Computational Insights on the Mechanism of Photo-Deactivation of a Type of Pt(Ⅱ) complexes

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[Abstract] The nonradiative decay process of a type of Pt(C^C)(acac) complexes chelated with phenylthiazole and acac ligand are investigated by using density functional theory(DFT) and time-dependent DFT (TD-DFT) method, for revealing the influence of fluorine atoms substituted at the acac ligand on the phosphorescent emission decay. The calculation results show that these complexes have similar MESX but different possible nonradiative pathways which result in different energy barriers. The low Φ (<0.01) of Pt(C^C)(acac) with fluorine atoms at acac ligands can be explained by the small energy barrier.

[Introduction] Phosphorescent organmetallic complexes, particularly iridium(III) and platinum(II) complexes, have attracted much attention due to theirs extreme widely used in variety photocatalysis and photoelectrochemistry.[1,2] The Pt(II) complexes with a square-planar coordination geometry is favorable to the electron−hole creation and separation.[3] More importantly, the square planar geometry makes the platinum complexes flexible in structure, as different cyclometalated ligands. To understand current materials and design high efficient new complexes, most theoretical calculations applied in exploration of radiative processes, which are focused on the component of metal to ligand charge transfer [3]MLCT in the transition character of emitting state, the energy of singlet−triplet splitting $\Delta E(S_1-T_1)$, and the transition dipole moment in the $S_0 \rightarrow S_1$ transition. However, the mechanism of emission decay is not established and there is no clear understanding on the origin of the dramatically differences on the nonradiative process. In the present study, we have studied the emission decay of a type of Pt(II) emitters using DFT method.

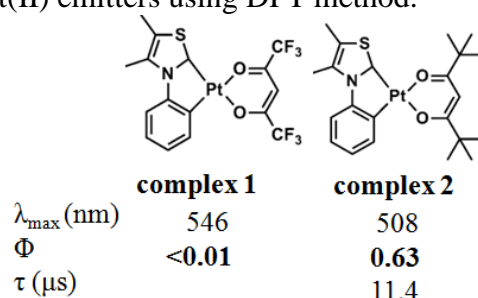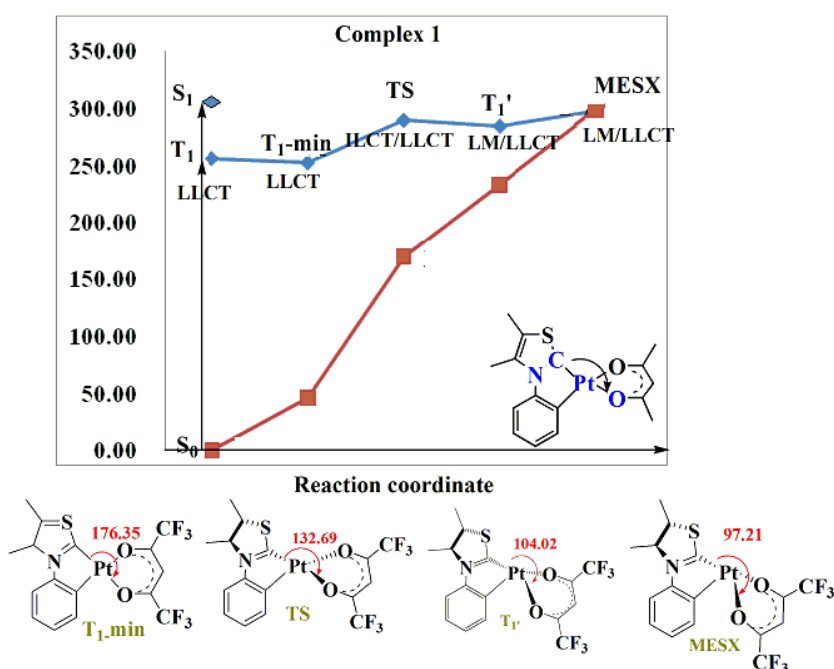|	complex 1	complex 2
λ_{max} (nm)	546	508
Φ	<0.01	0.63
τ (μs)		11.4

