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428 Chemistry Building

In the field of photochemistry and photophysics, a high interest in substituting for rare and expensive ruthenium has risen in these years. With the goal in mind, iron seems to be a propriate metal candidate due to its abundance in the earth crust.¹ Besides, low-spin (LS) iron(II) polypyridyls have isoelectronic configuration to its ruthenium(II) polypyridyl analogues, which leads to similar visible light absorption mechanism in terms of electron transfer process from metal to ligand. However, the main reason regarding current failure of replacing ruthenium with iron is majorly attribute to the extremely short metal-to-ligand charge transfer (MLCT) excited state lifetime. Unlike the 2nd or 3rd row transitional metal complexes, metal-centered states such as ³T₁, ⁵T₂ serve as a channel for ultrafast deactivation from the MLCT excited state in LS iron(II) polypyridyls.² Ideally, this short MLCT excited state lifetime for d⁶ electron configuration LS iron(II) polypyridyls is able to be effectively prolonged by either choosing to destabilize the metalcenter states or stabilize the MLCT excited state. On the contrary, rather than adjusting ligand field strength over iron(ll) complexes, restricting corresponding vibrational motions arising from the MLCT relaxation is a relatively uncharted strategy to extend the MLCT lifetime.³ Although this idea is practical,⁴ the most challenging portion is to quantify the relaxation dynamics of the MLCT excited state because of unthermalized property of the MLCT excited state manifolds. Therefore, instead of directly probing the MLCT deactivation, two primary constituting components of the MLCT deactivation will be investigated in this research: the MLCT formation as well as ground state recovery processes. (Fig.1) The dynamics of the two specific transition processes will reveal potential vibrational motions on corresponding reaction coordinates may couple into the MLCT deactivation. Besides, this fruitful information can be also transformed into basis on molecular design of iron(II) complexes in which binding motifs is a critical factor that can affect photophysical dynamics.

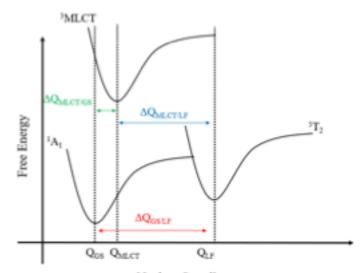




Figure 1. General potential energy diagram of reaction coordinate for LS iron(ll) polypyridyls.

References

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