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Four new cyclometalated phenylisoquinoline-based Ir(III) complexes: Syntheses, structures, properties and DFT calculations



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ABSTRACT

Four new cyclometalated phenylisoquinoline-based iridium(III) complexes $[Ir(C^N)_2(bipy)]PF_6$ (**5a-5d**) (bipy = 2,2'-bipyridine) have been synthesized and fully characterized, where the C^N ligands are 1-(4-(trifluoromethyl) phenyl)isoquinoline, 4-(isoquinolin-1-yl)benzaldehyde, 4-(isoquinolin-1-yl)benzonitrile and 1-(3-fluoro-4-methylphenyl)isoquinoline, respectively. The crystal structures of **5a** and **5c** have been determined. The photophysical and electrochemical properties of these new complexes **5a-5d** have been studied. All Ir(III) complexes exhibit orange phosphorescence in dichloromethane solution at room temperature with a maximum at 593–618 nm, quantum yield of 0.046–0.16. The frontier molecular orbital diagrams and the lowest-energy electronic transitions of **5a–5d** have been calculated with density functional theory (DFT) and time-dependent DFT (TD-DFT).

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Currently, a considerable amount of interests have been drawn to the application of iridium(III) complexes in organic light-emitting devices (OLEDs), as they have high phosphorescence quantum efficiency, long excited-state lifetime and excellent color tunability [1-3]. In general, the structure and even the position of the substituents on the ligand framework play important roles in tuning the photophysical properties of Ir(III) complexes [4,5]. Meanwhile, substantial researches on iridium complexes have showed that the introduction of a strongly electronwithdrawing group in the cyclometalating ligand could eventually cause a great increase of the luminescence efficiency [6,7]. These results prompted us to systematically study the effects on emissive colors and quantum efficiencies of different electron-withdrawing substituents on cyclometalating ligand. Therefore, we chose 1-phenylisoquinoline (piq) as the cyclometalated ligand with electron-withdrawing substituents $(-CF_3, -CHO, -CN \text{ and } -F)$ to synthesize a series of ionic iridium(III) complexes 5a-5d. The photophysical and electrochemical properties of these complexes were investigated, and the lowestenergy electronic transitions were analyzed based on density functional theory (DFT) and time-dependent DFT (TDDFT).

The C^N ligands 4-(isoquinolin-1-yl)benzaldehyde (**3b**) and 1-(3fluoro-4-methylphenyl)isoquinoline (**3d**) were both synthesized by the suzuki reaction between 1-chloroisoquinoline and 1.1 equivalents of substituted phenylboronic acids [8]. The other two C^N ligands 1-(4-(trifluoromethyl)phenyl)isoquinoline (**3a**) and 4-(isoquinolin-1yl)benzonitrile (**3c**) were prepared according to the literature procedure [9,10]. The reaction of **3a–3d** with iridium trichloride hydrate yielded four new precursors [(C^N)₂Ir(μ -Cl)]₂ (**4a–4d**). The corresponding iridium(III) complexes (**5a–5d**, Scheme 1) were then produced by the reaction of **4a–4d** with the N^N ligand 2,2'-bipyridine [11]. Characterization of all these new compounds has been accomplished by ¹H NMR and mass spectroscopies. In ¹H NMR spectra of **5a–5d**, the ratio of the C^N to N^N ligands is 2:1, which suggests that the chemical formula of each Ir(III) complex is [(C^N)₂Ir(N^N)](PF₆).

The structures of complexes **5a** and **5c** were determined at room temperature [12]. As shown in Fig. 1, the Ir(III) ion in each cationic complex is in a distorted octahedral $[(C^N)_2 Ir(N^N)]^+$ coordination geometry with the C and N atoms of two phenylisoquinoline-based (C^N) ligands and the N atoms of bipyridine (N^N) ligand. The average distances of Ir – N (2.108 Å for **5a**, 2.097 Å for **5c**) and Ir – C (2.003 Å for **5a**, 2.000 Å for **5c**) are typical for this type of complexes [13,14]. In particular, the Ir – N bond lengths from N^N ligands are shorter than those from C^N ligands. Also, the two N atoms of the C^N ligands are transposition to each other. The X-ray data show a large torsion angle for complex **5a** [C8–C9–C10–C16, -14.70°], which suggest that the $-CF_3$

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Scheme 1. Synthetic routes of C^N ligands 3a-3d and Ir(III) complexes 5a-5d.

group can cause larger molecular deformation. However, the torsion angle [C8–C9–C11–C12] of complex **5c** with – CN group is only 0.63°, indicating that the 4-(isoquinolin-1-yl)benzonitrile ligand is almost coplanar.

The absorption spectra of complexes **5a–5d** in CH₂Cl₂ solution are presented in Fig. 2 and the spectral data are summarized in Table 1. In common with most Ir(III) complexes [15–17], the absorption spectra of **5a–5d** are dominated by multiple bands originating from ligand-centered π – π * transitions and MLCT transitions. The strong absorption bands of the higher energies (below 350 nm) are mainly assigned to the spin-allowed intraligand ¹(π – π *) transitions [18]. The moderate absorption peaks of lower-energies (350–550 nm) are likely due to charge-transfer (CT) transitions, with their nature being both spin-allowed (singlet-to-singlet metal-to-ligand charge transfer, ¹MLCT) [19] and spin-forbidden (singlet-to-triplet metal-to-ligand charge transfer, ³MLCT and ligand-centered ³ π – π * transition) [20].

Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations have been performed for complexes **5a–5d** to gain insights into the lowest-energy electronic transition (435 nm for **5a**, 456 nm for **5b**, 442 nm for **5c**, 434 nm for **5d**). The representative molecular frontier orbital diagrams have been presented in Fig. 3 and the calculated spin-allowed electronic transitions and electron density distributions are listed in Tables S1 and S2. The electron density in the HOMO/HOMO-1 of all the complexes **5a–5d** resides significantly on the cyclometalating ligands and the core Ir(III) atom. The electron density in LUMO + 1 (**5a**) and LUMO + 2 (**5c**) locates mainly on the cyclometalating ligand. All these electronic transitions are ascribed as LLCT and MLCT $\pi \to \pi^*$ transition, which are consistent with the actual absorptions.

All complexes are luminescent at room temperature in CH_2Cl_2 solution (Fig. 4). Upon photoexcitation at ca. 360 nm, the complexes **5a–5d** show intense orange luminescence with the emission peak appeared at 593–618 nm, and display the wavelength order as **5b** > **5c** > **5a** > **5d** (Table 1). The results are in good agreement with those of the lowestenergy electronic transition in UV–Vis spectra and DFT calculations (Table S1). As compared with **5b** and **5c**, **5a** and **5d** exhibit the blueshifted emission spectra, which can be explained by steric hindrance of 4-CF₃, 4-Me and 3-F group. According to analogous iridium(III) cyclometalates reported in references [21,22], the photoluminescence spectra of **5a–5d** display the vibronically structured emission bands arose from a mixture of ${}^{3}LC ({}^{3}\pi-\pi^{*})$ and ${}^{3}CT ({}^{3}MLCT)$ excited states.

Phosphorescence relative quantum yields (Φ) of **5a–5d** in dichloromethane solution were measured to be 0.046–0.16 (Table 1) at room temperature by using typical phosphorescent *fac*-Ir(ppy)₃ as a standard ($\Phi = 0.40$) [4,23]. Compared with the parent complex [Ir(piq)₂(bpy)](PF₆) ($\Phi = 0.089$) [24], the introduction of the C–F bond or – CF₃ group in complexes **5b** and **5d** results in the increase of the luminescence quantum yield dramatically. This is probably due to the presence of the C–F bonds that could reduce the radiationless deactivation rate in comparison with C–H bonds [6,25]. Additionally, the electron-withdrawing substituents (–CHO and –CN) in the same site of the ligand lead to a decrease in the phosphorescence quantum yield for complexes **5a** and **5c**.

The electrochemical properties of the complexes **5a–5d** were studied by cyclic voltammetry (Fig. 5). All complexes show a pair of reversible redox peaks, with potentials of 1.27–1.65 V. The positive oxidation potential is attributed to the metal-centered Ir^{3+}/Ir^{4+} oxidation couple [26,27], because the higher oxidation potentials are ascribed to the stronger electron-withdrawing ability of the substituent on phenylisoquinoline ligands. Based on the electrochemical data, the complexes can be arranged in the increasing order as follows: **5c** > **5a** > **5b** > **5d**, which is consistent with the actual electron-withdrawing ability of $-CN > -CF_3 > -CHO > -F$. The HOMO energy deduced by the equation $E_{HOMO} = -(E_{ox} + 4.8 \text{ eV})$ [28] is listed in Table 1, as well as compared with the theoretical calculation results. From the results, it can be seen that the HOMO orbital energy also reveals the order as **5c** > **5a** > **5d**.

In conclusion, four new cyclometalated phenylisoquinoline-based iridium(III) complexes $[Ir(C^N)_2(N^N)]PF_6$ (**5a–5d**) with the N^N ligand 2,2'-bipyridine and four different C^N cyclometalating ligands have been synthesized. The photophysical properties, electrochemical behaviors and theoretical calculations have been investigated. X-ray diffraction studies of complexes **5a** and **5c** indicate that the coordinations of the iridium atoms are both distorted octahedral. Analyses of DFT and TDDFT calculations for **5a–5d** indicate that the lowest-energy electronic transitions are attributed to MLCT and LLCT $\pi \rightarrow \pi^*$ transition. Each Ir(III) complex shows orange emission with a maximum main peak and a shoulder peak, which is suggested to be a mixture of ³LC (³ π – π^*) and ³CT (³MLCT) excited states. The results will facilitate the



Fig. 1. ORTEP view of complexes **5a** (top) and **5c** (bottom) with an atom-numbering scheme at the 50% probability level. Hydrogen atoms, solvent molecules and PF_6 anion are omitted for clarity.



Fig. 2. Electronic absorption spectra of 5a-5d in CH₂Cl₂ at room temperature.

