

Molecular Structural Dynamics of Photoactive Transition Metal Complexes in Solar Energy Conversion Studied by Ultrafast Optical Spectroscopy and LITR-XAS

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Abstract. Transition metal complexes play important roles in solar energy conversion due to their intense absorption within the solar spectrum, their capability of transferring electron and energy through the metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT) excited state, and their capability of binding substrates through coordination geometry changes. Hence, structural dynamics of these complexes in their excited states need to be understood in order to gain knowledge of controlling solar energy conversion processes. We will present our recent studies on structural dynamics of two metal complexes using both ultrafast optical spectroscopy and laser initiated time-resolved x-ray absorption spectroscopy (LITR-XAS). In order to fully understand the roles of transition metal complexes in solar energy conversion, structural dynamics of these molecules in their excited states on ultrafast time scales are needed. We will discuss mainly two different transition metal complex systems, 1) ultrafast structural dynamics in the MLCT state of $[\text{Cu(I)(dmp)}_2]^+$ in different solvents, and 2) excited state structural dynamics of metalloporphyrins in solution. In the first system, a structural dynamics study using ultrafast up-conversion revealed time scale of the internal structural changes in the MLCT state, which provides guidance in future ultrafast structural determination using fs x-ray sources, such as LCLS. In the second system, a few examples of excited state metalloporphyrin structures obtained by LITR-XAS will be discussed with potential applications in photocatalysis and solar energy conversion.

Keywords: time-resolved X-ray absorption spectroscopy, pump-probe XAFS, LITR-XAS, excited state structures, metalloporphyrins, MLCT state structures of transition metal complexes, solar energy conversion.

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INTRODUCTION

Transition metal complexes play important roles in solar energy conversion due to their intense absorption within the solar spectrum, their capability of transferring electron and energy through the metal to ligand charge transfer (MLCT) or ligand to metal charge transfer (LMCT) excited states, and their capability of binding substrates through coordination geometry changes(1, 2). These properties enable transition metal complexes essential building blocks for conversion light to electricity, fuel and mechanical energy. The excited state molecules created by optical photons with energies within solar energy spectrum are critical initial reactants for solar energy conversion. Their structural dynamics are keys for efficient energy transfer, electron transfer and photocatalysis. Laser-initiated time-resolved (LITR) x-ray methods(3-5), such as XAS (x-ray absorption

spectroscopy), XRD (x-ray diffraction) and WAXS/SXD (wide angle x-ray scattering/solution x-ray diffraction), developed in recent years have started to provide direct structural information of the excited states with atomic resolution. While these methods are still at the beginning stages of the development and far from routinely conducted experiments, it is important to proceed beyond prototype experiments for demonstration of the feasibilities. While the fs x-ray sources just become available or will be available in a few years, it is important to understand the actual processes to be probed and their scientific impacts. Using two examples from our recent studies on structural dynamics of metal complexes with both ultrafast optical spectroscopy and LITR-XAS, we will discuss the above issues.

In this report, we will discuss two different transition metal complex systems, 1) ultrafast structural dynamics of $[\text{Cu(I)(dmp)}_2]^+$ in different

solvents, and 2) excited state structural dynamics of metalloporphyrins. In the first system, we will focus on combined approaches with ultrafast fluorescence up-conversion spectroscopy, transient absorption spectroscopy and LITR-XAS to resolve the dynamics of the MLCT excited state motions. In the second system, we will focus on recent results on the excited state structural dynamics of metalloporphyrins and their implications to the excited state properties. On one hand, both studies demonstrate the importance of the structural information to our understanding of photophysical and photochemical properties of these molecules and the impact on rational design of molecular systems for solar energy conversion applications. On the other hand, these studies provide guidance in future ultrafast structural determination using fs x-ray sources, such as LCLS (Liner Coherent Light Source).

