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Introduction

Phosphorescent transition-metal complexes have drawn great research and industry attention because of their excellent performance when used as colorful emitters in organic lightemitting diodes (OLEDs). Among them, cyclometalated Ir^{III} complexes are regarded as the most successful phosphorescent material¹ owing to their high photoluminescence efficiency, relatively short lifetimes and flexible color tunability.² For both the homoleptic and heteroleptic Ir^{III} complexes, the cyclometalating C[^]N ligands play essential roles in determining the phosphorescent energy and emitting color of the complexes, although occasionally the ancillary ligand is also important, like iridum(m)bis[(4,6-di-fluorophenyl)-pyridinato-N,C²]picoliin nate (Firpic).3 Accordingly, two typical strategies have been utilized to tune the emissive color of the iridium complexes. One method is to design different $C^{\wedge}N$ ligand frameworks. For this purpose, a flexible combination of different arenes and heterocycles has generated various C[^]N ligand frameworks. For example, the phosphorescence peak wavelength of a group of 2-aryl-pyridine based homoleptic iridium complexes is readily

Iridium complexes containing 2-aryl-benzothiazole ligands: color tuning and application in highperformance organic light-emitting diodes[†]

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Three 2-aryl-benzothiazole chromophores were designed and synthesized for use as major cyclometalating ligands of iridium complexes, in which the aryl groups were *N*-phenyl-3-carbazolyl, 2-(9,9-dioctyl)fluorenyl and *N*-phenyl-2-carbazolyl. The homoleptic tris-cyclometalated and heteroleptic bis-cyclometalated iridium complexes, **1–5**, were synthesized using these ligands. By adjusting the chemical structures and then the electronic state of these complexes, we were able to continuously tune the phosphorescence from yellow to saturated red with peak wavelengths in the order of **1** < **2** < **3** < **4** < **5**. The quantum chemical calculations and the electrochemical data clearly demonstrate the origin of the phosphorescence color tuning. The organic light-emitting diodes (OLEDs) containing these iridium complexes as doped emitters exhibited yellow to red electrophosphorescence with excellent performance. Particularly, the complex **1** based device produced high efficiencies for yellow OLEDs up to now. Furthermore, **1** was used to fabricate two-element white OLEDs in combination with a blue phosphor and high efficiencies of 57.9 cd A⁻¹ and 21.9% were achieved, which are among the best efficiencies for two-emitting-component white OLEDs reported so far.

tuned from 504 to 596 nm by varying the aryl moiety from 3-carbazolyl to 2-benzo[b]thiophenyl.⁴ Another typical strategy is to incorporate different substituents in either C-related arenes or N-related heterocycles while fixing the $C^{\wedge}N$ ligand skeleton. For example, incorporating different substituents at different positions of the 2-phenylpyridine ligand framework has resulted in a continuous tuning of the phosphorescence of their homoleptic iridium complexes from sky blue (468 nm) to orange-red (595 nm).5 All these methods are successful in tuning the phosphorescence color since in most cases the cyclometalating C^AN ligands are involved in their lowest-energy triplet excited state, either the ligand-centered ${}^{3}\pi$ - π * state or the metal-to-ligand-charge-transfer (³MLCT) triplet state, which is responsible for the phosphorescence. For most of the Ir^{III} complexes, the highest occupied molecular orbital (HOMO) consists of arene π - and Ir d-orbitals, while the lowest unoccupied molecular orbital (LUMO) is located largely on the N-related heterocycle that is usually electron-deficient. In general, the phosphorescence of the Ir^{III} complex red shifts when the electron-donating substituent is introduced into the HOMO-lying arene part and/or the electron-deficient group is incorporated in the LUMO-lying heterocycle moiety of the C[^]N ligands. Whereas a hypsochromic shift will occur when the electron-deficient substituent is introduced into the HOMOlying arene and/or the electron-rich group is incorporated into the LUMO-lying heterocycle.

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Among the reported cyclometalating $C^{\wedge}N$ ligands, 2-phenylbenzothiazole and its derivatives have drawn increasing attention and many Ir^{III} complexes containing this ligand framework have been developed as efficient electrophosphorescent emitters for OLED application.6 For example, a high EL efficiency of 89 cd A^{-1} was obtained in our previous report when the 2-phenyl-benzothiazole ligand was decorated by CF₃ at the 6-position of a benzothiazole ring.^{6f} A two-element white OLED with a peak current efficiency of 68 cd A⁻¹ was also fabricated with the related derivative as an orange emitter.^{6d} However, most of the Ir^{III} complexes containing 2-phenyl-benzothiazole as major ligands, with a few exceptions,^{6b,g} are limited to the yellow-emissive range. The red-emissive analogues containing benzothiazole moieties are still absent, which in turn are identically important for application in both red and RGB white OLEDs. As far as we know, besides 2-phenyl-benzothiazole, few other benzothiazole-containing chromophores7 have been developed as the cyclometalating ligand framework to prepare corresponding Ir^{III} complexes up to now.

