

ULTRAFAST ELECTRON TRANSFER AND SPIN FLIP IN A HETEROBIMETALLIC COMPLEX

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A major channel of energy loss in solar energy conversion is nonradiative charge recombination, whereby photochemical or photovoltaic energy is lost to the surroundings as heat. Understanding the mechanism of charge recombination, particularly the timescale and coupling to nuclear and spin degrees of freedom, is critical for understanding how to promote long-lived charge separation. In this regard, bimetallic molecules with metal-to-metal charge transfer (MMCT) transitions are valuable model systems because the charge recombination reaction can be initiated with light by directly populating the charge transfer state.

We employed femtosecond optical transient absorption (OTA) spectroscopy to monitor charge recombination following MMCT excitation in a heterobimetallic Fe(II)Co(III) complex. The measurements uncovered a long-lived excited state with a 500 ps lifetime. Time-dependent density functional theory (DFT) allowed for assignment of this state as a metal-centered high spin state. The combined experimental and theoretical approach pointed to an ultrafast intersystem crossing and charge recombination to a local, intermediate-spin, metal-centered excited state, followed by a slower intersystem crossing to the long-lived high-spin state. These results uncover the intricate mechanism of charge recombination in this molecule by elucidating the spectral signatures, lifetimes, assignments, energetics, and nuclear geometries of the states involved. The coupling of the electron transfer to vibrations and spin in this complex could account for the ultrafast timescale of the charge recombination and could be a target for promoting long-lived charge transfer states through synthetic tuning.