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Synthesis, Photophysical and Electroluminescent Properties of Iridium(III) Complexes with 2-Aryl-thiazole and Oxadiazol-substituted Amide Derivative Ligands

Jiali Yang ^a, Fuli Zhang ^{b,*}, Xiaobin Dong ^b, Bo Yu ^b, Mengyang Zhang ^b, Donghui Wei

^c, Zhongyi Li^b, Bin Wei^{a,*}, Chi Zhang^b, Suzhi Li^b, Guangxiu Cao^b and Bin Zhai^{b,*}

^a Key Laboratory of Advanced Display and System Applications, Ministry of Education, School of Mechatronic Engineering and Automation, Shanghai University, Shanghai 200072, P. R. China.

^b Engineering Technical Research Centre for Optoelectronic Functional Materials of Henan Province, Key Laboratory of Biomolecular Recognition and Sensing of Henan Province, College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, P. R. China.

^c College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China.

*Corresponding author.

E-mail: zzu_zfl@126.com (Fuli Zhang); bwei@shu.edu.cn (Bin Wei); zhaibin_1978@163.com (Bin Zhai).

Abstract

By using aryl-thiazole as cyclometalated ligand and oxadiazol-substituted amide as ancillary ligand, three novel iridium(III) complexes have been synthesized and characterized, and the photophysical and electrochemical properties have been investigated. Complexes **1–3** exhibit efficient phosphorescence emissions at 542, 555 and 585 nm with photoluminescence quantum yields (PLQYs) of 0.04, 0.03 and 0.02 in

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CH₃CN solutions, respectively. In the 10 wt% doped 2,4-diphenyl-6-bis(12phenylindolo)[2,3-a]carbazole-11-yl)-1,3,5-triazine (Dictrz) film, the PLQYs (0.88 for complex **1**, 0.47 for complex **2** and 0.37 for complex **3**) increase significantly owing to the great restriction of rotations and vibrations in rigid host. The organic light-emitting diodes based on these complexes show good performance with the maximum current efficiencies of 20.06, 22.20 and 13.45 cd A⁻¹ and maximum power efficiencies of 13.54, 17.31 and 9.48 lm W⁻¹ with the CIE coordinates of (0.46, 0.53), (0.49, 0.50) and (0.59, 0.40) for complexes **1–3**, respectively.

Keywords: Organic light-emitting diodes; Iridium complex; Aryl-thiazole; Oxadiazolsubstituted amide

1. Introduction

Since the pioneering work done by Forrest and Ma in 1998,^{1, 2} who used Platinum and Osmium complexes to fabricate organic light-emitting diodes (OLEDs), luminescent heavy transition metal complexes have been attracting increasing attention.³⁻⁵ These organo-transition metal compounds exhibit a phosphorescence from the lowest excited electronic triplet state to the electronic singlet ground state allowed by spin–orbit coupling (SOC) induced by the central metal. Consequently, phosphorescent heavy-metal complexes can harvest both singlet and triplet excitons due to their effective intersystem crossing (ISC) and achieve an maximum internal quantum efficiency (IQE) of 100% in phosphorescent OLEDs (PHOLEDs), which are four times than those of the fluorescence-based OLEDs. In comparison with other phosphorescent emitters, cyclometalated iridium(III) complexes have exhibited enormous potential in

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OLEDs owing to their short lifetime of triplet excited states, high photoluminescence quantum yields (PLQYs), and particularly broad range of emission colors from near ultraviolet to visible and near infrared regions.⁶⁻¹⁹

Generally, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are crucial for the photophysical properties, some popular strategies are adopted to regulate the light emission color of cyclometalated iridium(III) complexes. One is to attach electron-donating or electronwithdrawing moieties of cyclometalated ligands to enlarge or reduce the energy gaps between HOMOs and LUMOs. For example, the PL spectrum (peak at 475 nm) of $Ir(dfppy)_{2}pic$ (Firpic, dfppy = 4,6-difluorophenylpyridinato- $N_{1}C2'$, pic = picolinate) is blue-shifted relative to that (peak at 506 nm) of the Ir(ppy)₂pic (ppy is 2phenylpyridine)²⁰ when 4 and 6 positions of cyclometalated ligand ppy are substituted by two electron-withdrawing fluorine atoms in the phenyl ring.²¹ Another approach is to extend or narrow the π -conjunction of cyclometalated ligands by merging or interrupting aromatic rings. By adopting large conjugated 1-phenylisoquinoline (piq) as the cyclometalating ligand in place of ppy, the emission peak of $Ir(ppy)_3$ is tuned to 620 nm for Ir(piq)₃ in N₂-saturated toluene solution.²² As is well known, 2phenylbenzothiazole (Hbt) has been widely used as cyclometalated ligand of yellow- or orange-emitting phosphors due to its convenient modification. Some functional substituents, such as -OMe, -Me, -CF₃ and halogen atoms, have been incorporated to the frame of (bt)₂Ir(acac) (acac is acetylacetone) molecule to develop the new phosphors.²³⁻²⁵ Interestingly, few reports studied the influence of conjugation degrees of the 2-aryl-thiazole cyclometalated ligands on the electronic states and optoelectronic properties of their iridium complexes. In this article, using 2-phenylthiazole (Hpt), Hbt,

