

**Theoretical investigation of the influence of heterocycle on the
radiative and non-radiative decay processes for iridium(III)
complex**

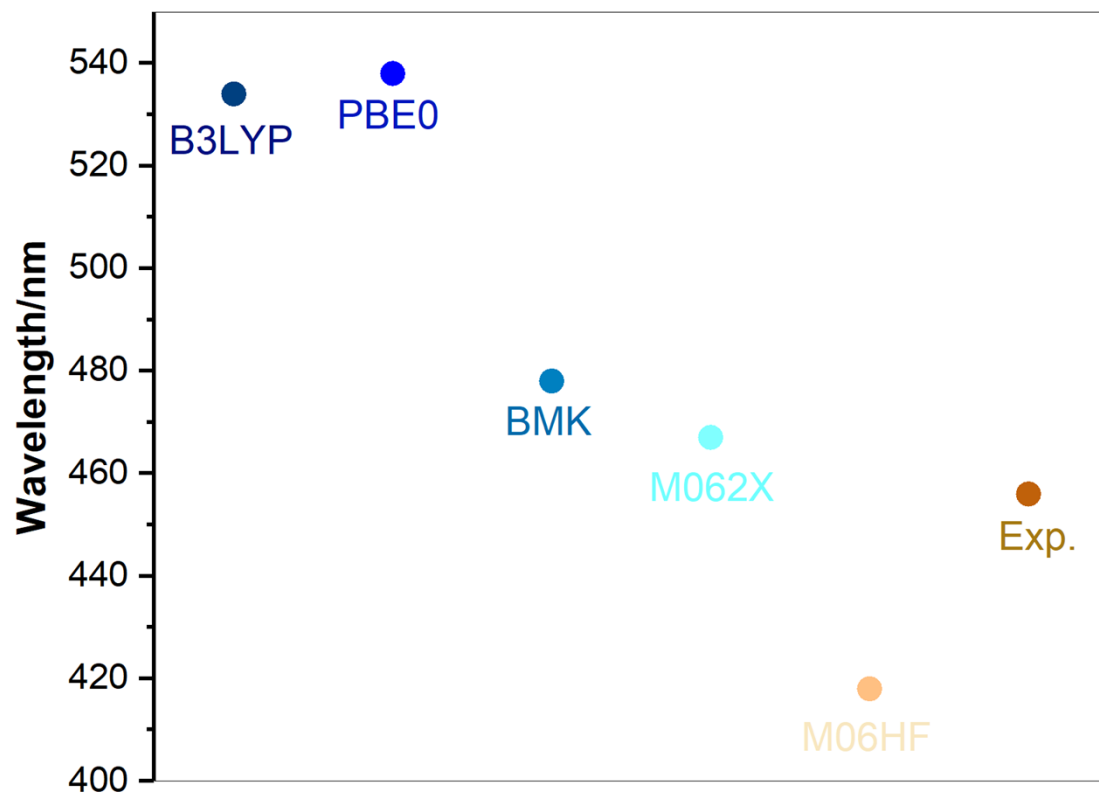


Figure S1. The test of different functionals for emission wavelength of **Ir-3**, together with the available experimental value.

