Synthesis and Characterization of High-Efficiency Red Phosphorescent Iridium(III) Complexes with 1-(4-(Trifluoromethyl)phenyl)isoquinoline Ligand

Zheng Zhao,¹ Xiao-Han Yang,¹ Zi-Wen Tao,¹ Han-Ru Xu,¹ Kai Liu,¹ Guang-Ying Chen,² Zheng-Rong Mo,² Shui-Xing Wu,¹ Zhi-Gang Niu,^{1,2} and Gao-Nan Li^{1,*}

¹ Key Laboratory of Electrochemical Energy Storage and Energy Conversion of Hainan Province, College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, China

² Key Laboratory of Tropical Medicinal Plant Chemistry of Ministry of Education, Hainan Normal University, Haikou 571158, China

* Corresponding author: E-mail: ligaonan2008@163.com (G.-N. Li)

Received: 05-05-2019

Abstract

Two new tfmpiq-based bis-cyclometalated iridium(III) complexes, [(tfmpiq)₂Ir(imdzppo)] (**2a**) and [(tfmpiq)₂Ir(idzpo)] (**2b**) (where tfmpiq = 1-(4-(trifluoromethyl)phenyl)isoquinoline, imdzppo = 2-(imidazo[1,2-a]pyridin-2-yl)phenol, idzpo = 2-(2H-indazol-2-yl)phenol), have been synthesized and fully characterized. The single crystal structure of **2b** has been determined. The relationship between the structures and photophysical properties of both complexes are considered, and the DFT calculations have been used to further support the deduction. These Ir(III) complexes emit red light with quantum yields of 39.9–51.9% in degassed CH₂Cl₂ solution at room temperature. Also, their emission originates from a hybrid ³MLCT/³LLCT/³LC excited state. All these results show that iridium(III) complexes **2a–2b** are suitable for red-phosphorescent materials in OLEDs.

Keywords: Iridium(III) complex; 1-(4-(Trifluoromethyl)phenyl)isoquinoline; Red phosphorescence; DFT calculation

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention on the development of modern optoelectronic technologies such as full-color displays and solid-state lighting sources.^{1–3} Particularly, cyclometalated iridium(III) complexes ([Ir(C^N)₃] or [(C^N)₂Ir(LX)]) are the most valuable emitting materials in the fabrication of OLEDs, owing to their relatively short excited-state lifetime, high phosphorescence efficiency and excellent color-tuning capability.^{4,5} As compared to other colors, red electrophosphorescent emitting phosphors are difficult to maintain high device efficiency, since their quantum efficiencies tend to decrease as the emission wavelength increases in accordance with the energy gap law.^{6–8} Thus, the design and syntheses of highly efficient red-emitting iridium complexes remain a challenge.

1-Phenylisoquinoline (piq) is one typical ligand framework to construct red iridium complexes. A large number of piq-based Ir(III) complexes have been reported during the past decade.^{9–13} Among these examples, iridium complexes of fluorinated phenylisoquinoline show strong electroluminescence brightness and efficiency. This is because the fluorine groups could not only modify the electronic properties but also decrease the rate of nonradioactive deactivation and improve phosphorescence quantum yields.¹⁴ Therefore, in 2006, K.-H. Fang and co-workers first reported Ir(tfmpiq)₂acac (acac = acetylacetonate) complex, which emitted red phosphorescence with a wavelength maximum at 631 nm, and the quantum yield was up to 31%.¹⁵ Subsequently, in 2014, S. Zhang et al. developed red Ir(tfmpiq)₂tpip complex (tpip = tetraphenylimidodiphosphinate), which achieved emission at 622 nm with quantum efficiency of 15%.¹⁶ In the same

year, we employed 2,2-bipyridine as the ancillary ligand to synthesize $\text{Ir}(\text{tfmpiq})_2\text{bipy}$ complex, which exhibited a maximum emission peak at 594 nm with quantum yield of 14%.¹⁷ Recently, in 2016, S. Aoki group reported tris-cyclometalated iridium complex, $\text{Ir}(\text{tfpiq})_3$, which displayed red phosphorescence at 600 nm with quantum yield of 25%.¹⁸

However, these conventional ancillary ligands used in tfmpiq -based iridium (III) complexes didn't show significantly red-shift with high quantum efficiencies. Thus, we wanted to attempt other types of ancillary ligands for $\text{Ir}(\text{tfmpiq})_2(\text{LX})$ complexes, aiming to increase quantum efficiencies and further reduce the energy gap to reach to longer wavelength region. Our group previously reported four btp-based deep-red phosphorescent iridium(III) complexes with different ancillary ligands.¹⁹ Among them, the Ir(III) complex with the picolinic acid as ancillary ligand could achieve a more red-shift relative to ones with N^N ancillary ligands. The N^O-type ancillary ligand containing –OH group could dramatically raise the highest occupied molecular orbital (HOMO) level and lead to a narrow HOMO-LUMO energy gap. Unfortunately, the quantum yield is very low (12%), as results of the fluorine-free main ligands in $[\text{Ir}(\text{btq})_2\text{pic}]$ complex.