Enlightened by the remarkable EL performance of the current 2-phenyl-benzothiazole based iridium complexes, our interest is to exploit more 2-aryl-benzothiazole chromophores as cyclometalating C^N ligands to prepare novel Ir^{III} complexes. In this paper, we report the synthesis of three 2-aryl-benzothiazole chromophores (Scheme 1), in which the aryl groups are N-phenyl-3-carbazolyl (L1), 2-(9,9-dioctyl)fluorenyl (L2), and N-phenyl-2-carbazolyl (L3), respectively. It should be noted that the fluorene and carbazole rings have similar skeletons, but are linked to the benzothiazole moiety via different sites, resulting in a different extent of conjugation within these ligands. Ligands L2 and L3 have identical linear conjugation between the benzothiazole moiety and a biphenyl, which is longer than that of the benzothiazole and a phenyl in ligand L1. Carbazole has been selected as the important building block due to the following reasons: (1) it is an excellent hole injecting and

transporting group,⁸ (2) its electron-donating feature will tune the electronic state and then the emission color of the resulting iridium complexes. These 2-aryl-benzothiazole chromophores were used to prepare the homoleptic tris-cyclometalated and heteroleptic bis-cyclometalated iridium complexes, 1–5 (Scheme 2). The photophysical, electrochemical, and electroluminescent properties of these iridium complexes were investigated systematically. We demonstrated that the phosphorescence of these benzothiazole-containing iridium



Scheme 2 Synthetic routes for the cyclometalated iridium(III) complexes 1–5.



Scheme 1 Structures and synthetic routes for the ligands L1, L2, and L3.

complexes are able to be tuned over a wide spectral range from yellow to saturated red by adjusting the π -conjugation length of the 2-aryl-benzothiazole ligand, introducing electron-donating groups into the HOMO-locating aryl moiety of the ligands, or incorporating high-field-strength ancillary ligands. In addition, high-performance monochromatic and white OLEDs were achieved using these novel benzothiazole-containing iridium complexes as doped emitters.

Results and discussion

Preparation and characterization

Scheme 1 outlines the synthetic routes of the cyclometalating ligands L1-L3. The important intermediates, including N-phenylcarbazole-3-carbaldehyde,9 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene,10,11 and N-phenylcarbazole-2-boronic acid,12 were synthesized according to the literature methods. The cyclometalating ligand L1 was obtained by the cyclizative condensation of o-aminothiophenol with the corresponding aldehyde precursor.13 Whereas Suzuki coupling of the commercially available 2-bromobenzothiazole with the 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene and Nphenylcarbazole-2-boronic acid generated the ligands L2 and L3, respectively, in high yields.^{11,12} The target iridium complexes 1-5 were synthesized following the traditional procedures as shown in Scheme 2. First the cyclometalation of the iridium trichloride hydrate with each cyclometalating ligand generated the corresponding chloro-bridged dimmer [Ir(C^{\N})₂Cl]₂.¹⁴ Further reaction of this dimer intermediate with the same ligand in refluxing diglyme afforded the desired homoleptic tris-cyclometalated Ir^{III} complexes 1 and 3.5b On the other hand, the heteroleptic IrIII complexes 2, 4, and 5 were obtained by refluxing the corresponding chloro-bridged dimmer with acetylacetone in 2-ethoxyethanol in the presence of Na₂CO₃.¹⁴ We tried to prepare the desired homoleptic complex of ligand L3 by using the corresponding chloro-bridged dimer, the heteroleptic complex 5, and $Ir(acac)_3$ as the starting materials. However, we finally failed to obtain it after trying all these typical pathways.^{5b,15} All the obtained iridium complexes were well dissolved in common organic solvents and thus purified by column chromatography over silicagel. They were fully characterized by ¹H and ¹³C NMR, Maldi-TOF or ESI-MS mass spectrometry, and elemental analysis.

Photophysical properties

Fig. 1 shows the absorption spectra and photoluminescence spectra of complexes **1–5** in dilute dichloromethane solution. The pertinent data of these Ir^{III} complexes is summarized in Table 1. As shown in Fig. 1a, these complexes all displayed characteristic absorption spectra of Ir^{III} complexes, which are dominated by multiple absorption bands originating from the ligand-centered π - π * transitions and MLCT (metal-to-ligand-charge-transfer) transitions.¹⁶ The intense absorption bands in the short wavelength region appear to be the spin-allowed ligand-centered $^{1}\pi$ - π * transitions. The weaker absorption bands over 400 nm should correspond to the excitations to the ¹MLCT and ³MLCT, and the spin-orbit coupling enhanced

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Fig. 1 UV-vis absorption (a) and PL (b) spectra of complexes **1–5** in dilute dichloromethane solution.