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and 2-(2-naphthyl)-1,3-benzothiazole (Hnbt) as cyclometalated ligands and N-(5phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide (HPOXD) as ancillary ligand, respectively, three new phosphorescent iridium complexes [Ir(pt)₂(POXD)] (1), $[Ir(bt)_2(POXD)]$ (2), and $[Ir(nbt)_2(POXD)]$ (3) were designed and synthesized. By adjusting the conjugation length of the cyclometalated ligands, emissions peaking at 542, 555 and 585 nm, respectively, of complexes 1–3 in CH₃CN solution were acquired. In addition, 1,3,4-oxadiazole derivatives have proved to be good electron injection and transport materials due to their high electron affinity and good thermal/chemical stability.²⁶⁻³¹ Recently, our group has reported efficient iridium complexes and devices using HPOXD as ancillary ligands to improve the complexes' electron transporting ability and consequently achieve high device performance.^{17, 32, 33} For example, the electron mobility of POXD-based complex [Ir(ppy)₂(POXD)] is in the range of 7.41- $8.57 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under an electric field from 1100 (V cm⁻¹)^{1/2} to 1300 (V cm⁻¹)^{1/2}, higher than that $(4.74-4.86 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ of the popular electron transport material Alg₃ under the same electric fields.¹⁷ Herein, we present the results of our investigation on the synthesis, structural characterization, photophysical and electroluminescent properties of these novel Ir(III) complexes.

2. Experimental

2.1. General experiments

All solvents and materials were purchased from commercial sources and used as received unless otherwise stated. The cyclometalated ligands Hpt and Hbt were purchased from J&K Chemical Ltd. (Shanghai). ESI mass spectrometry was performed with a Waters Xevo G2-S QT of mass spectrometer. ¹H NMR spectra were recorded with a Bruker DPX 400 spectrometer. Elemental analysis was determined with an

Elementar Vario EL CHN elemental analyzer. The absorption and PL spectra were performed with а UV-vis spectrophotometer (Agilent Cary 60) and а fluorospectrophotometer (Hitachi F-7000), respectively. The excited state lifetimes of the complexes were measured by time-correlated single-photon counting technique at the peak emitting wavelength upgrade on a transient spectrofluorimeter (Edinburgh Instruments, FLSP920). PLQYs in CH₃CN solutions were measured with quinine sulfate ($\varphi = 0.545$ in 1 M H₂SO₄)³⁴ as the reference. Cyclic voltammetry was performed on a CHI 820C electrochemical station (Shanghai Chenhua Co., China) in CH₃CN solutions $(1 \times 10^{-3} \text{ M})$ at a scan rate of 100 mV s⁻¹ with a platinum plate as the working electrode, a Ag wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was n-Bu₄NPF₆ (0.1 M) and ferrocene was selected as the internal standard. The solutions were bubbled with argon for 10 min before measurements.

2.2. Syntheses

Syntheses of ligand Hnbt. A mixture of 2-naphthaldehyde (1.09 g, 7 mmol) and 2aminobenzenethiol (0.88 g, 7 mmol) in dimethyl sulfoxide (10 mL) was refluxed at 200°C for 1 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water, and the formed precipitate was filtered and dried. The crude compound was purified by column chromatography on silica gel (200–300 mesh) with petroleum ether/ethyl acetate (15:1) as the eluent, yielding of the product, 2-(2-naphthyl)-1,3-benzothiazole (Hnbt) as a white solid. Yield: 72%. ¹H NMR (400 MHz, CDCl₃, δ): 8.57 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.98–7.92 (m, 3H), 7.89–7.86 (m, 1H), 7.56–7.49 (m, 3H), 7.40 (t, J = 8.0 Hz, 1H).

