*]thiazole, fbt = 6-fluoro-2-phenylbenzo[*d*]thiazole, cf₃bt = 2-phenyl-6-(trifluoromethyl)benzo[*d*]thiazole, dfbt = 5,7-difluoro-2-phenylbenzo[*d*]thiazole, tpip = tetraphenylimidodiphosphinate) have been synthesized and investigated. All complexes emit yellow lights peak at 564–574 nm with quantum efficiencies (Φ_{em}) of 27.1–48.4% and excited state lifetimes of 2.40–2.81 µs in degassed CH₂Cl₂ solution at room temperature, respectively. Correspondingly, the organic light-emitting diodes (OLEDs) using these complexes as emitters achieve yellow electrophosphorescence with good device characteristics. Due to its highest photoluminescence quantum yield (48.4%), the device based on (dfbt)₂Ir(tpip) displays the best device performances with a maximum current efficiency ($\eta_{c,max}$) up to 69.8 cd A⁻¹ and a maximum external quantum efficiency (EQE_{max}) up to 24.3%. Furthermore, all devices showed low efficiency roll-off ratios. The EQE still could be retained at 17.7%, 16.4%, 18.3% and 20.6% for four devices at a luminance of 1000 cd m⁻², respectively. These results suggest that these materials have potential application in efficient OLEDs.

Introduction

Organic light-emitting diodes (OLEDs) have attracted great interest in the development of modern optoelectronic technologies such as low-cost, more-efficient flat-panel displays and the next generation solid-state lighting sources.¹⁻³ In particular, luminescent iridium(III) complexes play an important role in the fabrication of efficient OLEDs, owing to their high photoluminescence quantum yields, good stability and flexible color tunability.⁴⁻⁵

In order to achieve highly efficient full-color and white OLEDs (WOLEDs), the yellow- or orange-emitting Ir(III) phosphors are also the most important research directions, since they can be used in combination with deep blue emitters to fabricate twoemitting-component WOLEDs.6 In this regard, many different classes of Ir(III) complexes have been synthesized and investigated.⁷⁻¹³ Among them, 2-phenylbenzothiazole (bt) is one typical ligand framework to construct orange-yellow Ir(III) complexes. Since the first yellow-emitting Ir(III) complex $(bt)_2$ Ir(acac) (acac = acetylacetonate) was reported,¹⁴ a number of bt derivatives with substituents on the ligands have been developed for OLED applications.^{6, 15} These early examples of neutral bt-based iridium(III) complexes adopt acetylacetonate (acac) as ancillary ligand, and their electroluminescent properties are not very satisfying. To further improve the efficiencies of yellow and orange phosphorescent materials, it is necessary to

attempt different types of ancillary ligands. From our previous work, tetraphenylimidodiphosphinate (tpip) derivatives with polar P=O bonds and phenyl rings were used as ancillary ligands,¹⁶ which can improve the electron mobility of the emitters and benefit their device performances.¹⁷ Besides, we found that the fluorinated main ligands can modify the optical properties of iridium complexes. Particularly, the bulky $-CF_3$ group can affect the packing of molecular and the according steric protection around metal can restrain the self-quenching of luminescence. Again, the C–F bonds with lower vibrational frequency can reduce the rate of nonradioactive deactivation, which would enhance the photoluminescence quantum yields.¹⁸

In consideration of these factors, in this study we synthesized four Ir(III) complexes (Scheme 1) with bt derivatives (fbt = 6fluoro-2-phenylbenzo[d]thiazole, 2-phenyl-6cf₃bt = (trifluoromethyl)benzo[d]thiazole, dfbt = 5,7-difluoro-2phenylbenzo[d]thiazole) as the cyclometalated ligands and tpip as the ancillary ligand. All complexes emit yellow lights peak at 564-574 nm in degassed CH₂Cl₂ solution at room temperature and the fluorinated substituents in the main ligands have great effects on their photophysical properties. Using these complexes as emitters, all device show good electroluminescence properties with maximum current efficiencies ($\eta_{c,max}$) of 57.1–69.8 cd A⁻¹

and maximum external quantum efficiencies (EQE_{max}) of 18.5–24.3\%.

Experimental section

Materials and measurements

All reagents and chemicals were purchased from commercial sources and used without further purification. ¹H, ¹⁹F and ³¹P spectra were recorded on a Bruker AM 400 MHz instrument, and chemical shifts were reported in ppm relative to Me₄Si as internal standard. ESI-MS and MALDI-TOF-MS spectra were recorded on an Esquire HCT–Agilent 1200 LC/MS spectrometer and a Bruker Autoflex^{II} TM TOF/TOF instrument, respectively. UV– vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F–7000 spectrophotometer as deaerated CH₂Cl₂ solutions

at room temperature and 77 K. The thermoanalytical analysis (TGA) was performed under a flow of nitrogen using a simultaneous NETZSCH STA 449C thermal analyzer. Luminescence lifetime curves were measured on an Edinburgh Instruments FLS920P fluorescence spectrometer and the data were treated as one-order exponential fitting using OriginPro 8 software. Cyclic voltammetry (CV) was performed on a CHI 1210B electrochemical workstation, with a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode, an Ag/Ag⁺ electrode as the reference electrode, and 0.1 M*n*-Bu₄NClO₄ as the supporting electrolyte. All solutions were deaerated by nitrogen bubbling for 30 min before measurements. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)₃) and the unknown sample.⁷



Scheme 1. Synthetic routes of four Ir(III) complexes (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip).

Syntheses

All reactions were performed under nitrogen atmosphere. The synthetic routes of ligands and complexes are also showed in Scheme 1. Tetraphenylimidodiphosphinate (tpip) and its potassium salt (Ktpip) were synthesized according to our previous work.¹⁹ 2-Amino-5-fluorobenzenethiol and 2-amino-5-(trifluoromethyl)benzenethiol were prepared according to the literature methods.²⁰

General syntheses of benzothiazole ligands (3a-3c).

