



DFT studies on the ligand effect on electronic and optical properties of three series of functionalized Ir(III) complexes



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ABSTRACT

With the help of DFT and TDDFT, a series of functionalized mononuclear iridium (III) complexes were systematically investigated to make clear the effect of auxiliary ligands on their electronic and photophysical properties. It can be found that introducing electron withdrawing group ($-\text{CF}_3$) on benzene moiety can stabilize HOMO level, thus leading to wider HOMO-LUMO gap and blue shift in spectrum. More importantly, introducing $-\text{CF}_3$ on benzene moiety can also significantly improve the radiative decay rate (k_r). On the other hand, the incorporation of electron donating groups (such as $-\text{Ph}(\text{CH}_3)_3$) into pyridine moiety on ligand reduce k_r . The complexes **1c-3c** and **1d-3d** have improved charge balance ability and larger percentage of metal character. The results revealed the nature of the different substituents have a significant effect on the HOMO, LUMO energy levels and k_r , resulting in the change of emission color and the quantum efficiency (Φ_p).

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1. Introduction

Phosphorescent functionalized materials based on late transition metal are becoming increasingly successful in full-color flat panel display and solid-state lighting (SSL) [1–5]. The strong spin-orbital coupling (SOC) involved in transition metal ions lead to good efficiency of intersystem crossing (ISC) from singlet (S_1) to triplet excited state (T_1). Consequently, the mixing of S_1 and T_1 not only break out of the spin-forbidden nature in the radiative relaxation of T_1 , but also obviously shortens the lifetime of T_1 , thus enhancing phosphorescent efficiency [6–10]. Among third-row transition-metal complexes, iridium^{III} based complexes are most interesting due to their wide range of emission colors, excellent thermal stability, short lifetimes of T_1 and wonderful emission efficiency. The color purity, efficiency and brightness of organic light-emitting diodes (OLEDs) are obviously influenced by the nature of

different ligands. And the modification of ligand is helpful in adjusting the photophysical characteristics of emitting complexes. Therefore, to explore the ligand effect on electronic structures and optical properties is particularly important.

Herein, the theoretical calculations using density functional theory (DFT) methods have been performed to search for the potential efficient phosphorescent Ir^{III} complexes according to the reported Ir (dfppy)₂(taz) (**1a**) and Ir (dfppy-tfm)₂(taz) (**2a**) (Fig. 1) [11]. A series of derivatives were fabricated and investigated by systematically modifying the auxiliary ligand or by incorporating different substituent groups [Ir (dfppy-tfm-bz)₂(taz) (**3a**), Ir (dfppy)₂(pic) (**1b**), Ir (dfppy-tfm)₂(pic) (**2b**), Ir (dfppy-tfm-bz)₂(pic) (**3b**), Ir (dfppy)₂(bno) (**1c**), Ir (dfppy-tfm)₂(bno) (**2c**), Ir (dfppy-tfm-bz)₂(bno) (**3c**), Ir (dfppy)₂(dpz) (**1d**), Ir (dfppy-tfm)₂(dpz) (**2d**), Ir (dfppy-tfm-bz)₂(dpz) (**3d**); dfppy-tfm-bz = 2-(3,5-difluoro-4-(trifluoromethyl) phenyl)-4-mesitylpyridine, pic = picolate, bno = benzo-[1,5]naphthyridin-6(5H)-one, dpz = 3,6-diphenylpyridazine]. The influence of ligands on the electronic structures and spectroscopic properties of these heteroleptic Ir(III) complexes have been investigated in detail, which will contribute to our designing new types of efficient Ir(III) complexes for industrial applications.