1. ULTRAFAST STRUCTURAL DYNAMICS OF $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ IN DIFFERENT SOLVENTS

In our previous work, structural origins of the MLCT excited-state behavior of $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) was investigated using LITR-XAS (6, 7). Absorption of a visible photon promotes an electron from Cu^{I} to one of the dmp ligands, achieving intramolecular charge separation with a $\text{Cu}^{\text{II}*}$ center coordinated to one reduced and one neutral dmp ligand (8-10). The initial Franck-Condon MLCT state has the identical pseudotetrahedral coordination geometry as the ground state, but the $\text{Cu}^{\text{II}*}$ center with a d^9 electronic configuration is susceptible to a Jahn-Teller distortion resulting in a MLCT state with flattened tetrahedral coordination (Figure 1) (11). The MLCT excited state lifetimes of this complex are highly solvent dependent, which are around 100 ns in noncoordinating solvents, and 1-2 ns in coordinating solvents. It was believed that a radiative decay pathway is though the formation of a penta-coordinate complex with a strongly coordinating solvent molecule, resulting in the “exciplex” quenching.

The respective elongation and the shortening of the average Cu-N bond distance for the MLCT state of the $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ in noncoordinating toluene and in coordinating acetonitrile, respectively(6,7), signaling the difference in the interactions of the copper with the fifth ligand. Such variation was also seen by a broad range of the MLCT state lifetimes in various Lewis base solvents with different electron donating capabilities. The variation of the MLCT state structure in different solvents confirmed that the origin of distinctly different excited-state behavior is due to

formation of MLCT state-solvent complexes with different electronic interactions. When the interaction is strong, the MLCT state lifetime is shortened significantly and the luminescence is quenched, which has been characterized by the “exciplex” formation in previous literature. Therefore, the pump-probe XAFS measurements in the time domain provide new insights into the fundamental aspects of structural factors that may influence photoinduced electron and energy – transfer processes(12).

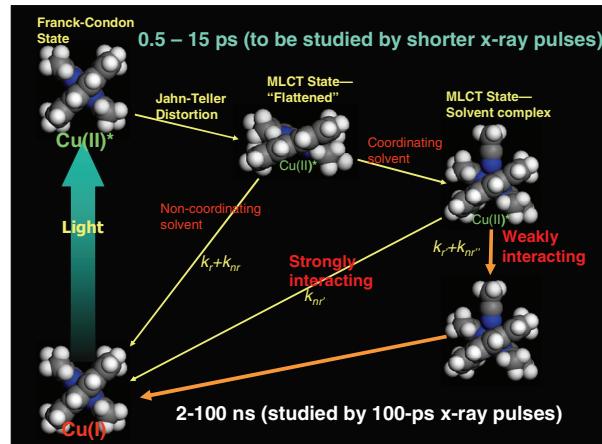


FIGURE 1. Structural dynamics of the MLCT state of $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ which has been demonstrated by the previous LITR-XAS studies.

In addition to the LITR-XAS studies, we used the ultrafast optical transient absorption and fluorescence

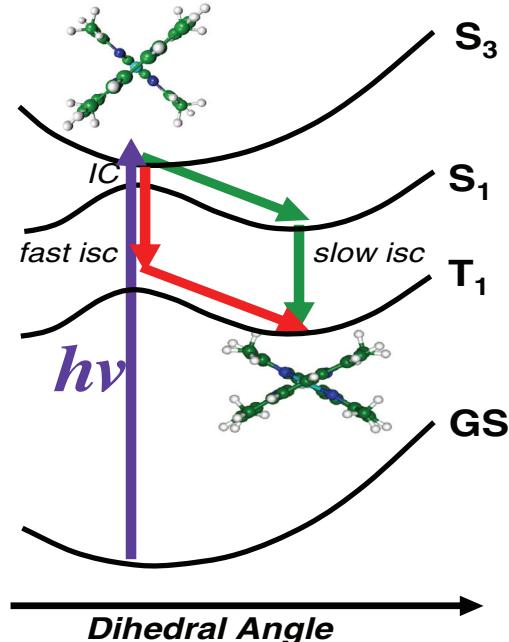


FIGURE 2. MLCT excited state pathways the of $[\text{Cu}^{\text{I}}(\text{dmp})_2]^+$ which has been demonstrated by the ultrafast optical spectroscopy.

up-conversion to probe the time scale for the initial fast flattening motions in order to determine if these motions can be probed by future fs x-ray sources. Based on the optical studies, a potential surface diagram for $[\text{Cu}^{\text{l}}(\text{dmp})_2]^+$ can be constructed in FIG. 2.

