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The effect of different conjugated structures in main ligand on the photophysical properties for a series of iridium(III) complexes from a theoretical perspective

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ABSTRACT

The electronic structure and photophysical properties of five iridium(III) complexes have been studied using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The influence of different conjugated structures on their photophysical properties has been explored. Ionization potentials, electron affinities and reorganization energy have also been obtained to evaluate the charge transfer and balance properties between hole and electron. The lowest energy emissions from the CAM-B3LYP level for these complexes are localized at 472, 503, 523, 635 and 699 nm, respectively. The theoretical investigation would be useful to design potential phosphorescent materials for application in the organic light-emitting diodes.

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1. Introduction

Over the past three decades, organic light-emitting diodes (OLEDs) have attracted great attentions as the potential candidate for next-generation flat-panel displays and solid-state lighting [1–8]. The phosphorescent transition metal complexes such as Ru(II), Rh(III), Os(II), Ir(III) and Pt(II) complexes have exhibited potential applications in the fabrication of OLEDs. Among them, iridium(III) complexes are of paramount importance, which is attributed to their high thermal stability, short lifetime in excited states and strong spin–orbit coupling (SOC) effect of heavy metal. Many researchers have reported iridium(III) complexes containing the triazole-based ligands: synthesis, characterization, and application to OLEDs [9–13]. Enrico Orselli et al. have investigated the photophysical properties of 1,2,3-triazolyl-pyridine derivatives as chelating ligands for blue iridium(III) complexes [14]. Mathias Mydlak et al. have synthesized several blue-emitting iridium(III) complexes with different 1,2,3-triazole ligands [15]. Fernández-Hernández have reported the synthesis and both photophysical and electrochemical characterization of new iridium(III) complexes utilizing 1,4-disubstituted-1*H*-1,2,3-triazoles as cyclometalating ligands [16].

Noviyan Darmawan et al. [17] have investigated the photophysical properties of a series of blue and deep-blue emitting iridium(III) complexes, consisting formally of a cationic Ir centre and a N,N′-heteroaromatic (N^N) ligand bearing negatively charged side groups, i.e., sulfonate and borate. Herein, four complexes have been designed on the basis of the prepared complex 2a [17]. That is, five Ir(III) complexes with the structure Ir(Xdfppy)(ptmfb), (Xdfppy represents the main ligand, ptmfb = trifluoro((4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-methyl)borate) have been studied using the density functional theory (DFT) and time-dependent density functional theory (TDDFT). Comparison of electronic structures and spectral properties among the five complexes was performed. We hope that the theoretical study can provide useful information for designing new Ir(III) complex with potential applications in OLEDs.

2. Computational method

The ground state geometry for each molecule was optimized by density functional theory (DFT) [18] method with hybrid Hartree–Fock/density functional model (PBE0) based on the Perdew-Burke-Erzenrhof (PBE) [19]. On the basis of the ground- and excited-state equilibrium geometries, the time-dependent DFT (TDDFT) approach was applied to investigate the absorption and emission spectral properties. The “double-ξ” quality basis set LANL2DZ

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[20,21] associated with the pseudopotential was employed on atom Ir. The 6-31G(d,p) basis set was used for nonmetal atoms in the gradient optimizations. 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 minima. In addition, the positive and negative ions with regard to the "electron-hole" creation are relevant to their use as OLEDs materials. Thus, ionization potentials (IP), electron affinities (EA), and reorganization energy (λ) were obtained by comparing the energy levels of neutral molecule with positive ions and negative ions, respectively. All calculations were performed with the polarized continuum model (PCM) in CH_2Cl_2 medium. The calculated electronic density plots for frontier molecular orbitals were prepared by using the GaussView 5.0.8 software. All calculations were performed with the Gaussian 09 software package [22].

3. Results and discussion

3.1. Geometries in the ground state S_0 and triplet excited state T_1

Four assumed structures **2**, **3**, **4** and **5** have been proposed on the basis of synthesized complex **1** [17] in Fig. 1(a). The optimized ground state geometric structure for complex **1** is shown in Fig. 1 (b) along with the numbering of some key atoms. Selected bond distances, bond angles and dihedral angles for complexes **1**–**5** (**1**–**5** indicates **1**, **2**, **3**, **4** and **5**, the same hereafter) have been presented in Table 1.

The computed geometries for all these complexes possess a distorted octahedral arrangement around the metal core, within C_1 point group symmetry. Molecular geometry for **1** was optimized starting from the available crystal datum [17]. In comparison with X-ray data of **1**, very good agreement were obtained for Ir—C and Ir—N bond lengths. For C1—Ir—N3, C2—Ir—N2 and N1—Ir—N4 of complex **1**, no more than 2° of deviation was found between the experimental and computed bond angles. The bond angles C1—Ir—N3, C2—Ir—N2 and N1—Ir—N4 of complexes **1**–**5** range from 171° to 174°. In order to have a better understanding of structural modification from S_0 to T_1 state, the main optimized geometric parameters of T_1 have also been summarized in Table 1. The changes of selected Ir(III)-related bond lengths from the ground to the excited state for complexes **1**–**5** are shown in Fig. 2. The Ir—C1, Ir—C2, Ir—N1 and Ir—N4 bonds for complexes **1**–**5** in the T_1 states are slightly contracted compared with those in the S_0 states. Nevertheless, the Ir—N2 and Ir—N3 bonds for complexes **1**–**5** in the T_1 states are elongated compared with those in the S_0 states. The dihedral angles C1—C2—N3—N2 and N1—N2—N4—C2 in the T_1 state for complexes **1**–**5** show slight decrease and increase, respectively, in comparison to those in the S_0 state.

