



Theoretical investigation on the electronic structures and photophysical properties of a series of iridium(III) complexes based on amidate ancillary ligand



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ABSTRACT

The electronic and photophysical properties of a series of iridium(III) complexes based on amidate ancillary ligand have been investigated using the density functional theory (DFT) and time-dependent density functional theory (TDDFT). Ionization potential (IP), electron affinities (EA) and reorganization energy ($\lambda_{\text{hole/electron}}$) have also been obtained to evaluate the charge transfer and balance properties between hole and electron. The absorption and emission properties can be altered by the different electron-withdrawing and electron-donating substituents in the N-acetylaniline. The calculated lowest energy emissions for **1–6** are localized at 542, 538, 535, 557, 538, and 495 nm, respectively. It can also be seen that the complex **4** and **6** have possibly the largest and smallest k_r values than among these complexes. It is anticipated that the theoretical work can be useful for designing promising phosphorescent materials for use in the organic light-emitting diodes.

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1. Introduction

It is well-known that organic light-emitting diodes (OLEDs) have attracted great interest for their wide applications in full-color flat-panel displays and other lighting sources [1–4]. Among the materials used as emitters in OLEDs, transition metal [such as Ru(II), Os(II), Ir(III), and Pt(II)] phosphorescent complexes are of great interest due to the strong spin–orbit coupling (SOC) effects which can promote singlet-to-triplet intersystem crossing (ISC) processes [5–13]. Especially, the phosphorescent cyclometalated Ir(III) complexes are regarded as the promising light-emitting materials due to their unique photophysical properties, such as high phosphorescent efficiencies, short lifetimes, and excellent emission wavelength tenability [14–20]. The iridium(III) is capable to harvest both singlet and triplet states from electrically generated excitons, leading to the internal quantum efficiency of the device up to 100% theoretically [21–23].

The photophysical properties of a series of quinolyl-substituted iridium(III) compounds with an amidate ancillary ligand and a four-membered-ring structure have synthesized and investigated by Yang et al. [24]. In the present work, the electronic structures,

spectral properties, and quantum efficiency of six Ir(III) complexes **1–6** with the structure $(pq)_2\text{Ir}(\text{O}\dot{\text{N}})$ (pq and $\text{O}\dot{\text{N}}$ represent the phenylquinolyl and substituted amidate ancillary ligand, respectively) have been investigated using the density functional theory (DFT) and time-dependent density functional theory (TDDFT), aiming at exploring the effect of different substituent groups at the ancillary ligand on the photophysical properties. It is anticipated that this study can provide useful information for searching for the good Ir(III) phosphors in OLEDs.

2. Computational details

The ground state geometry for each molecule was optimized by the density functional theory (DFT) method with Becke's three-parameter hybrid method combined with the Lee–Yang–Parr correlation functional (denoted as B3LYP) [25–27]. The geometry optimizations of the lowest triplet states (T_1) were performed by unrestricted B3LYP approach. On the basis of the ground- and excited-state equilibrium geometries, the time-dependent DFT (TDDFT) approach associated with the SCRf (self-consistent reaction field) theory using the integral equation formalism polarized continuum model (IEFPCM) [28,29] in dichloromethane (CH_2Cl_2) medium was applied to investigate the absorption and emission spectral properties. The equilibrium solvation regime is employed for the geometry optimization of the solute molecule in the ground

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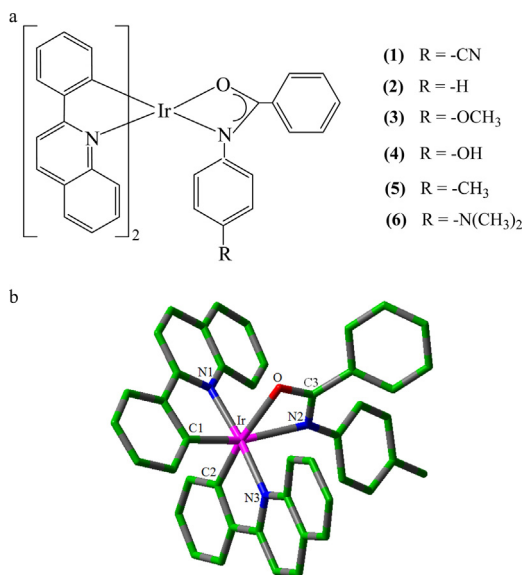


Fig. 1. (a) Sketch map of the structures of iridium(III) complexes **1–6**. (b) Representative optimized structure of **5** (H atoms omitted).

and excited states, while the nonequilibrium solvation regime is employed for vertical transitions. The “double- ξ ” quality basis set LANL2DZ associated with the pseudopotential was employed on atom Ir [30,31]. The 6–31+G(d) 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. The calculated electronic density plots for frontier molecular orbitals were prepared by using the GaussView 5.0.8 software. The absorption spectra were simulated by using the GaussSum 2.5 software [32] with the full width at half maximum (FWHM) of 3000 cm^{-1} based on the present TDDFT computational results. All calculations were performed with the Gaussian 09 software package [33].

