

Dynamics of metal-coordinated coumarin dyes for photoswitching applications

PhD Seminar

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Photoacids are molecules that exhibit changes in the acidity of particular protons in the electronic excited state. While these changes are typically used to facilitate photoinduced proton transfer, they can also be utilized to drive configurational photoswitching events. Here we have augmented the coumarin derivative 4-methylaesculetin (4ME) with dipicolylamine (DPA) to form a photoswitchable tetrahedral binding pocket for transition metal ions. Coordinating divalent first row transition metals in these pockets allows us to study the ultrafast configurational dynamics of these complexes using a combination of X-ray and optical transient absorption spectroscopies on timescales ranging from sub-picosecond to a few nanoseconds. This approach reveals the kinetics of metal unbinding/rebinding and the concomitant photophysical relaxation of the dye-centered excited state through metal-centered ligand field states. We have observed that in most metal-bound dye cases, unbinding of the metal from the dye occurs within 1 picosecond, followed by rebinding of the metal and relaxation to the lowest metal-centered state in 5-100 picoseconds and ultimately relaxation to the ground state on timescales on the order of 100s of nanoseconds. Notably, in the case of the Fe^{2+} complex, we do not observe the dye-centered state at all, demonstrating that the metal-centered state is populated within our instrument response time of ~ 150 femtoseconds. Finally, the lack of ligand-field states in the Zn^{2+} complex allows us to observe the photophysical dynamics of the metal-coordinated dye-centered state on the nanosecond timescale, revealing a greater degree of tautomerization than observed for the metal-free dye. By understanding the dynamics of the 4ME-DPA complex, we can optimize the design of the dye for specific applications. These switches, when coupled with energy transfer from a dye, can be utilized in supramolecular energy transfer relays or as a method to physically separate charge transfer states to slow recombination pathways.