Herein, we chose fluorinated 1-phenylisoquinoline (tfmpiq) as the cyclometalated ligand and N^O-type ligand (imdzp / idzpo) as the ancillary ligand to synthesize two iridium(III) complexes (Scheme 1). Their photophysical and electrochemical properties are investigated, and the lowest-energy electronic transitions and the lowest-lying triplet excited state are calculated with density functional theory (DFT) and time-dependent DFT (TD-DFT).

2. Experimental

2.1. Materials and Instrumentations

$\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Energy Chemical and all reagents were used without further purification unless otherwise stated. All solvents were dried using standard procedures. Solvents used for electrochemistry and spectroscopy were spectroscopic grade. The target ligands, 1-(4-(trifluoromethyl)phenyl)isoquinoline (**1**),²⁰ 2-(imidazo[1,2-a]pyridin-2-yl)phenol (**a**)²¹ and 2-(2H-indazol-2-yl)phenol (**b**)²² were prepared according to the literature procedures.

¹H NMR spectra were recorded on a Bruker AM 400 MHz instrument. Chemical shifts were reported in ppm relative to Me_4Si as internal standard. MALDI-TOF-MS spectra were recorded on a Bruker Autoflex^{II} TM TOF/TOF instrument. Elemental analyses were performed on a Vario EL Cube Analyzer system. UV-vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F-7000 spectrophotometer in deaerated CH_2Cl_2 solutions at 298 K and 77 K.

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 $n\text{-Bu}_4\text{NClO}_4$ as the supporting electrolyte.

2.2. Synthesis of $(\text{tfmpiq})_2\text{Ir}(\text{imdzp})$ (**2a**)

A mixture of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ (295 mg, 0.84 mmol) and the 1-(4-(trifluoromethyl)phenyl)isoquinoline (500 mg,

Scheme 1. Synthetic routes of Ir(III) complexes **2a–2b**.

1.82 mmol) in 15 mL of 2-ethoxyethanol and H₂O (v:v = 2:1) was heated at 120 °C under nitrogen for 12 hours. Upon cooling to room temperature, the orange-red precipitate was collected by filtration and washed with cooled ether and MeOH. After drying, the crude product of chloro-bridged dimer complex [(tfmpiq)₂Ir(μ-Cl)]₂ was used directly in next step without further purification. Then a slurry of the crude chloro-bridged dimer (100 mg, 0.065 mmol), 2-(imidazo[1,2-a]pyridin-2-yl)phenol (35 mg, 0.16 mmol) and Na₂CO₃ (55 mg, 0.52 mmol) in 2-ethoxyethanol (10 mL) was heated at 120 °C under nitrogen for 10 hours. After the solvent was removed, the mixture was poured into water and extracted with CH₂Cl₂ three times, and then evaporated. The residue was purified by flash column chromatography (petroleum ether : dichloromethane = 5:1~1:1) to afford the iridium complex **2a** as a red solid (55 mg, yield: 45%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.95 (d, *J* = 8.0 Hz, 1H), 8.92 (d, *J* = 6.4 Hz, 1H), 8.78 (d, *J* = 4.8 Hz, 2H), 8.29 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.81–7.92 (m, 10H), 7.71–7.75 (m, 3H), 7.38–7.40 (m, 2H), 7.18 (d, *J* = 4.8 Hz, 2H), 7.08–7.10 (m, 2H), 6.61 (d, *J* = 6.4 Hz, 1H), 6.21 (s, 1H). MALDI-TOF calcd for C₄₅H₂₇F₆IrN₄O: 946.172 ([M+H]⁺). Found: 946.504. Anal. Calcd. for C₄₅H₂₇F₆IrN₄O: C 57.14, H 2.88, N 5.92. Found: C 57.10, H 2.97, N 5.89.

