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Theoretical study on a series of iridium complexes with low efficiency roll-off property

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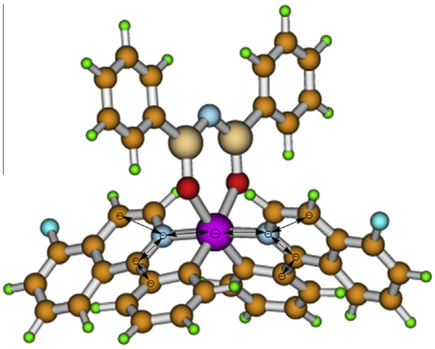
HIGHLIGHTS

- A series of Ir (III) complexes were investigated by DFT and TD-DFT method.
- The Ir complexes appeared here have an advantage of low efficiency roll-off property.
- The materials appeared here are practical for OLED industrialization.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of heteroleptic cyclometalated Ir (III) complexes for OLEDs application have been investigated theoretically to explore their electronic structures and spectroscopic properties. The geometries, electronic structures, and the lowest-lying singlet absorptions and triplet emissions of $(piq)_2Ir(acac)$ (labeled **1**) and theoretically designed models $(piq)_2Ir(dpis)$ (labeled **2**), $(4Fpiq)_2Ir(dpis)$ (labeled **3**), $(4F5M\text{-}piq)_2Ir(dpis)$ (labeled **4**), $(4,5\text{-}2F\text{-}piq)_2Ir(dpis)$ (labeled **5**) and $(5\text{-}F\text{-}piq)_2Ir(dpis)$ (labeled **6**) were investigated with density functional theory (DFT)-based approaches, where, piq = 1-phenylisoquinolato, acac = acetylacetonate and dpis = diphenylimidodisilicate. Their structures in the ground and excited states have been optimized at the DFT/B3LYP/LANL2DZ and TDDFT/B3LYP/LANL2DZ levels, and the lowest absorptions and emissions were evaluated at B3LYP and M062X level of theory, respectively. Furthermore, the energy-transfer mechanism of these complexes also be analyzed here, and the result shown that the complexes **1–6** are having the low efficiency roll-off property. Except that, the oscillator strength analyze shown that the complexes **2–6**, which were designed by theory, are suitable for OLED since their high oscillator strength property.

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Introduction

Luminescent transition metal complexes are employed in a diverse range of applications, notably as phosphorescent emitters for organic light-emitting diodes (OLEDs) and for solid-state lighting in the future [1]. In this regard, cyclometalated iridium (III) complexes have received special attention as dopants for harvesting the otherwise nonemissive triplet states formed in OLEDs [2]. The complexes are charge neutral and generally have good chemical and photochemical properties, such as high thermal stability, strong spin–orbit coupling effect of heavy metal, which can, to a large extent, partially remove the spin-forbidden nature of the

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T1 → S0 radiative relaxation. Among them, iridium (III) complexes are regarded as the most effective materials in OLEDs, because of which, they would display bright phosphorescent emission spanning the whole visible spectra, making them suitable to serve as ideal phosphors for OLEDs applications.

Nowadays, many interesting Ir complexes emitting in green, red, blue, and other color regions have been developed with good device performances [3]. Unfortunately, most of them cannot satisfy to be used for applications in displays, solid-state lighting, and so on, since that a fast reduction in efficiency known as roll-off, however, occurs when the drive current increases, This leads to a much lower luminance and more power consumption [4]. In 2011, Zheng et al. reported the first sky blue phosphorescent material ($(dfppy)_2Ir(tpip)$) with low efficiency roll-off [3k], and in order to perfect the luminous mechanism of it, we also gave a lecture to analysis it by theory [5]. so, in this article, we theoretical design another ligand dpis like tpip.

In order to verification the methods we used are suitable for Ir complexes, we theoretically investigated the molecular structures, the absorption and phosphorescence properties of iridium (III) complexes $(piq)_2Ir(acac)$ (labeled **1**) in this paper, and the results we got are similar to the experimental datas.

Furthermore, based on the designing idea of $(dfppy)_2Ir(tpip)$, the diphenylimidodisilicate (dpis) ligand is used on designing a series of red Ir complexes here: $(piq)_2Ir(dpis)$ (labeled **2**), $(4Fpiq)_2Ir(dpis)$ (labeled **3**), $(4F5M\text{-}piq)_2Ir(dpis)$ (labeled **4**), $(4,5\text{-}2F\text{-}piq)_2Ir(dpis)$ (labeled **5**) and $(5\text{-}F\text{-}piq)_2Ir(dpis)$ (labeled **6**). And we also investigated the electronic structures, a part of the frontier molecular orbital composited by fragments (FMOfs) and the frontier molecular orbital composited by atom orbitals (FMOas), absorption and phosphorescence properties of iridium (III) complexes **1–6** by DFT and TDDFT method. It is worth noting that we discussed the mechanism of charge transfer in the process of emitting in the final of this paper, and the computational result shown that the Ir complexes with dpis ligand not only have a lower efficiency roll-off, who are similar to $(dfppy)_2Ir(tpip)$ (our previous work) [5], but also cause the electrons actively, so we hope that the materials we design can be synthesis in future.

