Novel, highly efficient blue-emitting heteroleptic iridium(III) complexes based on fluorinated 1,3,4-oxadiazole: tuning to blue by dithiolate ancillary ligands†

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Novel blue-emitting phosphorescent iridium(III) complexes with fluorinated 1,3,4-oxadiazole derivatives as cyclometalated ligands and dithiolates as ancillary ligands have been synthesized and fully characterized; highly efficient OLEDs have been achieved using these complexes in the light-blue to blue-emitting region.

Phosphorescent heavy metal complexes play a very important role in organic light-emitting diodes (OLEDs) because their strong spin–orbit coupling, caused by the heavy metal atom, makes intersystem crossing between the singlet and triplet excited states more efficient. In theory, mixing the singlet and triplet excited states can lead to internal phosphorescence quantum efficiencies as high as 100%.[1] In particular, cyclometalated iridium(III) complexes show high phosphorescent efficiencies and relatively short lifetimes, and thus behave as one of the most promising class of phosphorescent dyes in OLEDs. Numerous highly efficient green- and red-emitting OLEDs have been reported using iridium complexes or dendrimers as phosphorescent dyes.[2] However, blue-emitting iridium complexes, which are important for the realization of RGB full-color displays and the creation of white light-emitting devices (WOLEDs), are still scarce.[3]

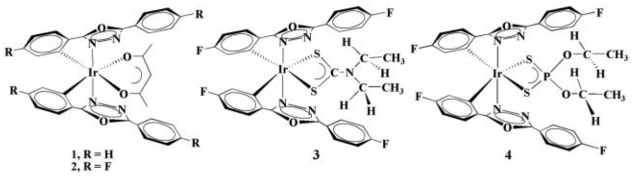
Blue emission from iridium complexes results from large HOMO–LUMO energy gaps. To achieve this goal, one strategy is to lower the HOMO energies of cyclometalated iridium(III) complexes by attaching electron withdrawing fluoride to the phenyl ring of the cyclometalated ligand, such as in the first triplet state of blue light-emitter iridium(III) bis(4,6-difluorophenylpyridinato)picolate (FIrpic),[4] or by using ancillary ligands with strong fields, such as in the highly efficient phosphorescent blue-emitter iridium(III) bis(4,6-difluorophenylpyridinato)tetrakis(1-pyrazolyl)-borate (Fir6).[5] Another strategy is to increase the LUMO energies of cyclometalated iridium(III) complexes by replacing the pyridyl fragment of phenylpyridine ligands with other *N*-heterocyclic moieties, such as pyrazole, triazole, *N*-heterocyclic carbenes, *etc.*[6]

Oxadiazole derivatives have recently received considerable attention in electro-active and opto-active materials due to their high electron affinities, which make them good candidates for electron injection and transportation.[7] Polymers containing oxadiazole units in the side chain or main chain have been widely used in electronic devices for improving their electron transporting ability. Small molecule oxadiazole derivatives, such as 2-(4-*tert*-butylphenyl)-5-biphenyl-1,3,4-oxadiazole (PBD), have also been commonly used as electron transporting and hole blocking materials in OLEDs. However, reports of oxadiazole-based metal complexes have been very limited.

In this communication, we choose for the first time 1,3,4-oxadiazole derivatives as cyclometalated ligands, which have similar structure to triazole, and dithiolates with strong ligand field as ancillary ligand, such as *N*,*N′*-diethyldithiocarbamate (Et_2dtc) or *O*,*O′*-diethyldithiophosphate (Et_2dtp), to develop new blue phosphorescent iridium(III) complexes. We also anticipate that oxadiazoles, as part of the ligand framework, could increase their electron transporting ability and consequently facilitate charge trapping across the bulk for high performance OLEDs.[8]

Cyclometalated iridium(III) complexes (Scheme 1) were prepared in two steps through dichloride-bridged diiridium complex intermediates. All complexes were structurally characterized by ^1H NMR (and, where applicable, ^{31}P, ^{19}F and ^{13}C NMR, and 2D-COSY spectra), elemental analysis and mass spectroscopy. The molecular structure of **4** was determined by X-ray crystallography and is depicted in Fig. 1.‡ The iridium center is located in a distorted octahedral environment by the chelating of two cyclometalated ligands with *cis*-C,C and *trans*-N,N dispositions (C–Ir–C angle: 91.6(2)°, N–Ir–N angle: 168.99(18)°) (see ESI†).

