

Title

Ab Initio Molecular Dynamics Simulations of Dye-Catalyst Complexes for Photocatalytic Water Oxidation

Authors

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Abstract oral presentation

[Ru-bda]-complexes (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid) have emerged as extremely effective water oxidation catalysts, rendering them a potential candidate for incorporation into dye-sensitized photoelectrochemical cells. Unfortunately, the performance of these catalysts declines dramatically when anchored to a photoanode surface due to their catalytic mechanism involving the interaction of two metal centers (I2M). This reduced performance prompted us to investigate the catalytic cycle following an alternative mechanism in which the O-O bond is formed through a water nucleophilic attack (WNA). We have extensively studied this alternative mechanism for a [Ru-bda]-dye dyad with hybrid-DFT based MD simulations.¹ These simulations yield previously unattained insights into the dynamical flexibility of the first coordination sphere of the Ru center and on the energetics of the catalyst. Moreover, they also highlight the importance of including a fraction of exact exchange in the exchange correlation functional for a proper description of spin localization within the dyad. Although this catalyst can operate also via the WNA mechanism, we predict a relatively high free-energy barrier for the O-O bond formation step, which would slow down considerably the catalytic cycle. Therefore, we have been exploring new avenues to accelerate the photocatalytic water splitting process. In a recent paper, we have mapped out the electronic reactant and product states for a proton-coupled electron transfer reaction in the water oxidation catalytic cycle of the afore mentioned [Ru-bda]-dye and found a conical intersection of these states along the proton transfer reaction coordinate.² Building on these findings, we have performed spin-flip TDDFT based surface-hopping simulations to explore the dynamical response of the complex following an optical excitation into the electronic product state.³ Our simulations reveal that populating the electronic product state triggers an ultrafast proton transfer event within a 100 fs timescale. These results suggest that the catalysis could be accelerated dramatically by exposing the system to optimally tuned laser pulses that drive this optical transition. These state-of-the-art excited state non-adiabatic MD simulations provide important insights into the elementary mechanisms driving photocatalytic water oxidation.

References

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2. de Haas, T., et al. *Strategies to Enhance the Rate of Proton-Coupled Electron Transfer Reactions in Dye-Water Oxidation Catalyst Complexes*. *ChemPhotoChem*, 2022. 7.e202200274
3. de Haas, T., et al. *Non-Adiabatic Surface Hopping Dynamics of Ultra-Fast Proton Coupled Electron Transfer in Dye-Catalyst Complex for Water Oxidation*. Manuscript in preparation.