Benzaldehyde (0.60 g, 5.65 mmol) was mixed with a substituted 2-aminothiophenol (0.71 g, 5.65 mmol) in 20 mL of DMSO and an equimolar amount of $Na_2S_2O_3$ was then added. The reaction was heated at 120 °C for 3 hours. After cooling, H_2O was added and the precipitate collected was dissolved in CH_2Cl_2 , washed

with brine. Then solvent was removed and the resulting solid was purified by column chromatography (petroleum ether : ethyl acetate = 30 : 1) to give the ligands of 3a-3c as white solid.

2-Phenyl-benzo[*d*]thiazole (**3a**, 0.96 g, yield: 84.2%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.07~8.10 (m, 3H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.46~7.50 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H). MS (ESI): m/z 212.05 [M+H]⁺.

6-Fluoro-2-phenylbenzo[*d*]thiazole (**3b**, 0.73 g, yield: 80.3%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.04~8.07 (m, 2H), 8.01 (dd, J = 4.8 Hz, 8.8 Hz, 1H), 7.58 (dd, J = 2.8 Hz, 8.0 Hz, 1H), 7.50 (t, J = 4.0 Hz, 3H), 7.20~7.25 (m, 1H). MS (ESI): m/z 230.04 [M+H]⁺.

2-Phenyl-6-(trifluoromethyl)benzo[*d*]thiazole (3c, 0.75 g, yield: 82.6%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.10~8.20

(m, 4H), 7.73 (d, J = 8.8 Hz, 1H), 7.51~7.53 (m, 3H). MS (ESI): m/z 280.03 [M+H]⁺.

Synthesis of 5,7-difluoro-2-phenylbenzo[d]thiazole (3d)

N-(3,5-Difluorophenyl)benzamide (1d). Benzoyl chloride (1.14 g, 8.13 mmol) was added dropwise to a solution of 3,5-difluoroaniline (1.0 g, 7.75 mmol) and Et₃N (1.18 g, 1.62 mL) in dry DCM (30 mL) at 0 °C. After the addition, the reaction mixture was warmed up to room temperature and stirred overnight. Then the mixture was diluted with water and extracted with DCM. The combined organic phases were washed with brine and evaporated. The crude product was recrystallized from the mixture of ethyl acetate and petroleum ether (V : V = 1 : 1) to give compound 1d (1.58 g, yield: 87.5%) as white solid, which was used in next step without further purification.

N-(3,5-Difluorophenyl)benzothioamide (2d). To a solution of 1d (1.50 g, 6.43 mmol) in toluene (50.0 mL) was added Lawesson's reagent (2.60 g, 6.43 mmol). The solution was refluxed for 8 hours, and then concentrated. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 10 : 1) to give the product of 2d (1.35 g, yield: 84.2%) as yellow solid.

5,7-Difluoro-2-phenylbenzo[d]thiazole (**3d**). To a solution of K₃Fe(CN)₆ (5.28 g, 16.05 mmol) in H₂O (10 mL) at 90 °C was added dropwise a solution of **2d** (1.00 g, 4.0 mmol) and NaOH (0.96 g, 24.13 mmol) in H₂O/EtOH (20 mL / 4 mL). The solution was heated at this temperature for another 8 h. The mixture was cooled to room temperature, diluted with water and extracted with DCM. The combined organic phases were washed with brine and evaporated. The residue was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1) to give the product **3d** (0.75 g, yield: 75.1%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.06~8.08 (m, 2H), 7.49~7.60 (m, 4H), 6.93 (dt, $J_1 = 9.2$ Hz, $J_2 = 2.0$ Hz, 1H). MS (ESI): m/z 248.04 [M+H]⁺.

General syntheses of iridium complexes.

A mixture of IrCl₃ (1.0 mmol) and the ligands **3a–3d** (2.2 mmol) in 9 mL of ethoxyethanol and H₂O (V : V = 2 : 1) was heated at 120 °C for 24 h, respectively. Upon cooling to room temperature, the precipitates were collected by filtration and washed with water and MeOH. After drying, the cholorobridged dimers were used directly in next step without further purification. A mixture of the above dimers (0.2 mmol) and Ktpip (2.5 equiv.) in 10 mL of ethoxyethanol was heated at 120 °C for 12 h. After the solvent was removed, water was added and the reaction mixture was extracted with CH₂Cl₂ three times, and then evaporated. The residues were purified by flash column chromatography (petroleum ether : dichloromethane = 10 : 1) to afford the target Ir(III) complexes, which were further purified by sublimation in vacuum.

(bt)₂**Ir(tpip)** (yield: 48.7%) ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.89 (d, J = 8.4 Hz, 2H), 7.81~7.87 (m, 4H), 7.61 (d, J =

7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.31~7.36 (m, 6H), 7.21~7.25 (m, 4H), 7.11 (t, J = 7.6 Hz, 2H), 6.81~6.88 (m, 4H), 6.68~6.76 (m, 6H), 6.57 (t, J = 7.6 Hz, 2H), 6.27 (d, J = 7.6 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃): (ppm) 23.06. MALDI-TOF calcd for C₅₀H₃₆IrN₃O₂P₂S₂: 1029.135 ([M+H]⁺), found: 1029.467. Anal. calcd. for C₅₀H₃₆IrN₃O₂P₂S₂: C 58.35, H 3.53, N 4.08. Found: C 58.39, H 3.62, N 4.05.

(**fbt**)₂**Ir**(**tpip**) (yield: 46.3%) ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.86 (dd, J = 4.8 Hz, 8.8 Hz, 2H), 7.83~7.88 (m, 4H), 7.58 (d, J = 7.6 Hz, 2H), 7.35~7.37 (m, 6H), 7.19~7.25 (m, 6H), 6.92 (t, J = 7.2 Hz, 2H), 6.79~6.86 (m, 6H), 6.59 (t, J = 6.8 Hz, 2H), 6.35~6.40 (m, 2H), 6.24 (d, J = 7.6 Hz, 2H). ¹⁹F NMR (367 MHz, CDCl₃) δ (ppm) -116.87. ³¹P NMR (162 MHz, CDCl₃): (ppm) 23.06. MALDI-TOF calcd for C₅₀H₃₄F₂IrN₃O₂P₂S₂: 1065.116 ([M+H]⁺), found: 1065.324. Anal. Calcd. For C₅₀H₃₄F₂IrN₃O₂P₂S₂: C 56.38, H 3.22, N 3.95. Found: C 56.29, H 3.26, N 3.98.