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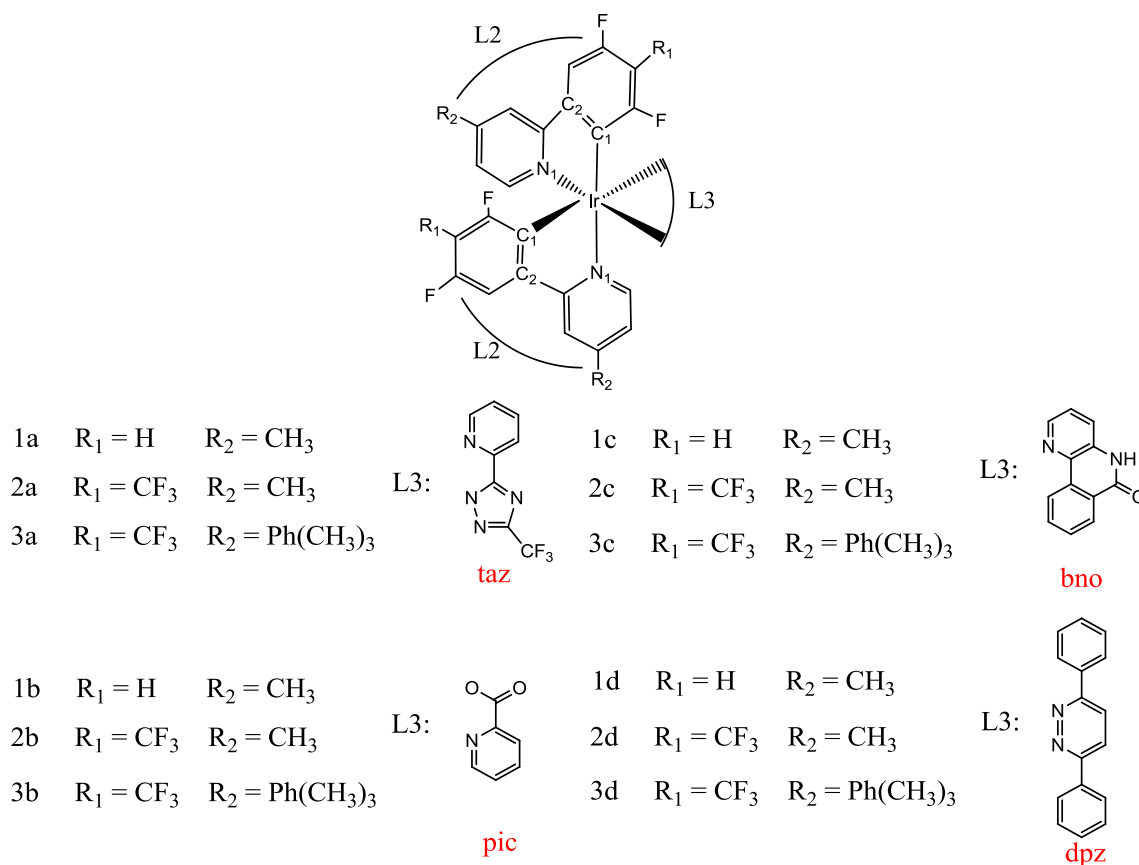


Fig. 1. Schematic structures of these investigated complexes.

2. Computational details

Calculations on singlet (S_0) and triplet (T_1) states of these complexes were carried out by DFT and TDDFT approach with B3LYP functional [12]. On the basis of S_0 and T_1 states, the TDDFT was utilized to investigate the absorption and phosphorescence properties. In all the calculations, a 'double- ζ ' quality basis set LANL2DZ associated with relativistic effective core potential (ECP) was employed on Ir atom, and 6-31G(d) basis set was used for other atoms [13]. There were no symmetry constraints on these complexes. The absorption and phosphorescence properties were calculated in CH_2Cl_2 in association with the polarizable continuum model (PCM) [14]. All calculations were performed with Gaussian 09 software package [15].

3. Results and discussion

3.1. Geometries of ground states and lowest lying triplet excited states

The calculated bond lengths, bond-angles, and dihedral-angles for ground and excited states of these complexes are presented in Table 1 and Table S1, along with the experimental data.

In ground state (S_0), the Ir–C1 and Ir–N1 distances and the dihedral angles are almost the same compared to the crystal data, suggesting the calculations are reliable in predicting the structures of these complexes. The C1–Ir–N1–C2 dihedral angles indicate these three ligands are approximately perpendicular to each other. It indicates that all these complexes adopt pseudo-octahedral coordination modes, showing the introduction of different ligand (L3)

causes minor difference on geometrical parameters for these complexes. The Ir–N distance on L3 is in the sequence of 'b', 'a', 'c' and 'd' (for example, **1a**: 2.13 Å; **1b**: 2.08 Å; **1c**: 2.16 Å; **1d**: 2.21 Å), indicating the different coordination ability of different ligands (L3). On the other hand, the bond lengths of Ir–C1 for 'a', 'b', and 'c' complexes decrease in their lowest lying triplet excited states (T_0), which is caused by the slightly stronger interaction between metal and ligands. However, the bond lengths of Ir–C1 do not show a clear change for **1d**, **2d** and **3d**. Moreover, the bond lengths of Ir–N1 decrease for 2a, 1b, 2b and 3b in their T_1 states, but other complexes show the opposite.

The natural charges on Ir^{III} of S_0 and T_1 states were calculated by NBO method and listed in Table 2 [16]. In all case, the natural charges on the Ir atom at S_0 state are evidently less ionic than formal Ir³⁺ ion, which indicates observable donation from adjacent ligands to the 5d AOs of Ir³⁺. The changing trends on Ir of these complexes from S_0 to T_1 state increase in the order of **2a** < **3a** < **2b** < **3b** < **1b** < **1a** < **2c** < **3c** < **2d** < **3d** < **1c** < **1d**. It reveals that 'bno' and 'dpz' are more efficient in electronic transfer from the 5d orbital of Ir^{III} to the ligands on going from S_0 to T_1 state.

3.2. Frontier molecular orbitals

The frontier molecular orbitals are very important because they are closely related to the spectral properties. Therefore, the contour plots of HOMO and LUMO and the energy gaps are illustrated in Fig. 2. And the contribution of metal and ligands are listed in Table S2 (Supporting materials).

For 'a' series complexes, HOMO mainly resides on benzene moiety and Ir atom, while LUMO resides mainly on pyridine of L2

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