2. 3. Synthesis of (tfmpiq)₂Ir(idzpo) (**2b**)

Complex **2b** (52 mg, yield: 46%) was obtained by the method similar to the preparation of **2a** using 2-(2H-indazol-2-yl)phenol instead of 2-(imidazo[1,2-a]pyridin-2-yl)phenol. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 9.01 (d, *J* = 8.4 Hz, 1H), 8.87 (d, *J* = 6.4 Hz, 1H), 8.84 (d, *J* = 8.4 Hz, 1H), 8.49–8.51 (m, 2H), 8.25 (d, *J* = 6.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.87–8.89 (m, 1H), 7.67–7.83 (m, 5H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 6.4 Hz, 1H), 7.30 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H), 7.13–7.15 (m, 2H), 7.04–7.09 (m, 2H), 6.85–6.88 (m, 1H), 6.69–6.73 (m, 1H), 6.44–6.48 (m, 1H), 6.32–6.36 (m, 1H), 6.16–6.21 (m, 2H). MALDI-TOF calcd for C₄₅H₂₇F₆IrN₄O: 946.172 ([M+H]⁺). Found: 946.386. Anal. Calcd. for C₄₅H₂₇F₆IrN₄O: C 57.14, H 2.88, N 5.92. Found: C 56.97, H 2.81, N 5.99.

2. 4. Crystallographic Studies

X-ray diffraction data were collected with an Agilent Technologies Gemini A Ultra diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) at room temperature. Data collection and reduction were processed with CrysAlisPro software.²³ The structure was solved and refined using full-matrix least-squares based on *F*² with program SHELXS-97 and SHELXL-97²⁴ within Olex2.²⁵ Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC

1836887 (**2b**). Copies of the data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

2. 5. Computational Method

All calculations were carried out with Gaussian 09 software package.²⁶ The density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed with no symmetry constraints to investigate the optimized geometries and electron configurations with the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid density functional theory.^{27–29} The LANL2DZ basis set was used for the iridium(III), whereas the 6-31G* basis set was adopted for the ligands. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent.^{30,31}

3. Results and Discussion

3. 1. Synthesis and Characterization

Scheme 1 outlines the synthetic routes for iridium complexes **2a–2b** investigated in this work. The main ligand, 1-(4-(trifluoromethyl)phenyl)isoquinoline (tfmpiq), was prepared from the synthesis of 1-chloroisoquinoline and (4-(trifluoromethyl)phenyl)boronic acid according to the literature procedure.²⁰ The two constitutional isomer ligands, 2-(imidazo[1,2-a]pyridin-2-yl)phenol (imdizzo) and 2-(2H-indazol-2-yl)phenol (idzpo), were formed by an Ortoleva–King reaction and a P^{III}/P^V = O redox cycling reaction, respectively.^{21,22} Complexes **2a–2b** were obtained in moderate yields from the above ligands by a conventional two-step reaction. In the first step, a chloro-bridged dimer was formed by the reaction of iridium trichloride hydrate with an excess of main ligand. Then this dimer was cleaved via treatment with ancillary ligand in the presence of Na₂CO₃ to produce the heteroleptic iridium complex. The two complexes were structurally characterized by ¹H NMR spectroscopy, mass spectrometry and elemental analysis.

3. 2. Structural Description

The crystal of **2b** was obtained by slow evaporation of CH₂Cl₂/MeOH solution and the structure was determined through X-ray diffraction analysis (Fig. 1a). The crystallographic data and structure refinement details are listed in Table 1; selected bond lengths and bond angles are collected in Table 2.

As shown in Fig. 1a, the Ir(III) adopts a distorted octahedral geometry with the C[^]N ligands in *cis*-C,C' and *trans*-N,N' configurations. The average distance of Ir–C

Fig. 1. (a) ORTEP view of **2b** with the atom-numbering scheme at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Selected non-covalent contacts of the C–H...O, C–H...F and C–H...N types (dashed red lines). Atoms involved in hydrogen bonds are shown as balls of arbitrary radii. All other atoms and covalent bonds are represented as wires or sticks.

bonds ($\text{Ir}-\text{C}_{\text{av}} = 1.989 \text{ \AA}$) is shorter than that of the Ir–N bonds ($\text{Ir}-\text{N}_{\text{av}} = 2.082 \text{ \AA}$), as reported in other iridium(III) complexes.^{32,33} Notably, bonds between iridium and the N[^]O ligand ($\text{Ir}-\text{N}3 = 2.156 \text{ \AA}$, $\text{Ir}-\text{O}1 = 2.153 \text{ \AA}$) are longer than those between iridium and the C[^]N ligands ($\text{Ir}-\text{C}15 = 1.985 \text{ \AA}$, $\text{Ir}-\text{C}31 = 1.993 \text{ \AA}$, $\text{Ir}-\text{N}1 = 2.040 \text{ \AA}$, $\text{Ir}-\text{N}2 = 2.051 \text{ \AA}$), resulting from strong *trans* influence of the carbon donors.³⁴ The angles of atoms on the para positions of the octahedron range from $171.61(18)^\circ$ to $172.59(17)^\circ$, which are close to straight lines. For comparison, the two C–Ir–N bite angles of the C[^]N ligand are 79.23° and 79.47° , while the N–Ir–O bite angle of the ancillary ligand is 82.78° . This may be due to the rigid effect of the five-membered ring at the metal center.³⁵ In addition, the hydrogen-bonding interactions in the crystal structure are