(cf₃bt)₂Ir(tpip) (yield: 52.6%) ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.98 (d, *J*=8.8Hz, 2H), 7.86~7.91 (m, 4H), 7.78 (s, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.39~7.40 (m, 6H), 7.20~7.24 (m, 4H), 6.82~6.89 (m, 6H), 6.71~6.73 (m, 4H), 6.62 (t, *J* = 7.6 Hz, 2H), 6.25 (d, *J* = 7.6 Hz, 2H). ¹⁹F NMR (367 MHz, CDCl₃) δ (ppm) - 61.60. ³¹P NMR (162 MHz, CDCl₃): (ppm) 23.15. MALDI-TOF calcd for C₅₂H₃₄F₆IrN₃O₂P₂S₂: 1165.110 ([M+H]⁺), found: 1165.352. Anal. calcd. for C₅₂H₃₄F₆IrN₃O₂P₂S₂: C 53.60, H 2.94, N 3.61. Found: C 53.51, H 3.02, N 3.72.

(dfbt)₂Ir(tpip) (yield: 42.9%) ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.55 (d, J = 10.0 Hz, 2H), 7.87~7.91 (m, 4H), 7.62 (d, J =7.2 Hz, 2H), 7.29~7.37 (m, 10H), 6.82~6.94 (m,8H), 6.64 (t, J =8.0 Hz, 4H), 6.23 (d, J = 8.0 Hz, 1H). ¹⁹F NMR (367 MHz, CDCl₃) δ (ppm) -111.08, -111.09, -113.32, -113.33. ³¹P NMR (162 MHz, CDCl₃): (ppm) 23.95. MALDI-TOF calcd for C₅₀H₃₂F₄IrN₃O₂P₂S₂: 1101.098 ([M+H]⁺), found: 1101.311. Anal. calcd. for C₅₀H₃₂F₄IrN₃O₂P₂S₂: C 54.54, H 2.93, N 3.82. Found: C 54.41, H 2.97, N 3.90.

Results and discussion

Preparation and characterization of compounds

The syntheses of the cyclometalating ligands 3a-3d and their derived complexes $(bt)_2Ir(tpip)$, $(fbt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ are shown in Scheme 1. The ligands 3a-3cwere conveniently synthesized by the improved method, which used benzaldehyde and the corresponding substituted 2aminothiophenol as raw materials. The difluorinated ligand 3dwas easily synthesized through a traditional three-step reaction. First, the amide compounds 1d was prepared between benzoyl chloride and the corresponding substituted aniline by the acylation reaction in good yield (87.5%), and the thioamide 2d was then generated with Lawesson's reagent in high yield over 80%. Sequential the main ligand 3d was prepared by the cyclization reaction under K₃Fe(CN)₆ catalysis. The Ir(III) dimers [(C^N)₂Ir(μ -Cl)]₂ were synthesized by IrCl₃ with 2.2 equiv of **3a–3d** in a 2 : 1 mixture of 2-ethoxyethanol and deionized water according to a similar method reported by Nonoyama.²¹ And then the Ir(III) complexes (**bt**)₂**Ir(tpip**), (**fb**)₂**Ir(tpip**), (**cf**₃**bt**)₂**Ir(tpip**) and (**dfbt**)₂**Ir(tpip**) were obtained by the reaction of $[(C^{N})_{2}Ir(\mu - CI)]_{2}(1.0 \text{ equiv.})$ with Ktpip (2.5 equiv.) in 2-ethoxyethanol.

Structural description

The crystal structures of complexes $(bt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ were determined by X-ray crystallography and the ORTEP diagrams are depicted in Fig. 1. The corresponding crystallographic data and structure refinement details are listed in Table S1, and selected bond lengths and bond angles are collected in Table S2. As shown in Fig. 1, the iridium metal center in each complex adopts the distorted octahedral coordination geometry with the C and N atoms of the cyclometalated ligands and the O atoms of ancillary ligand. The nitrogen atoms in the cyclometalated ligands adopt a *trans*

conformation to one another, while the bound carbon atoms are cis positions with respect to the iridium center, as indicated in other Ir(III) complexes.²²⁻²³ The lengths of Ir-C and Ir-N bonds are in the range from 1.983(8) ~ 1.986(5) Å and 2.052(6) ~ 2.068(4) Å, respectively, close to those in previously reported complexes.²⁴⁻²⁵ It is noteworthy that the Ir-O_{tpip} bond lengths $(2.197(3) \sim 2.260(3)$ Å) are slightly longer than the average value (2.088 Å) of Ir-O bond reported in the Cambridge Crystallographic Database, which may be attributed to the strong trans-influence of the carbon donors. The O-Ir-O and C-Ir-N bond angles are in agreement with the corresponding parameters described in similarly constituted Ir(III) complexes.¹⁷ In addition, the terminal thifluoromethyl groups of complex (cf₃bt)₂Ir(tpip) are disordered over two sites (F1 1, F2 1 and F3 1 with 0.58 occupancy, F1 2, F2 2 and F3 2 with 0.42 occupancy; F1 3, F2 3 and F3 3 with 0.60 occupancy, F1 4, F2 4 and F3 4 with 0.40 occupancy).



Fig. 1 ORTEP views of $(bt)_2Ir(tpip)$ (CCDC No. 1832345), $(cf_3bt)_2Ir(tpip)$ (CCDC No. 1832346) and $(dfbt)_2Ir(tpip)$ (CCDC No. 1832347) with the atom-numbering scheme at the 50% probability level. The terminal thifluoromethyl groups of complex $(cf_3bt)_2Ir(tpip)$ are disordered over two sites. Hydrogen atoms and solvent molecules are omitted for clarity.