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General syntheses of iridium complexes 1–3. A mixture of $IrCl_3$ (1.00 mmol) and ligands Hpt, Hbt and Hnbt (2.05 mmol) in 2-ethoxyethanol (20 mL) and water (100 mL) was refluxed for 24 h. After cooling to room temperature, the mixture was filtered, and the precipitate was washed with H₂O and petroleum ether to give the crude cyclometalated Ir(III) chloro-bridged dimer. The slurry of crude chloro-bridged dimer (0.43 mmol) and 2.2 equivalent KPOXD¹⁷ (0.95 mmol) were dissolved in 2methoxyethanol (20 mL). The mixture was then refluxed at 120 °C for 12 h under an argon atmosphere. The crude compound was filtered after the solution cooled to room temperature and purified by column chromatography on silica gel (200–300 mesh) with petroleum ether/ethyl acetate (4:1) as the eluent, yielding of iridium complex powder.

Ir(pt)₂(POXD) (1). Overall yields: 50%. ¹H NMR (400 MHz, CDCl₃, δ): 8.08 (d, J = 4.0 Hz, 1H), 7.97–7.91 (m, 1H), 7.80 (dd, J = 4.0 and 8.0 Hz, 2H), 7.62 (d, J = 4.0 Hz, 2H), 7.55–7.45 (m, 5H), 7.40–7.29 (m, 7H), 7.16 (d, J = 4.0 Hz, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.84–6.78 (m, 3H), 6.66 (t, J = 8.0 Hz, 1H), 6.43 (d, J = 8.0 Hz, 1H), 6.19 (t, J = 8.0 Hz, 1H). ESI-MS [m/z]: 872.9 (M + H)⁺. Anal. found: C 52.31, H 3.10, N 7.99. Anal. Calcd for C₃₈H₂₇N₅O₂PS₂Ir: C 52.28, H 3.12, N 8.02.

Ir(bt)₂(POXD) (**2**). Overall yields: 62%. ¹H NMR (400 MHz, CDCl₃, δ): 9.02 (d, J = 8.0 Hz, 1H), 7.81–7.70 (m, 4H), 7.64 (t, J = 8.0 Hz, 3H), 7.50–7.31 (m, 11H), 7.15 (t, J = 4.0 Hz, 2H), 7.01–6.92 (m, 6H), 6.75 (t, J = 8.0 Hz, 1H), 6.54 (dd, J = 8.0 and 12.0 Hz, 2H), 6.26 (d, J = 8.0 Hz, 1H). ESI-MS [m/z]: 973.9 (M + H)⁺. Anal. found: C 56.74, H 3.23, N 7.24. Anal. Calcd for C₄₆H₃₁N₅O₂PS₂Ir: C 56.78, H 3.21, N 7.20.

Ir(nbt)₂(POXD) (**3**). Overall yields: 64%. ¹H NMR (400 MHz, CDCl₃, δ): 9.12 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 20.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.79–7.70 (m, 5H), 7.57–7.49 (m, 6H), 7.35–7.28 (m, 6H), 7.20–6.86 (m, 12H), 6.52 (s, 1H). ESI-MS [m/z]:

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1074.1 (M + H)⁺. Anal. found: C 60.47, H 3.31, N 6.49. Anal. Calcd for $C_{54}H_{35}N_5O_2PS_2Ir$: C 60.43, H 3.29, N 6.53.

2.3. Quantum Chemical Calculations

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were conducted to gain insights into the electronic states and the orbital distribution. The B3LYP^{35, 36} density functional was used to optimize the geometries of the Ir complexes in the acetonitrile solvent using the integral equation formalism polarized continuum model (IEFPCM).³⁷ The 6-31G(d, p) and Lanl2DZ basis sets were applied for the main group atoms and Ir atom, respectively. All the calculations were performed using the Gaussian 09 program.³⁸ The visualization of molecular orbitals was accomplished using the GaussView program.

2.4. Fabrication and characterization of OLEDs

Device was fabricated upon a glass substrate, which was precoated with an about 100 nm thick layer of indium-tin-oxide (ITO) with a sheet resistance of about 10 Ω sq⁻¹, then degreased with solvents, cleaned by exposure to oxygen plasma and ultraviolet-ozone ambient. All the organic layers and cathode were fabricated by vacuum evaporation deposition under a low pressure of 1× 10⁻⁴ Pa. The luminance–voltage–current density characteristics were measured with a PR655 spectrometer and a Keithley 2400 programmable voltage-current source in ambient atmosphere without further encapsulation.

3. Results and discussion

3.1. Synthesis and Structural Characterization



Scheme 1 Synthetic routes for complexes 1–3.