Table 1. Crystallographic data for complex **2b** · H₂O.

Empirical formula	C ₄₅ H ₂₉ F ₆ IrN ₄ O ₂
M _r (g/mol)	963.92
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	12.5501(5)
<i>b</i> (Å)	18.1261(7)
<i>c</i> (Å)	16.6857(5)
α (°)	90
β (°)	95.252(3)
γ (°)	90
<i>V</i> (Å ³)	3779.8(2)
<i>Z</i>	4
<i>D</i> _{calcd} (Mg/m ³)	1.694
<i>F</i> (000)	1896
Absorption coefficient (mm ^{−1})	3.607
<i>R</i> _{int}	0.0354
GOF (<i>F</i> ²)	1.026
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0378, 0.0796
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0592, 0.0909

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table 2. Selected bond distances (Å) and angles (°) for complex **2b** · H₂O.

Ir1–N1	2.040(4)	Ir1–N3	2.156(4)
Ir1–O1	2.153(4)	Ir1–C31	1.993(5)
Ir1–N2	2.051(4)	Ir1–C15	1.985(5)
N1–Ir1–O1	93.51(15)	C31–Ir1–N2	79.47(19)
N1–Ir1–N2	172.47(17)	C31–Ir1–N3	171.61(18)
O1–Ir1–N3	82.78(15)	C15–Ir1–O1	172.59(17)
C31–Ir1–O1	90.02(17)	C15–Ir1–N3	98.77(17)
C15–Ir1–N1	79.23(19)	C15–Ir1–C31	88.93(19)

Table 3. Hydrogen bonding arrangements for complex **2b** · H₂O (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C1–H1...O1	0.93	2.52	3.075(6)	118
C12–H12...F2	0.93	2.42	2.732(1)	100
C30–H30...N1	0.93	2.58	3.091(6)	115

presented in Fig. 1b and the details are summarized in Table 3. From Fig. 1b, the three selected non-covalent contacts of the C–H...O, C–H...F and C–H...N types are attributed to intramolecular hydrogen bonds, making three five-membered rings, respectively.

3. 3. Electronic Absorption Spectra

The UV-vis absorption spectra of complexes **2a–2b** measured in CH₂Cl₂ solution at room temperature are depicted in Fig. 2, and the data are provided in Table 4. The absorption spectra reveal strong absorption bands below 400 nm, which are assigned to intraligand π – π^* transitions centered on the C[^]N main ligand and the N[^]O ancillary ligand. The weak absorption bands extending from 400 nm to 550 nm are attributed to the metal to ligand ¹MLCT/³MLCT transitions.^{36–38} In comparison

Table 4. Photophysical and electrochemical data of **2a–2b**.

Complex	Absorption ^a λ_{abs} (nm)	Emission $\lambda_{em}^{298\text{ K}}$ (nm) ^a	Emission $\lambda_{em}^{77\text{ K}}$ (nm) ^b	Φ_{em}^c (%)	E_{ox}^a (V)	HOMO ^d (eV)	HOMO ^e (eV)
2a	237, 293, 360, 399, 464	618, 662(sh)	621, 666(sh)	39.9	0.87	–5.67	–4.91
2b	234, 288, 342, 397, 477	628, 670(sh)	630, 680(sh)	51.9	1.05	–5.85	–5.20

^aData were collected from degassed CH₂Cl₂ solutions at 298 K. ^bData were collected from degassed CH₂Cl₂ solutions at 77 K. ^c*fac*-Ir(ppy)₃ as referenced standard (0.4).⁴¹ ^dHOMO energies are deduced from the equation HOMO = –(E_{ox} + 4.8 eV).

^eObtained from theoretical calculations.

Fig. 2. Electronic absorption spectra of **2a–2b** in CH₂Cl₂ at room temperature.

with **2a**, the lowest lying absorption band for complex **2b** is slightly red-shifted, presumably depending on the different N-heterocycle ancillary ligands. This assumption will be proved by electrochemistry analyses and DFT calculations.

