

DETERMINING THE CHARGE TRANSFER PROPERTIES OF METAL-COORDINATED COUMARIN DYES USING X-RAY AND OPTICAL TRANSIENT ABSORPTION SPECTROSCOPIES

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Organic dyes present a promising alternative to the more expensive ruthenium and iridium complexes commonly used in photoredox reactions. Ideally, such a framework should offer facile tunability of the excited state redox potential while maintaining sufficiently long excited state lifetimes for intermolecular charge transfer. Here we have augmented the coumarin derivative 4-methylesculetin with dipicolylamine to form a tetrahedral binding pocket that can then coordinate different divalent first-row transition metals, allowing us to tune the excited state redox potential by simply adding a salt. Using X-ray transient absorption spectroscopy, we have observed photoinduced reductive shifts in the K-edge spectra of the corresponding complexes of Mn^{2+} through Zn^{2+} that are consistent with the varying degrees of intramolecular charge transfer to the metals predicted by density functional theory calculations. We have also combined these X-ray measurements with optical transient absorption spectroscopy to characterize the relaxation dynamics of these complexes on timescales ranging from 100s of femtoseconds to 10s of microseconds. As expected, the Zn^{2+} complex exhibits little to no charge transfer character, and any electronic or nuclear rearrangement at the metal site fully relax within the temporal resolution of our measurement. On the other hand, all other metal complexes exhibit long-lived charge transfer states that persist for 100s of nanoseconds. Notably, the relaxation dynamics of the Co^{2+} complex include an additional time component of approximately 10 nanoseconds that is entirely absent in the other metal complexes.