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# Effect of phenylamine moiety on the structure, optical properties, and phosphorescence efficiencies of some red-emitting iridium(III) complexes: A theoretical study

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ABSTRACT

Quantum-chemistry methods are used to investigate the effect of phenylamine chromophore on the electronic structure, optical properties, and phosphorescence efficiencies of a series of *fac*-iridium(III) complexes, Ir-$(g0)_3$**(1)**, meta-substituted Ir compounds [Ir-$(g0)_2$-$(g1)_1$]**(1a)**, [Ir-$(g0)_1$-$(g1)_2$]**(1b)**, [Ir-$(g1)_3$]**(1c)** and para-substituted Ir compounds [Ir-$(g0)_2$-$(g1')_1$]**(2a)**, [Ir-$(g0)_1$-$(g1')_2$]**(2b)**, [Ir-$(g1')_3$]**(2c)**, where g0 = L-phenylisoquinolinato, g1 = 4-(isoquinolin-1-yl)-*N*,*N*-diphenylbenzenamine, g1′ = 3-(isoquinolin-1-yl)-*N*,*N*-diphenylbenzenamine. The calculations show that introduction of phenylamine chromophore at meta position of phenyl ring (**1a**–**1c**) slightly changes the ground-states geometries but largely increases the energy of HOMO and decreases IP values hence improves the ability of hole injection, which is consistent with the experimental report. The introduction of diphenylamine substitutions on the para position (**2a**–**2c**) is effective for extending the π-electron delocalization, which results in strengthening metal-ligand bond and dramatically increasing the HOMO energy. More important, the **2a**–**2c** have enhanced metal-to-ligand charge transfer $^3$MLCT participation in the phosphorescent spectra, decreased the singlet-triplet splitting energy ($\Delta E_{S1-T1}$), as well as dramatically small energy differences between the highest occupied orbitals splitting ($\Delta dd_{occ}$) and large lowest unoccupied d-orbitals splitting ($\Delta dd^*$) at the both $S_0$ and $T_1$ geometries, these account for the quantum yield and efficiency of phosphorescence. The calculated ionization potentials (IPs), electronic affinities (EAs), and reorganization energy (λ) confirm that the hole and electron injection and transfer ability were enhanced by importing the diphenylamine. Furthermore, based on the analyses of triple energy differences between host and guest, charge carrier mobility, optical overlap, it is found that these Ir complexes maybe good guest materials in CBP. Thus, the introduction of phenylamine at para position is effective approach to obtain highly efficient red phosphorescent emitters.



## 1. Introduction

In recent decades, the photophysical properties of $d^6$ transition-metal complexes such as Re(I) [1,2], Ru(II) [3–5], Os (II) [6,7], and Ir(III) [8–10] have attracted enormous attention in the scientific community because of their potential applications in many areas [11,12]. Among them, the Ir(III) complexes are generally regarded as the most effective emitters in organic light-emitting

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diodes OLEDs [13,14] for their high phosphorescence efficiencies, high thermal stability, and relative short phosphorescent lifetime.

To date, considerable success has been achieved in making OLEDs with green phosphorescent Ir(III) complexes as dopants [15,16]. However, it is not easy to develop pure red emitters with high quantum efficiency, because their luminescence quantum yields tend to decrease with increasing peak emission wavelength according to the energy gap law [17,18]. Therefore, researchers have tried their best to design desirable red dopants by introducing various electron-withdrawing or electron-donating groups to the main cyclometalating ligands, and/or even ancillary ligands of the Ir core [19–22]. Among these works, Tsuboyama et al. [23] synthesized a series of cyclometalated iridium complexes, $Ir(piq)_3$, $Ir(tiq)_3$ and $Ir(fliq)_3$ (Hpiq = 1-phenylisoquinolinato-$C^2$,N, Htiq = 1-thiophen-2-ylisoquinolinato-$C^3$,N, Hfliq = 1-(9,9-dimethyl-9*H*-fluoren-2-yl)isoquinolinato-$C^3$,N), in 2003. It was reported that the OLEDs using $Ir(piq)_3$ as a red emitter exhibited excellent power efficiency of 8.01 m/W at 100 cd/m$^2$, external quantum efficiency of 10.3%, and sufficient Commission International de L'Eclairage (CIE) characteristics at (0.68, 0.32). Unfortunately, there was still a shortage of these red dyes giving relatively supersaturated red emission spectra. More recently, Zhou et al. synthesized a series of pure red-emitting Ir(III) complexes with triphenylamine dendrons (**Ir-G1** and **Ir-G2**) [24]. They also reported that all the devices based on **Ir-G1** and **Ir-G2** emit pure red light with the electroluminescence (EL) maximum at around 640 nm, excellent CIE color coordinates of (0.70, 0.30), and high external quantum efficiency (11.65% for Ir-G1 and 7.36% for Ir-G2).