Table 1

Photonhysical	and e	electrochemical	data for	complexes	5a-5d
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Complex	Absorption λ_{abs} (nm)	Emission λ_{em} (nm)	$\Phi_{\rm em}{}^{\rm a}$	E _{ox} (eV)	HOMO ^b (eV)	HOMO ^c (eV)
5a	285, 341, 356, 379, 435	594	0.14	1.63	-6.43	-6.044
5b	294, 345, 360, 398, 456	618	0.046	1.54	-6.34	-6.043
5c	288, 343, 359, 384, 442	604	0.074	1.65	-6.45	-6.177
5d	293, 345, 357, 374, 434	593	0.16	1.37	-6.17	-5.266

^a fac-Ir(ppy)₃ as referenced standard (0.4) [4,23].

 $P HOMO = -(E_{ox} + 4.8 \text{ eV}).$

^c Obtained from theoretical calculations.

design of new phenylisoquinoline-based ligands for light-emitting iridium complexes.

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Appendix A. Supplementary material

CCDC 962809 and 962810 contain the supplementary crystallographic data of **5a** and **5c**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. Other supplementary data associated with this article: Crystallographic data for **5a** and **5c** in CIF format. Calculated spin-allowed electronic transitions and electron density distributions for **5a–5d**. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche. 2014.02.031.

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Fig. 3. The frontier molecular orbital diagrams of complexes 5a-5d from DFT calculations.

 $(M\,+\,1);$ Synthesis of 3d: 3d was obtained by a method similar to the preparation of 3b. Yield: 86%. 1H NMR (400 MHz, CDCl3) δ 8.59 (d, J = 5.2 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.63 7.69 (m, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.32 7.39 (m, 3H), 2.38 (s, 3H). MS-ESI: m/z calculated: 237.1.2; found: 238.1 (M+).

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Fig. 4. Normalized emission spectra of 5a-5d in CH₂Cl₂ at room temperature.



Fig. 5. Cyclic voltammograms of 5a-5d measured in CH₃CN solution containing $n-Bu_4NCIO_4$ (0.1 M). The scan rate was 100 mV/s.

(d, J = 8.0 Hz, 2H), 8.77 (d, J = 8.0 Hz, 2H), 8.38 (d, J = 7.6 Hz, 2H), 8.19 (t, J = 7.6 Hz, 2H), 7.95 ~ 7.98 (m, 2H), 7.82 ~ 7.86 (m, 4H), 7.76 (d, J = 5.6 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.37 ~ 7.45 (m, 6H), 6.43 (s, 2H). MS-ESI: m/z calculated: 893.2; found: 893.3 (M⁺); Synthesis of **5b**: **5b** was obtained by a method similar to the preparation of **5a**, Yield 62%. ¹H NMR (400 MHz, CDCl₃) δ 9.64 (s, 2H), 8.93 (d, J = 7.2 Hz, 2H), 8.71 (d, J = 7.6 Hz, 2H), 8.46 (d, J = 7.6 Hz, 8.46 (d, J = 7.68.4 Hz, 2H), 8.14 ~ 8.18 (m, 2H), 7.97 (t, J = 6.4 Hz, 2H), 7.80 ~ 7.86 (m, 6H), 7.62 (t, J = 8.0 Hz, 2H), 7.39 ~ 7.54 (m, 6H), 6.75 (s, 2H). MS-ESI: m/z calculated: 813.2; found: 813.3 (M⁺); Synthesis of 5c: 5c was obtained by a method similar to the preparation of **5a**, Yield 78%. ¹H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, J =5.6 Hz, 2H), 8.76 (d, J = 8.8 Hz, 2H), 8.41 (d, J = 7.2 Hz, 2H), 8.20 (t, J = 8.0 Hz, 2H), 7.86 (d, J = 4.8 Hz, 2H), 8.41 (d, J = 7.2 Hz, 2H), 8.20 (t, J = 8.0 Hz, 2H), 7.87 ~ 7.89 (m, 4H), 7.76 (d, J = 4.8 Hz, 2H), 7.54 (d, J = 6.4 Hz, 2H), 7.42 ~ 7.46 (m, 6H), 6.51 (s, 2H). MS-ESI: m/z calculated: 807.2; found: 807.3 (M⁺); Synthesis of 5d: 5d was obtained by a method similar to the preparation of 5a, Yield: 54%. ¹H NMR (400 MHz, CDCl₃) δ 8.85 ~ 8.92 (m, 2H), 8.71 (t, J = 8.0 Hz, 1H), 8.12 ~ 8.18 (m, 2H), 8.08 (d, J = 9.2 Hz, 1H), 8.00 ~ 8.04 (m, 1H), 7.89 ~ 7.94 (m, 2H), 7.73 ~ 7.83 (m, 6H), 7.33 ~ 7.43 (m, 4H), 7.20 ~ 7.28 (m, 3H), 6.99 ~ 7.03 (m, 1H), 5.99 ~ 6.01 (m, 1H), 1.99 ~ 2.08 (m, 6H). MS-ESI: m/z calculated: 821.2; found: 821.3 (M⁺).

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