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Supporting Information

Theoretical Investigation of Triplet Energy Potential Surfaces for ($C^{\wedge}C^{*}$) Cyclometalated Platinum(II) Complexes and Corresponding Control Strategies

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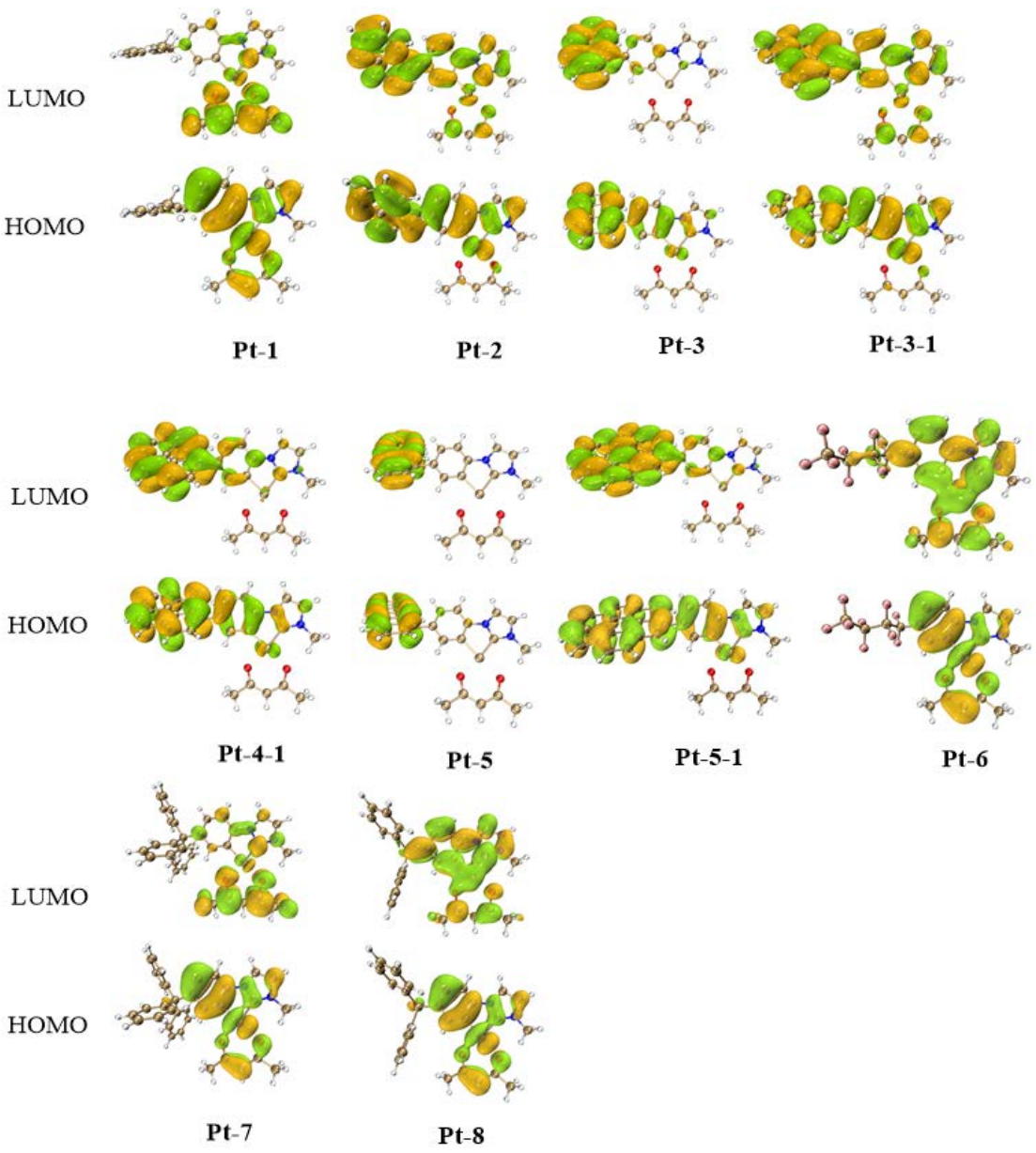

Figure S1. HOMO and LUMO of monometallic Pt(II) complexes at the S_0 equilibrium geometry.