 ${}^{3}\pi-\pi^{*}$ states.¹⁷ In comparison with the homoleptic analogue, the heteroleptic bis-cyclometalated iridium complex of each ligand shows a regular bathochromic effect in their absorption spectra, especially in the short wavelength range. For example, a red-shift of 7 nm was detected in the absorption spectrum of complex 2 relative to 1. In comparison with complexes 1 and 2, complexes 3 and 4 revealed a red-shift of approximately 30 nm in their absorption spectra, complex 5 showed a further redshift. This should be as a result of the extended π conjugation in ligands L2 and L3 in comparison with ligand L1.

Fig. 1b shows the photoluminescence (PL) spectra of these iridium complexes in dilute dichloromethane solution. Upon photoexcitation at 400 nm, all these complexes show intense room-temperature phosphorescence with vibronic fine structures in the PL spectra. With reference to the spectroscopic data of other similar iridium complexes in the literature, all the iridium complexes in the present study may possess dominantly the ${}^{3}\pi$ - π * lowest excited states. The vibronic splitting in the emission profiles implies the phosphorescence may come mainly from the predominantly ligand-centered ${}^{3}\pi$ - π * excited states, rather than from the ³MLCT excited states, which are otherwise characterized by broad and featureless emission spectra.17 The emission wavelengths of these complexes strongly depend on the structures of the cyclometalating ligands. For the 3-carbazolyl-containing homoleptic tris-cyclometalated complex 1, the phosphorescence is located in the yellow range with a peak at 551 nm and a shoulder at 580 nm. With the cyclometalating ligand going from L1 to 2-fluorenebased L2, the triscyclometalated iridium complex 3 shows redshifted phosphorescence at 587 nm with a shoulder at 634 nm

Table 1 Photophysical and electrochemical data obtained experimentally for the iridium complexes

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Compound	$\lambda_{abs}{}^{a}$ [nm]	$\lambda_{\rm em}{}^a$ [nm]	${\Phi_{\mathrm{p}}}^{b}$	$\tau_{\rm p}^{\ c} [\mu { m s}]$	$E_{\text{onset}}^{\text{ox}} d \left[\mathbf{V} \right]$	HOMO/LUMO ^{e} [eV]	$E_{g}^{f}[eV]$
1	322, 369, 399, 443	551, 580 sh	0.42	2.77	0.60	-5.00/-2.64	2.36
2	329, 379, 403, 465	559, 588 sh	0.34	2.76	0.68	-5.08/-2.78	2.30
3	358, 417, 465, 504	587, 634 sh	0.20	2.56	0.69	-5.09/-2.91	2.18
4	353, 422, 476, 506	596, 643 sh	0.16	2.20	0.78	-5.18/-2.97	2.21
5	361, 433, 502, 542	630	0.18	3.53	0.47	-4.87/-2.87	2.00

^{*a*} Measured in CH₂Cl₂ at 293 K with a concentration of 10⁻⁵ M, sh = shoulder. ^{*b*} Measured in degassed CH₂Cl₂ relative to *fac*-[Ir(ppy)₃] ($\Phi_p = 0.4$), $\lambda_{exc} = 400 \text{ nm.}^{c}$ Measured in degassed CH₂Cl₂ at a concentration of 10⁻⁵ M at 293 K. ^{*d*} 0.1 M [Bu₄N]PF₆ in CH₂Cl₂, scan rate 100 mV s⁻¹, *versus* SCE couple. ^{*e*} HOMO = -*e*($E_{onset}^{ox} + 4.4$), LUMO = HOMO + E_{g} . ^{*f*} Estimated from the absorption edge (λ_{edge}) of solid films by the equation $E_{g} = 1240/\lambda_{edge}$.

in comparison with complex **1**. This red-shift of phosphorescence should be ascribed to the extended π -conjugation length within the cyclometalating ligand, since ligand **L2** can be regarded as π -conjugated between the benzothiazole ring and a biphenyl, which is definitely longer by one additional phenyl than **L1**.