Although the detailed description of the ultrafast optical spectroscopic studies is beyond the scope of the manuscript, the two main conclusions from these ultrafast optical studies are 1) the flattening of the tetrahedral Frank-Condon state (FIG. 1) is an inner sphere process, independent of solvents, which has been demonstrated by invariance of the sub-ps and ps time constants in solvents with large variation of viscosities, and even in solid state polymer matrix; 2) the excited state intersystem crossing and fluorescence decay constants are strongly structural dependent on the dihedral angles between the two dmp ligands, where the intersystem crossing (ISC) slows down as the dihedral angle changes from near 90° at the Franck-Condon state to the flattened conformation, demonstrated by ultrafast fluorescence up-conversion results, and 3) the time scale of the flattening is on the order of 100 fs or faster, which implies future challenges in monitoring this coherent flattening with ultrafast x-ray sources. Nevertheless, the solvent ligation process following the flattening is expected to be slower and creates significant changes in XANES features, which can be easily observed with sub-ps or ps x-ray pulses. Our study indicates the importance of obtaining dynamics information of the ultrafast molecular motions in the excited states before LITR-XAS studies. Several other molecular systems with MLCT state lifetimes much longer than the current 75-ps x-ray pulses at the Advanced Photon Source have been studied and the data analyses are in process.

2. STRUCTURAL DYNAMICS OF EXCITED STATE METALLOPORPHYRINS

Metalloporphyrin excited states frequently act as electron donor/acceptor or light harvesting antenna in solar fuel/electric production processes due to their analogous structure and properties in natural photosynthesis. In addition, the versatility of the central metal in metalloporphyrins creates various possibility of using these compounds in photochemical reactions to induce bond formation or cleavage(13, 14). Using LITR-XAS method, the transient ligation species as well as transient oxidation changes of the metal in metalloporphyrins can be studied with 100-ps time resolution. Recently, we carried out studies on the singlet and triplet excited state structures of zinc tetraphenylporphyrin (ZnTPP) with and without the axial ligation. The experiments were conducted under

the special timing mode of the Advanced Photon Source with a hybrid fill pattern, where one super bunch with 16 mA is separated from other 56 bunches grouped by 8 septuplets. The separation between the single super bunch and the 56-bunch pulse train is

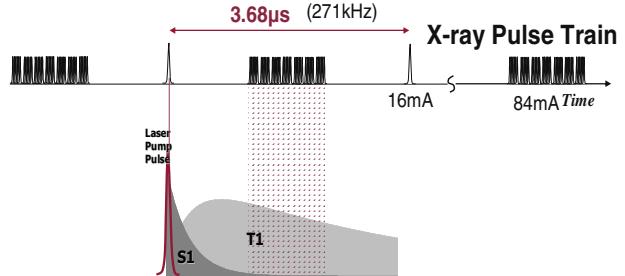


FIGURE 3. X-ray pulse sequence used in simultaneously probing S_1 and T_1 states of ZnTPP.

1.8 μs . The lifetime of the singlet state ZnTPP in toluene is 2 ns at room temperature while that of the triplet state is about 1.2 μs in the presence of air. Both of the lowest energy singlet (S_1) and triplet (T_1) states of ZnTPP are $\pi-\pi^*$ transitions that do not involve metal d orbitals of Zn directly, although the HOMO a_{2u} has significant electron densities on four N atoms directly linked to Zn (FIG. 4A)(15). Therefore, the lowest energy singlet state S_1 will unavoidably perturb the electron density on N atoms, creating Zn-N distance change. The energy levels of the different states of this molecule are presented in FIG. 4B, where the photoexcitation to S_1 and S_2 states, the internal conversion from S_2 to S_1 and intersystem crossing from S_1 to T_1 are clearly indicated. The former takes only a few ps and the latter, around 2 ns at room temperature. Hence, it is feasible to probe the structure of the lowest energy singlet state S_1 using the super single bunch by setting the time delay between the laser pulse and x-ray pulse within 100 ps, and to probe that of the lowest energy triplet state T_1 using