Methodology

The geometries of ground-state and the lowest-lying triplet excited-state have been investigated by the DFT and the time-dependent DFT (TD-DFT) methods with Becke's LYP (B3LYP) exchange–correlation functional with the double-ζ quality basis set: 6-31G* [6] and LanL2DZ [5,7] respectively, in addition, one f-type polarization function ($\alpha_f = 0.938$) [8] was augmented to the Ir atom [9]. And there were no symmetry constraints on these complexes. A relativistic effective core potential (ECP) for Ir atom replaces the inner core electrons leaving the outer layer[$(5s^2)(5p^6)$] electrons and the $(5d^6)$ valence electrons [7b]. The basis sets were depicted as Ir (8s6p3d/3s3p2d), C, N, O, F (10s4p1d/3s2p1d), Si(16s10p1d/4s3p1d) and H (4s/2s). This combination of basis set is adequate to describe the ground and excited state geometries of the Ir complexes, and it has been verified and discussed elsewhere [10].

The respective optimized geometries of ground and excited states and the spectral data were associated with the polarized continuum model (PCM) in CH_2Cl_2 medias, since the experimental spectral data are obtained in CH_2Cl_2 solution, with the default parameters embedded in Gaussian09 to obtain a valid approximation of chemical environment, which have been shown to provide accurate interpretation and predication for the transition metal complexes in numerous applications in our previous work [5,11]. The M062x functional together with the same basis set mentioned above were adopted to evaluate the emission nature [12]. Furthermore, the stable configurations of these complexes can be confirmed by frequency analysis, in which no imaginary frequency was found for all configurations at the energy minimal. All calculations have been performed with Gaussian09 suite of program with a tight self-consistent field convergence threshold for both gradient and wave function convergence [13].

Results and discussion

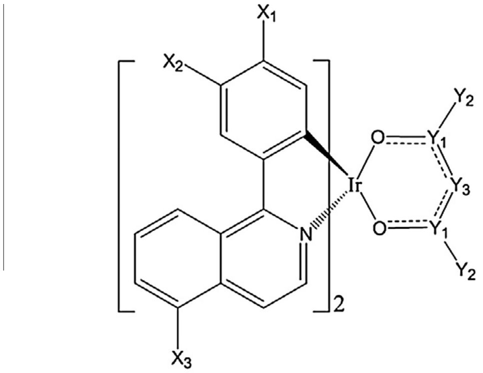
Geometries in the ground state S0 and the lowest-lying triplet state T1

The ground-state geometries were optimized by the DFT method with Becke's LYP (B3LYP) exchange–correlation function, and the optimized geometries of the lowest-lying triplet excited-state were obtained by TD-DFT/B3LYP approach. There were no symmetry constraints on these complexes.

The sketch maps of the complexes are shown in Fig. A.1. And the optimized ground-state geometrical structures for the complexes are shown in Fig. A.2 ($(piq)_2Ir(acac)$ (labeled **1**)) and Fig. B.1, along with the numbering of some key atoms. The main geometry structural parameters of the ground states (S_0) of the complexes are summarized in Table A.1 together with the BP86/TZ2P/TZP, B3LYP/TZP/DZP computational structure datas and experimental datas of the complex **1** [14], from which, we can find that our calculated structural parameters in the complex **1** are in good agreement with BP86/TZ2P/TZP, B3LYP/TZP/DZP and experimental values.

All complexes maintain the quasi-octahedral geometry around the metal centers as being observed in other typical six-coordinated Ir (III) complexes. But, it should be noted that there are subtle distortion among the structural parameters of them. As the ground states (S_0), compere to complex 1, the bond lengths Ir–O of complexes **2–6** are increasing 0.44–0.59 Å, and the bond angles N1–Ir–O1 are decreasing 0.2–0.5 degree, this should be attributed to the phenyl (abbreviated as Ph), which cause the steric hindrance of the molecules increased, connecting to the atoms Si. In addition, the atom F, whose atomic radius is larger and electron-withdrawing ability is stronger than atom H, cause the electron cloud come on closer to the main ligands of complexes, so that, the bond lengths Ir–O of complexes **3–6** are shorter than **2**.

The structure parameters of lowest-lying triplet states (T_1) are also listed in Table A.1. Compared with the ground states, the



$X_1=X_2=X_3=H$,	$Y_1=C, Y_2=Me, Y_3=CH$	**1**=$(piq)_2Ir(acac)$
$X_1=X_2=X_3=H$,	$Y_1=Si, Y_2=Ph, Y_3=N$	**2**= $(piq)_2Ir(dpis)$
$X_1=F, X_2=X_3=H$,	$Y_1=Si, Y_2=Ph, Y_3=N$	**3**=$(4Fpiq)_2Ir(dpis)$
$X_1=F, X_2=Me, X_3=H$,	$Y_1=Si, Y_2=Ph, Y_3=N$	**4**=$(4F5M\text{-}piq)_2Ir(dpis)$
$X_1=X_2=F, X_3=H$,	$Y_1=Si, Y_2=Ph, Y_3=N$	**5**=$(4,5\text{-}2F\text{-}piq)_2Ir(dpis)$
$X_1=X_2=H, X_3=F$,	$Y_1=Si, Y_2=Ph, Y_3=N$	**6**=$(5\text{-}F\text{-}piq)_2Ir(dpis)$

Fig. A.1. Sketch structures of the complexes.

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