3. 4. Emission Properties

Photoluminescence (PL) emission spectra of complexes **2a–2b** in degassed CH₂Cl₂ solution at 298 K and 77 K are displayed in Fig. 3 and the corresponding data are also summarized in Table 4. In both cases, the emission spectra show the broad emission maxima at 618–628 nm together with a shoulder peak at 662–670 nm, which makes them red emitters. For their emission, the excited states are attributed to a mixing of ³MLCT and ³LC state.^{39,40} As seen, the emission band of **2b** is also red-shifted relative to **2a**, in good agreement with absorption analyses. When the temperature is decreased to 77 K, the emission maxima of **2a–2b** are a slightly bathochromic shift compared to the 298 K spectra, as reported in our earlier literature.¹³ Clearly, these complexes exhibit vibronic bands at 77 K, which again demonstrate that their emission states are hybrid states with ³MLCT and ³LC characters.

Phosphorescence relative quantum yields (Φ_{em}) of **2a** and **2b** in dichloromethane solution at room temperature were measured to be 39.9 and 51.9% (Table 4) respectively,

Fig. 3. Normalized emission spectra of **2a–2b** in degassed CH₂Cl₂ solution at 298 K (left) and 77 K (right).

using typical phosphorescent *fac*-Ir(ppy)₃ as a standard ($\Phi_{em} = 0.40$).⁴¹ As expected, complexes **2a–2b** have relatively high quantum yields, due to the effect of fluorinated backbones.^{42,43} Specially, the quantum efficiency of **2b** is larger than that of **2a**. The results manifest nitrogen atoms at 1,2-positions are more effective than 2,8-positions.

3. 5. Theoretical Calculations

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed for complexes **2a–2b** to gain insights into the lowest-energy

electronic transitions. The most representative molecular frontier orbital diagrams for these complexes are presented in Fig. 4. The calculated spin-allowed electronic transitions are provided in Table 5, as well as compared with the experimental absorption spectra data. The electron density distributions are summarized in Table S1.

As shown in Fig. 4, the HOMOs of these complexes are mainly localized on the metal center and the phenyl ring of ancillary ligands, whereas the LUMOs are primarily dominated on the whole C^N ligands. Besides, the HOMO-1 of complex **2a** is located on iridium ion, the cyclometalated ligands and a little part of the ancillary ligands. The theory calculations of DFT reveal that the lowest-energy spin-allowed transitions of **2a–2b** are derived from HOMO/HOMO-1→LUMO and HOMO→LUMO transitions (Table 5), consequently assigned to metal-to-ligand charge transfer transitions and ligand-to-ligand $\pi-\pi^*$ transitions. These calculations support the photophysical properties discussed above.

To gain the origins of emission for complexes **2a–2b**, we also employed the DFT calculations to investigate the triplet excited-state characters. The results of the TD-DFT calculations for the triplet states are listed in Table 6. For both the studied complexes, the two lowest lying triplet states (T_1 and T_2) are predominantly from HOMO→LUMO, HOMO-1→LUMO, HOMO→LUMO+1, HOMO-1→LUMO+1 HOMO-2→LUMO and HOMO-3→LUMO transitions. According to electron density distributions in Table S1, the HOMOs are mainly localized at the ancillary ligands, while LUMOs/LUMO+1s at the C^N ligands. The HOMO-1s/HOMO-2s/HOMO-3s are composed of Ir *d*-orbital, C^N ligands and ancillary ligands. Thereby, both of the two lowest-lying triplet states (T_1 and T_2) have a mixed $^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$ character for the two

Fig. 4. The frontier molecular orbital diagrams of complexes **2a–2b** from DFT calculations.

complexes, except T_2 of **2a** with limited $^3\text{MLCT}$ contribution. The lowest-lying triplet states of **2a** have similar transition paths with those of **2b**, indicating that the different positions of N atoms on ancillary ligands have no obvious effect on emissive behavior.

3. 6. Electrochemical Properties

The electrochemical behaviors of both iridium complexes were investigated by cyclic voltammetry and the electrochemical waves are shown in Fig. 5. The respective electrochemical data and estimated HOMO energy levels are also reported in Table 4. Complexes **2a–2b** exhibit a

Table 5. Major configuration, transition characters, oscillator strength and calculated/experimental absorption wavelengths for **2a–2b**.