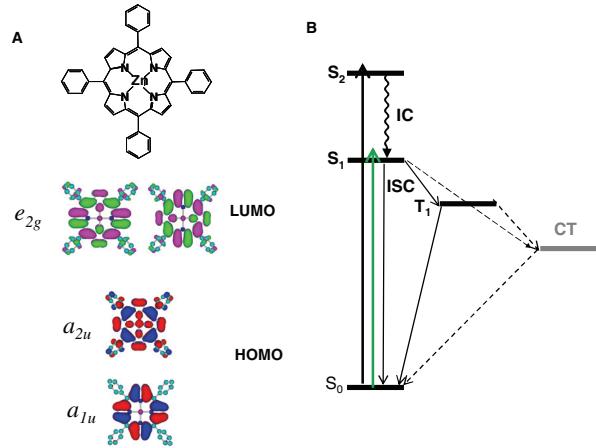


FIGURE 4. a) Molecular structure of ZnTPP with wavefunction distributions of the HOMO and LUMO,

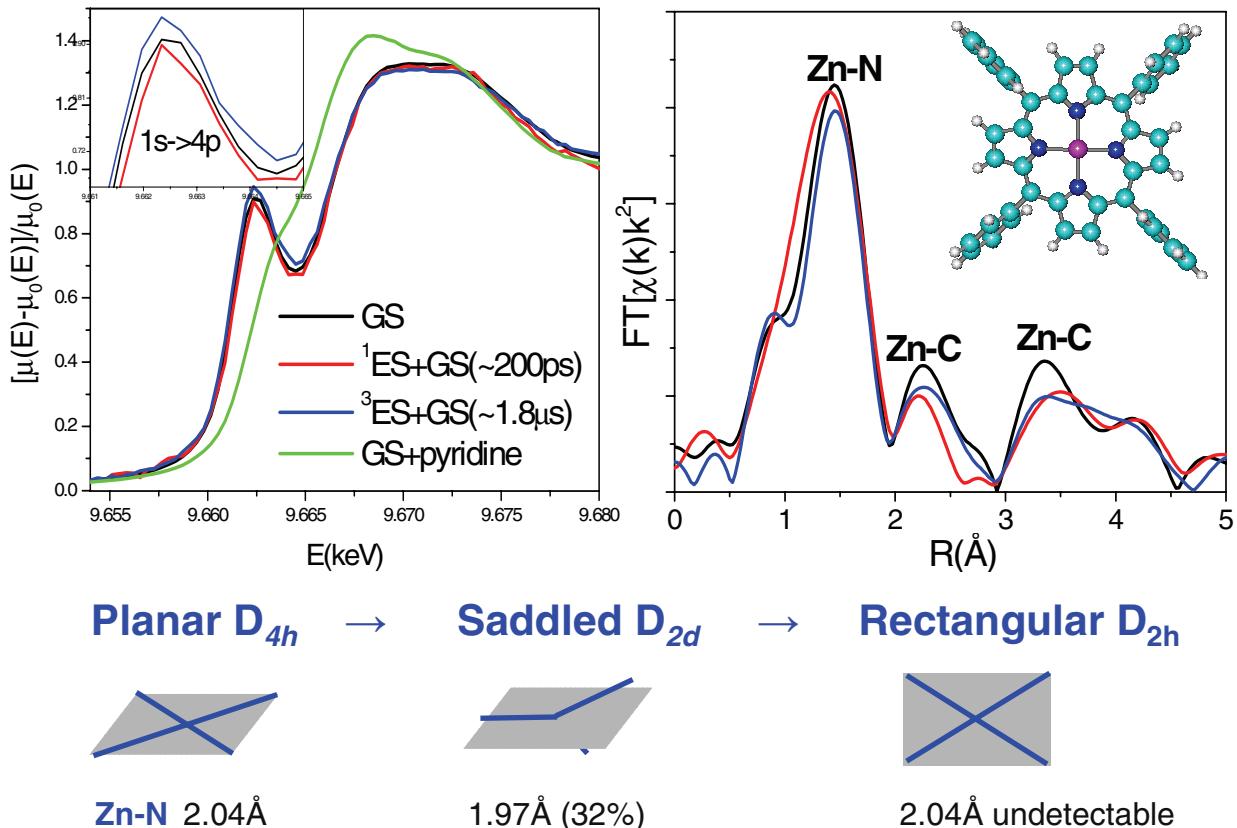


FIGURE 5. XANES and XAFS results of ZnTPP excited state along with those of its ground state and penta-coordinated ZnTPP-pyridine adduct.

the pulse train separated by 1.8 μs following the super-bunch overlapping in time with the S_1 state. The XAFS results indicate the significant structural changes in the singlet state (FIG. 5), but very indicating possible electron density distribution on N atoms that may be the origin for the structural changes. Little structural change was observed in the triplet state. In the XANES region, slightly variation in the 1s to $4p_z$ peak is observed, which may be related to small differences in covalency due to the variation of the electron density in $4p_z$. Apparently, there is no significant change in coordination geometry in the either excited states extracted from the XANES spectra.

However, the S_1 state ZnTPP in toluene shows observed changes on the average Zn-N bond distance that shortens by 0.07 \AA from 2.04 \AA for the ground state to 1.97 \AA . Considering the planar structure of the ground state ZnTPP in crystal and in solution, the most likely distortion to achieve shortened Zn-N bonds is to have a saddled structure where two of the four Zn-N bonds are oriented above and the other two are below the original plane defined by ZnN_4 in the ground state structure (FIG. 5). Although the distortion of the T_1

state structure from that of the ground state has been documented in literature as changing the symmetry of the molecule from D_{4h} to D_{2h} , where the square shaped molecule becomes a rectangle(16), we did not observe detectable changes in the Zn-N bond lengths. This could be due to the following reasons: 1) the T_1 state has a lifetime of 1.2 μs in the presence of air as in the experiment, which was too short for the pulse train separated 1.8 μs from the excitation laser pulse to detect sufficient population of the excited state; and 2) the distortion from a square to rectangle is insensitive in both XANES and XAFS features. In order to model the structural changes observed in the experiments and rationalize the nuclear displacement with their electronic configuration in the excited state, we are currently explore the TDDFT (time-dependent density functional theory) calculations on the excited state structures.