Thermal property

The thermal properties of these Ir(III) complexes are very important for efficient OLEDs. If iridium complexes as emitter are suitable for OLED application, they should have high enough melting point (T_m) and decomposition temperature (T_d) to ensure that the material could be deposited onto the solid face and survived long periods of application without any decomposition. The thermal properties of investigated complexes were characterized by thermogravimetric analysis (TGA) under a nitrogen steam. They all possess the decomposed temperatures higher than 300 °C, indicative of their good thermal stability (Table 1). From the TG curves in Figure S1, it can be seen that decomposition temperatures are 369 °C for (**bt**)₂**Ir**(**tpip**), 345 °C for (**fbt**)₂**Ir**(**tpip**), 355 °C for (**cf₃bt**)₂**Ir**(**tpip**) and 348 °C for

(dfbt)₂Ir(tpip), respectively, which are high enough for their application in stable OLEDs.

Photophysical property

The UV-vis absorption spectra of complexes $(bt)_2Ir(tpip)$, $(fbt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ in CH₂Cl₂ solution are depicted in Fig. 2(a), and the data are provided in Table 1. All Ir(III) complexes show similar absorption spectra and the intense absorption bands at higher energies (250–350 nm) are attributed to spin-allowed ligand centred (LC) ${}^1\pi \rightarrow \pi^*$ transitions typically. The relatively weak absorption bands at lower energies extending into the spectral region (350-550 nm) are reasonable to arise as singlet metal-to-ligand charge-transfer (1MLCT), triplet metal-to-ligand charge transfer (3MLCT) states

Published on 21 May 2018. Downloaded by KENT STATE UNIVERSITY on 21/05/2018 15:45:18.

and/or LLCT (ligand-to-ligand charge transfer) transition.²⁶ In comparison with (bt)₂Ir(tpip), the lowest lying absorption bands for complexes (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) are strongly red-shifted, whereas that of (fbt)₂Ir(tpip) is weakly blue-shifted.

The observed trend may reflect electron properties of substituents on the cyclometallated main ligand. This assumption will be proved by electrochemistry analyses and DFT calculations discussed below.



Fig. 2 Absorption and emission spectra of (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) in degassed CH₂Cl₂ solution.

Complex	Absorption $\lambda_{abs} (nm)^a$	Emission				Thermal	Thermal property		
		λ_{em}^{RT} $(nm)^{a}$	$egin{array}{lll} arPhi_{ m PL}\ (\%)^b \end{array}$	τ $(\mu s)^a$	$k_r (10^5 s^{-1})^c$	$k_{nr} (10^5 \text{ s}^{-1})^c$	λ_{em}^{77K} $(nm)^d$	T _m (°C) ^e	T _d (°C) ^f
(bt)2Ir(tpip)	230, 269, 312, 328, 364, 402, 444, 486	566, 605(sh)	27.1	2.43	1.12	3.00	564	358	369
(fbt)2Ir(tpip)	227, 267, 310, 326, 362, 400, 443, 484	564, 601(sh)	32.5	2.81	1.16	2.40	563	317	345
(cf ₃ bt) ₂ Ir(tpip)	227, 269, 314, 330, 369, 412, 451, 502	574, 613(sh)	36.9	2.65	1.39	2.38	574	323	355
(dfbt)2Ir(tpip)	228, 263, 319, 334, 371, 413, 452, 504	567	48.4	2.40	2.02	2.15	567	328	348

Table 1 Photophysical and thermal stability data of complexes (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip)

^{*a*} Data were collected from degassed CH₂Cl₂ solutions at room temperature. ^{*b*} *fac*-Ir(ppy)₃ as referenced standard (0.4).^{7 *c*} Radiative decay rate (k_r) and nonradiative decay rate (k_{nr}) were estimated from the measured quantum yields and lifetimes. ^{*d*} Data were collected from degassed CH₂Cl₂ solutions at 77 K. ^{*e*} T_m: melting temperature. ^{*f*} T_d: decomposition temperature corresponding to a 5% weight loss.

Photoluminescence (PL) emission spectra of complexes $(bt)_2Ir(tpip)$, $(fbt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ in degassed CH_2Cl_2 solution at room temperature (RT) and 77 K are displayed in Fig. 2(b), and the corresponding data are also summarized in Table 1. The emission spectra of Ir(III) complexes at RT show a broad band covering a range from 564 to 574 nm, together with a shoulder peak at 601–613 nm, which make them as yellow emitters. Their excited states are mainly a ³MLCT state with a

contribution of a ³LC transition centered on the main ligand.²⁷ The main peaks display the wavelength orders as $(fbt)_2Ir(tpip) < (bt)_2Ir(tpip) < (dfbt)_2Ir(tpip) < (cf_3bt)_2Ir(tpip)$, mirroring that observed for the lowest-energy absorption bands. The higher-energy emission of $(fbt)_2Ir(tpip)$, compared with that of $(bt)_2Ir(tpip)$, could be dependent on the electron-withdrawing fluorine atom in the phenyl ring of the bt ligand. On the contrary, for $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$, the thifluoromethyl group

at 3-position and the F atoms at 3,5-position on the bt ligand can lower the emission energy and therefore lead to redshifted emission. Upon cooling to 77 K, all the Ir(III) complexes show phosphorescence spectra with well-resolved vibronic progression. It is interesting to note that all the complexes show exceptionally small blue-shifts compared to those measured at RT.²⁸⁻³⁰

Phosphorescence relative quantum yields (Φ_{em}) of (bt)₂Ir(tpip), (fbt)2Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) in dichloromethane were measured to be 27.1-48.4% (Table 1) at room temperature by using typical phosphorescent fac-Ir(ppy)₃ as a standard ($\Phi_{em} = 0.40$). Generally, the presence of the C-F bonds can lead to the reduced radiationless deactivation rate (see k_{nr} in Table 1).^{31–} ³² Thus, the quantum efficiencies of complexes (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) with fluorine atoms are higher than that of complex (bt)₂Ir(tpip), and the quantum yield value of complex (dfbt)₂Ir(tpip) is the most largest one. Subsequently, the luminescence excited state lifetimes (τ) of all the four emitters were measured at RT in degassed CH2Cl2 solution, ranging from 2.40 to 2.81 µs (Table 1), which indicate that the emissive excited states of all Ir(III) complexes have triplet characters.³³ From the quantum yields Φ_{em} and the lifetimes τ values, the radiative decay rate (k_r) and the nonradiative decay rate (knr) were calculated through the equations: $k_r = \Phi_{em} / \tau$ and $k_{nr} = (1 - \Phi_{em}) / \tau^{34}$ (Table 1). As can be seen, the k_r value of (dfbt)₂Ir(tpip) is the largest one and the knr value is the smallest one within investigated complexes. Hence, complex (dfbt)₂Ir(tpip) is the most strongly emissive one in the family of complexes, which also benefits its device performances.

