

# Theoretical investigation on the structural and optical properties of a series of pyridyl-substitutes Os (II) complexes

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**Abstract** –The electronic structures and spectroscopic properties of Os (II) complexes with a series of pyridyl substituents [Os(L)<sub>2</sub>(PH<sub>3</sub>)<sub>2</sub>](L= (1) ptz, ptzH=(2-pyridyl)-1,2,4-triazole; (2) bptz, bptzH=3-tert-butyl-5-(2-pyridyl)-1,2,4-triazole; (3) fptz, fptzH=3-(trifluoromethyl)-5-(2-pyridyl)-1,2,4-triazole, and (4) fbtz, fbtzH=3-(trifluoromethyl)-5-(4-tert-butyl-2-pyridyl)-1,2,4-triazole were investigated theoretically (Fig.1). The structures of the complexes were fully optimized at the B3LYP and UB3LYP method for the ground- and excited- states, respectively. The absorptions and emissions in dichloromethane solution were calculated at the time-dependent density functional theory (TD-DFT) level associated with the polarized continuum model (PCM). DFT calculations of both the singlet (ground) and the triplet states of the complexes suggest that the HOMO levels are a mixture of Os and ligand orbitals, while the LUMO is predominantly ligand-based. All the complexes have intense absorption bands in the UV region assigned into <sup>1</sup>( $\pi \rightarrow \pi^*$ ) transitions and weaker MLCT (metal-to-ligand charge transfer) transition that extent to the visible region with the admixture of the [d(Os) $\rightarrow \pi^*(pz)$ ] (MLCT) and [ $\pi \rightarrow \pi^*$  (pz)] (ILCT) transition. The phosphorescent emission of 1~4 at 654, 687, 624 and 603 nm were assigned as mainly <sup>3</sup>MLCT accompanied with a limited <sup>3</sup>ILCT transitions (Fig.2). The results showed that the different substituents affected the compositions of HOMO or LUMO of the excited state, thus accordingly induced the phosphorescent emission spectra shift.

Theoretical and experimental investigation on structures and spectroscopic properties of the third-row transition metal complexes with organic ligands continue to attract much attention mainly due to their potential application such as chemical sensors [1], sensitizers in solar energy conversion [2], and the fabrication for organic light emitting diodes (OLEDs)[3]. Recently, much attention has been paid to synthesize and characterize the emission materials with various types of ligands and to gain more understanding on their associated photophysical properties considering applications as OLEDs. Several red OLED devices based on osmium (II) phosphors have already been obtained [4] and it has been shown that Os (II) complexes trap both electrons and holes on the complex site, enhancing the device efficiency. Otherwise, the solvent has a remarkable effect on both emission energies and lifetimes. In particular it is to be noted that the emission of the complexes is almost completely quenched in H<sub>2</sub>O, however, the emission of the complexes is usually observable in CH<sub>2</sub>Cl<sub>2</sub> solutions at room temperature.

Although recently, many experimental works about the Os (II) complexes with phosphine ligand have been archived because they can be utilized as a kind of light emitting transition metal material to fabricate phosphorescent OLED, there are a few theoretical studies on excited states and luminescent properties for the Os (II) complexes with phosphine ligand. In the present study, the structure and electronic properties of the ground and lowest excited states for four pyridyl-substitutes Os (II) phosphine complexes have been investigated by ab initio density functional theory (DFT) method. By analyzing the composition, symmetry and electronic distribution of the molecular orbital for the ground state and excited state, we obtained the electronic transition properties of the absorption and emission spectra quantitatively. The nature of the low-lying excited states, which all typically metal-to-ligand charge-transfer (MLCT) excitations, is then explored using the TD-DFT approach to derive vertical excitation energies, which are compared with archived spectroscopic data. The calculations revealed that the judicious selection of the ancillary ligands will tune the luminescence of the complexes.

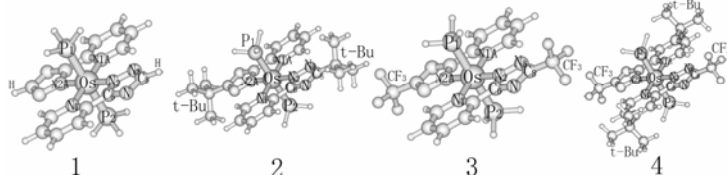


Fig.1 structures of 1~4 in the ground state with the B3LYP method.

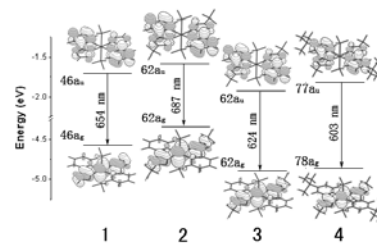


Fig.2 The emissions at 654,687, 617 and 603 nm for 1~4 under the TD-DFT calculations.

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