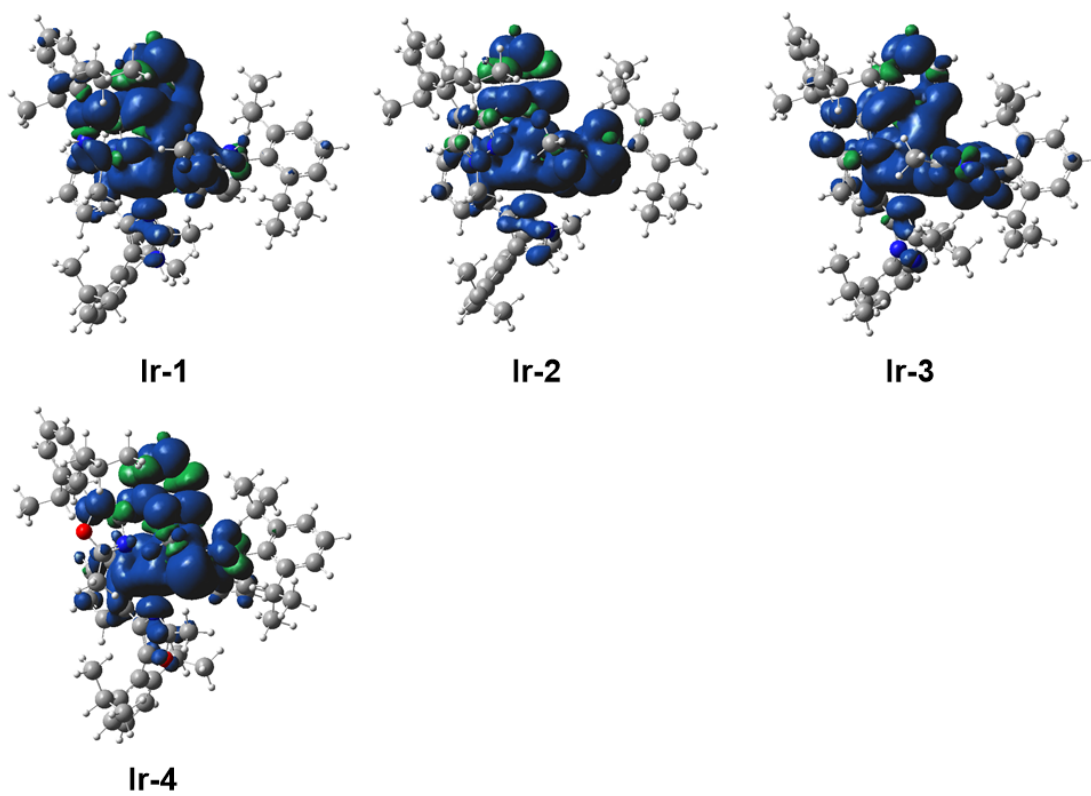


Figure S2. Spin densities computed on the transition state for investigated complexes (isovalue= 0.02).