Chemical structures and synthetic protocols of iridium compelxes **1–3** are shown in Scheme 1. The cyclometalated ligand Hnbt and potassium salt KPOXD of ancillary ligand used in this work were synthesized according to the reported procedures.^{17, 25} Complexes **1–3** were synthesized by reacting the dimeric iridium(III) intermediates $[(pt)_2Ir(\mu-Cl)_2Ir(pt)_2]$, $[(bt)_2Ir(\mu-Cl)_2Ir(bt)_2]$ and $[(nbt)_2Ir(\mu-Cl)_2Ir(nbt)_2]$ with KPOXD according to the literature procedure.^{17, 39, 40} We purified the crude products by column chromatography on silica gel (200–300 mesh) with petroleum ether/ethyl acetate as eluent, and fully characterized them by ¹H NMR, ESI (electron spray ionization) mass spectroscopy, elemental analysis (see the Experimental Section).

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Fig. 1 The molecular structures of complexes 2 (a) and 3 (b). Hydrogen atoms are omitted for clarity.

The crystal structures (CCDC numbers are 1836142 and 1889387, respectively) of complexes **2** and **3** were further examined using single-crystal X-ray diffraction analysis. As shown in Fig. 1, the Ir center exihibits a pseudo-octahedral geometry with two cyclometalated ligands adopting C,C-*cis*, N,N-*trans* configurations, which resembles those observed in other cyclometalated iridium complexes.^{40, 41} The Ir–C_(C^N), Ir–N_(C^N), Ir–N_(N^O) and Ir–O_(N^O) bond lengths, as well as the ligand bite angles, are similar to those of previously reported iridium complexes.^{32, 33} The downside is that single crystals of **1** could not be obtained.

3.2. Photophysical Properties



Fig. 2 Normalized absorption and emission pectra of complexes 1–3 in CH₃CN solution (a) and Dictrz doped film (b).

	$\lambda_{abs} [nm]$ ($\epsilon [\times 10^4$	Emission at roo	Electrochemical data ^[d]		
	$M^{-1}cm^{-1}]$ [a]	$\lambda_{em} [nm]/\Phi_{em}/\tau[\mu s]$		- E [V]	E . [V]
		CH ₃ CN ^[b]	Dictrz film ^[c]		L _{red} [V]
1	224(5.77)/			0.58	-2.49
	292(3.70)/	542/4%/0.14	542/88%/1.85		
	385(0.44)				
	217(6.52)/				
2	313(2.83)/	555/3%/0.45	557/47%/1.09	0.71	-2.21
	401(0.51)				
3	228(11.66)/			0.56	-2.12
	327(6.54)/	585/2%/0.56	593/37%/1.64		
	418(0.47)				

Table 1. Photophysical characteristics of complexes 1–3.

^[a] In CH₃CN solution (1 × 10⁻⁵ M). ^[b] In degassed CH₃CN solution. λ_{ex} : 385 nm. ^[c] Dictrz film was deposited on quartz substrate with thickness of about 100 nm. λ_{ex} : 385 nm. ^[d] Electrochemical data versus Fc⁺/Fc (Fc is ferrocene) were collected in CH₃CN solution (10⁻³ M).

The absorption and photoluminescent (PL) spectra of complexes 1-3 are shown in Fig. 2 and detailed photophysical characterizations are depicted in Table 1. The broad and strong absorption bands in the UV region below about 400 nm assigned to spin-allowed $1\pi-\pi^*$ transitions of the cyclometalated main ligands and ancillary ligands. The relatively weak absorption bands (see Fig. S1 in Supporting Information) extending to about 525 nm are attributed to excitations to 1MLCT (metal-to-ligand charge-transfer), 1LLCT (ligand-to-ligand charge-transfer), 3MLCT , 3LLCT , and ligand-centered (LC)

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 ${}^{3}\pi-\pi^{*}$ transitions.⁴²⁻⁴⁶ It is notable that the absorption peaks shift toward longer wavelength with the changes of cyclometalating ligand from Hpt to Hbt and Hnbt due to a gradual enlargement of conjugacy.

