

## GROUND- AND EXCITED-STATE CHARACTERIZATION OF A Ni-BIPYRIDINE PHOTOCATALYST USING X-RAY SPECTROSCOPY

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Photo-assisted catalysis using Ni complexes is an emerging field for cross-coupling reactions in organic synthesis. However, the mechanism by which light enables and enhances reactivity is poorly understood. Optical techniques can lend insight into the ground- and excited-states of the photocatalysts but lack the specificity to interrogate electronic and geometric structural changes at specific atoms. Through static and transient L- and K-edge X-ray absorption spectroscopy of a prototypical bipyridine-based Ni(II) photocatalyst, we are able to determine that the ground-state of complex features an unexpected mixed-spin character. We are also able to unambiguously determine that the long-lived (5 ns) excited state is a tetrahedral metal-centered triplet state. The mixed-spin character of the ground state can have profound impact on the excited-state properties and reactivity that are not well understood. In addition, these findings can drive future synthetic design of improved photocatalysts via judicious tuning of the electronic and geometric properties of the ligands.