Exploring the intrinsic charge separation and recombination rates in ligand-to-metal charge transfer excited states of bimolecular photocycles.

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Abstract

The current interest on increasing the efficiency of solar-energy harvesting methods unfolded a competitive search for the ideal photoactive complex for photo-redox catalysis. A crucial part of designing the ideal molecular system with an optimal performance is to elucidate the dynamics of the photoexcited transitions and the charge transfer mechanisms that can intervene in a photo-catalytic cycle for energy production. [1-4]

In this work, we aim to elucidate the luminescent ligand-to-metal charge transfer (LMCT) excited state in bimolecular electron transfer reactions, by focusing on rhenium (II) (Re^{II}) complexes with photo-redox active ^{2}LMCT excited states. Thanks to its nanosecond lifetimes and high excited state oxidation potentials, Re^{II} can be reduced by a large range of electron donors. [5-7]

Ultrafast transient absorption spectroscopy with 20-fs time resolution is therefore used to investigate the the excited state dynamics in solution, and ultimately trace the full photocycle between a Re^{II} complex and the electron donor (Fig 1). The intrinsic rates of the photocycle are unraveled by using high concentrations of electron donor (~5.7 M), which allows to work in the regime of close contact between the electron donor and the Re^{II} complex and disentangle the rate of diffusion.

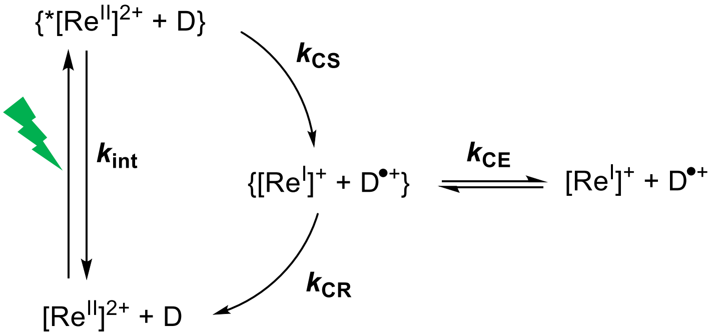

Fig 1. *Photocycle between a rhenium(II) photosensitizer $[Re]^{2+}$, and the electron donor, D. k_{int} = intrinsic decay rate of excited $[Re]^{2+}$; k_{CS} = rate of charge separation; k_{CR} = rate of charge recombination; k_{CE} = rate of cage escape.*

References.

[1] *Science*, **2019**, *363*, 249 – 253; [2] *J. Am. Chem. Soc.* **2020**, *142*, 8565–8569; [3] *J. Am. Chem. Soc.* **2021**, *143*, 15661–15673; [4] *J. Am. Chem. Soc.* **2024**, *146*, 10286-10292; [5] *J. Am. Chem. Soc.* **1994**, *116*, 3599–3600; [6] *J. Am. Chem. Soc.* **2006**, *128*, 16494–16495; [7] *Inorg. Chem.* **2015**, *54*, 11136 – 11149.