On the other hand, for each cyclometalating ligand, the heteroleptic bis-cyclometalated iridium complex shows a regular red shift of the phosphorescence in comparison with its tris-cyclometalated analogue. For example, the phosphorescence of the heteroleptic complex 2 has a peak at 559 nm with a shoulder at 588 nm, which was red shifted by 8 nm relative to its homoleptic analogue 1. A red shift by 9 nm was also observed for the heteroleptic complex 4 in comparison to its homoleptic analogue 3. The bathochromic effect in the phosphorescence of the heteroleptic iridium complexes with the acac ancillary ligand was frequently observed and ascribed to the high-fieldstrength effect from the acetylacetonate anion.18 With the cyclometalating ligand going from L2 to 2-carbazole based L3, the phosphorescence of the corresponding heteroleptic iridium complex 5 shows dramatic red-shift relative to that of 4. The phosphorescence of complex 5 is in the saturated red region with a peak at 630 nm. L2 and L3 have identical π -conjugation lengths between the benzothiazole and the biphenyl. Thus the large red shift observed in the phosphorescence of complex 5 should be attributed to the additional electron-donating effect of the N moiety which is located at the para-site of the C-Ir bond and strongly activates the HOMO level of this complex. Therefore, through combination of the three strategies, *i.e.* expanding the effective π -conjugation length of the cyclometalating ligand, introducing an electron-donating element into the aryl moiety of the ligands, and incorporating a high-field-strength ancillary ligand, the phosphorescence of this series of iridium complexes 1-5 is continuously tuned from yellow to saturated red with peak wavelengths in the order of 1 < 2 < 3 < 4 < 5.

The photophysical properties of these complexes were further probed by measuring their relative phosphorescent quantum yields in dilute degassed dichloromethane solutions at room temperature with *fac*-Ir(ppy)₃ as a standard ($\Phi_{\rm P} = 0.40$, Hppy = 2-phenylpyridine).¹⁹ Most of these Ir^{III} complexes showed high $\Phi_{\rm p}$ (Table 1). Especially, complex 1 showed the highest $\Phi_{\rm p}$ of 0.42 and even the red-emitting 5 showed a $\Phi_{\rm p}$ as high as 0.18. It is interesting that the $\Phi_{\rm p}$ of these complexes shows a regular decreasing trend with the emission wavelength shifting to red. This is reasonable since it is generally accepted that the smaller the energy band gap, the higher the possibility of non-radiative decay of the excited states.²⁰ The relative high phosphorescent quantum yields of these iridium complexes indicate that they should be promising phosphors for high-performance electrophosphorescent devices. The phosphorescent lifetimes of these complexes were determined to be in the range of 2.20–5.90 μ s, which is indicative of strong spin-orbit coupling leading to efficient intersystem crossing from the singlet to the triplet state.

Electrochemical analysis

The electrochemical behavior of these complexes was investigated by means of cyclic voltammetry (CV) measurements. Upon the anodic sweep in deoxygenated dichloromethane solutions, one or two reversible peaks for all the complexes were detected, which should be assigned to the metal-centered Ir^{III}/Ir^{IV} oxidation couple and/or the possible oxidation of the fluorene and carbazole groups on the cyclometalating ligands.²¹ These oxidation potentials are lower for the homoleptic complexes 1 and 3 than their corresponding heteroleptic complexes 2 and 4, which is in accordance with the fact that the acac ligand with the stronger ligand-field strength could stabilize the HOMO level. Notably, by comparison with the fluorene-based complexes, the incorporation of 2-carbazole and 3-carbaozle in the ligands shifts the oxidation potentials of the iridium complexes to less-positive values and the HOMO to higher levels, indicating a greater ease for 1, 2, and 5 to loose an electron and to accept the injected hole from the anode or other functional layers in the OLEDs. On the other hand, the stabilization effect on the iridium complex caused by the extended π -conjugation length in the ligand frameworks can be verified by the lowering of both the HOMO and LUMO of complexes 3 and 4 (Table 1) in comparison with complexes 1 and 2, respectively. Similar to the 2-fluorene based complex 4, the 2-carbazole based complex 5 shows a similar decrease of LUMO in comparison with complex 2 due to the extended π -conjugation length. However, the HOMO of complex 5 is dramatically raised to a higher level (-4.87 eV) than that (-5.18 eV) of complex 4, resulting in a further smaller HOMO-LUMO band gap and further red-shift of phosphorescence in complex 5. This further red-shift should be as a result of the electron-donating feature of the N atom located at the para-site of the C-Ir bond

and its destabilization effect on the HOMO level. All these electrochemical observations are consistent with the photophysical results. The measured oxidation potentials for these complexes are in the range of 0.59-0.78 V vs. saturated calomel electrode (SCE). On the basis of the onset potential of the first oxidation (E_{onset}^{ox}) and the absorption edge data, the HOMO and LUMO energy levels can be estimated from the empirical formulae: $E_{\text{HOMO}} = -e(E_{\text{onset}}^{\text{ox}} + 4.4)$ and $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$ (where E_g is the optical energy gap obtained from the absorption threshold of the film sample).²² The electrochemical and electronic data of these complexes is collected in Table 1.