Electrochemical property and theoretical calculation

In order to gain insights into the orbital distributions and to investigate the electronic effects caused by the fluorination on the C^N ligands, theoretical calculations of complexes $(bt)_2Ir(tpip)$, $(fbt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ were carried out using density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The HOMO–LUMO energy-level diagrams and the energy gap of these complexes are presented in Fig. 3(a). The calculated spin-allowed electronic transitions are provided in Table S3, as well as compared with the experimental absorption spectra data. The electron density distributions are summarized in Table S4.

As can be clearly seen for all the Ir(III) complexes (Fig. 3(a)), the HOMOs are mainly dominated by the metal center and the phenyl parts of the C^N ligands, and the LUMOs are localized on the whole C^N ligands. Therefore, the lowestenergy spin-allowed electronic transitions for all complexes (HOMO→LUMO) are ascribed as metal-to-ligand charge transfer (MLCT) in combination with partial ligand-to-ligand charge transfer (LLCT), which are consistent with the actual absorptions (Table 1 and Table S3). Moreover, the HOMO levels of complexes (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) are lower than complex (bt)₂Ir(tpip), owing to the fluorinated substituents on the phenyl moiety of the C^N ligands. Specially, the decreasing trends of $(cf_3bt)_2Ir(tpip)$ and (dfbt)₂Ir(tpip) are more pronounced than (fbt)₂Ir(tpip). Similar results have also been obtained for the LUMO levels of these Ir(III) complexes. Different decreasing trends of the HOMO/LUMO levels induce distinct HOMO-LUMO energy gap. For example, the energy bandgap of (fbt)₂Ir(tpip) (3.49 eV) is larger than (bt)₂Ir(tpip) (3.48 eV), whereas those of $(cf_3bt)_2Ir(tpip)$ (3.37 eV) and $(dfbt)_2Ir(tpip)$ (3.40 eV) are smaller, thereby leading to blue-shifted and red-shifted in the actual UV-visible spectra, respectively.



Fig. 3 (a) Molecular orbital energy-level diagrams of HOMOs and LUMOs; (b) cyclic voltammogram curves in CH_2Cl_2 solution containing *n*-Bu₄NClO₄ (0.1 M) at a sweep rate of 100 mV·s⁻¹ of the Ir(III) complexes (**bt**)₂**Ir(tpip**), (**ft**)₂**Ir(tpip**), (**ft**)₂**Ir(tpip**) and (**dfbt**)₂**Ir(tpip**).

The electrochemical properties of $(bt)_2Ir(tpip)$, $(fbt)_2Ir(tpip)$, $(cf_3bt)_2Ir(tpip)$ and $(dfbt)_2Ir(tpip)$ were investigated by cyclic voltammetry, and the oxidation/reduction waves are shown in Fig. 3(b). On the

basis of their oxidation potentials, the HOMO and LUMO energy levels calculated are summarized in Table S5. The energy gaps ($E_{opt,g}$) were estimated from the UV-vis absorption edges and the HOMO levels were calculated from the oxidation peak potential (E_{ox}) of the complexes.³⁵ Then the LUMO levels were determined according to the equation LUMO = HOMO + $E_{opt,g}$.

All the complexes exhibit a one electron reversible oxidation couple around 1.03–1.16 V. The oxidation processes are linked to metal-centered orbitals with a contribution from cyclometalated fragments, as already confirmed by DFT calculations (Fig. 3(a)). It is noteworthy that the trend in E_{ox} is $(bt)_2Ir(tpip) < (fbt)_2Ir(tpip) <$ $(cf_3bt)_2Ir(tpip) < (dfbt)_2Ir(tpip)$, while the order of the HOMO energy levels is $(bt)_2Ir(tpip) > (fbt)_2Ir(tpip) >$ $(cf_3bt)_2Ir(tpip) > (dfbt)_2Ir(tpip)$. These results suggest that the presence of fluorine atoms on the cyclometalated ligands

impoverishes the electron densities in the Ir-phenyl moiety and stabilizes of the HOMO orbitals. Remarkably, the oxidation processes for complexes (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) are more harder than analogue (fbt)₂Ir(tpip), indicating that the stabilization effect on the HOMO level can be further strengthened by an increase in the number of fluorine atoms. Moreover, the E_{ox} difference between $(cf_3bt)_2Ir(tpip)$ (1.15 eV) and $(dfbt)_2Ir(tpip)$ (1.16 eV) is very small, reflecting the similar electronic properties of the thifluoromethyl group at 3-position and the F atoms at 3,5position on the bt ligand. The LUMO energy levels were obtained from the HOMO and $E_{opt,g}$ values. It can be observed that the LUMO and HOMO energy levels have the same variation tendency based on experimental and theoretical data. In addition, the HOMO/LUMO energy levels inferred from the CV data are systematically slightly lower compared to the DFT data, as reported in the literature.^{35b}



Fig. 4 Energy level diagrams of phosphorescent OLEDs and the molecular structures of the materials used in the devices.

