

Short communication

Synthesis, structural characterization, opto-electrical properties of Ir(III) complexes with imidazolium-based carbene ligands

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ABSTRACT

A series of Ir(III) complexes with N-heterocyclic carbenes (NHC) ligands (**1–3**) were synthesized and characterized. The opto-electrical properties of these complexes were investigated spectroscopically, electrochemically and theoretically. All complexes exhibit ligand-based $^1\pi,\pi^*$ transitions in the UV region, $^1\text{MLCT}$ absorption in the UV region, and weak low energy $^3\pi,\pi^*$ transition in visible region. These complexes all exhibit blue phosphorescence at both room temperature and 77 K, which is dominated by $^3\pi,\pi^*$ character. DFT calculation results indicate their lowest unoccupied molecular orbitals (LUMO) from -0.47 to -0.33 eV and the highest occupied molecular orbitals (HOMO) from -4.97 to -5.33 eV. The opto-electrical properties can be influenced drastically by NHC ligands, which would be useful for rational design of optical functional materials.

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Cyclometalated Ir(III) complexes have received considerable attention in the past decade, due to their high phosphorescence quantum efficiencies and applications in phosphorescent organic light-emitting devices (PhOLEDs) [1–5], biological-labeling reagents [6], low-power upconversion [7–8], photocatalysts [9–11] and nonlinear optics [12–13]. These applications are intrinsically based on their rich photochemical and photophysical properties. Their high emission efficiency is caused by strong spin-orbital coupling of Ir center, which leads to the mixed singlet and triplet excited states, “spin-forbidden” triplet states for photon emission, and creates the possibility of full utilization of both the singlet and triplet excitons [14]. In addition, their photophysical properties, especially emission wavelength and excited-state lifetime, can be tuned by changing cyclometalated ligands to meet the different requirements for diverse applications [15].

By structural modifications of the employed cyclometalated ligands, the emission colors of Ir complexes can be readily tuned from blue to red [16]. However, the preparation of blue light-emitting complexes, especially the deep blue emitters suitable for fabrication of stable PhOLEDs are much more difficult to achieve than the red and green ones [17]. For the most common blue phosphor, vacuum deposition and decomplexation cause degradation over a short period of running, leaving the blue pixels with a much shorter lifetime than both the red and green [18–20]. On the other hand, for the necessity of having a high triplet energy to yield blue colour, problems may arise with finding a host material with a triplet energy

higher than that of the emitter but which can also act as a good transport material for electrons and holes [21–25]. In this context, design and synthesis of cyclometalated Ir(III) complexes with blue light-emitting and stable optical properties still remain a major challenge.

N-heterocyclic carbenes (NHCs) have been the subject of significant study as good σ -donating neutral ligands in organometallic and coordination chemistry. The carbene moiety is a two electron donor ligand, which makes the cyclometalated ligand a bidentate monoanionic ligand ($C^{\wedge}C$ ligand), similar to the cyclometalating ligands ($C^{\wedge}N$ ligand) that have been used to make stable Ir trischelates [26]. The NHC ligands also form more strong bonds with transition metals [27], which imparts to the complexes an adequate balance between stability and activity. Their tunable character also allows the control of the steric and electronic properties on the metal center. Compared with other reported complexes [28–29], the Ir(III) complexes bearing NHC ligands are easy to be modified and proved an efficient way to achieve blue emitters. Furthermore, with the σ -donating neutral NHC ligands, Ir(III) complexes usually exhibit high triplet energy gaps and could be potentially utilized as blue emitters for OLEDs and electrochemical cells.

Early in 2005, Sajoto and co-workers [30] reported a series of triscyclometalated Ir(III) complexes with NHC ligands, which display efficient blue to near-UV luminescence at room temperature (RT), and stronger *trans* influence than pyrazolyl based Ir(III) complexes. Venkatesan group [31] synthesized a series of bis-N-heterocyclic carbene Pt(II) bis-arylacetylide complexes, which exhibit triplet intraligand (^3IL) based phosphorescence with metal-to-ligand charge-transfer (MLCT) characters. Kido group [32] also reported a blue cyclometalated Ir carbene complex, which is a promising candidates