It is noteworthy that in the aliphatic regions of the ^1H NMR spectra of complexes **3** and **4**, two groups of multiplets, centered at about 4.20 and 3.80 ppm, were observed. These were assigned to two kinds of proton environment in the same methylene group of the dithiolate ligands by 2D-COSY and NOE spectra. As shown in Fig. 1, protons H31a and H29b give the same chemical shift due to the restriction of van der Waals interactions between H and N2 or N4, whereas protons H31b and H29a are magnetically equivalent,



Scheme 1 Structures of the iridium(III) complexes.

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† Electronic supplementary information (ESI) available: Synthesis, characterization, crystal structure and electroluminescent properties of the reported complexes. See DOI: 10.1039/b616493e

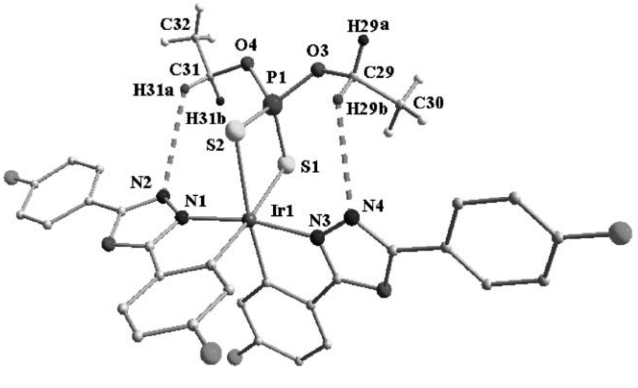

Fig. 1 View of the molecular structure of **4**, showing the van der Waals interactions between H and N atoms.

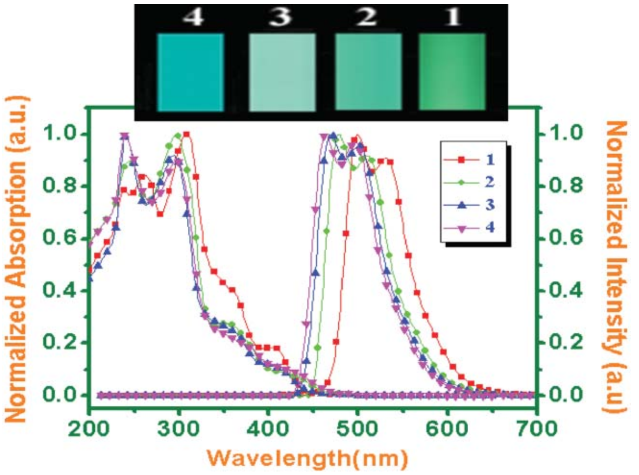

Fig. 2 Absorption and PL spectra of the complexes recorded in CH_2Cl_2 solution, as well as photoluminescent images of a PMMA (polymethylmethacrylate) film of 5% weight ratio at 298 K.

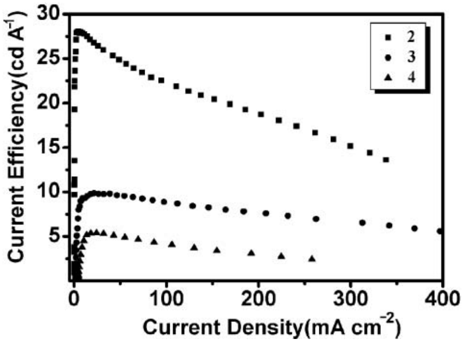

Fig. 3 Current efficiency–current density (η_c–J) curves of the devices, using **2–4** as dopants at a 5% doping level.

attributed to random rotation. The weak van der Waals interactions were confirmed by variable temperature ^1H NMR experiments in d_8-toluene. The two groups of multiplets at room temperature became closer and finally coalesced with rising temperature.