Quantum chemical calculations

In order to gain further insight into the photophysical and electrochemical behaviors of these phosphors and to understand the origin of color tenability induced by substitution, density functional theory (DFT) calculations were performed for complexes 2, 4, and 5 using B3LYP hybrid functional theory with Gaussian 03.23 These Ir^{III} complexes have very similar structures with octahedral geometry. Fig. 2 depicts the selected molecular orbitals involved in the lowest-lying transitions of these complexes.

As shown in Fig. 2, the HOMO orbital of each of these complexes is located on both the central iridium atom and the aryl group of the 2-arylbenzothiazole ligand, but with different contributions from the aryl group. For the carbazole-containing complexes, the HOMO orbital of complex 2 is mainly located on the two benzene rings of the carbazole moiety, and that of complex 5 is mainly distributed on the biphenyl part of the carbazole moiety with additional contribution from the 9-site N atom and the appending phenyl ring. However the HOMO orbital of the fluorenyl-containing complex 4 is only located on the single phenyl ring that is directly bonded to the benzothiazole. Apparently, the HOMO orbitals for these carbazolecontaining complexes 2, and 5 are more delocalized and destabilized than 4. This is consistent with the electrochemical result shown in Table 1 that the HOMO levels for 2, and 5 are higher to some extent than that of 4 due to the stronger electron donating character of carbazole groups than fluorene. In comparison with that of complex 2, the HOMO of its analogue,



Fig. 2 The distribution of the HOMOs and LUMOs for complexes 2, 4, and 5.

complex 5, is more extended to the 9-site N atom and the appending phenyl ring. This should be because the N-phenyl moiety is located in the para-site of the C-Ir bond in complex 5 and its electron-donating character will have a stronger stabilization effect on the HOMO level of this molecule than in complex 2. The LUMO orbitals of all these iridium complexes cover the whole benzothiazole part and spread more and more to the aryl moiety with the phosphor going from 2, to 4, to 5. Since the ligands L2 and L3 have similar molecular skeletons, the LUMO orbitals of 4 and 5 are identically located on the whole ligands including the benzothiazoles and the biphenyl rings on the fluorene and 2-carbazole moieties. It is obvious that the 2-fluorenyl and 2-carbazolyl rings effectively expand the π -conjugation length of the ligand frameworks in comparison with the 3-carbazolyl, which results in more delocalized and stabilized LUMOs for 4 and 5 than 2. This is consistent with the much lower LUMO levels obtained by experiment for 4 and 5. In comparison with 2, the 2-fluorenyl-based complex 4 possesses both a stabilized HOMO and LUMO due to the extended π -conjugation length. However, the much larger downwards shift of the LUMO than the HOMO finally produces a further red shift in its phosphorescence. In comparison with complex 4, complex 5 has a more destabilized HOMO due to additional contribution from the electron-donating carbazole and identically stabilized LUMO due to the same π -conjugation in the ligand, and consequently exhibits further red-shift in phosphorescence relative to complex 4. Therefore, the phosphorescence peak wavelength of these heteroleptic complexes exhibits a regular tunability in the order of 2 < 4 < 5.

Electroluminescent properties

To illustrate the electroluminescent properties of these complexes, the monochromatic OLEDs A-E were fabricated using these complexes as the doped emitter. With the exception of 5, these complexes were significantly stable against thermal sublimation and thus the OLEDs A-D were prepared with the emitting layer deposited by the vacuum thermal evaporation approach. The device configuration was ITO/PEDOT:PSS (40 nm)/NPB (20 nm)/CBP:Ir^{III} phosphor (x wt%, 30 nm)/TPBI (45 nm)/LiF (1 nm)/Al, in which 4,4'-N,N'-dicarbazolebiphenyl (CBP) served as a host material for the iridium complexes, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as the hole injecting layer, and 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and 1,3,5-tris[N-(phenyl)benzimidazole]-benzene (TPBI) as the hole-transporting and electron-transporting materials, respectively. Since complex 5 was found to decompose before sublimation, its OLED was fabricated by spin coating a mixed solution of 5 in small molecular host materials as the emitting layer. The solution-processed OLED E containing 5 has the configuration of ITO/PEDOT:PSS (40 nm)/5 (5 wt%): m-TDATA (50 wt%): PBD (45 wt%) (30 nm)/TPBI (45 nm)/LiF (1 nm)/Al, in which *m*-TDATA (4,4',4''-tris[(3-methylphenyl)phenylamino]triphenylamine) acts as the hole-transporting host and PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) as the electron transporting one. For the purpose of optimization, the doping level of each iridium phosphor was varied in the range

5 to 10 wt%. Table 2 summarizes the best performance data for each device at the optimized doping level of the Ir phosphor.

