

# Spin-Orbit Coupling Induced Heterogeneous Excited-State Dynamics of 6-Coordinate Transition Metal Protodyes

Verma, Archana

Characterizing excited-state behavior of inorganic complexes is pivotal to developing efficient dyes for dye-sensitized solar cells. In this study, femtosecond spectroscopy characterized inorganic protodyes to identify if symmetry can reduce the heterogeneity induced by spin-orbit coupling. Matveev et al. (2015) did not identify ultrafast dynamics in  $[\text{IrBr}_6]^{2-}$ . Electronic dynamics of the Oh  $[\text{IrBr}_6]^{2-}$  was compared to the D4h  $[\text{Ir}(\text{CN})_2\text{Br}_4]^{2-}$ .  $[\text{IrBr}_6]^{2-}$  and  $[\text{Ir}(\text{CN})_2\text{Br}_4]^{2-}$  were synthesized and analyzed by mass spectrometry, UV-Vis spectrophotometry, transient absorption, coherent wavepacket evolution analysis (CWEA), and 2D electronic spectroscopy (2DES).  $[\text{IrBr}_6]^{2-}$  had six absorption bands, but did not fluoresce. CWEA was able to identify excited state potential energy levels at 650nm and 725nm (corresponding to the wavelength of the absorbed photon). Transient absorption showed ultrafast relaxation which was undetected by Matveev et al. (2015), and the ultrafast 2DES slice showed an accessible triplet state at low energy excitations (~750nm). The D4h  $[\text{Ir}(\text{CN})_2\text{Br}_4]^{2-}$  has only four absorption bands. CWEA indicated an accessible conical intersection.  $[\text{Ir}(\text{CN})_2\text{Br}_4]^{2-}$  has a conical intersection, and a triplet state accessible at ultrafast lifetimes at high energy excitations (~550nm). Varied symmetry altered some aspects of electronic dynamics (UV-Vis spectra, energy at which triplet state is accessible), it did not eliminate heterogeneity, suggesting spin-orbit coupling drives heterogeneity in timescale and wavelength. Future moieties to investigate include  $[\text{Ir}(\text{Pph}_3)\text{Br}_4]$  to expand to larger systems and  $[\text{Ir}(\text{F}_2\text{ppy})\text{Br}_4]$  to isolate whether molecular orbital energy level splitting or less defined spin states induces the heterogeneity.

## Awards Won:

Second Award of \$2,000

American Chemical Society: Third Award of \$2,000