Cyclic voltammetry was used to investigate the electrochemical behavior of these complexes (Table 1). As revealed previously by theoretical calculations, reduction is considered to mainly occur in the heterocyclic portion of cyclometalated ligands, whereas oxidation processes largely involve the Ir–aryl center.[9] Consistent with this conclusion, the LUMO energy levels of complexes **2–4** were little affected by the similar oxadiazole frameworks, whereas their HOMO levels change significantly due to the different ancillary ligands.

Fig. 2 shows the absorption and photoluminescent (PL) spectra of these complexes in CH_2Cl_2 solution. The intense absorptions in the ultraviolet region between 200 and 320 nm can be assigned to spin-allowed π–π* transitions from the cyclometalated ligands. The relatively weak absorption bands in the range 320–370 nm are well resolved and ascribed to a spin-allowed metal-to-ligand charge transfer (^{1}MLCT) transition. The long tails extending to lower energies (in the range 370–470 nm) can most likely be associated with both ^{3}MLCT and $^3\pi$–π* transitions, which gain considerable intensity by mixing with the ^{1}MLCT transition through spin–orbit coupling.[2a,5a]

As shown in Fig. 2, the emission spectra of all the complexes exhibit vibronic fine structure, implying that the lowest excited triplet states of these complexes are likely to be dominant by a ligand-based $^3\pi$–π* transition.[2a] Compared to Ir(ppy)$_2$(acac), with an emission peak at 516 nm, **1**, with the pyridyl replaced by oxadiazole moiety, exhibited a 16 nm hypsochromic shift. **2**, with fluorine atoms incorporated at the 4-positions of the phenyl rings, revealed an additional 21 nm blue-shift in the emission maxima with respect to **1**, attributed to the strong electron-withdrawing ability of fluorine. Further hypsochromic shifts of 9 nm for **3** and 13 nm for **4**, relative to **2**, respectively, took place when the acetylacetonate in **2** was replaced by a strong field dithiolate ancillary ligand. The above alteration of emission wavelength is in good correlation with the energy gap evaluated from the results of cyclic voltammetry.

To illustrate the electroluminescent properties of these complexes, typical OLED devices using complex **2–4** as dopants were fabricated. The devices consisted of multi-layer films of configuration ITO/NPB (40 nm)/CBP + dopant (30 nm)/BCP (10 nm)/AlQ_3 (30 nm)/LiF(1 nm)/Al (100 nm). The electroluminescence

Table 1 Absorption, emission and electrochemical data of complexes **1–4**

Complex	λ_{abs}(log ε) Abs/nm[a]	λ_{max} Em/nm[a]	Q. Y.[b]	$E_{1/2}^{ox}$/V[c,e]	$E_{1/2}^{red}$/V[d,e]	HOMO/eV[f]	LUMO/eV[g]
1	246(3.9), 298(4.0), 355(3.2), 424(2.7), 465(2.0)	500, 529	0.35	0.65	−2.67, −2.55	−5.30	−2.45
2	230(3.8), 312(4.0), 369(3.3), 432(2.8), 468(2.1)	479, 510	0.44	0.80	−2.72, −2.57	−5.47	−2.40
3	238(3.8), 323(4.0), 402(3.3), 436(2.7), 472(2.0)	470, 501	0.32	0.86	−2.70, −2.58	−5.52	−2.39
4	241(3.9), 313(4.0), 397(3.2), 434(2.8), 469(2.2)	466, 498	0.10	0.93	−2.71, −2.59	−5.57	−2.38

[a] Recorded in CH_2Cl_2 at 298 K. [b] Quantum yield measured in CH_2Cl_2 solution relative to quinine bisulfate (10^{-5} M in 1.0 M H_2SO_4, Φ_f = 0.546). [c] Measured in CH_2Cl_2 solution with a concentration of 10^{-3} M at 298 K. [d] Measured in THF solution with a concentration of 10^{-3} M at 298 K. [e] Potential values are reported *vs.* Fc^+/Fc. [f] Determined from the onset oxidation potential. [g] Determined from the onset reduction potential.

