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An isomeric strategy for enhancing phosphorescence efficiency of iridium(III) complexes with *N*-heterocyclic naphthyridine ligands: A theoretical study

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ABSTRACT

The electronic structures and photophysical properties of six isomeric Ir(III) complexes with different *N*-heterocyclic naphthyridine ligands were investigated by density functional theory (DFT) and time dependent DFT (TD-DFT) approach. The radiative transition rates (k_r) were determined through calculated the spin–orbital coupling (SOC) matrix elements $\langle T_m|H_{SOC}|S_n\rangle$ and the energy levels (E_{Sn} and E_{Tm}). The non-radiative transition rates (k_{nr}) were estimated through analysis of the structural distortions, the *d*-orbital splittings and the energy differences between the S_0 and T_1 states $\Delta E(T_1 - S_0)$. As the results, the E_{Sn}, the E_{Tm} and the energy splittings ($\Delta E_{S_1-T_m}$ and $\Delta E_{T_m-T_{m-1}}$) can be regulated by the position of two nitrogen atoms in naphthyridine ring for studied complexes. Moreover, Ir(III) complex inclusive of quinoxaline heterocyclic ring presents large k_r and k_{nr}, so its phosphorescence quantum efficiency is difficult up to be 100%. While two Ir(III) complexes bound to quinazoline heterocyclic ring show weakly emissive because of large k_{nr}. Notably, the presence of the cinnoline heterocyclic ring in the Ir(III) complex makes singlet–triplet intersystem (ISC) rate and k_r fast but k_{nr} slow, then leads to its high phosphorescence quantum efficiency.

1. Introduction

Phosphorescent transition-metal complexes have come into the focus of research, due to their potential application as highly efficient electroluminescent emitters in organic light emitting diodes (OLEDs) [1]. The strong spin–orbital coupling of heavy-atom effect, increases the probability of efficient intersystem crossing (ISC) from the excited singlet state to the light emitting excited triplet state [2], and breaks the principle of triplet spin-forbidden, makes the complexes harvest both singlet and triplet excitons, so the internal quantum efficiency even can reach as much as 100% [3].

Thompson and Förrest synthesized a series of homoleptic or heteroleptic iridium(III) complexes with strong-field C^N or N^N cyclometalating ligand [4]. Ir(III) complexes have been recognized as the excellent phosphors because of their highly phosphorescence quantum yields, good photo- and thermal stabilities, facile color tuning through ligand structure control, relatively short phosphorescence lifetime, and high color purity [5]. Moreover, the third-row transition complexes with quasi-octahedral geometries, have a large Δdd^* (the splitting between the highest occupied and the lowest unoccupied *d* orbitals) and a small Δdd_{occ} (the energy gap between the two highest occupied *d*-orbitals). A large Δdd^* may result in an thermal unaccessible metal-centered (MC) *dd* excited states and reduce non-radiative quenching [6]. A small Δdd_{occ} means a strong spin–orbital coupling (SOC) and a higher radiative transition rate k_r [7]. Iridium complexes are the most successful family of phosphors for OLEDs in the visible range especially for green and blue emitters, however, in contrast to the well-developed short-wavelength phosphorescent materials, long-wavelength orange to red-emitting iridium complexes are prone to low quantum yields due to the smaller energy gap [8]. Therefore, how to overcome its intrinsic defects via modifying cyclometalating ligand is still a cutting-edge research topic for high efficient red-emitting complexes. The most commonly adopted strategy is inserted an additional sp^2-hybridized N in the pyridyl chelating ring to form naphthyridine-containing heterocycles such as quinoxaline [9], quinazoline [9b,10], and cinnoline [11] derivatives etc. This tuning strategy, which involving direct nitrogen-for-carbon substitution at the π-framework, should be as good as