In contrast to the wide experimental investigations, theoretical study on the electronic structures and properties of transition metal complexes is limited [25–30]. In order to foresee the structure–property relationships and provide a valuable guide for design highly efficient red phosphorescent emitters, we theoretically investigated the electronic structures, electronic spectra, charge carrier injection and transport properties of a series of *fac*-Ir(III) complexes in this paper. In the first place, we focused on investigating the experimental synthesized complex **1** and meta-substituted Ir complex Ir-G1 (named **1c** in this paper). To explore the influence of the number of the phenylamine on the structure and optical properties of Ir complexes, [Ir-$(g0)_2$-$(g1)_1$] **(1a)** and [Ir-$(g0)_1$-$(g1)_2$]**(1b)** (as shown in Fig. 1) were calculated and compared with **1** and **1c**. Moreover, in order to explore the effect of ligand substituent position on the properties of Ir complexes, we designed the para-substituted Ir congeners [Ir-$(g0)_2$-$(g1')_1$]**(2a)**, [Ir-$(g0)_1$-$(g1')_2$]**(2b)**, [Ir-$(g1')_3$]**(2c)**, see Fig. 1. The geometries, frontier molecular orbitals, absorption spectra and phosphorescent emission properties of these Ir complexes are discussed in detail. The charge injection and transfer ability are evaluated by analysis of ionization potential (IP), electronic affinity (EA), and reorganization energy ($\lambda$). Furthermore, the comparison of participation of triplet metal to ligand charge transfer $^3$MLCT contributions, singlet-triplet splitting energy ($\Delta E_{S1-T1}$) and d-orbital splitting of these complexes are used to demonstrate the relationships between electronic structure and quantum yields. The aim of this work is to provide a useful understanding of the relationship between electronic structure and photophysical property, and to give some information for designing efficient red emitters for OLEDs.

## 2. Computational details

In order to identify a reliable method to predict the ground-state geometry of this type of Ir complex, complex **1** was selected to do the calculation test with different theoretical approaches (B3LYP [31], TPSSh [32], PBEPBE [33], M062X [34], CAMB3LYP [35]), and the structural parameters of complex **1** were collected in Table S1 in Supporting information. Considering the frontier molecular orbital energies were very important to reveal the photophysical properties of materials, therefore, the orbital energies of complex **1** were also collected in Table S1. Taking the optimized structure and frontier molecular orbital energy of complex **1**, B3LYP method gave more satisfied results than other methods. Therefore, B3LYP was employed to optimize the ground-state geometries of complexes **1**, **1a**–**1c**, **2a**–**2c** as well as their ionic structures. The ground-state geometries of complexes **1**, **1c**, and **2**c were optimized with $C_3$ symmetry constraints. Based on these ground-state optimization geometries, the energies of the excited singlet state of these compounds were computed by time-dependent (TD) [36,37] B3LYP associated with the polarized continuum model (PCM) [38,39]. On the basis of these optimized

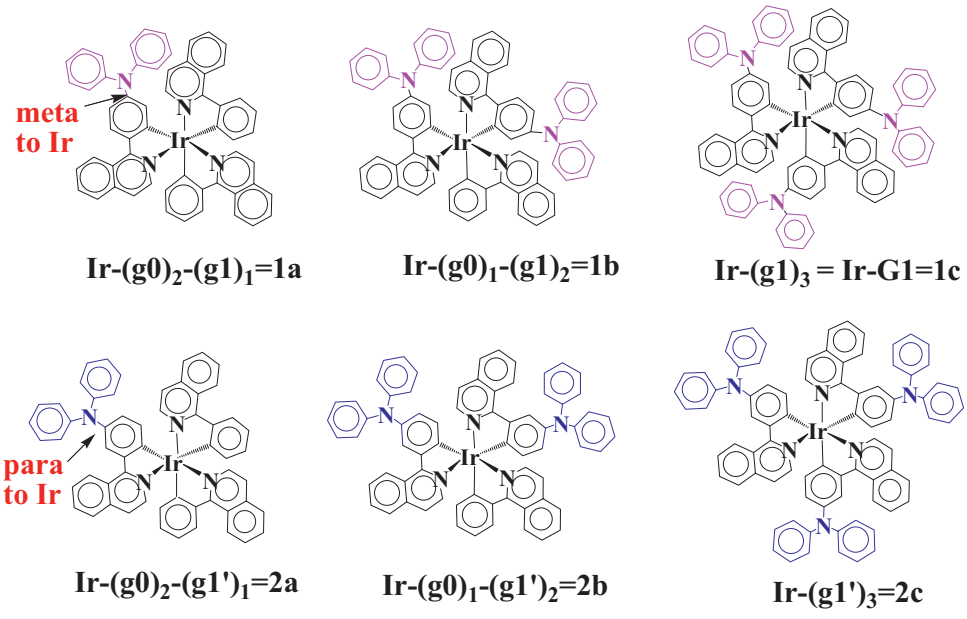


**Fig. 1.** Sketch structure of studied compounds.