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for OLED device with a high $\eta_{p,max}$ of 35.9 lm W^{-1} (28.6 cd A^{-1} , EQE 18.6%). In addition, another research effort in the area of NHC complexes originated from the desire of developing highly active, phosphine-free catalysts [33–34]. Jiménez and co-workers [35] reported a series of Ir complexes based on hemilabile O-donor- and N-donor-functionalized NHC ligands, which are efficient precatalysts for the transfer hydrogenation of cyclohexanone in 2-propanol/KOH. Although many of these previous studies are intriguing, reports on the photophysical, electrochemical and crystal structural properties of Ir(III) complexes with NHC ligands are still limited. By introducing different designed NHC ligands to Ir(III) complexes, we envision to blue-shift their low-energy absorption and emission bands, affording new optical functional materials.

In this work, we designed and synthesized three NHC Ir(III) complexes with different aryl substituents on the phenyl component (**1–3**, Chart 1). Their behavior is noteworthy with regards to the use of similar derivatives as phosphorescent dopants in application of OLEDs [36–38]. The detailed structural characterization, electrochemical and photophysical properties of these complexes were systematically investigated with the aim of understanding the structure-property correlations and developing novel functional materials, such as blue phosphorescent emitters and nonlinear optical materials.

Fig. 1 shows an ORTEP view of the crystal structures of complexes **1** and **2**. The crystallographic data, selected bond lengths and angles are listed in Table S1 and Table S2, respectively. Both of the two complexes have the three cyclometalating ligands in an octahedral coordination geometry around the Ir center. The Ir–C and Ir–C_{carbene} bond lengths for the two structures are statistically equivalent. The average Ir–C (2.072 (10) Å) and Ir–C_{carbene} (2.008 (10) Å) bond lengths of **1** are within one sigma of the corresponding averages for **2** (average Ir–C = 2.087 (7) Å, average Ir–C_{carbene} = 2.040 (7) Å). The structural data suggests a nearly identical coordination environment around the Ir center for the two complexes, and thus, both are expected to have ligand field states with similar energies. Moreover, the bond length of Ir–C_{carbene} is much shorter than that of the Ir–N bond in similar Ir complex. Compared with complex Ir(ppz)₃ (ppz = 1-phenylpyrazolyl-*N,C'*) with average Ir–N of 2.124(5) Å [28], the Ir–C_{carbene} distance in **1** and **2** (2.008 (10) Å and 2.040 (7) Å) is significantly shorter than the average Ir–N distance in Ir(ppz)₃ (2.124(5) Å). The resulting larger ligand field strength would further destabilize the metal-centered *d-d* excited states, which could become thermally inaccessible from the typical emissive triplet excited state, making the carbene complexes suitable to serve as efficient phosphors [39]. Moreover, the average Ir–C_{phenyl} distance in **1** and **2** (2.072 (10) Å and 2.087 (7) Å) is longer than the average Ir–C_{phenyl} distance in Ir(ppz)₃ (2.021(6) Å), indicating that the carbene is a stronger field ligand than the pyrazolyl or pyridyl counterparts, and therefore, the NHC Ir complexes should have high energy ligand field states. Meanwhile, the NHC ligands are twisted from planarity around the bridging C_{phenyl}–N_{carbene} bond in both **1** and **2**. The distortion is probably due to steric repulsion between adjacent hydrogen atoms on the phenyl

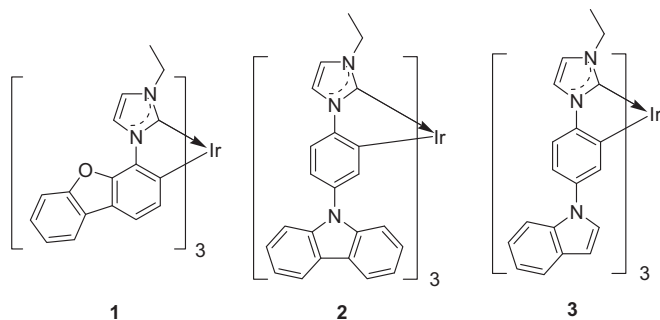


Chart 1. Chemical structures of complexes 1–3.