Figure 1. The scheme of studied molecules[4]

[Methods]: The SC-AFIR method is implemented in GRRM program is used to locate the minimum energy seam of crossing (MESXs). The DFT and TDDFT methods are used for the calculation using Gaussian09 Program. The optimized geometries of the ground and excited states are carried by B3LYP/LANL2DZ(Pt), 6-31G+(d) (C, H,O,S, N,F) level.

[Results and Discussion]

The nonradiative decay process is happened from the T_1-min→TS[T_1-min/$T_{1'}$]→MESX. The emission decay leads to elongate the metal-ligand bond and distort the FC geometries. The N-C-Pt-O angle changes from 177.50°, 176.35°, 104.92°, and 97.21° in T_1-min, TS, $T_{1'}$, MESX, respectively. Together with the emission decay, the nature of the T_1 state changes

from ligand to ligand charge transfer (LLCT) to Ligand to metal center (LM), which is consistent with the previous report, that is, the most nonradiative decay processes of Ir(Ⅲ) or Pt(II) emitters is happened on the metal-centered state (^3MC). Furthermore, although the MESX of complex 1 is higher than T_1 state at the FC, the energy barrier MESX can be easily reached when the ISC happened. The energy barrier from the T_{1-min} to TS is found to be 37.36kJ/mol.

For complex 2, the nonradiative decay process is similar with that of complex 1. The most possible emission decay is happened on the ^3MC state. But the energy barrier of complex 2 is 65.47kJ/mol, which is much higher than that of complex 1. Thus the quenching pathway of complex 1 is more favorable compared with that of complex 2. The calculated results can fully explain the experimental data(Φ <0.01 and 0.63 for complex 1 and 2, respectively)[4].
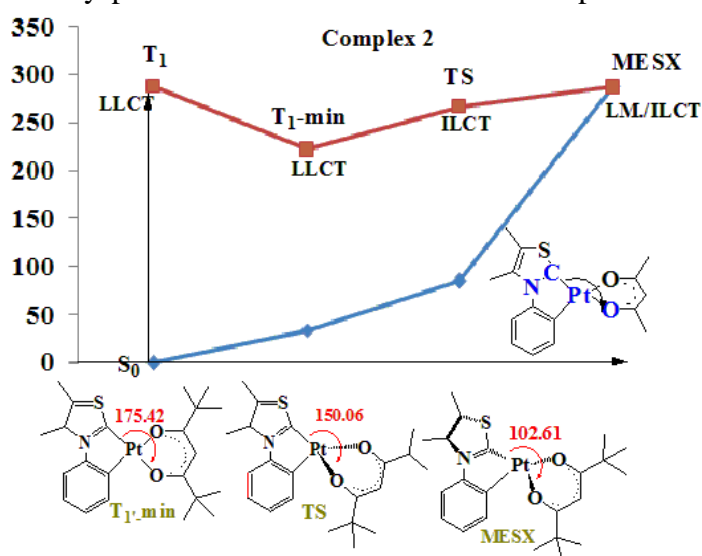
[References]

[1] Yu, M.; Zhao, Q.; Shi, L.; Li, F.; Zhou, Z.; Yang, H.; Yi, T.;Huang, C. Chem. Commun. 2008, 2115−2117.

[2] Yersin, H. Highly Efficient OLEDs with Phosphorescent Materials; Wiley: Weinheim, 2008.

[3] Wang, L.; Wen, J.; He, H.; Zhang, J. Dalton Trans. 2014, 43, 2849−2858.

[4] Leopold, H.; Heinemeyer, U.; Wagenblast, G.; Münster, I.; Strassne, T.; Chem. Eur. J. 2017, 23, 1118 – 1128