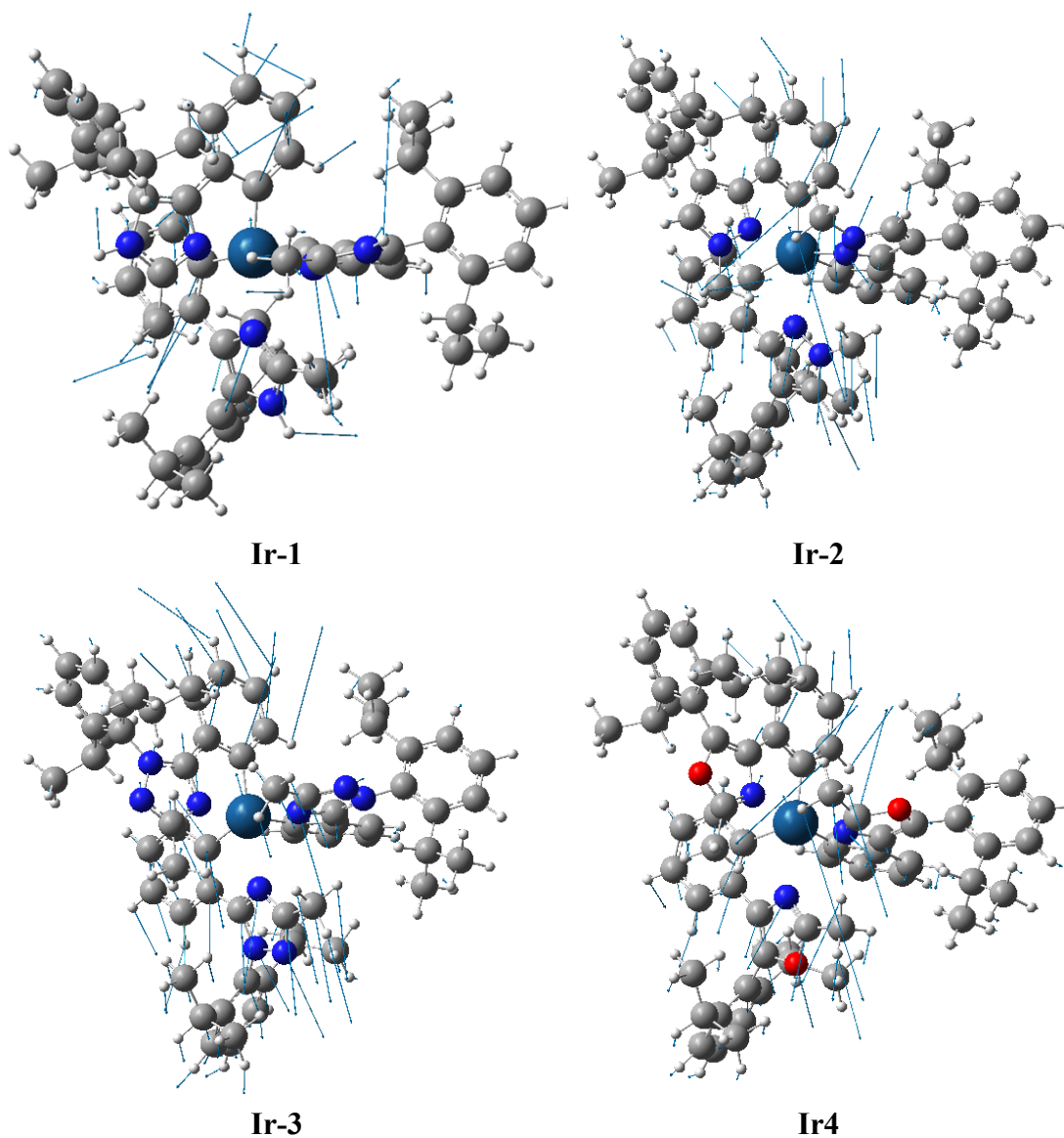


Figure S3. The vibrationa forms of transition states for studied complexes.

