Theoretical perspective of FIrpic derivatives: relationship between structures and photophysical properties

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ABSTRACT

The phosphorescent properties of a series of potential blue-emitting Ir(III) complexes $(C^\wedge N)_2 Ir(N^\wedge N')$ are studied by means of the density functional theory/time-dependent density functional theory (DFT/TDDFT). Their possibilities to be blue-emitting phosphors are theoretically evaluated by the electroluminescence (EL) performance and phosphorescence quantum yield. The effect of two different substituents attached on the difluorophenyl ring is explored by comparison of the complexes in groups I (**1a**–**4a**) and II (**1b**–**4b**). Furthermore, to explore the influence of the stronger electron-donating/withdrawing group substituted on the primary ligand, the properties of complexes **1c** and **1d** are estimated. All the substituents are added on the para-position of the corresponding ring. The comparable radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) result in the similar quantum yield for complexes in two groups. Besides, the balance of the reorganization energies for complexes **2b**–**4b** is better than others.

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1. Introduction

Electroluminescent metal complexes would probably play a crucial role in the next-generation display device and solid-state lighting source through the phosphorescent organic light-emitting diode (OLED) technology [1–4]. Because of the spin-forbidden rule, the efficiency of fluorescent organic systems is limited by 25%, while phosphorescent metal complexes could potentially emit light from both the singlet and triplet excitons through the spin-orbit coupling (SOC). Since the SOC effect could be strengthened with the increase of the atomic number of metal atom, metal based complexes, such as ruthenium (Ru), rhenium (Re), platinum (Pt), iridium (Ir), europium (Eu), and terbium (Tb) species [5–10], have been employed to improve the efficiency of phosphorescent emission. Among them, Ir(III) complexes have attracted much more attentions as compared with other complexes [11,12]. The octahedral symmetry of Ir(III) complex can suppress the triplet-triplet annihilation originated from the aggregation of phosphors effectively leading to a high phosphorescent quantum yield.
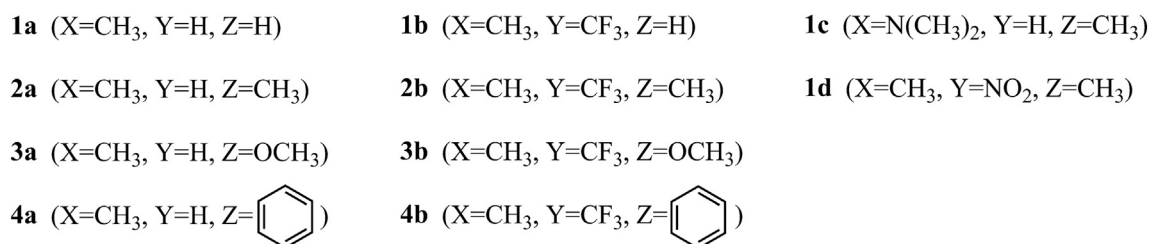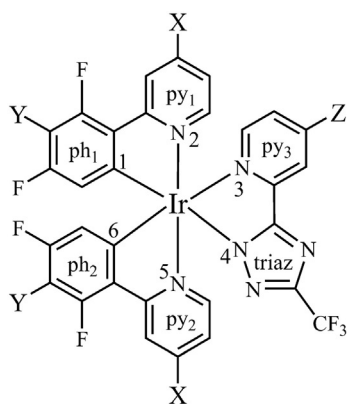
Unfortunately, the stable and efficient blue-emitting metal phosphor, particularly for the deep-blue emitting one, is still rare as compared to the red- and green-emitting phosphors. The emitting color, especially in the visible region, is dominated by the energy difference between HOMO and LUMO of the phosphor. Thus, controlling the variation of the HOMO and LUMO energy level by selective addition of the

electron-donating/withdrawing substituent(s) has become a powerful tool to develop ideal blue-emitting complexes [13,14]. The Ir(III) complex, tris(2-phenylpyridnato-N,C^2)iridium(III) [Ir(ppy)$_3$] (**TPPI**), is a green emitter with the HOMO mainly distributed in the phenyl ring and the LUMO extended over the pyridine ring. As a consequence, the energy gap of the **TPPI** could be enlarged by attachment of the electron-withdrawing group on phenyl ring to decrease the HOMO energy and/or incorporation of the electron-donating group on pyridine ring to increase the LUMO energy. According to this strategy, the **FIrpic**, one of the representative blue emitters for the phosphorescent OLEDs, was developed by addition of the fluorine atoms at C-2 and C-4 positions on the phenyl ring of the 2-phenylpyridine primary ligand together with replacement of one 2-phenylpyridine ligand with picolinate ancillary ligand [15,16]. However, the emitting color for **FIrpic** is blue-green rather than pure blue. Alternatively, both an electron-withdrawing trifluoromethyl (—CF$_3$) group at C-3 position on the phenyl ring and an electron-donating methyl group at C-4 position on the pyridine ring are introduced into the ligand leading to an Ir(III) complex that presents an obvious blue-shift in the phosphorescent emission relative to **TPPI** [17]. Furthermore, one of 2-phenylpyridine ligands is replaced by an 5-(2′-pyridyl)-3-trifluoromethyl-1,2,4-triazole ancillary ligand to form a new blue emissive complex with the shorter emission wavelength than the well-known **Firpic** [17].