Complex		Major Configuration	Transition	Character	Oscillation Strength	Calcd (nm)	Exptl (nm)
2a	S_1	HOMO → LUMO (93%)	LLCT	$\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$	0.0308	576	464
	S_2	HOMO-1 → LUMO (94 %)	MLCT/LC	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}} \rightarrow \pi_{\text{tfmpiq}}^*$	0.0401	501	
2b	S_1	HOMO → LUMO (91%)	MLCT/LLCT	$d\pi_{\text{Ir}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$	0.0641	526	477

Table 6. Contribution of triplet transitions and transition characters for complexes **2a–2b**.

Complex		Major Configuration	Transition	Character
2a	T_1	HOMO → LUMO (57 %)	$^3\text{LLCT}$	$\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
		HOMO-1 → LUMO (26 %)	$^3\text{MLCT}/^3\text{LC}$	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}} \rightarrow \pi_{\text{tfmpiq}}^*$
	T_2	HOMO → LUMO+1 (61%)	$^3\text{LLCT}$	$\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
		HOMO → LUMO (15%)	$^3\text{LLCT}$	$\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
2b	T_1	HOMO → LUMO (31 %)	$^3\text{MLCT}/^3\text{LLCT}$	$d\pi_{\text{Ir}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
		HOMO-1 → LUMO (30%)	$^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
	T_2	HOMO-1 → LUMO+1 (25%)	$^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
		HOMO-2 → LUMO (14%)	$^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$
		HOMO-3 → LUMO (12%)	$^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$	$d\pi_{\text{Ir}}/\pi_{\text{tfmpiq}}/\pi_{\text{imdzppo}} \rightarrow \pi_{\text{tfmpiq}}^*$

Fig. 5. Cyclic voltammograms for complexes **2a–2b** in CH_2Cl_2 solution containing $n\text{-Bu}_4\text{NClO}_4$ (0.1 M) at a sweep rate of 100 mV/s.

quasi-reversible/irreversible oxidation peak (E_{ox}) at 0.87 and 1.05 V, respectively. As inferred from DFT calculations (Table S1), the HOMOs are mainly localized on the Ir ion (13.88 % for **2a**, 24.74 % for **2b**) and ancillary ligands (75.74 % for **2a**, 58.06 % for **2b**). Therefore, the oxidation is assigned to Ir(III) to Ir(IV) with some contribution from ancillary ligand. On the basis of the potentials of the oxidation, the HOMO energy is deduced by the equation $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8 \text{ eV})$,⁴⁴ and the trend is quite consistent with theoretical calculation values (Table 4). As it can be seen from these results, through changes of nitrogen atoms from 2,8-positions to 1,2-positions, the HOMO level of **2b** is more stable and the oxidation process is more difficult than those of analogue **2a**.

4. Conclusions

In conclusion, two red-emitting iridium(III) complexes (**2a–2b**) equipped with tfmpiq cyclometalated ligand and imdzppo/idzpo ancillary ligand, have been successfully synthesized and characterized. Their photophysical properties, electrochemical behaviors and theoretical calculations have been systematically studied. The calculated absorptions of the two complexes **2a–2b** are in full agreement with the experimental data, which indicate that the lowest lying absorptions are assigned to MLCT/LLCT transitions. Both Ir(III) complexes exhibit red phosphorescence in dichloromethane solution at 298 K and at 77 K, and the lowest lying triplet excited states have a mixed $^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$ character. By changing the positions of N atoms in the ancillary ligand, we have confirmed complex **2b** had a further red-shift relative to **2a** in the emission spectra. These research results will facilitate the design of new piq-based ligands for red-emitting iridium complexes.

5. Acknowledgments

This work was supported by the Natural Science Foundation of Hainan Province (218QN236, 219MS043, 217115), the 2018 National Innovation Experiment Program for University Students and Program for Innovative Research Team in University (IRT-16R19).