3.2. Molecular orbital properties

The photophysical properties are closely bound up with the change in the ground-state electronic structure. Therefore, it is important to study the ground-state electronic properties focusing on the frontier molecular orbital (FMO) components and the energy levels. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) for complexes **1**–**5** is displayed in Fig. 3. The detailed information of FMO compositions for complexes **1**–**5** has been presented in Tables S1–S5 (Supplementary Materials).

The HOMOs of complexes **1**–**5** reside mainly on the Ir atom and A moiety. For example, the HOMO of complex **1** distributes over the d-orbital of Ir (35%) and the π-orbital of the A moiety (63%). The LUMO of complex **1** resides mainly on the B moiety. The LUMO of complex **2** resides mainly on the A and B moiety. It is different for complexes **3**–**5**, which have the LUMOs mainly distribution on the A moiety. The HOMOs and LUMOs distribution characteristic also can be seen from Fig. 3. In contrast to **1**, the orbital energy levels of HOMO and LUMO for **2** are slightly changed. However, the orbital energy levels of HOMO and LUMO for **4** and **5** are obviously changed. The energy gaps between of LUMO and HOMO ($\Delta E_{L\text{-}H}$) decrease in the order of **1** (4.32 eV) > **2** (4.24 eV) > **3** (4.09 eV) > **4** (3.91 eV) > **5** (3.79 eV), which indicates the extended π-conjugation has some effect on the $\Delta E_{L\text{-}H}$ value. The investigation on the energy gaps will be useful for study the variation trend of the absorption. It is known that the proper energy matching between host and dopants is a fundamental issue with regard to the configuration of OLEDs; different HOMO and LUMO energies will have a significant effect on hole and electron injection balance and the position of the recombination zone as well as device performance.

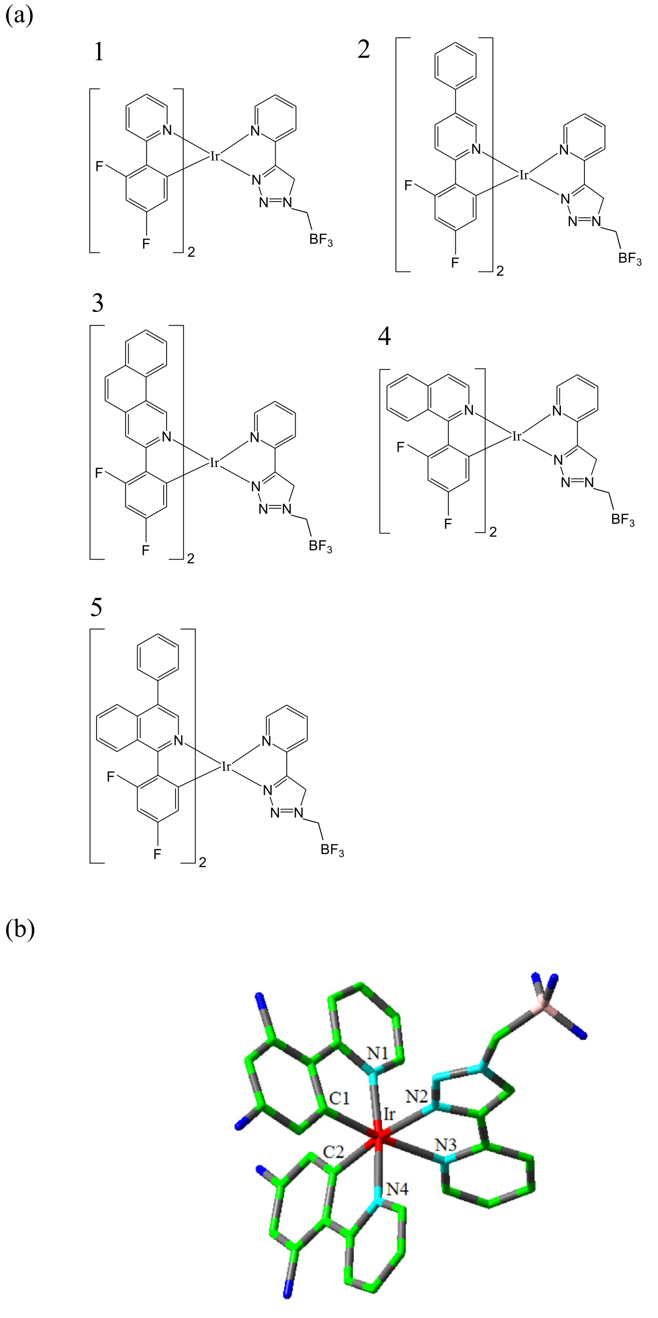

Fig. 1. (a) Sketch map of the structures of iridium(III) complexes **1**–**5**. (b) Representative optimized structure of **1** in the ground state at the PBE0 level (H atoms omitted).

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