The other metalloporphyrins under investigation are Ni(II)- and Cu(II)-porphyrins(17, 18). The former has a very flexible non-planar structure due to the small size of Ni in the macrocycle. The excited state lifetimes of Ni-porphyrins are very short in comparison with ZnTPP, due to additional

deactivation pathways of the excited state, such as vibrational relaxation, intersystem crossing and interactions with solvent molecules. Several years ago, we investigated the structure of the photodissociation product of Ni-tetr phenyl porphyrin in solution with a sextuplet x-ray pulse cluster as a probe limited to 14-ns time resolution(17). Using currently available single x-ray pulses with 75-ps duration, we are in a process to reinvestigate the photophysics of Ni-porphyrin with much higher time resolution than before. We have observed a wide range of the lifetime of the excited states for various Ni-porphyrins with different peripheral groups in various solvents, and are in a process to rationalize the structural changes with the excited state lifetimes in different porphyrin derivatives. Moreover, we started to measure the transient structure after the photocleavage in a bis-Fe(III)porphyrin system. The LMCT state of the molecule can be induced via UV excitation which eventually triggers the Fe-O bond cleavage producing one high valence Fe(IV) and one low valence Fe(II). The electronic structural difference between the closed configuration of the ground state and the open configuration of the excited state are reflected in the LITR-XAS spectra collected within 200 ps after the LMCT transition. The direct structural information of the excited state metalloporphyrins obtained in our experiment provides for the first time the possibility of mapping out the structure and reactivity correlation in photochemical reactions.

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