OLEDs performance

To evaluate the electroluminescent (EL) properties of these complexes, OLEDs with a configuration of ITO/ MoO3 (molybdenum oxide, 5 nm)/ TAPC (4,4'-(cyclohexane-1,1diyl)bis(N,N-di-p-tolylaniline, 30 nm)/ 2,6DCzPPy (bis[4-(N,N-ditolylamino)-phenyl]cyclohexane) : Ir(III) complex (8 wt%, 10 nm)/ TmPyPB (1,3,5-tri[(3-pyridyl)-phen-3yl]benzene, 40 nm)/ LiF (1nm)/ Al (100 nm) were named as D1-D4 using (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip), respectively. The schematic energy diagrams of phosphorescent OLEDs and the molecular structures of the materials used in the devices are depicted in Fig 4. Herein, we employed MoO₃ and LiF to serve as hole injecting layer (HIL) and electron injecting layer (EIL), respectively. TAPC was used as hole transport/electron block layer (HTL/EBL), while TmPyPB was used as electron transport/hole block layer (ETL/HBL). The bipolar material 2,6DCzPPv was chosen as the host because its' nearly equal electron mobility (μ_e) and hole mobility (μ_h) values (1~8×10⁻⁵ $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at an electric field between 6.0×10^5 and 1.0×10^6 $V \cdot cm^{-1}$), which benefits the electron-hole balance in the emissive layer (EML).³⁶⁻³⁸

The EL spectra, luminance-voltage-current density (L-V-J), current efficiency–luminance (η_c -L) and power efficiency– luminance $(\eta_{p}-L)$ characteristics of four OLEDs are shown in Fig. 5, and the key EL data are summarized in Table 2. It should be noted that the peaks of EL emission at 567, 566, 571 and 573 nm for the single EML device D1-D4 match well with the PL spectra of these complexes in the solution, which suggest that the energy can be transferred from 2.6DCzPPy to the emitters. Their corresponding Commission Internationale de l'Eclairage (CIE) coordinates are (0.52, (0.48), (0.50, 0.50), (0.48, 0.52) and (0.53, 0.46), which are corresponded to the yellow region. From Fig. 5 and Table 2, it can be seen that the four devices all have good EL performances, because four Ir(III) complexes have similar photophysical and electrochemical properties due to the similar main ligands and the same ancillary ligand. As well known, the phosphorescence quantum yield (Φ_{PL}) played a decisive role in determining the OLEDs performances. Due to

the lowest Φ_{PL} of (bt)₂Ir(tpip) (27.1%), the device D1 shows the relatively poor performances with a maximum current efficiency ($\eta_{c,max}$) of 57.1 cd A⁻¹ (3.9 V) with a maximum external quantum efficiency (EQE_{max}) of 19.2%, a maximum power efficiency ($\eta_{p,max}$) of 25.6 lm W⁻¹ and a maximum luminance (L_{max}) of 38628 cd m⁻², respectively. Relatively, the complexes (fbt)₂Ir(tpip) and (cf₃bt)₂Ir(tpip) have higher Φ_{PL} values of 32.5% and 36.9%, and the devices D2 and D3 also display better performances with a $\eta_{c,max}$ of 58.0 cd A⁻¹ with an EQE_{max} of 18.5%, a $\eta_{p,max}$ of 32.0 lm W⁻¹ and a $\eta_{c,max}$ of 68.1 cd A⁻¹ with an EQE_{max} of 23.4%, a $\eta_{p,max}$ of 38.2 lm W⁻¹, respectively. The complex (**dfbt**)₂**Ir(tpip**) has the highest Φ_{PL} efficiency of 48.4%, therefore, the device **D4** reveals a record best EL properties with a $\eta_{c,max}$ of 69.8 cd A⁻¹ with an EQE_{max} of 24.3%, a $\eta_{p,max}$ of 37.8 lm W⁻¹, respectively. Furthermore, all devices showed low efficiency roll-off ratios. For instance, even at a luminance of 1000 cd m⁻², the EQE could still be retained at 17.7%, 16.4%, 18.3% and 20.6% for the devices **D1-D4**, respectively.



Fig. 5 Characteristics of devices D1–D4: (a) normalized EL spectra at 8 V; (b) luminance–voltage–current density curves; (c) current efficiency–luminance curves; (d) power efficiency–luminance curves.

Device	$V_{\text{turn-on}}^{a}$ (V)	L_{\max}^{b} [cd m ⁻² (V)]	$\eta_{c,\max}^{c} (cd A^{-1}) \\ (EQE_{max}, \%)^{d}$	$\eta_{\text{c},\text{L1000max}}^{e} (\text{cd A}^{-1}) \\ (\text{EQE}_{\text{max}}, \%)^{f}$	$\eta_{p,\max}^{g}$ (lm W ⁻¹)	λ_{\max}^{h} (nm)	CIE^i (x, y)
D1	3.9	38628(13.5)	57.1(19.2)	52.8(17.7)	25.6	567	(0.52, 0.48)
D2	4.0	28604(14.7)	58.0(18.5)	51.3(16.4)	32.0	566	(0.50, 0.50)
D3	4.0	37114(14.7)	68.1(23.4)	53.3(18.3)	38.2	571	(0.52, 0.48)
D4	4.1	37046(15.1)	69.8(24.3)	59.3(20.6)	37.8	573	(0.53, 0.46)

Table 2 EL performances of single-EML devices D1-D4

^{*a*} Turn-on voltage recorded at a luminance of 1 cd m². ^{*b*} Maximum luminance. ^{*c*} Maximum current efficiency. ^{*d*} Maximum external quantum efficiency (EQE). ^{*e*} Current efficiency at 1000 cd m⁻². ^{*f*} EQE at 1000 cd m⁻². ^{*g*} Maximum power efficiency. ^{*h*} Values were collected at 8 V. ^{*i*} CIE (Commission Internationale de l'Eclairage) coordinates (CIE) at 8 V.

It is noteworthy that devices D2 and D3 showed more severe efficiency roll-off than that of devices D1 and D4, which may be attributed to the difference excited state lifetimes of these Ir(III) complexes ((bt)₂Ir(tpip) : 2.43 μ s, (fbt)₂Ir(tpip) : 2.81 μ s, (cf₃bt)₂Ir(tpip) : 2.65 μ s, (dfbt)₂Ir(tpip) : 2.40 μ s). The longer

lifetime will lead to exciton quenching through triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA), thereby resulting in more serious efficiency roll-off.³⁹ In general, the good EL properties are first attributed to the application of tpip as the ancillary ligand, which has good electron mobility caused by the P=O bonds and four phenyl rings of tpip in the

emissive layer. The emitters with good electron mobility will lead to a well-balanced charge carrier transport and efficient recombination. In addition, the LUMO levels of the dopants are low and they are just in the range of the host materials, which also benefits the electron transport property.