As shown in Fig. 2a, in CH₃CN solution, the PL peaks of the complexes have red shift with the changes of cyclometalating ligand from Hpt to Hbt and Hnbt, which is consistent with their absorption spectra. Complex 1 shows greenish yellow emission peaked at 542 nm, with a PLOY of 0.04 and an excited state lifetime of 0.14 us (see Fig. S2 in Supporting Information), which resemble to those of previously reported cationic iridium complex [Ir(ppy)₂(bpy)]PF₆ (bpy is 2,2'-bipyridine).⁴⁷ Complex 2 shows yellow emission peaked at 555 nm, with a PLQY of 0.03 and an excited state lifetime of 0.45 μs. In contrast, complex **3** gives orange emission peaked at 585 nm, with a PLQY of 0.02 and an excited state lifetime of 0.56 μ s. Their radiative decay rates (k_r) calculated are 2.86 \times 10⁵ s⁻¹, 0.67 \times 10⁵ s⁻¹ and 0.36 \times 10⁵ s⁻¹, respectively, whereas their nonradiative decay rates (k_{nr}) calculated are 68.57×10^5 s⁻¹, 21.56×10^5 s⁻¹ and 17.50×10^{-1} 10^5 s⁻¹, respectively, from the PLQYs and the lifetime values. The rapid nonradiative decay is responsible for the low quantum yield of the excited states. The PL spectra of complexes 1-3 in CH₃CN solution are vibronically structured, indicating that at room temperature, the emitting triplet states of these complexes are dominated by LC ${}^{3}\pi - \pi^{*}$ character.

In sharp contrast to the PLQYs in solutions, the doped (10 wt %) films of complexes 1-3 in Dictrz⁴⁸ exhibit significantly better PLQYs of 0.88, 0.47 and 0.37, respectively, accompanied by remarkable increase of excited state lifetimes (1.85, 1.09 and 1.64 µs, respectively, see Fig. S3 in Supporting Information), which plausibly result from the great restriction of rotations and vibrations in rigid host.^{42, 49} In addition, as shown in

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Fig. 2b, complexes 1–3 in doped films show more structured PL spectra with the emission peaks at 584, 505 and 507 nm, respectively, indicating dominant LC ${}^{3}\pi - \pi^{*}$ character in their emitting triplet states.

3.3. Electrochemical Properties and Theoretical Calculations

The electrochemical behaviors of complexes 1-3 were measured by cyclic voltammetry (CV) *versus* ferrocenium/ferrocene (Fc⁺/Fc) using *n*-Bu₄NPF₆ (0.1 M) as the supporting electrolyte in CH₃CN solution. Fig. 3 depicts the CV curves and redox potentials are summarized in Table 1. All complexes exhibit reversible oxidation processes with the oxidation potentials at 0.58, 0.71 and 0.56 V, respectively, which are almost identical to those of other thiazole-based iridium complexes.⁵⁰ Complexes 1-3 undergo irreversible reduction processes with the reduction potentials at -2.49, -2.21 and -2.12 V, respectively. The HOMO (-5.38 eV for 1, -5.51 eV for 2 and -5.36 eV for 3, respectively) and LUMO (-2.31 eV for 1, -2.59 eV for 2 and -2.68 eV for 3, respectively) levels of the complexes were calculated from the oxidation and reduction potentials.



Fig. 3 Cyclic voltammograms of complexes 1-3. Potentials were recorded versus Fc^+/Fc .

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To provide deeper insight into the photophysical and electrochemical properties of complexes 1-3, DFT calculations at the B3LYP/6-31G ** + LANL2DZ level were carried out. The frontier molecular orbital composition, including the HOMOs and LUMOs of complexes 1-3 are displayed in Fig. 4. HOMOs of complexes 1 and 2 were composed of phenyl groups of cyclometalated ligands, oxadiazole group of POXD and the iridium center. For complex 3, HOMO resides on the iridium center and naphthyl group of Hnbt ligand. LUMOs of complexes 1 and 2 were almost entirely distributed on one of the cyclometalated ligands. In particular, LUMO of complex 3 was located on two cyclometalated ligands.



Fig. 4 Isodensity plots of the frontier orbitals of complexes 1–3. All of the molecular orbital surfaces correspond to an isocontour value of |C| = 0.025.

The electronic transition dipole of low-lying triplet states of complexes 1-3 were calculated by TD-DFT approach in order to investigate the nature of the emitting excited states. The vertical excitation energies and orbitals involved in the excitations for calculated triplets below 3.0 eV were summarized in Table 2. For T₁, T₂ and T₃