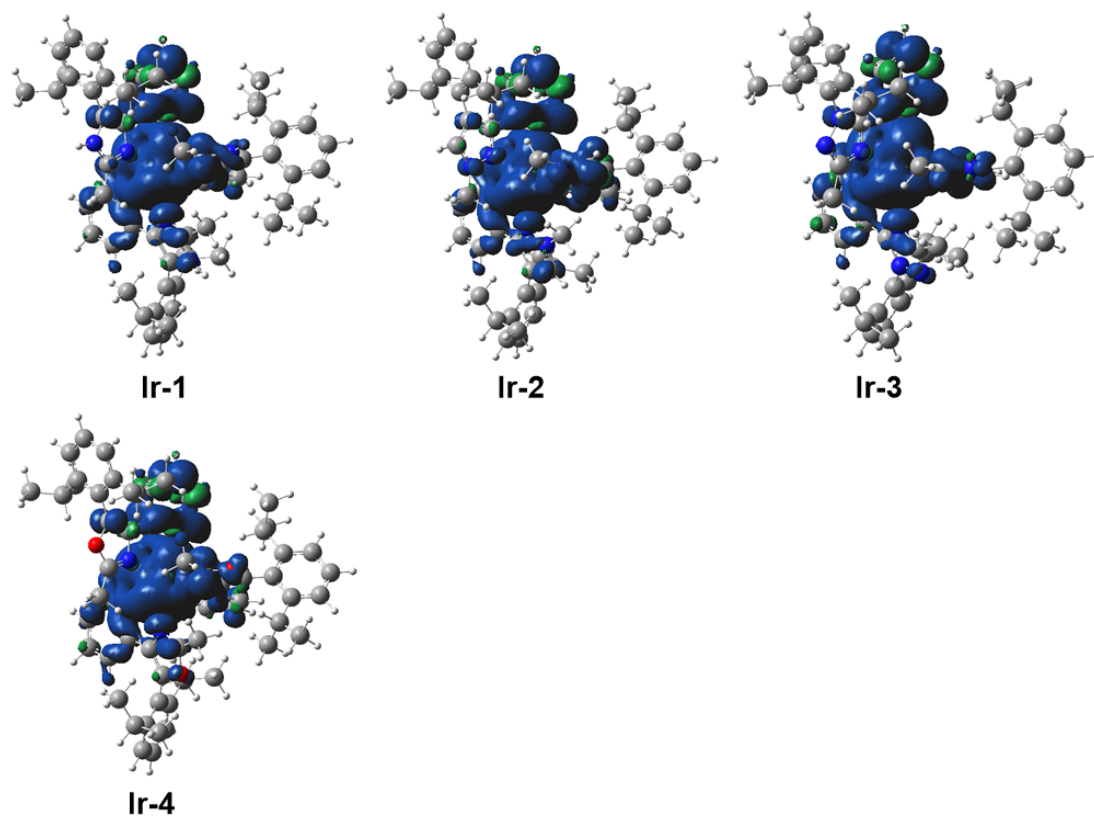


Figure S4 Spin densities computed on the 3MC states for investigated complexes (isovalue= 0.02).