References

- Y. S. Li, J. L. Liao, K. T. Lin, W. Y. Hung, S. H. Liu, G. H. Lee, P. T. Chou, Y. Chi, *Inorg. Chem.* **2017**, *56*, 10054–10060. DOI:10.1021/acs.inorgchem.7b01583
- R. D. Costa, E. Orti, H. J. Bolink, F. Monti, G. Accorsi, N. Armaroli, *Angew. Chem. Int. Ed.* **2012**, *51*, 8178–8211. DOI:10.1002/anie.201201471
- B. W. D'Andrade, S. R. Forrest, *Adv. Mater.* **2004**, *16*, 1585–1595. DOI:10.1002/adma.200400684
- C. H. Fan, P. Sun, T. H. Su, C. H. Cheng, *Adv. Mater.* **2011**, *23*, 2981–2985. DOI:10.1002/adma.201100610
- C. H. Chen, L. C. Hsu, P. Rajamalli, Y. W. Chang, F. I. Wu, C. Y. Liao, M. J. Chiu, P. Y. Chou, M. J. Huang, L. K. Chu, C. H. Cheng, *J. Mater. Chem. C* **2014**, *2*, 6183–6191. DOI:10.1039/C4TC00523F
- J. Qiao, L. Duan, L. T. Tang, L. He, L. D. Wang, Y. Qiu, *J. Mater. Chem.* **2009**, *19*, 6573–6580. DOI:10.1039/b906675f
- S. C. Lo, E. B. Namdas, P. L. Burn, I. D. W. Samuel, *Macromolecules* **2003**, *36*, 9721–9730. DOI:10.1021/ma030383w
- C. T. Chen, *Chem. Mater.* **2004**, *16*, 4389–4400. DOI:10.1021/cm049679m
- A. Tsuboyama, H. Iwawaki, M. Furugori, T. Mukaide, J. Kamatani, S. Igawa, T. Moriyama, S. Miura, T. Takiguchi, S. Okada, M. Hoshino, K. Ueno, *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979. DOI:10.1021/ja034732d
- Y. J. Su, H. L. Huang, C. L. Li, C. H. Chien, Y. T. Tao, P. T. Chou, S. Datta, R. S. Liu, *Adv. Mater.* **2003**, *15*, 884–888. DOI:10.1002/adma.200304630
- C. L. Li, Y. J. Su, Y. T. Tao, P. T. Chou, C. H. Chien, C. C. Cheng, R. S. Liu, *Adv. Funct. Mater.* **2005**, *15*, 387–395. DOI:10.1002/adfm.200305100
- S. Huo, J. C. Deaton, M. Rajeswaran, W. C. Lenhart, *Inorg. Chem.* **2006**, *45*, 3155–3157. DOI:10.1021/ic060089v
- G. N. Li, S. B. Dou, T. Zheng, X. Q. Chen, X. H. Yang, S. Wang, W. Sun, G. Y. Chen, Z. R. Mo, Z. G. Niu, *Organometallics* **2018**, *37*, 78–86. DOI:10.1021/acs.organomet.7b00740
- F. Babudri, G. M. Farinola, F. Naso, R. Ragni, *Chem. Commun.* **2007**, *0*, 1003–1022. DOI:10.1039/B611336B
- K. H. Fang, L. L. Wu, Y. T. Huang, C. H. Yang, I. W. Sun, *Inorg. Chim. Acta* **2006**, *359*, 441–450. DOI:10.1016/j.ica.2005.10.003
- S. Zhang, L. S. Xue, C. Wu, Y. X. Zheng, J. L. Zuo, *Chin. J. Inorg. Chem.* **2014**, *30*, 134–141. DOI: 10.11862/CJIC.2014.073
- Z. G. Niu, D. Liu, J. Zuo, Y. Zou, J. M. Yang, Y. H. Su, Y. D. Yang, G. N. Li, *Inorg. Chem. Commun.* **2014**, *43*, 146–150. DOI:10.1016/j.inoche.2014.02.031