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states of complex 1, the orbitals involved are the HOMO–3, HOMO–2, HOMO–1, HOMO, LUMO, LUMO+1, LUMO+2 and LUMO+3 orbitals, rendering these states the nature of mixed ³MLCT ($d\pi(Ir) \rightarrow \pi^*(pt), d\pi(Ir) \rightarrow \pi^*(POXD)$), ³LC $\pi - \pi^*$ ((pt-based) and (POXD-based)) and ³LLCT ($\pi(pt) \rightarrow \pi^*(POXD), \pi(POXD) \rightarrow \pi^*(pt)$) characters. The T₁, T₂ and T₃ states of complex 2 can be rendered the nature of mixed ³MLCT ($d\pi(Ir) \rightarrow \pi^*(bt), d\pi(Ir) \rightarrow \pi^*(POXD)$), ³LC $\pi - \pi^*$ ((bt-based) and (POXD-based)) and ³LLCT ($\pi(bt) \rightarrow \pi^*(POXD), \pi(POXD) \rightarrow \pi^*(bt)$) characters. For complex 3, however, the T₁, T₂ and T₃ states can be attributed to ³MLCT ($d\pi(Ir) \rightarrow \pi^*(nbt)$), ³LC $\pi - \pi^*$ ((nbtbased). Considering that the vibronically structured emission spectra and the red-shift of PL spectra with the conjugation degrees of cyclometalated ligands increasing, we tentatively assign the emission of complexes 1–3 to be mainly from cyclometalated ligand-based ³ $\pi - \pi^*$ states.

	States	E [a] [eV]	Dominant excitations [b]	Nature
1	T1	2.41	$H \rightarrow L (0.46)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow *(pt)$
			$H - 1 \rightarrow L (0.17)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow *(pt)$
			$H - 2 \rightarrow L (0.13)$	$d\pi(Ir)$ - $\pi(pt) \rightarrow \pi^*(pt)$
	T2	2.45	$\mathrm{H} \rightarrow \mathrm{L} + 1 \; (0.59)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow *(pt)$
			$H - 2 \rightarrow L (0.15)$	$d\pi(Ir)-\pi(pt) \rightarrow \pi^*(pt)$
			$H - 3 \rightarrow L + 1 \ (0.14)$	$d\pi(Ir)-\pi(pt) \rightarrow \pi^*(pt)$
	T3	2.74	$\mathrm{H}-1 \rightarrow \mathrm{L}+2~(0.35)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow \pi^*(POXD)$
			$\mathrm{H}-1 \rightarrow \mathrm{L}+3~(0.23)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow \pi^*(POXD)$
			$\mathrm{H} \rightarrow \mathrm{L} + 2 \; (0.22)$	$d\pi(Ir)-\pi(pt)-\pi(POXD) \rightarrow \pi^*(POXD)$
2	T1	2.40	$H \rightarrow L (0.45)$	$d\pi(Ir)-\pi(bt)-\pi(POXD) \rightarrow \pi^*(bt)$
			$H - 1 \rightarrow L (0.31)$	$d\pi(Ir)-\pi(bt)-\pi(POXD) \rightarrow \pi^*(bt)$
			$H - 2 \rightarrow L (0.17)$	$d\pi(Ir)-\pi(bt) \rightarrow \pi^*(bt)$
	T2	2.42	$\mathrm{H} \rightarrow \mathrm{L} + 1 \; (0.69)$	$d\pi(Ir)-\pi(bt)-\pi(POXD) \rightarrow \pi^*(bt)$
	Т3	2.65	$H \rightarrow L (0.52)$	$d\pi(Ir)-\pi(bt)-\pi(POXD) \rightarrow \pi^*(bt)$
			$H - 2 \rightarrow L(0.31)$	$d\pi(Ir)-\pi(bt)-\pi(POXD) \rightarrow \pi^*(bt)$
3	T1	2.09	$H \rightarrow L (0.81)$	$d\pi(Ir)-\pi(nbt) \rightarrow \pi^*(nbt)$
			$H - 2 \rightarrow L + 1 (0.14)$	$d\pi(Ir)-\pi(nbt) \rightarrow \pi^*(nbt)$
	T2	2.14	$H \rightarrow L + 1 \ (0.73)$	$d\pi(Ir)-\pi(nbt) \rightarrow \pi^*(nbt)$
			$H - 2 \rightarrow L (0.24)$	$d\pi(Ir)-\pi(nbt) \rightarrow \pi^*(nbt)$
	Т3	2.55	$H \rightarrow L (1.00)$	$d\pi(Ir)-\pi(nbt) \rightarrow \pi^*(nbt)$

Table 2 Selected triplet states for complexes 1–3 calculated from TDDFT approach.

[a] Excitation energies calculated for the triplet states. [b] H and L denote HOMO and LUMO, respectively; data in parentheses are the contributions of corresponding excitations.