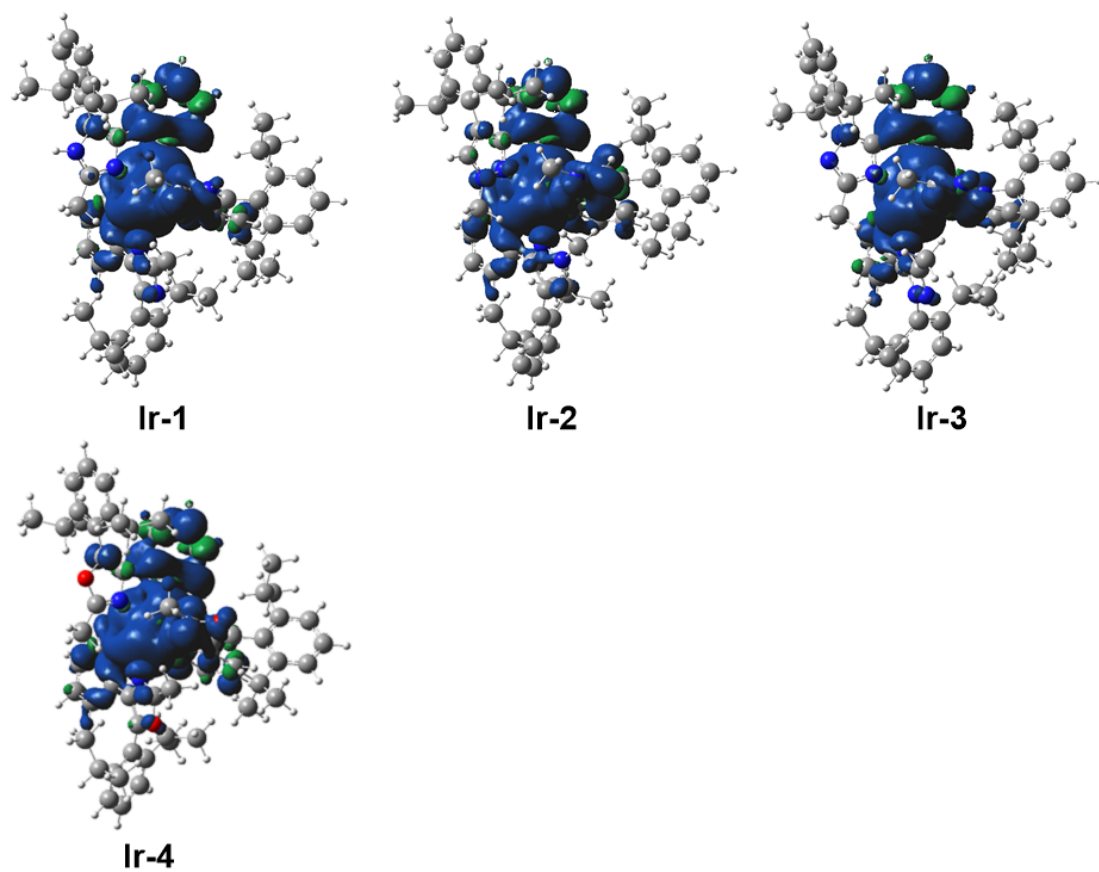


Figure S5 Spin densities computed on the minimal energy crossing points (MECP) for investigated complexes (isovalue= 0.02).

The Methodology for radiative decay rate constants

In a non- or scalar-relativistic scene, the triplet excited states are three threefold degenerate. However, SOC splits the triplet excited states into three different sublevels which are separated by energy in the absence of external magnetic field. Therefore, the energy difference between the sublevels is called zero-point splitting energy, i.e., ZFS. And the radiative decay rate from each sublevel can be calculated by the following equations:

$$\kappa_i^r = \frac{1}{\tau_i} = \kappa^r(S_0, T_{em}^i) = \frac{4\alpha_0^3}{3t_0} \Delta E_{S_0-T_{em}^i}^3 \sum_{j \in \{x,y,z\}} |M_j^i|^2$$

where τ_i refers to radiative lifetime from sublevel i ($i=1, 2, 3$) of triplet excited states to the ground state, α_0 is the fine-structure constant, $t_0 = (4\pi\epsilon_0)^2 \hbar^3 / m_e e^4$, $\Delta E_{S_0-T_{em}^i}$ is the transition energy between the triplet excited states and the ground state, M_j^i is on behalf of the spin-orbit coupled $T_{em} \rightarrow S_0$ transition dipole moment which can be showed as follow:

$$M_j^i = \sum_{n=0}^{\infty} \frac{\langle S_0 | \hat{\mu}_j | S_n \rangle \langle S_n | \hat{H}_{SO} | T_{em}^i \rangle}{E(S_n) - E(T_{em}^i)} + \sum_{m=1}^{\infty} \frac{\langle S_0 | \hat{H}_{SO} | T_m \rangle \langle T_m | \hat{\mu}_j | T_{em}^i \rangle}{E(T_m) - E(S_0)}$$

Based on the linear response theory, the transition dipole moment from the i th sublevel of triplet excited states and ground state can be evaluated and the Cartesian components $j \in \{x, y, z\}$ are used to represent spin eigenfunctions. The operators $\hat{\mu}_j$, \hat{H}_{SO} represent the electric dipole and spin-orbit Hamiltonian, respectively.

According to a thermal population distribution determined by Boltzmann statistics of the three sublevels, the total radiative decay rate constant can be computed by the following equation:

$$\kappa^r = \frac{\kappa_1^r + \kappa_2^r \exp(-ZFS_{1,2} / \kappa_B T) + \kappa_3^r \exp(-ZFS_{1,3} / \kappa_B T)}{1 + \exp(-ZFS_{1,2} / \kappa_B T) + \exp(-ZFS_{1,3} / \kappa_B T)}$$

In general, the values of $ZFS_{1,2}$ and $ZFS_{1,3}$ for transition metal complexes are typically $< 200 \text{ cm}^{-1}$. Thus, at the ambient temperature, the equation can be reduced to

$$\kappa^r = \frac{1}{3} \sum_{i=1}^3 \kappa_i^r$$

Based on the equation of spin-orbit coupled $T_{em} \rightarrow S_0$ transition dipole moment, the radiative decay rate is not only related to the energy differences, spin-orbit couplings between S_n and T_1 states, but also related to the energy differences, spin-orbit couplings between S_0 and T_1 states.