Disentangling the Injection Kinetics of Ru(II)-Polypyridyl Dyes on TiO_2

Scientific Achievement

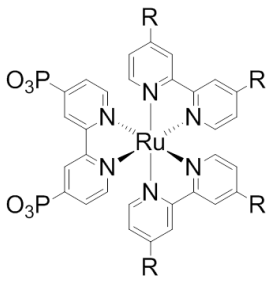
Found that the complex kinetics of Ru(II) MLCT states on TiO_2 are largely due to injection from manifold excited states.

Significance and Impact

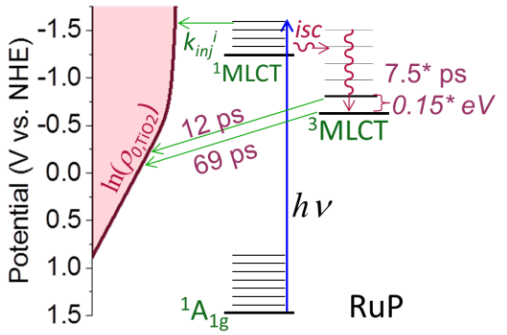
Provides guidance on synthetic design of chromophore-catalyst assemblies for solar fuels production

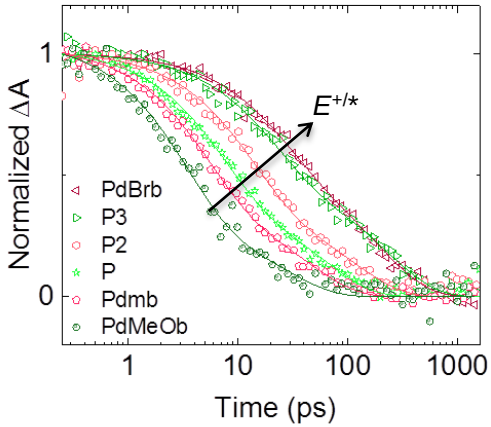
Research Details

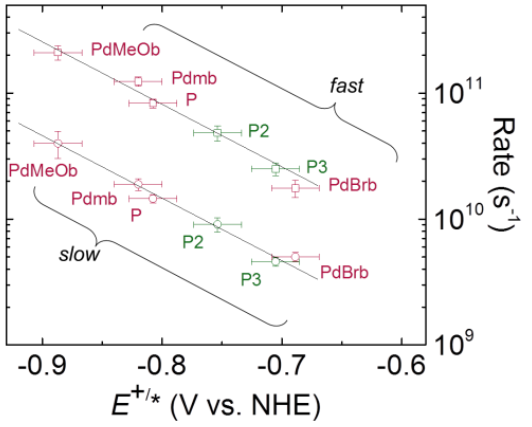
- 12 Ru(II) dyes on TiO_2 investigated by emission spectral fitting, electrochemistry, spectroelectrochemistry, fsTA and kinetic analysis
- Slow component: Injection from thermally relaxed MLCT state
- Fast component (<30 ps): Injection from hot excited states (~0.15 eV higher in energy)
- All Ru(II)-polypyridyl dyes exhibit a common cooling time of ~7.5 ps



Dye	R
PdMeOb	OMe
Pdmb	Me
P	H
PdBrb	Br
P2	$H;PO_3H_2$
P3	PO_3H_2







Upper left 6 of 12Ru(II)-polypyridyl dyes studied on TiO_2 in pH 1 perchloric acid.

Lower left Transient decay traces at 376 nm for the dyes on TiO_2 excited with 420 nm light (100 nJ/pulse). The points correspond to observed time points and solid lines are bi-exponential functions fit by non-linear least squares

Lower right Plot of longer time constant (slow) and shorter time constant times the pre-exponential (fast). Overlaid exponential curves are best fits of Marcus-Gerischer theory.

Upper right Semi-quantitative Jablonski diagram showing the injection kinetics for RuP. Values with * indicate constants associated with all Ru(II)-polypyridyl dyes.

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Disentangling the Physical Processes Responsible for the Kinetic Complexity in Interfacial Electron Transfer of Excited Ru(II) Polypyridyl Dyes on TiO_2. In Preparation

Work was performed at the University of North Carolina at Chapel Hill