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3.4. Electroluminescent Properties of OLED Devices

In order to evaluate the electroluminescent properties of these complexes, 1-3 were employed as doped emitters to fabricate the OLEDs with the structure of ITO/HAT-CN (20 nm)/NPB (10 nm)/TCTA (20 nm)/Dictrz: x% Ir complex (10 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm) (HAT-CN is dipyrazino[2,3-f:2',3'-h]quinoxaline 2,3,6,7,10,11-hexacarbonitrile, NPB is N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)benzidine, TCTA is 4.4'.4"-tris(carbazol-9-vl)triphenvlamine, TmPvPB is 1.3,5-tri(mpyrid-3-yl-phenyl)benzene). HAT-CN acted as hole-injecting layer; NPB and TCTA were used as hole-transporting materials; The aromatic thermally activated delayed fluorescence compound Dictrz have a triplet energy $(E_{\rm T})$ of 3.0 eV,^{48, 51} which served as hosts for complexes 1 ($E_T = 2.30 \text{ eV}$), 2 ($E_T = 2.24 \text{ eV}$) and 3 ($E_T = 2.12 \text{ eV}$). The higher $E_{\rm T}$ of host can prevent the energy transfer of triplet excitons from the emitters back to the host material more effectively; TmPyPB was employed as electrontransporting material; Liq/Al acted as electron-injection layer and cathode. The device architecture and chemical structures of the materials used are shown in Fig. 5. Doping concentrations were varied from 1, 5 to 10 wt % in order to optimize the device performance.

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Fig. 5 Device architecture and chemical structures of the materials used in the OLEDs.

The electroluminescence (EL) spectra and potential (V) –luminance (L) – current density (J) curves of the OLEDs are depicted in Figs. 6–8. As shown in Figs. 6(a), 7(a) and 8(a), devices based on **1**, **2** and **3** emit greenish yellow, yellow and orange light with major EL peak at 540, 553 and 594 nm with the Commission International de l'Eclairage (*CIE*) coordinates of (0.46, 0.53), (0.49, 0.50) and (0.59, 0.40), respectively, which closely resemble those of PL spectra in solution and Dictrz doped film, indicating that EL originated from the triplet excited states of complexes **1–3**. However, at low doping concentrations of the dopant (1% and 5 wt %), a weak emission from host Dictrz was observed, indicating incomplete energy transfer from Dictrz to complexes **1–3**. With an increase of the doping concentration to 10%, emission from host disappeared.

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As can be seen in Figs. 6(b), 7(b) and 8(b), as increasing the dopant content of complexes in OLEDs, evolution trend of luminance with applied bias are similar, but current density have different evolution trend with applied bias. The diffient evolution trend of current density may stem from the different extent of carrier trapping and energy transfer in the host-guest emitting system of Dictrz-complexes 1–3. From Figs. 6(a), 7(a) and 8(a), we can judge that there existed the incomplete energy transfer from Dictrz to complexes when the doping concentration is lower than 10%. On the other hand, the energy barrier (0.6 eV) between electron transport layer and adjacent host is big. The host doped with a guest molecule of a deep LUMO level can effectively reduce the barrier and faciliate electron injection. This leads to different evolution trend of current density with applied bias. The current density within one OLED can be described as $J = J_I - J_r$, in which J_I is the injected current, and J_r is the recombation current, respectively. As increasing the dopant content of complexes in OLEDs, the current density for complex 1 slightly decreased from 1% to 5% due to increase in recombination current (J_r) , which can be demonstrated from the efficient energy transfer as depicted in PL spectra of Fig. 6(a). And then, with the doping concentration increased from 5% to 10%, the current density rose due to efficient electron injection (J_1) into Dictrz through complex 1. For complex 2, as the ascent concentration from 1% to 5%, the current density increased because the electrons may hop more efficiently through the channel of complex 2 due to the little gap between the LUMO of dopant and the adjacent electron transport layer. Despite the elevated recombination current, the enhanced electrons is bigger than recombined ones in dye sites. While the concentration of the complex 2 increased to 10%, the accumulated charge may cause the concentration quenching giving rise to the nonradiative triplet-polaron annihilation

(TPA), which lead to the severe drop of current density. With regards to complex **3**, the current increased dramatically due to dominant trapping effect of electrons in complex **3** for very small barrier. Comparatively, notwithstanding the existence of TPA, the barrier-free interface facilitate the high efficient injection, leading the more increased injected charge than the quenching current.



Fig. 6. (a) normalized EL spectra and (b) L–V–J characteristics of OLEDs with a structure of ITO/HAT-CN (20 nm)/NPB (10 nm)/TCTA (20 nm)/Dictrz: x% complex 1 (10 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), x = 1, 5 or 10.



Fig. 7. (a) normalized EL spectra and (b) L–V–J characteristics of OLEDs with a structure of ITO/HAT-CN (20 nm)/NPB (10 nm)/TCTA (20 nm)/Dictrz: x% complex 2 (10 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), x = 1, 5 or 10.