Conclusions

In summary, four bis-cyclometalated Ir(III) complexes based on 2-phenylbenzothiazole derivatives with tpip as the ancillary ligand were investigated in detail. Due to the HOMOs and LUMOs are primarily located on the metal center and on main ligands of these Ir(III) complexes, the modification of the main ligands can affect their photophysical and electrochemical properties greatly. All the complexes emit from a predominantly ³MLCT state with a mixed ³LC contribution in the yellow region of the visible spectra. The phosphorescent OLEDs comprising (bt)₂Ir(tpip), (fbt)₂Ir(tpip), (cf₃bt)₂Ir(tpip) and (dfbt)₂Ir(tpip) as yellow dopants realize state-of-art device performances with EQE_{max} of 19.2%, 18.5%, 23.4% and 24.3%, respectively, with low efficiency roll-off. These results suggest that these Ir(III) complexes are potential yellow phosphorescent materials for OLEDs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51773088, 21501037), the Natural Science Foundation of Jiangsu Province (BY2016075-02), the Natural Science Foundation of Hainan Province (218QN236) and Hainan Province Natural Science Foundation of Innovative Research Team Project (2017CXTD007).

Conflicts of interest

There are no conflicts to declare.

Notes and references

¹ State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China, yxzheng@nju.edu.cn zuojl@nju.edu.cn

2 College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, P. R. China, ligaonan2008@126.com

[†]Electronic Supplementary Information (ESI) available: H, ¹⁹F and ³¹P NMR spectra and mass spectrometry of ligands and iridium complexes. The crystallographic data, selected bonds and angles of complexes (**bt**)₂**Ir(tpip**), (**fbt**)₂**Ir(tpip**) and (**dfbt**)₂**Ir(tpip**). TGA curves, frontier orbital energy and electron density distribution of complexes (**bt**)₂**Ir(tpip**), (**fbt**)₂**Ir(tpip**), (**cf**₃**bt**)₂**Ir(tpip**) and (**dfbt**)₂**Ir(tpip**).

- Y. S. Li, J. L. Liao, K. T. Lin, W. Y. Hung, S. H. Liu, G. H. Lee, P. T. Chou and Y. Chi, *Inorg. Chem.*, 2017, 56, 10054.
- R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, Angew. Chem., Int. Ed. 2012, 51, 8178.

- 3. B. W. D. Andrade and S. R. Forrest, Adv. Mater., 2004, 16, 1585.
- 4. M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750.
- E. Matteucci, A. Baschieri, A. Mazzanti, L. Sambri, J. Ávila, A. Pertegás, H. J. Bolink, F. Monti, E. Leoni and N. Armaroli *Inorg. Chem.* 2017, 56, 10584.
- R. J. Wang, D. Liu, H. C. Ren, T. Zhang, X. Z. Wang and J. Y. Li, J. Mater. Chem., 2011, 21, 15494.
- K. A. King, P. J. Spellane and R. J. Watts, J. Am. Chem. Soc., 1985, 107, 1431.
- (a) D. X. Ma, T. Tsuboi, Y. Qiu and L. Duan, *Adv. Mater.*, 2017, **29**, 1603253.
 (b) B. H. Zhang, G. P. Tan, C. S. Lam, B. Yao, C. L. Ho, L. H. Liu, Z. Y. Xie, W. Y. Wong, J. Q. Ding and L. X. Wang, *Adv.Mater.*, 2012, **24**, 1873.
 (c) B. M. J. S. Paulose, D. K. Rayabarapu, J. P. Duan and C. H. Cheng, *Adv. Mater.*, 2004, **16**, 2003.
- (a) G. L. Zhang, H. Q. Guo, Y, T, Chuai and D. C. Zou, *Mater. Lett*, 2005, **59**, 3002. (b) V. G. Vladimir, H. Norman, D. L. Daniel, J. M. William, A. P. Viacheslav and Y. Wang, *Chem. Commun.*, 2001, **16**, 1494.
- (a) J. C. Axtell, K. O. Kirlikovali, P. I. Djurovich, D. Jung, V. T. Nguyen, B. Munekiyo, A. T. Royappa, A. L. Rheingold and A. M. Spokoyny, *J. Am. Chem. Soc.*, 2016, **138**, 15758. (b) Y. H. Lee, J. Park, J. Lee, S. U. Lee and M. H. Lee, *J. Am. Chem. Soc.*, 2015, **137**, 8018.
- (a) P. Tao, W. L. Li, J. Zhang, S. Guo, Q. Zhao, H. Wang, B. Wei, S. J. Liu, X. H. Zhou, Q. Yu, B. S. Xu and W. Huang, *Adv. Funct. Mater.*, 2016, **26**, 881. (b) J. H. Jou, Y. X. Lin, S. H. Peng, C. J. Li, Y. M. Yang, C. L. Chin, J. J. Shyue, S. S. Sun, M. Lee, C. T. Chen, M. C. Liu, C. C. Chen, G. Y. Chen, J. H. Wu, C. H. Li, C. F. Sung, M. J. Lee and J. P. Hu, *Adv. Funct. Mater.*, 2014, **24**, 555. (c) C. L. Ho, W. Y. Wong, G. J. Zhou, B. Yao, Z. Xie and L. Wang, *Adv. Funct. Mater.*, 2007, **17**, 2925.
- J. Zhang, L. Zhou, H. A. Al-Attar, K. Z. Shao, L. Wang, D. X. Zhu, Z. M. Su, M. R. Bryce and A. P. Monkman, *Adv. Funct. Mater.*, 2013, 23, 4667. (b) J. P. Duan, P. P. Sun and C. H. Cheng, *Adv. Mater.*, 2003, 15, 224.
- 13. C. L. Li, Y. J. Su, Y. T. Tao, P. T. Chou, C. H. Chien, C. C. Cheng and R. S. Liu, *Adv. Funct. Mater.*, 2005, **15**, 387.
- S. Lamansky, P. Djurovich, D. Murphy, F. A. Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, J. Am. Chem. Soc., 2001, 123, 4304.
- (a) I. R. Laskar and T. M. Chen, *Chem. Mater.*, 2004, **16**, 111; (b) N. Deligonul, A. R. Browne, J. A. Golen, A. L. Rheingold and T. G. Gray, *Organometallics*, 2014, **33**, 637; (c) Y. Feng, P. Li, X. Zhuang, K. Ye, T. Peng, Y. Liu and Y. Wang, *Chem. Commun.*, 2015, **51**, 12544; (d) C. Yang, F. Mehmood, T. L. Lam, S. L. F. Chan, Y. Wu, C. S. Yeung, X. G. Guan, K. Li, C. Y. S. Chung, C. Y. Zhou, T. T. Zou and C. M. Che, *Chem. Sci.*, 2016, **7**, 3123.
- Q. L. Xu, C. C. Wang, T. Y. Li, M. Y. Teng, S. Zhang, Y. M. Jing, X. Yang, W. N. Li, C. Lin, Y. X. Zhen, J. L. Zuo and X. Z. You, *Inorg. Chem.*, 2013, **52**, 4916.
- (a) Y. C. Zhu, L. Zhou, H. Y. Li, Q. L. Xu, M. Y. Teng, Y. X. Zheng, J. L. Zuo, H. J. Zhang and X. Z. You, *Adv. Mater.*, 2011, 23, 4041; (b)
 M. Y. Teng, S. Zhang, S. W. Jiang, X. Yang, C. Lin, Y. X. Zheng, L.
 Y. Wang, D. Wu, J. L. Zuo and X. Z. You, *Appl. Phys. Lett.*, 2012, 100, 073303; (c) Y. H. Zhou, J. Xu, Z. G. Wu and Y. X. Zheng, *J. Organomet. Chem.*, 2017, 848, 226; (d) Y. H. Zhou, Q. L. Xu, H. B.
 Han, Y. Zhao, Y. X. Zheng, L. Zhou, J. L. Zuo and H. Zhang, *Adv. Opt. Mater.*, 2016, 4, 1726.
- (a) K. Reichenbächer, H. I. Süss and J. Hulliger, *Chem. Soc. Rev.*, 2005, 34, 22. (b) F. Babudri, G. M. Farinola, F. Naso and R. Ragni, *Chem. Commun.*, 2007, 1003.
- R. Wang, D. Liu, H. Ren, T. Zhang, H. Yin, G. Liu and J. Li, Adv. Mater., 2011, 23, 2823.
- R. I. C. Hernández, J. C. Basurto, C. A. F. Sandoval, I. I. P. Martínez, B. N. Torres, M. L. V. Tanaca, F. T. Cach, J. J. N. Fidencio and J. T. Ferrara, *Med. Chem. Res.*, 2016, 25, 211.
- 21. M. Nonoyama, Bull. Chem. Soc. Jpn. 1974, 47, 767
- 22. Z. G. Niu, D. Liu, J. Zuo, Y. Zou, J. M. Yang, Y. H. Su, Y. D. Yang and G. N. Li, *Inorg. Chem. Commun.*, 2014, **43**, 146.
- V. Thamilarasan, A. Jayamani, P. Manisankar, Y. I. Kim and N. Sengottuvelan, *Inorg. Chim. Acta*, 2013, 408, 240.
- 24. G. N. Li, Y. Zou, Y. D. Yang, J. Liang, F. Cui, T. Zheng, H. Xie and Z.

