PHOTO-INDUCED ELECTRON TRANSFER WITHIN THE MARCUS PICTURE AND BEYOND

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Photo-induced electron transfer (PET) processes are the cornerstone of natural photosynthetic processes. Detailed understanding of the light-induced processes is essential for the design of efficient and long-term stable artificial photocatalysts in the scope of solar energy conversion. As well as the light-harvesting capability of the photosensitizer, the thermodynamics and kinetics of the subsequent competitive PET phenomena govern photocatalytic efficiency. In particular, such PET processes are involved in charge separation or undesired processes such as charge recombination and degradation (Figure 1). Among the most famous concepts to assess such electron transfer processes is semi-classical Marcus theory.

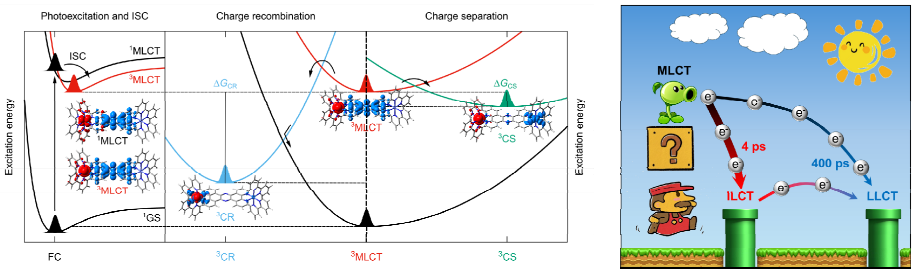

Figure 1: Competitive PET channels in transition metal-based photocatalysts and theoretical extension to model these in a *n*-state model beyond Marcus theory by means of dissipative quantum dynamics.[5]

In this contribution, we present our hierarchical quantum chemical approach to unravel the thermodynamics and kinetics of competitive PET processes associated with catalytic turn-over, charge-recombination and degradation in transition metal-based supramolecular photocatalysts.[1-3] Within the Marcus picture – a two-state model – both intramolecular[1,2] as well as intermolecular PET[3,4] processes are investigated along efficient internal reaction coordinates and *ab initio molecular dynamics*, respectively. However, such two-state models are insufficient to account for the plethora of electronic excited states involved in photoactive dyad and triad architectures. Therefore, a concept beyond Marcus theory is introduced to cover incomplete population transfer and super-exchange phenomena between an arbitrary number of (excited) states via path-integral-based dissipative quantum dynamics.[5] Implementation of diabatization schemes (e.g. Edmiston-Ruedenberg) into pysisyphus – our external optimizer aware of excited states – allowed us to extend our molecular perspective to electrode materials, i.e. to model electron transfer processes of molecular entities embedded in redox-active polymers.[6]

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