18. Y. Tamura, Y. Hisamatsu, S. Kumar, T. Itoh, K. Sato, R. Kuroda, S. Aoki, *Inorg. Chem.* **2017**, *56*, 812–833. DOI:10.1021/acs.inorgchem.6b02270
19. G. N. Li, Y. Zou, Y. D. Yang, J. Liang, F. Cui, T. Zheng, H. Xie, Z. G. Niu, *J. Fluoresc.* **2014**, *24*, 1545–1552. DOI:10.1007/s10895-014-1443-7
20. H. H. Rhoa, Y. H. Parkb, Y. H. Leeb, N. G. Parkc, Y. Had, Y. S. Kimd, *Mol. Cryst. Liq. Cryst.* **2006**, *444*, 145–155. DOI:10.1080/15421400500365326
21. A. J. Stasyuk, M. Banasiewicz, M. K. Cyrański, D. T. Gryko, *J. Org. Chem.* **2012**, *77*, 5552–5558. DOI:10.1021/jo300643w
22. T. V. Nykaza, T. S. Harrison, A. Ghosh, R. A. Putnik, A. T. Radosevich, *J. Am. Chem. Soc.* **2017**, *139*, 6839–6842. DOI:10.1021/jacs.7b03260
23. CrysAlisPro Version 1.171.36.21; Agilent Technologies Inc., Santa Clara, CA, USA, 2012.
24. G. M. Sheldrick, *Acta Cryst. A* **2008**, *64*, 112–122. DOI:10.1107/S0108767307043930
25. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341. DOI:10.1107/S0021889808042726
26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 09, Revision A.01, Gaussian, Inc. Wallingford, CT, **2009**.
27. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789. DOI:10.1103/PhysRevB.37.785
28. B. Miehlisch, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200–206. DOI:10.1016/0009-2614(89)87234-3
29. A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652. DOI:10.1063/1.464913
30. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681. DOI:10.1002/jcc.10189
31. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3093. DOI:10.1021/cr9904009
32. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, *Inorg. Chem.* **2001**, *40*, 1704–1711. DOI:10.1021/ic0008969
33. A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377–7387. DOI:10.1021/ja034537z
34. K. K. W. Lo, C. K. Chung, N. Y. Zhu, *Chem. Eur. J.* **2003**, *9*, 475–483. DOI:10.1002/chem.200390050
35. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* **2001**, *40*, 1704–1711. DOI:10.1021/ic0008969
36. C. H. Yang, J. Beltran, V. Lemaure, J. Cornil, D. Hartmann, W. Sarfert, R. Fröhlich, C. Bizzarri, C. L. De, *Inorg. Chem.* **2010**, *49*, 9891–9901. DOI:10.1021/ic1009253
37. F. Monti, F. Kessler, M. Delgado, J. Frey, F. Bazzanini, G. Accorsi, N. Armaroli, H. J. Bolink, E. Ortí, R. Scopelliti, M. K. Nazzeeruddin, E. Baranoff, *Inorg. Chem.* **2013**, *52*, 10292–10305. DOI:10.1021/ic400600d
38. T. Y. Li, X. Liang, L. Zhou, C. Wu, S. Zhang, X. Liu, G. Z. Lu, L. S. Xue, Y. X. Zheng, J. L. Zuo, *Inorg. Chem.* **2015**, *54*, 161–173. DOI:10.1021/ic501949h
39. S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukaide, J. Kamatani, S. Igawa, A. Tsuboyama, T. Takiguchi, K. Ueno, *Dalton Trans.* **2005**, *9*, 1583–1590. DOI:10.1039/b417058j
40. Z. G. Niu, T. Zheng, Y. H. Su, P. J. Wang, X. Y. Li, F. Cui, J. Liang, G. N. Li, *New J. Chem.* **2015**, *39*, 6025–6033. DOI:10.1039/C5NJ00975H
41. K. A. King, P. J. Spellane, R. J. Watts, *J. Am. Chem. Soc.* **1985**, *107*, 1431–1432. DOI:10.1021/ja00291a064
42. C. L. Ho, W. Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, *Adv. Funct. Mater.* **2008**, *18*, 928–937. DOI:10.1002/adfm.200701115
43. Y. Wang, N. Herron, V. V. Grushin, D. LeCloux, V. Petrov, *Appl. Phys. Lett.* **2001**, *79*, 449. DOI:10.1063/1.1384903
44. W. Lee, T. H. Kwon, J. Kwon, J. Y. Kim, C. Lee, J. I. Hong, *New J. Chem.* **2011**, *35*, 2557–2563. DOI:10.1039/c1nj20446g

Povzetek

Sintetizirali smo dva nova bis-ciklometalirana iridijeva(III) kompleksa s tfmpiq ligandom, $[(\text{tfmpiq})_2\text{Ir}(\text{imdizzo})]$ (**2a**) in $[(\text{tfmpiq})_2\text{Ir}(\text{idzpo})]$ (**2b**) (tfmpiq = 1-(4-(trifluorometil)fenil)izokinolin, imdizzo = 2-(imidazo[1,2-a]piridin-2-il) fenol, idzpo = 2-(2*H*-indazol-2-il)fenol), in ju okarakterizirali. Določili smo monokristalno strukturo **2b**. Določili smo razmerje med strukturo in fotofizikalnimi lastnostmi obeh kompleksov podprto tudi z DFT izračuni. Ir(III) kompleksa emitirata rdečo svetlobo s kvantnim izkoristkom 39.9–51.9 % v degaziranem CH_2Cl_2 pri sobni temperaturi. Emisija izvira iz hibridnega $^3\text{MLCT}/^3\text{LLCT}/^3\text{LC}$ vzbujenega stanja. Vsi ti rezultati kažejo, da sta iridijeva(III) kompleksa **2a-2b** primerna kot rdeča fosforescentna materiala v OLED.

Except when otherwise noted, articles in this journal are published under the terms and conditions of the Creative Commons Attribution 4.0 International License