On the basis of above studies, Yoon et al. [18] have synthesized several phosphorescent Ir(III) complexes (See Scheme 1) by incorporation of the proper groups into 2-phenylpyridine primary ligands coupled with the substituted pyridyltriazolate (**pytz**) ancillary ligand with the goal to develop new Ir(III) phosphors to emit light effectively in a

1a (X=CH₃, Y=H, Z=H)   **1b** (X=CH₃, Y=CF₃, Z=H)   **1c** (X=N(CH₃)₂, Y=H, Z=CH₃)

2a (X=CH₃, Y=H, Z=CH₃)   **2b** (X=CH₃, Y=CF₃, Z=CH₃)   **1d** (X=CH₃, Y=NO₂, Z=CH₃)

3a (X=CH₃, Y=H, Z=OCH₃)   **3b** (X=CH₃, Y=CF₃, Z=OCH₃)

4a (X=CH₃, Y=H, Z=⬡)   **4b** (X=CH₃, Y=CF₃, Z=⬡)

Scheme 1. Sketch structures for all the investigated Ir(III) complexes.

deeper blue wave band than **FIrpic** or the Ir(III) complex synthesized by Yamashita et al. [17]. Employing the trial-and-error approach to design new complexes is time-consuming and expensive. In contrast, theoretical calculation might be a reliable and vital tool to rationalize properties of the known chemical species and to predict the novel one [19–21]. Although the predicted complexes are still needed to be synthesized or measured by experimental methods, it is expected that an in-depth understanding of the structure-property relationship might open a high-efficiency way to explore the new complexes. To uncover the relationship between substitution pattern and property of the complex, the geometries, electronic structures, quantum yields, and electroluminescent (EL) performance of all complexes are deeply studied by density functional theory (DFT) and time-dependent DFT (TDDFT) calculations. It has been testified that both the nature and the position(s) of the substituted group(s) have an influence on the performance of phosphorescent complex [11,22].

2. Theoretical background and computational details

2.1. Theoretical background

The performance of a triplet phosphor is evaluated from two aspects: one is the EL efficiency; the other one is the internal quantum yield. The quantum yield is related to the radiative rate constant (k_r) and nonradiative rate constant (k_{nr}), which is expressed as follows, where τ_{em} is the emission decay time:

$$\Phi_{em} = k_r \tau_{em} = k_r/(k_r + k_{nr}) \tag{1}$$

It is clear that a higher quantum yield is ensured by a larger k_r and a smaller k_{nr}. The k_r could be [23]:

$$k_a = \frac{1}{\tau_a} = \frac{64\pi^4(\Delta E_{TS})^3}{3h^4c^3} \sum_{\gamma}^{x,y,z} |M_\gamma(T_1^\alpha)|^2 \tag{2}$$

where $M_y(T_1^\alpha)$ is determined by the relationship:

$$M_\gamma(T_1^\alpha) = \sum_m \frac{\langle T_m^\alpha|H_{SO}|S_0\rangle}{E(S_0)-E(T_m)}\langle T_1^\alpha|M_\gamma|T_m^\alpha\rangle + \sum_n \frac{\langle S_n|H_{SO}|T_1^\alpha\rangle^*}{E(T_1)-E(S_n)}\langle S_n|M_\gamma|S_0\rangle \tag{3}$$

which can be identified from the corresponding quadratic response (QR) function [24]. As the competing parameter, the k_{nr} could not be evaluated accurately, which is estimated by the thermal population of ³MC state in this work.

Except for the quantum yield, the charge mobility is the other key factor to estimate the performance of OLED devices. The ionization potential (IP) and the electron affinity (EA) are normally used to qualitatively evaluate the hole- and electron-injection abilities, respectively [25,26]. According to the Marcus/Hush model [27,28], the charge (hole or electron) transfer rate k (cm²/Vs) can be represented by the formula [29]:

$$k = \left(\frac{\pi}{\lambda k_B T}\right)^{1/2}\frac{V^2}{\hbar}\exp\left(-\frac{\lambda}{4k_B T}\right) \tag{4}$$

where k_B is the Boltzmann constant, T is the temperature, λ is the reorganization energy, and V is the coupling matrix element between the ions and molecules which is dictated by the overlap of orbitals. Due to the limited intermolecular charge transfer range in the solid state, the mobility of charges has been demonstrated to be dominantly related to the reorganization energy (λ) for OLED materials [27]. A small λ value contributes to an efficient charge transport process. Normally, the λ for hole and electron transfer can be simply defined by the following respective expression:

$$\lambda_{hole} = [E^+(M)-E(M)] - [E^+(M^+)-E(M^+)] = IP_v - HEP \tag{5}$$

$$\lambda_{electron} = [E(M^-)-E^-(M^-)-E(M)-E^-(M)] = EEP - EA_v \tag{6}$$