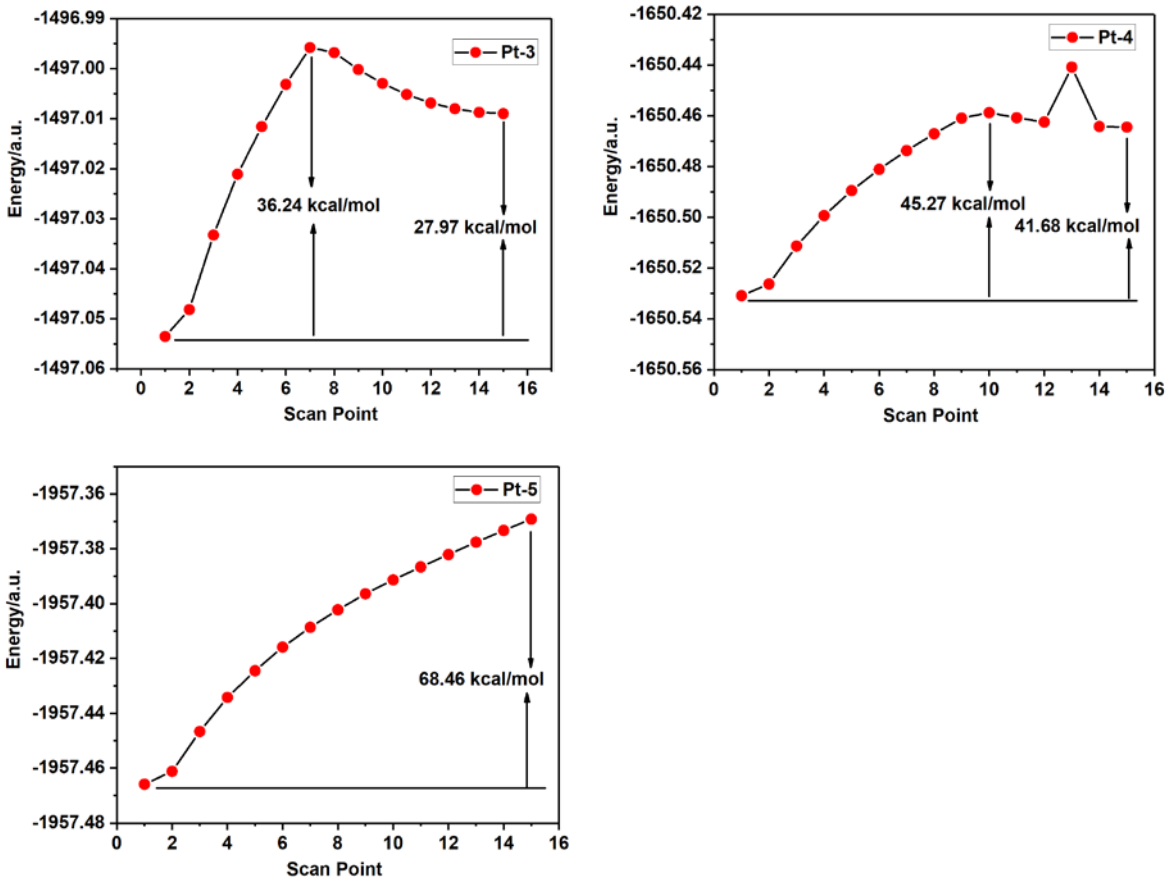

Figure S2. Potential energy surface scans for **Pt-3**, **Pt-4** and **Pt-5** between T_1 and ^{3}MC states, respectively.

The details about calculations of radiative rate constants

Based on the optimized geometries of the lowest triplet states, the phosphorescence radiative decay rates were computed using the quadratic response (QR) time-dependent (TD)-B3LYP approach. The rate constants (*k*r) for phosphorescence radiative decay from the three spin sublevels (indexed by *i*) of the T_1 states, can be expressed as follow:

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

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, $t_0 = \left(4\pi\varepsilon_0\right)^2\hbar^3/m_e e^4$, $\Delta E_{S_0-T_{em}^i}$ is the transition energy between the T_1 and S_0 statse, M_j^i is on behalf of the spin-orbit coupled $T_1 \rightarrow S_0$ transition dipole moment, which can be shown as follow and calculated using the QR TD-B3LYP approach.

$$M_j^i = \sum_{n=0}^{\infty}\frac{\langle S_0|\hat{\mu}_\mathrm{j}|S_n\rangle\langle S_n|\hat{H}_{SO}|T_{em}^i\rangle}{E\left(S_n\right)-E\left(T_{em}\right)} + \sum_{m=1}^{\infty}\frac{\langle S_0|\hat{H}_{SO}|T_m\rangle\langle T_m|\hat{\mu}_j|T_{em}^i\rangle}{E\left(T_m\right)-E\left(S_0\right)} \qquad \mathrm{j}\in\{x,y,z\} \tag{2}$$

The Cartesian components $j\in\{x,y,z\}$ are used to represent spin eigenfunctions. The operators $\hat{\mu}_\mathrm{j}$, $\hat{H}_{SO}$ represent the electric dipole and spin-orbit Hamiltonian, respectively.