CoE EQUITANT Seminar

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Shedding Light on Future Solar Fuels:

Investigating the photophysics of two inorganic water-splitting photocatalysts

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Solar driven hydrogen production from water is a sustainable alternative to fossil fuels, but suffers from the large energy requirements of water-splitting redox reactions. Efficient photocatalysts for water splitting need to generate long-lived charge-separated states with the ability to oxidize water or reduce aqueous protons. Several potential photocatalysts are investigated here using ultrafast transient absorption and emission techniques to observe the excited state dynamics of charge separation and recombination. Ruthenium(II) polypyridyl systems display metal-to-ligand charge-transfer (^{3}MLCT) excited states which undergo interligand electron transfer (ILET) with a dynamic rate, initially behaving as an ultrafast barrierless process, but transforming into a much slower activated process as excess energy is vibrationally released over 100 ps following excitation.[1] These Ru(II) complexes undergo slow electron transfer to a cobalt(II) catalytic center linked via 1,2,3-triazole, compared to other Ru(II)-Co(II) systems.[2] Citrate coated CeO_2 nanoparticles[3] demonstrate ultrafast trapping of holes upon excitation with UV light, forming significantly deeper traps than has been observed in other metal oxides. The corresponding electrons appear to form long lived Ce^{3+} sites, observable on timescales of minutes. The fate of both charge carriers is pH dependent, indicating that CeO_2 may be an effective water-splitting photocatalyst under basic conditions.

(1) Stark, C. W.; Schreier, W. J.; Lucon, J.; Edwards, E.; Douglas, T.; Kohler, B. Interligand Electron Transfer in Heteroleptic Ruthenium(II) Complexes Occurs on Multiple Time Scales. *J. Phys. Chem. A* **2015**, *119*, 4813–4824.

(2) Lombard, J.; Boulaouche, R.; Amilan Jose, D.; Chauvin, J.; Collomb, M.-N.; Deronzier, A. Synthesis and Properties of Trinuclear Polypyridyl Complexes Ru(II)–Co(II)–Ru(II) and Ru(II)–Co(III)–Ru(II): Their Photoinduced Interconversion. *Inorganica Chim. Acta* **2010**, *363*, 234–242.

(3) Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P. Fundamentals and Catalytic Applications of CeO_2 -Based Materials. *Chem. Rev.* **2016**, *116*, 5987–6041.

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