Fig. S1[†] shows the normalized electroluminescence (EL) spectra of these devices. Essentially, a wide EL color range spanning from yellow to red (550 of 1 to 638 nm of 5) was observed for these devices. Fig. S2[†] illustrates the EL spectra under different luminance for complex 2 based device B as an example. Apparently, the EL spectra were independent of the driving voltage and the luminance, indicating a high stability of the EL spectra for these phosphors. In addition, the same color tunability was obtained in EL as in PL with simply varying the organic ligands. Highly efficient electrophosphorescent OLEDs have been demonstrated with these new complexes and they exhibited low turn-on voltages of 3.2-4.9 V at a brightness of 1 cd m^{-2} . The luminance-voltage-current density (L-V-I) characteristics of OLEDs A-D and their efficiency curves are provided in Fig. 3 and 4, and S3,† respectively. The best performance was achieved for the yellow-emitting device A doped with 1 at the doping level of 7 wt%, with a maximum luminance (L_{max}) of 51 220 cd m⁻² at 11.5 V, a forward viewing maximum luminance efficiency $\eta_{\rm L}$ of 75.9 cd A⁻¹ at 5.5 V, a maximum power efficiency $\eta_{\rm p}$ of 48.2 lm W⁻¹ and a maximum external quantum efficiency (η_{ext}) of 23.0%. For device A, the EL spectrum at 8 V has a maximum peak at 550 nm and Commission International de l'Eclairage (CIE) coordinates of (0.46, 0.53), which falls in the yellow region of the CIE chromaticity diagram. Indeed, the efficiency of 75.9 cd A^{-1} (48.2 lm W^{-1} , 23.0%) is much higher than the highest value ever reported for yellow OLEDs²⁴ and is even comparable with the vacuum-deposited green OLEDs.25 This high performance for device A should be predominantly ascribed to the high phosphorescence quantum yield of 1 (0.42). Furthermore, the holetransporting carbazole moiety that brings about a more balanced electron and hole transportation and recombination in CBP host layer is critical in improving the EL efficiency. The performance of its heteroleptic analogue 2-doped device B is also remarkable with $L_{\rm max}$ of 55 350 cd m⁻², peak $\eta_{\rm L}$ of 56.3 cd A^{-1} , η_p of 35.4 lm W^{-1} and η_{ext} of 18.7% at a doping concentration of 7 wt%. Although these efficiencies are slightly lower than device A, they are still among the highest for yellowemitting OLEDs.

Device C fabricated with 10 wt% of the orange-red complex 3 also showed an impressive performance with an L_{max} of



Fig. 3 The luminance–voltage–current density (*L–V–J*) characteristics for OLEDs A–D.

32 830 cd m⁻², peak $\eta_{\rm L}$ of 33.9 cd A⁻¹, $\eta_{\rm p}$ of 21.9 lm W⁻¹ and $\eta_{\rm ext}$ of 14.2%. In particular, the device D containing dopant **4** exhibited an almost saturated red emission and good performance with a maximum efficiency of 19.6 cd A⁻¹, 10.3 lm W⁻¹ and 13.4% with CIE coordinates of (0.63, 0.37). To the best of our knowledge, these EL efficiencies of device C are some of the highest ever reported for orange-red emitting OLEDs based on vacuum-sublimated Ir dopants.²⁶

Complex 5 based device E emitted a saturated red light with a peak wavelength at 638 nm and a shoulder at 688 nm, which correspond to the CIE coordinates of (0.67, 0.32). In comparison with all the aforementioned vacuum deposited OLEDs, the performance of the partially solution-processed device E are not so remarkable (Fig. S4†), with a maximum luminance of 1706 cd m⁻² at 10 V, and peak η_L of 5.4 cd A⁻¹, η_p of 4.4 lm W⁻¹ and η_{ext} of 8.3%. The reduced performance in device E should be understandable if considering the device fabrication approach and the relatively lower phosphorescent quantum yield of complex 5. It is usually accepted that the solution-processed devices exhibit an inferior performance than those vacuum deposited ones due to the relatively worse film quality caused by the wet methods.

Besides their high efficiencies, another attractive feature of our present Ir^{III} complexes is the less efficient roll-off with increasing driving voltage (Fig. 4 and S2[†]). Taking complex **1** as an example, the luminance efficiency $\eta_{\rm L}$ and external quantum efficiency $\eta_{\rm ext}$ at a brightness of 1000 cd m⁻² are still as high as 75.3 cd A⁻¹ and 22.6%, respectively. The efficiency roll-off ratios