3. Results and discussion

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

The sketch map of the six complexes **1**, **2**, **3**, **4**, **5**, and **6** are presented in Fig. 1(a), and the optimized ground state geometric structure for **5** is shown in Fig. 1(b) along with the numbering of some key atoms. The main geometric parameters in the ground and lowest triplet states are summarized in Table S1 (Supplementary Information).

It can be seen that these complexes have distorted octahedral coordination geometry around the iridium center. Obviously, the variation of the substituents in the N-acetylaniline did not cause a difference in their crystal packing. In general, there are no large geometric differences among these complexes studied. The bond angle N1–Ir–N3 for all these complexes are close to 180° . The dihedral angles Ir–O–C3–N2 for these complexes are very small, which forms a nearly planar four-membered ring.

On the whole, for the triplet excited state T_1 , bond distances of Ir–C1 and Ir–C2 are shorter than those of in the singlet state (S_0). Meanwhile, the bond angle C1–Ir–N1, C2–Ir–N3, N1–Ir–N3 are

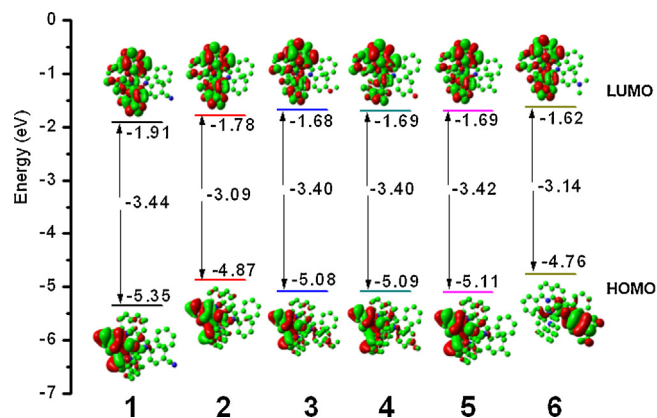


Fig. 2. Molecular orbital diagrams and HOMO and LUMO energies for complexes **1–6**.

Table 1

The calculated vertical IP (IP_v), adiabatic IP (IP_a), hole extraction potential (HEP), vertical EA (EA_v), and adiabatic EA (EA_a), electron extraction potential (EEP), and reorganization energies for electron ($\lambda_{\text{electron}}$) and hole (λ_{hole}), unit: eV.

	IP_v	IP_a	HEP	EA_v	EA_a	EEP	$\lambda_{\text{electron}}$	λ_{hole}
1	6.152	6.025	6.025	1.061	1.137	1.067	0.006	0.127
2	6.085	5.949	5.784	0.701	0.775	0.852	0.150	0.300
3	6.014	5.872	5.692	0.676	0.752	0.833	0.156	0.321
4	6.037	5.892	5.716	0.684	0.759	0.838	0.154	0.321
5	6.057	5.921	5.750	0.687	0.760	0.837	0.150	0.306
6	5.874	5.542	5.232	0.625	0.705	0.789	0.164	0.641

slightly larger compared with the ground state one. On the contrary, the bond angle C1–Ir–N2 in T_1 state is obviously reduced relative to those in the S_0 state. Besides, the dihedral angles of C1–N1–N2–N3 and C1–C2–N2–O in T_1 state are obvious increased with respect to those in S_0 state for all these complexes.

3.2. Molecular orbital properties

To explore the effect of the different substituent groups on the N-acetylaniline in these complexes, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and energy gap ($\Delta E_{L \rightarrow H}$) of these complexes are plotted in Fig. 2. The calculated FMOs compositions for **1–6** were listed in Tables S2–S7 (Supplementary Information).

The complex **1** with the electron-accepting substituent –CN has the smallest HOMO(LUMO) energies level and the largest $\Delta E_{L \rightarrow H}$ value among these complexes. It can be seen from Fig. 2 that complexes **3** and **4** have the same HOMO and LUMO energies level, including $\Delta E_{L \rightarrow H}$ values. The complex **2** have the smallest $\Delta E_{L \rightarrow H}$ value 3.09 eV. On the whole, the HOMO (LUMO) distributions for complexes **1–6** are very similar. For example, the LUMO of these complexes reside mostly on the C^N main ligands. As for the HOMO distribution, complexes **1–5** have the similar distribution on the Ir center and C^N main ligands, however, complex **6** has the different distribution, that is, mainly on the N \hat{O} ligand (92%). The reason can be due to the strong electron-donating substituent N(CH₃)₂ on the ancillary ligand.

3.3. Ionization potential (IP) and electronic affinity (EA)

It is known that the ionization potential (IP), electron affinity (EA), and charge mobility are key factors in the design of the optoelectronic properties of light-emitting layer materials in OLEDs. Ionization potential (IP), electron affinity (EA), reorganization energy (λ), hole and electron extraction potential (HEP and EEP) have been calculated and presented in the Table 1. The details

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