Table 2 EL performance of the devices

Dopant	Wt%	L_{max}/cd m^{-2}	Voltage/V[a]	$\eta_{c\ max}$/cd A^{-1}	$\eta_{p\ max}$/lm W^{-1}	V_{ON}/V[b]	EL$_{max}$/nm[c]	CIE (X, Y)[c]
2	3	17 296	23.9	19.09	4.57	4.7	480	(0.21, 0.35)
	5	26 015	26.3	28.06	6.46	4.9	482	(0.22, 0.37)
3	3	18 047	21.3	7.98	2.03	5.1	471	(0.16, 0.27)
	5	22 250	22.5	9.88	2.38	5.5	473	(0.16, 0.28)
4	3	2632	26.5	3.71	0.55	5.9	468	(0.14, 0.25)
	5	3659	21.5	5.41	1.01	6.1	469	(0.14, 0.26)

[a] Voltage at maximum brightness. [b] Turn-on voltage recorded at a brightness of 1 cd m^{-2}. [c] EL maximum recorded at a driving voltage of 12 V.

(EL) spectra are very close in appearance to the PL spectra of the complexes, indicating that the EL emission of the device originates from the triplet excited states of the phosphors. The current efficiency (η_c) as a function of current density (J) for the devices are displayed in Fig. 3. The performance data of the devices are summarized in Table 2.

The device based on **2** at a doping concentration of 5% showed a maximum current efficiency ($\eta_{c\ max}$) of 28.06 cd A^{-1} at a current density (J) of 4.93 mA cm^{-2}, a maximum power efficiency ($\eta_{p\ max}$) of 6.46 lm W^{-1} and a maximum brightness (L_{max}) of 26 015 cd m^{-2} at 26.3 V. To the best of our knowledge, this is among the best performances for iridium(III) complex-based OLEDs in the light-blue-emitting region. The device based on **3** at a doping concentration of 5% showed a maximum brightness of 22 250 cd m^{-2} at 22.5 V, a maximum current efficiency of 9.88 cd A^{-1} at J = 3.05 mA cm^{-2} and a maximum power efficiency of 2.38 lm W^{-1}. The luminous efficiency and brightness of this device are comparable with the best known blue-emitting heteroleptic iridium complex, FIrpic. Moreover, the device showed almost the same peak emission as the device based on FIrpic. However, it shows better blue-colour chromaticity (CIE, coordinates (0.16, 0.27)) than the device based on FIrpic (0.17, 0.34).[4] The device based on **4** at a doping concentration of 5% showed a maximum current efficiency of 5.41 cd A^{-1} at J = 2.49 mA cm^{-2}, a maximum power efficiency of 1.01 lm W^{-1} and a maximum brightness of 3659 cd m^{-2} at 21.5 V. The CIE coordinates are (0.14, 0.25), which is similar to the OLED based on iridium(III) bis(4,6-difluorophenylpyridinato)-5-(pyridine-2-yl)-1*H*-tetrazolate (0.15, 0.24).[3a]

In conclusion, we have developed a new family of blue-emitting iridium(III) complexes with fluorinated 1,3,4-oxadiazoles as cyclometalated ligands and dithiolates as ancillary ligands. We note that the application of dithiolates as the second ligand blue-shifts the emission of the iridium complexes, but more importantly, the corresponding blue-emitting complexes exhibit high efficiency in OLEDs. The color chromaticities of complexes **3–4** are sufficient to provide blue light for full color OLED displays. The optimization of the structures of the iridium complexes and their devices are in progress.

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Notes and references

‡ Crystal data of **4** at 293(2) K: $C_{32}H_{24}O_4N_4F_4S_2PIr$, M_r = 891.84, triclinic, space group P-1, D_c = 1.661 g cm^{-3}, Z = 2, a = 11.884(2), b = 12.611(3), c = 14.567(3) Å, α = 77.01(3), β = 66.69(3), γ = 62.94(3)°, V = 1783.0(6) Å^3, μ = 3.968 mm^{-1}. Bruker AXS Smart CCD diffractometer, Mo-K$_\alpha$ radiation, λ = 0.71073 Å, number of reflections measured = 16756, number of independent reflections = 8014, R_{int} = 0.0407, final R(F) = 0.0561 ($I > 2\sigma(I)$), w$R(F^2)$ = 0.1120. CCDC 626979. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616493e

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