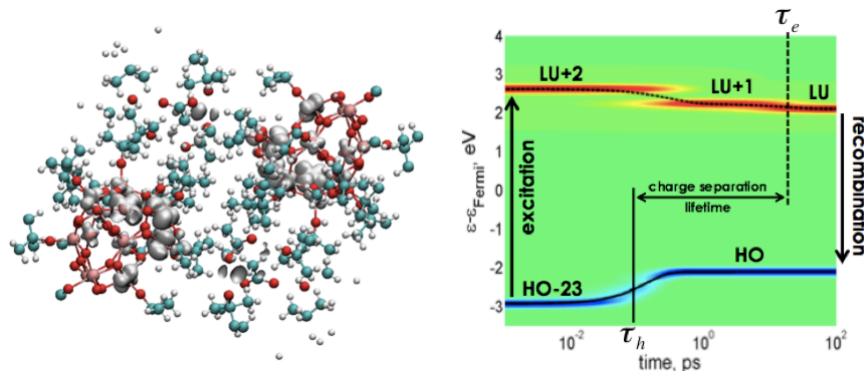


## Titanium Hydroxide and Polyoxotitanate Clusters: A Nanostructure Comparison

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A comparison of electronic structure and dynamics, calculated from first principles, is given for Titanium Hydroxide,  $\text{Ti}(\text{OH})_4$ ,<sup>1</sup> and small polyoxotitanate clusters,  $\text{Ti}_n$  ( $n=14-18$ ).<sup>2,3</sup> Controlled synthesis of  $\text{TiO}_2$  nanostructures allows fine-tuning of electronic and optical properties, resulting from quantum size effects, to increase efficiency within photovoltaic and water-splitting devices. Exact nuclear configurations of experimentally synthesized polyoxotitanate nanostructures are found using single crystal XRD. An organic matrix is used during synthesis of the polyoxotitanate clusters for crystallization but also affects the nanomaterial electronic structure. The organic system consists of organic ligands that functionalize the polyoxotitanate clusters through passivation of surface defects<sup>4</sup> and reduction of trap states in the band gap energy range. Computation of ground state electronic structures, found through DFT using PBE and HSE06 functionals within VASP software, allow for density of states, absorption spectra, and partial charge densities to be calculated. On-the-fly nonadiabatic couplings along computed molecular dynamic trajectories result in calculations of cascade thermalization, facilitated by molecular vibrations.<sup>5</sup> Following excitation, photogenerated electrons and holes migrate from initially populated states to metastable LUMO and HOMO states, respectively, cumulating in recombination described by non-radiative relaxation rates. The increased density of states in polyoxotitanate clusters, in comparison to molecular sized  $\text{Ti}(\text{OH})_4$ , results in smaller band gap energy and faster charge carrier relaxation rates. The impact organic ligands have on the polyoxotitanate cluster electronic structure is shown through comparison of bare and functionalized cluster models.



Nonadiabatic dynamics do not correspond to shown model, full details will be presented within the poster.

1. D. J. Vogel and D. S. Kilin, MRS Online Proceedings Library **1647**, gg08-07 (2014).
2. J. B. Benedict, R. Freindorf, E. Trzop, J. Cogswell and P. Coppens, Journal of the American Chemical Society **132** (39), 13669-13671 (2010).
3. J. B. Benedict and P. Coppens, Journal of the American Chemical Society **132** (9), 2938-2944 (2010).
4. A. Puzder, A. Williamson, F. Gygi and G. Galli, Physical Review Letters **92** (21), 217401 (2004).
5. D. A. Micha, The Journal of Chemical Physics **137** (22), - (2012).