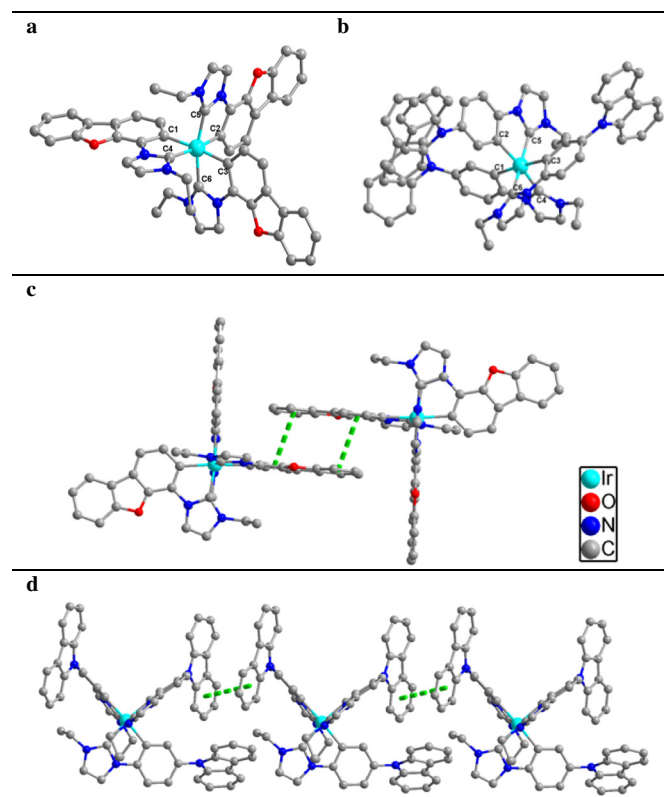


Fig. 1. (a) Thermal ellipsoid (ORTEP) plots of **1**; (b) Thermal ellipsoid (ORTEP) plots of **2**; (c) The packing of **1** in crystalline at RT; (d) The packing of **2** in crystalline at RT. The hydrogen atoms were omitted for clarity and green dash lines indicated intramolecular π – π interactions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and imidazolyl moieties. However, the average twist in **1** (4.270°) is smaller than that in **2** (5.506°). This variation in ligand distortion is most likely due to the crystal packing effects [28].

In the crystal packing of complex **1**, every two molecules packed together *via* face-to-face π – π stacking between dibenzofuran rings, where the two planes are nearly parallel (Fig. 1c). The interplanar distance between the dibenzofuran rings is 3.80 Å. For complex **2**, the molecular structures are packed by face-to-face π – π stacking among adjacent carbazole rings. The interplanar distance between the carbazole rings is 3.75 Å (green dash line) (Fig. 1d), which may allow intermolecular Ir– π and π – π interactions to occur.

The UV–Vis absorption of complexes **1–3** obeys Lambert–Beer's law in the concentration range studied (1×10^{-6} – $1 \times 10^{-4} \text{ mol L}^{-1}$) in CH_2Cl_2 , suggesting that no dimerization or oligomerization occurs within this concentration range. The UV–Vis absorption spectra of complexes **1–3** in CH_2Cl_2 solution is presented in Fig. 2a, and their photophysical parameters are listed in Table 1. In comparison to their respective ligands (2a–2c, Fig. S1), the strong absorption bands of the Ir complexes above 280 nm can be assigned to ligand $^1\pi,\pi^*$ transitions of the cyclometalating ligands (Fig. 2a), which are also in line with the other transition organometallic compounds reported previously [40–42]. It is noted that these bands are somewhat shifted, indicating the delocalization of the ligand-centered molecular orbitals *via* the interactions with the Ir *d* π orbitals and the stereo-hindrance effect of the ligands. In addition to the $^1\pi,\pi^*$ transitions of the cyclometalating ligands, weaker bands at lower energy ($\lambda = 280$ – 370 nm , $\epsilon \sim 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) are ascribed to $^1\text{MLCT}$ transitions. Finally, weak low energy band ($\lambda > 380 \text{ nm}$, $\epsilon \sim 3 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) is also present in all complexes, which can be assigned to spin-forbidden transitions directly to triplet states ($^3\pi,\pi^*$ transitions) [43]. Optical band gaps (E_g^{opt}) determined from the absorption

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