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**Tracking the charge and spin dynamics of electronic excited states in inorganic complexes<sup>1</sup>**

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Inorganic complexes have many advantageous properties for solar energy applications, including strong visible absorption and photocatalytic activity. Whether used as a photocatalyst or a photosensitizer, the lifetime of electronic excited states and the earth abundance of the molecular components represent a key property for solar energy applications. These dual needs have undermined the usefulness of many coordination compounds. Isoelectronic iron and ruthenium based complexes represent a clear example. Ru-polypyridal based molecules have been the workhorse of solar energy related research and dye sensitized solar cells for decades, but the replacement of low abundance Ru with Fe leads to million-fold reductions in metal to ligand charge transfer (MLCT) excited state lifetimes. Understanding the origin of this million-fold reduction in lifetime and how to control excited state relaxation in 3d-metal complexes motivates the work I will discuss. We have used the spin sensitivity of hard x-ray fluorescence spectroscopy and the intense femtosecond duration pulses generated by the LCLS x-ray laser to probe the spin dynamics in a series of electronically excited  $[\text{Fe}(\text{CN})_{6-2N}(2,2'\text{-bipyridine})_N]^{2N-4}$  complexes, with  $N = 1-3$ . These femtosecond resolution measurements demonstrate that modification of the solvent and ligand environment can lengthen the MLCT excited state lifetime by more than two orders of magnitude. They also verify the role of triplet ligand field excited states in the spin crossover dynamics from singlet to quintet spin configurations.

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