Table 2	EL performan	L performance of the Ir ^{III} complexes-doped monocharomatic OLEDs (A–E) and white-emitting device W										
Device	Dopant	Doping level [wt %]	$V_{\rm turn-on} \left[V \right]$	$L_{ m max}$ [cd m ⁻²]	$\eta_{\rm ext}{}^a$ [%]	$\eta_{\rm L}{}^a [{ m cd} { m A}^{-1}]$	$\eta_{ ext{P}}{}^{a}\left[ext{Im W}^{-1} ight]$	$\lambda_{ m em} \left[m nm ight]$	CIE (x, y)			
A	1	7	3.6	51 220	23.0, 22.6	75.9, 75.3	48.2, 42.1	550, 584 sh	(0.46, 0.53)			
В	2	7	3.2	55 350	18.7, 18.5	56.3, 56.1	35.4, 33.6	563, 595 sh	(0.50, 0.50)			
С	3	10	4.9	26 130	16.0, 15.0	32.9, 31.2	15.9, 12.9	585, 637 sh	(0.59, 0.41)			
D	4	10	4.3	19 070	13.4, 12.4	19.6, 18.1	10.3, 8.1	598, 651 sh	(0.63, 0.37)			
Е	5	5	2.9	1706	8.3	5.4	4.4	638, 688 sh	(0.67, 0.32)			
W	1, Firpic	1.5, 8	4.0	23 180	21.90, 18.61	57.91, 48.82	36.37, 21.55	472, 545	(0.31, 0.45)			

^{*a*} The numbers before the commas are the maximum values of the devices, those after the comma are values collected at a brightness of 1000 cd m^{-2} .



Fig. 4 The plots of luminance efficiency *versus* luminance for device A–D.

from the peak η_L (75.9 cd A⁻¹) and η_{ext} (23.0%) values to those at a brightness of 1000 cd m⁻² are only 0.8% and 1.56%, respectively.

The remarkable performance of 1 in its monochromatic OLED prompted us to explore its application in a two-emittingcomponent white OLED. The WOLED had the structure of ITO/ PEDOT:PSS (40 nm)/CBP:1 (x wt%) (10 nm)/mCP:Firpic (8 wt%) (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (device W), in which Firpic and mCP represent iridium(III)bis(4,6-(difluorophenyl)pyridinato-N, $C^{2'}$)picolinate and N,N'-dicarbazolyl-3,5-benzene, respectively. The 10 nm-thick CBP doped with 1 served as the yellow-emitting layer and 20 nm-thick mCP doped with 8 wt% Firpic as the sky-blue-emitting layer. In order to avoid the undesired dopant-dopant energy transfer if both the yellow and blue iridium phosphors were co-doped in one host layer, each of these two dopant emitters were arranged in individual emitting layers. mCP with a higher triplet energy was selected as the host for blue-emitting Firpic to ensure efficient host-to-dopant energy transfer and to avoid the unwanted back energy transfer. By fixing the concentration of FIrpic at 8 wt%, the doping concentrations of the 1 in CBP varied from 0.5 to 2 wt% in order to tune the purity of the white spectrum, as well as the device efficiency. Fig. 5 shows the EL spectrum of device W with 1.5 wt% of 1 in CBP, which was selected as the optimized doping concentration and exhibits a balanced white light emission with CIE coordinates of (0.31, 0.45). Two intense emission peaks at 472 nm and 545 nm were observed and assigned to the emission from Firpic and complex 1,



Fig. 5 EL spectrum of the WOLED at 6 V.

respectively. With increasing the driving voltage, the CIE coordinates varied only slightly from (0.31, 0.45) at 6 V, (0.29, 0.44) at 8 V to (0.28, 0.43) at 10 V. The white emission slightly shifted with more contribution from the blue emitter when increasing driving voltage and luminance, as indicated by the spectra change in Fig. S5.† This is reasonable since the higher-energy blue component in the device will be more electrically excited at higher electric field than at low field. However, the slight CIE variation still indicates the relatively high stability of the emission color in this WOLED.

The L-V-J characteristics and the efficiency plots are shown in Fig. 6. As can be seen, the threshold voltage of the device was 4.0 V and the luminance reached a maximum of 23 180 cd m^{-2} at 12 V. The peak efficiencies of this WOLED reached $\eta_{\text{ext}} =$ 21.9%, $\eta_{\rm L} = 57.9$ cd A⁻¹, and $\eta_{\rm P} = 36.4$ lm W⁻¹, respectively. The gradual efficiency roll-off was observed in device W with increasing the current density, which can be typically attributed to a combination of triplet-triplet annihilation and fieldinduced quenching effects in electrophosphorescent devices.18a However, at a practical brightness of 1000 cd m^{-2} , the efficiencies were maintained at 18.6%, 48.8 cd A⁻¹, and 21.6 lm W^{-1} . Apparently, there is still room for improvement of the efficiency and color purity for our present WOLED by optimizing the device configuration parameters and/or combining the present orange phosphors with more suitable blue emitters. In recent years, many encouraging results of two-emittingcomponent WOLEDs have been reported. Wu et al. realized highly efficient WOLEDs with a luminance efficiency $\eta_{\rm L}$ of 42.9 cd A^{-1} by doping yellow and blue phosphorescent dyes into a poly(N-vinylcarbazole) (PVK) host. Ma et al. reported a



