Electronic Coherence in Solar Energy Conversion Processes in Transition Metal Complexes: Visualization and Control

Lin X. Chen

Chemical Sciences and Engineering Division, Argonne National Laboratory
Department of Chemistry, Northwestern University

Solar energy conversion processes in natural photosynthesis are carried out via chlorophyll arrays and supramolecular transition metal cluster complexes. These photosynthesis machineries perform light-induced energy and electron transfer through coherent electronic couplings among themselves, which has been shown to facilitate long distant light harvesting effectively. This discovery prompted question in how to design synthetic light conversion systems to carry out the similar tasks where the correlations between electronic coherence and system functions needs to be examined and understood. Many multi-metal center transition complexes are motifs of redox active centers in nature where multi-electron redox processes occur to split water for hydrogen and oxygen. It has been puzzling how one can use a series of single photon events in light harvesting to perform multiple electron redox reactions. The key question is how different metal centers are coupled. These multi-metal complexes are molecular system but they also contains the smallest core metal clusters with metal-metal bonds. Recently, we start to examine the electronic coherence in multi-metal center transition complexes that are relevant to light harvesting and electron transfer induced by sunlight using ultrafast transient absorption anisotropy. The first study uses a conventional single color pump-probe transient absorption anisotropy with ~40 fs pulse durations to investigate the observed electronic coherence between two halves of a Pt(II) dimer in a platinum phenylbipyridine pyrazolate dimer complex(Figure 1).

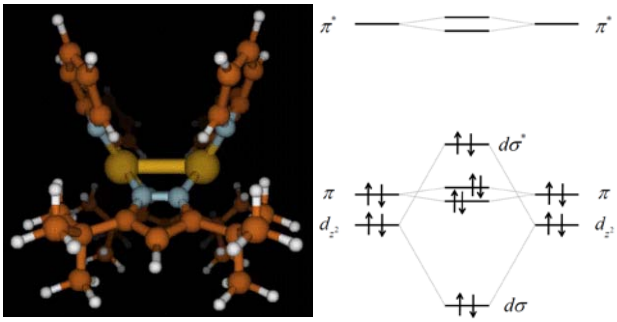

Figure 1. Left: Molecular structure of **[Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$**; Right: Molecular orbitals formed from two halves of the molecule (the monomer).

The Pt(II) dimer complex, **[Pt(ppy)(μ-^{t}Bu$_2$pz)]$_2$,** (synthesized by the Castellano Group in Bowling Green State University) has two interacting $5d_{z^2}$ orbitals from each Pt atom due to the bulky *ter*-butyl groups attached to the pyrazolate bridging units. Our study found that this interaction was mediated coherently via the coupling of the two metal-to-ligand-charge-transfer (MLCT) electronic transitions. These transitions are normally responsible for the light induced electron transfer converting the photon energy to drive electron injection to other parts of the systems, enabling the function of the materials as vehicles of providing the energy forms converted from the sunlight. The coupling of the

two MLCT or ligand centered (LC) transitions due to the Pt-Pt interaction created a new transition due to metal-metal-to-ligand-charge-transfer (MMLCT) transition.

When this transition was excited, we observed anticorrelated oscillations in the polarization directions parallel and perpendicular relative to the excitation polarization. The oscillations proceed sequentially with two distinct frequencies, 320 cm^{-1} from 0 − 200 fs after photoexcitation, and then 110 cm^{-1} from 200 − 2000 fs, respectively. The static Raman spectrum of the compound confirmed the later frequency, which has been assigned as the Pt-Pt stretch.

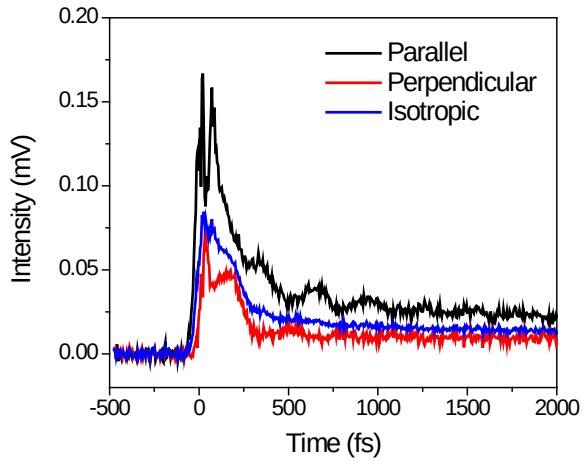

Figure 2. Parallel, perpendicular, and magic angle transient absorption signals as a function of the time delay from the excitation pulse (40fs fwhm) in toluene after photoexcitation of the MMLCT band at 510 nm.

Combined with the ultrafast fluorescence decay results of this compound, we discovered the following facts that could have important implications in coherent interactions in multiple metal center photoactive systems for solar energy conversion and multiple electron redox sites.

1. Contributions from the monomer centered MLCT transition are coherently coupled through an overlap between the $5d_{z^2}$ orbitals from the two Pt atoms, resulting in the electron density shifting alternatively between the two halves of the molecule;

2. The coherence between the two parts of the molecule has been surpringly preserved even after the ultrafast intersystem crossing from the initial singlet MMLCT to its triplet state, which implies that the intersystem crossing pathway is likely through the potential surface far from the equilibrium position where the barrier is minimum;

3. The vibrational motions of Pt-Pt stretching can modulate the coupling in the electronic transition and hence the electronic coherence.

The questions under discussions are mainly focused on (1) what roles of electronic coherence in synthetic systems are in their photoinduced energy and electron transport; (2) if we can design molecular systems that are efficient in solar conversion via enabling the electronic coherence, (3) what the structural factors are for such electronic coherence, and (4) how the electronic coherence facilitates reaction pathways on the potential surfaces which are far from equilibrium and what structural design will enable such properties,