

Probing the Mechanism of Energy Transfer in Luminescent Lanthanide Complexes by Ultrafast Optical and X-ray Absorption Spectroscopy

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Trivalent lanthanide complexes have a wide range of applications in science and industry due to their long-lived emission in the visible/near-IR spectrum,¹ which originates from transitions between lanthanide excited 4f states. We have demonstrated the ability of the 1-hydroxypyridin-2-one (HOPO) ligand to bind and efficiently sensitize Eu(III) through energy transfer (ET), resulting in bright lumiphores.² The structural motif across our library of Eu-HOPO complexes is extremely similar, yet there is a large variation in luminescence brightness across the series that is largely due to variations in ET efficiency. Also, both the dominant ET pathway and the effect of ligand structural perturbations on ET efficiency are unclear. Here, we utilize pump-probe optical and X-ray spectroscopies to probe the excited-state properties of Eu-HOPO complexes and determine both the dominant ET pathway (Förster resonant energy transfer or Dexter charge exchange) and the source of variation in the sensitizer efficiency in these systems. Ultrafast optical transient absorption (OTA) spectroscopy has revealed that Dexter charge exchange from the ligand triplet state has a ~100% yield, with the sensitizer efficiency largely dictated by the ligand singlet excited-state dynamics. Microsecond X-ray transient absorption (XTA) spectra at the Eu L_{III} edge exhibit changes in both the $2p \rightarrow 4f$ and $2p \rightarrow 5d$ absorption bands consistent with a change in 4f-5d orbital hybridization in the absence of structural reorganization,³ influencing sensitizer efficiency in these systems.⁴ Ongoing measurements focus on ultrafast XTA, where the timescale of 4f excited state population can be correlated with the ligand singlet and triplet decay times from OTA to determine the dominant ET mechanism in the Eu-HOPO complexes. These results will enable the further rational design of ligands optimized for highly-efficient sensitization of trivalent lanthanides.

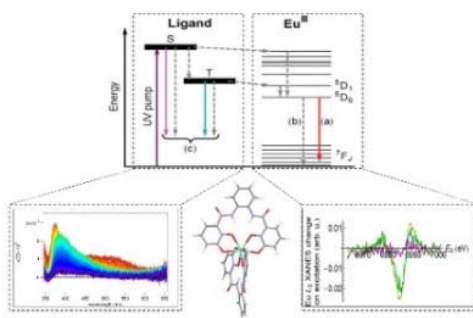


Figure 1. Dynamics of photoexcited Eu-HOPO complexes, as probed through optical transient absorption (left) and X-ray transient absorption (XTA)

References

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