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Fig. 8. (a) normalized EL spectra and (b) L–V–J characteristics of OLEDs with a structure of ITO/HAT-CN (20 nm)/NPB (10 nm)/TCTA (20 nm)/Dictrz: x% complex 3 (10 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm), x = 1, 5 or 10.

	<i>x</i> [a]	V _{turn-on} [b] [V]	<i>L</i> _{max} [c] [cd m ⁻²]	η _{c,max} [d] [cd A ⁻¹]	η _{p,max} [e] [lm W ⁻¹]	$\lambda_{ m EL} [{ m f}] \ [{ m nm}]$	<i>CIE</i> [g] (x, y)
1	1	4.5	2400	6.25	3.92	539, 578 (sh)	(0.38, 0.48)
	5	4.0	6650	12.85	9.19	539, 579 (sh)	(0.43, 0.52)
	10	4.0	13100	20.06	13.54	540, 580 (sh)	(0.46, 0.53)
2	1	3.5	11000	13.52	9.23	552, 595 (sh)	(0.46, 0.49)
	5	3.5	9040	17.01	10.58	552, 595 (sh)	(0.48, 0.50)
	10	3.4	26000	22.20	17.31	553, 596 (sh)	(0.49, 0.50)
3	1	4.0	2930	4.90	3.68	588, 633 (sh)	(0.42, 0.45)
	5	4.0	4640	7.78	5.43	591, 632 (sh)	(0.56, 0.41)
	10	3.5	8950	13.45	9.48	594, 633 (sh)	(0.59, 0.40)

Table 3. EL performances of the devices based on complexes 1–3.

[a] x: doping concentration. [b] $V_{turn-on}$: Turn-on voltage recorded at a luminance of 1 cd m⁻². [c] L_{max} : maximum luminance. [d] $\eta_{c,max}$: maximum current efficiency. [e] $\eta_{p,max}$: maximum power efficiency. [f] λ_{EL} : maximum EL wavelength. [g] *CIE*: Commission Internationale de l'Éclairage.

As shown in Figs. 6b, 7b, 8b, S4 (in Supporting Information) and Table 3, a maximum luminance (L_{max}) of 13100 cd m⁻², a maximum current efficiency ($\eta_{c, max}$) of 20.06 cd A⁻¹ and a maximum power efficiency ($\eta_{p, max}$) of 13.54 lm W⁻¹ for complex 1, a L_{max} of 26000 cd m⁻², a $\eta_{c, max}$ of 22.20 cd A⁻¹ and a $\eta_{ext, max}$ of 17.31 lm W⁻¹ for

complex 2 and a L_{max} of 8950 cd m⁻², a $\eta_{c, \text{max}}$ of 13.45 cd A⁻¹ and a $\eta_{\text{ext, max}}$ of 9.48 lm W⁻¹ for complex 3 are achieved. These devices exhibit inferior EL properties compared with those of other POXD-based iridium(III) complexes.^{17, 32} The relatively low efficiencies of these devices are presumably due to the inefficient energy transfer from the host to these complexes or TPA in emitting layer with high doping concentration (vide supra). The devices based on complexes 1 and 2 exhibit better electroluminescence properties compared with those based on complex 3, which can be ascribed to the higher PLQYs of Dictrz doped films in complexes 1 and 2.

4. Conclusion

In summary, by adjusting the conjugation degrees of the 2-aryl-thiazole-based cyclometalated ligands, greenish yellow, yellow to orange phosphorescent iridium(III) complexes (1–3) bearing N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide as ancillary ligand have been synthesized and fully characterized with their electrochemical, photophysical and device optoelectronic properties. The PhOLEDs with the structure of ITO/HAT-CN (20 nm)/NPB (10 nm)/TCTA (20 nm)/Dictrz: 10% complexes (10 nm)/TmPyPB (40 nm)/Liq (1 nm)/Al (100 nm) shows excellent performance with the maximum current efficiencies of 20.06, 22.20 and 13.45 cd A⁻¹ with the CIE coordinates of (0.46, 0.53), (0.49, 0.50) and (0.59, 0.40) for complexes 1–3, respectively.

Acknowledgements

We would like to thank the National Natural Science Foundation of China (Grant Nos. 21501117, U1704140, 21571123 and 21601119) and the Program for Science and Technology Innovation Talents in Universities of Henan Province (19HASTIT034) for financial support.

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By using aryl-thiazoles with different conjugation degree as cyclometalated ligands and oxadiazol-substituted amide as ancillary ligand, greenish yellow, yellow to orange phosphorescent iridium(III) complexes have been synthesized and fully characterized with their electrochemical, photophysical and device optoelectronic properties.