G. Niu, J Fluoresc, 2014, 24, 1545.

- S. Lamansky, P. Djurovich, D. Murphy, F. A. Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mmui, R. Bau and M. E. Thompson, *Inorg. Chem.* 2001, 40, 1704.
- (a) S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukaide, J. Kamatani, S. Igawa, A. Tsuboyama, T. Takiguchi and K. Ueno, *Dalton Trans.*, 2005, 9, 1583; (b) G. N. Li, S. B. Dou, T. Zheng, X. Q. Chen, X. H. Yang, S. Wang, W. Sun, G. Y. Chen, Z. R. Mo and Z. G. Niu, *Organometallics*, 2018, 37, 78.
- A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau and M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.
- K. K. W. Lo, C. K. Chung, T. K. M. Lee, L. H. Lui, K. H. K. Tsang and N. Y. Zhu, *Inorg. Chem.*, 2003, 42, 6886.
- 29. K. K. W. Lo, D. C. M. Ng and C. K. Chung, *Organometallics*, 2001, **20**, 4999.
- J. S. Y. Lau, P. K. Lee, K. H. K. Tsang, C. H. C. Ng, Y. W. Lam, S. H. Cheng and K. K. W. Lo, *Inorg. Chem.*, 2009, 48, 708.
- C. L. Ho, W. Y. Wong, Q. Wang, D. G. Ma, L. X. Wang and Z. Y. Lin, *Adv. Funct. Mater.*, 2008, 18, 928.
- Y. Wang, N. Herron, V. V. Grushin, D. L. Cloux and V. Petrov, *Appl. Phys. Lett.*, 2001, **79**, 449.
- 33. F. O. Garces, K. A. King and R. J. Watts, *Inorg. Chem.*, 1998, **27**, 3464.
- B. P. Straughan and S. Walker, Spectroscopy, 2nd Edn, Chapman, Hall, London, 1976, Vol. 3.
- 35. (a) P. Brulatti, R. J. Gildea, J. A. K. Howard, V. Fattori, M. Cocchi and J. A. G. Williams, *Inorg. Chem.*, 2012, **51**, 3813; (b) Z. G. Niu, T. Zheng, Y. H. Su, P. J. Wang, X. Y. Li, F. Cui, J. Liang and G. N. Li, *New J. Chem.*, 2015, **39**, 6025.
- J. Lee, N. Chopra, S. H. Eom, Y. Zheng, J. Xue, F. So and J. Shi, *Appl. Phys. Lett.*, 2008, 93, 123306.
- S. J. Su, T. Chiba, T. Takeda and J. Kido, *Adv. Mater.*, 2008, **20**, 2125.
 M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki and Y. Taga, *Appl. Phys. Lett.*, 2001, **79**, 156.
- 39. Y. Zhang, J. Lee and S. R. Forrest, Nat. Commun., 2014, 5, 5008.

Dalton Transactions Accepted Manuscript

Graphical abstract



Four yellow iridium(III) complexes with benzo[d]thiazole derivatives as main ligands displays good device performances with a maximum current efficiency up to 69.8 cd A^{-1} and a maximum external quantum efficiency up to 24.3%.