Fig. 6 The luminance–voltage–current density (*L–V–J*) characteristics (a) and the plots of efficiencies *versus* current density (b) for the white OLED.

vacuum-deposited phosphorescent WOLED exhibiting a peak $\eta_{\rm L}$ of 52.8 cd A⁻¹ and a $\eta_{\rm P}$ of 42 lm W⁻¹. In our own recent publication, an even higher efficiency of 68.6 cd A⁻¹ and $\eta_{\rm P}$ of 34 lm W⁻¹ was achieved for two-element WOLEDs. Apparently, even without any outcoupling enhancement, the maximum luminance efficiency of 57.9 cd A⁻¹ and peak power efficiency of 36.4 lm W⁻¹ in the present study are still among the best values ever reported for two-emitting-component WOLEDs.^{24,27}

Conclusions

In conclusion, five novel homoleptic and heteroleptic iridium complexes were designed and synthesized using three 2-arylbenzothiazole derivatives as major cyclometalating ligands. By expanding the effective π -conjugation length of the cyclometalating ligand framework, introducing an electron-donating element in the HOMO-locating moiety within the cyclometalating ligands, or incorporating a high-field ancilliary ligand, the phosphorescence peak of the iridium complex was successfully shifted to red. By these means, the phosphorescence color of these iridium phosphors was regularly tuned from yellow to saturated red. Amongst these strategies, it seems that the π -conjugation length of the cyclometalating ligand framework is the predominent factor over others to determine the phosphorescence energy and color of the iridium phosphors. High-performance monochromatic and white OLEDs were achieved by using these iridium phosphors as doped emitters. Notably, the yellow-emitting OLEDs containing complex 1 exhibited an excellent performance with 75.90 cd A^{-1} , 48.19 lm W^{-1} , and 23.00%, which represent the highest efficiencies for yellow electrophosphorescence up to now. The 2-carbazolyl-benzothiazole ligand based heteroleptic complex 5 exhibited standard red electrophosphorescence with CIE coordinates of (0.67, 0.32) and an efficiency of 8.3%. The twoemitting-component white OLED fabricated with the yellow 1 and another blue phosphor also produced high-efficiencies of 57.91 cd A^{-1} , 36.37 $\mathrm{lm}~\mathrm{W}^{-1}$, and 21.90%, which are also among the best values for two-element WOLEDs ever reported so far. Given the ease of synthesis and color tunability, as well as performance advantages, these iridium phosphors have significant potential for applications in multicolor displays and possibly in white light illumination sources by layer combination with other suitable emissive dopants.

Experimental

General information

¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz and 100 MHz Varian Unity Inova spectrophotometer. Mass spectra were taken on MALDI micro MX and HP1100LC/MSD MS spectrometers. The photoluminescence and UV-vis absorption spectra measurements were performed on a Perkin-Elmer LS55 spectrometer and a Perkin-Elmer Lambda 35 spectraphotometer, respectively. Luminescence lifetimes were measured on an Edinburgh FLS920 Spectrometer. Cyclic voltammograms of the these iridium complexes were recorded on an electrochemical workstation (BAS100B, USA) at room temperature in a 0.1 M $[{\rm Bu_4N}]{\rm PF_6}$ solution under nitrogen gas protection.

Quantum chemical calculations

Density functional theory (DFT) calculations using the B3LYP functional were performed. The basis set used for C, H, O, N, and S atoms was 6-31G while the LanL2DZ basis set was employed for the Ir atoms. There were no imaginary frequencies for both optimized structures. All these calculations were performed with Gaussian 03.

OLED fabrication and measurements

The pre-cleaned ITO glass substrates $(30 \Omega \square^{-1})$ were treated by UV-ozone for 20 min. For all devices, a 40 nm thick PEDOT:PSS film was first deposited on the ITO glass substrates, and baked at 120 °C for 30 min in air. For monochromatic OLEDs A-E and white device W, all the organic layers were deposited on top of PEDOT:PSS film by vacuum evaporation in a vacuum chamber with a base pressure less than 10^{-6} torr. For device E, the emitting layer was deposited on the PEDOT layer by spin coating the mixed solution of complex 5 in m-TDATA and PBD hosts. The EL spectra, CIE coordinates, and currentvoltage-luminance characteristics were measured with computer-controlled Spectrascan PR 705 photometer and a source-measure-unit Keithley 236 under ambient conditions. The forward viewing external quantum efficiency (η_{ext}) was calculated by using the luminance efficiency, EL spectra and human photopic sensitivity.

The details of the compound's syntheses can be found in ESI.†

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