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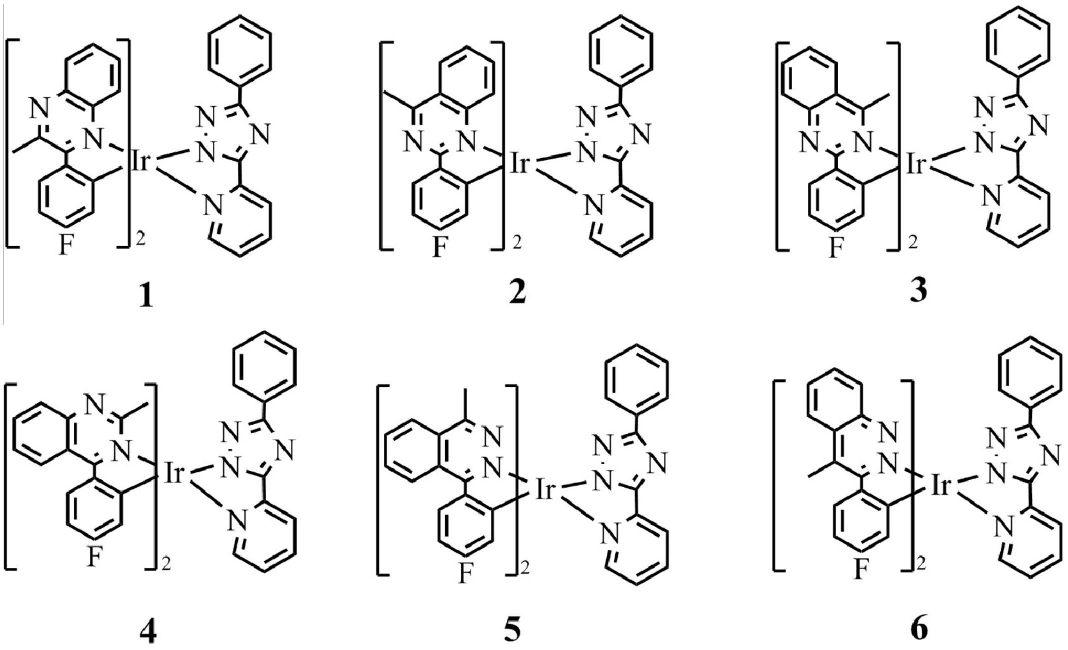
or even better than the traditional method of using the electron-donating or electron-withdrawing substituents. It exhibits shorter excited-state lifetimes, small efficiency roll-off and more thermally stabilities in theses dinitrogen-containing heterocycle complexes compared to those normal nitrogen-containing counterpares [8b,9a–12]. However, the phosphorescence quantum efficiency of these complexes are far from satisfied and need to be further explored. Unfortunately, to our knowledge, there has been no systematic comparison and analysis of the effect of the non-chelating sp^2-hybridized N on the phosphorescence quantum efficiency. Recently, one iridium complex bearing two 2-(4-fluorophenyl)-3-methyl-quinoxaline (fpq) ligands and an ancillary ligand: triazolylpyridine (trz) was reported and proved to be strong phosphorescent material with short-living phosphorescent decay. Complex $(fpq)_2Ir(trz)$ (hereafter noted by complex **1**) shows a superior operating lifetime in device compared to $[Ir(piq)_3]$ (a widely used kind of red emission material in OLED devices) [13]. Based on the structure of complex **1**, we altered the relative position of the two nitrogen atoms in the naphthyridine ring and proposed several additional modified structures [*trans*-2-fp-4-mqz]$_2$Ir(trz) (**2**), [*cis*-2-fp-4-mqz]$_2$Ir(trz) (**3**), [4-fp-2-mqz]$_2$Ir(trz) (**4**), [1-fp-4-mpl]$_2$Ir(trz) (**5**), [3-fp-4-mcn]$_2$Ir(trz) (**6**), in which fp = fluorophenyl, mpl = methylphthalazine, mcn = methylcinnoline, respectively (in Scheme 1). In this work, we are focused on the influence of the replacement position of the non-chelating nitrogen atom in the naphthyridine-containing heterocyclic ring on the phosphorescent properties of the isomeric Ir(III) complexes. Toward this goal, we implement a comprehensive quantum chemistry calculation on complexes **1–6** to explore the effect of the introducing positions of the non-chelating nitrogen atom (para-, meta- and ortho-positions) on the photophysical property of these complexes. The electronic structures, the frontier molecular orbitals (FMOs) and UV-absorption spectra are investigated, moreover, we explored mechanism of the phosphorescent emission for the series of Ir(III) complexes from microscopic theoretical perspectives, such as the relationship between the spin–orbital coupling (SOC) matrix elements $\langle T_m|H_{SOC}|S_n\rangle$, the energy splittings of the S_n and T_m states, and the radiative transition rates (k_r), meanwhile we analyzed the factors affecting the non-radiative transition rates for the complexes. Finally, we predicted their phosphorescence quantum efficiency (ϕ_p).

2. Computational details

The ground-state geometries were optimized by density functional theory (DFT) [14] with the Becke's three-parameter hybrid method combined with the Lee–Yang–Parr correlation functional (denoted as B3LYP) [15]. There were no symmetry constraints on these complexes. Vibrational frequencies were performed at the same theoretical level to confirm that each configuration is stable structure. The lowest lying triplet excited state geometries were optimized by the unrestricted B3LYP (UB3LYP) [16], and the calculated spin contamination are rather small (the expectation values of spin operator $\langle S^2\rangle$ were all below 2.03 for triplet excited state), which can be neglected. Recent calculations with TDDFT method for transition-metal complexes have been supported by experimental spectra and the reliability of TDDFT method was valid [17]. Thus, at the respective optimized geometries of the ground and excited states, the molecular orbital compositions, absorption and emission spectra of the complexes in dichloromethane (CH_2Cl_2) solvent were calculated by time-dependent DFT (TD-DFT) [18] method associated with the polarized continuum model (PCM) [19].

In the calculation, the choice of appropriate functionals and basis sets is crucial step for rational and precise prediction. So besides B3LYP, several other frequently used functionals including the PBE0, X3LYP, O3LYP, B3P86, B3PW91, CAM-BLYP and LC-BLYP [20] were picked out to evaluate the transition properties of complex **1**.

With regard to basis sets, the SDD ECP basis set for iridium is adequate to describe the ground state geometries of the Ir(III) complexes, which has been discussed by Li et al. [21]. As to the non-metal atoms (C, N, H and F atoms), we employed a couple of basis sets to obtain more accurate excitation energies and electronic transition properties closer to the experimental values. Finally, the combination of the SDD of ECP basis set for iridium together with the D95V basis set for rest of atoms performs better performance over the other collocations. The comparative details



Scheme 1. Chemical structures sketch of Ir(III) complexes **1–6**.