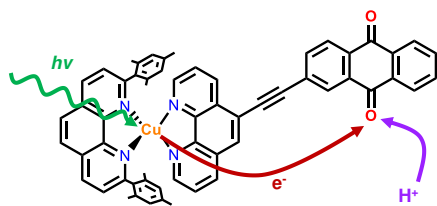


INVESTIGATION OF ULTRAFAST ELECTRON AND PROTON TRANSFER PROCESSES IN COPPER-ANTHRAQUINONE DONOR-ACCEPTOR MOLECULES

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We have investigated the photochemistry of molecular dyads composed of a light absorbing Cu(I) diimine species covalently linked to an anthraquinone moiety (CuAnQ). These donor-acceptor molecules serve as Earth-abundant prototypes for studying charge accumulation mechanisms in donor-acceptor-donor triads. We have utilized ultrafast optical and NIR spectroscopy to study the kinetics of the electron transfer, taking advantage of the optical and NIR signatures of the AnQ⁻ radical anion.



After excitation into a ¹MLCT band, we observe electron transfer from Cu to AnQ in 10's of picoseconds, forming a charge-separated state (CSS). The assignment of the CSS to Cu²⁺AnQ⁻ was confirmed by spectroelectrochemical study of the Cu⁺AnQ⁻ species. The CSS relaxes back to the ground state in 3 nanoseconds.

In the presence of a protic solvent, the charge-separated state further transforms into a new species. The spectral changes suggest this product results from protonation of the AnQ⁻ into the semiquinone radical (HAnQ[•]). Accompanying this protonation is an extension of the charge-separated state lifetime from 3 ns to 15 ns.

These results provide promise for future studies on the CuAnQCu triad, which can potentially form the double reduced Cu²⁺AnQ²⁻Cu²⁺ and Cu²⁺H₂AnQCu²⁺ CSSs. Preliminary experiments which indicate CO₂ binding to the Cu²⁺AnQ⁻ and Cu²⁺HAnQ[•] CSSs are still underway.