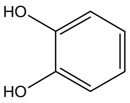
# *Ab Initio* Studies of the Photoinduced Electron Transfer from Molecular Donors to the $TiO_2$ Acceptor

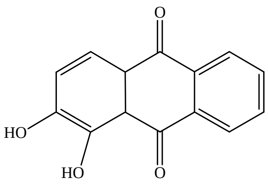
Oleg V. Prezhdo

Department of Chemistry
University of Washington
Seattle, WA 98195

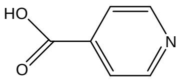
We report the results of the *ab initio* electronic structure calculations and real-time non-adiabatic molecular dynamics simulations of the ultrafast photoinduced electron transfer (ET) in the Gratzel solar cell from molecular electron donors to the $TiO_2$ acceptor



catechol



alizarin

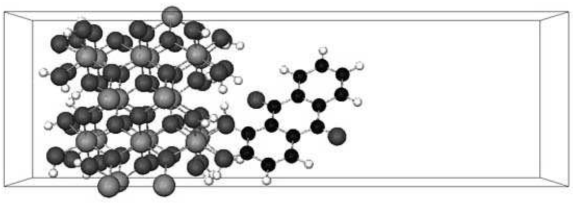


isonicotinic acid

The surprising differences observed in the electronic spectra of the catechol and alizarin molecules upon binding to titanium are elucidated. Catechol and alizarin are similar chromophores with analogous electronic spectra in the free state. Binding of alizarin to titanium red-shifts the spectrum. Binding of catechol to titanium produces a new optically active transition, at the same time preserving the features of the free catechol spectrum. Supported by the details of the calculations, the spectral differences in the catechol and alizarin systems are rationalized by the positioning of the catechol and alizarin $\pi$-molecular orbitals relative to the conduction band of $TiO_2$, which is formed by the d-orbitals of Ti atoms.

The presented theoretical study demonstrates three types of photoexcited states: *First*, the chromophore excited state that is below or near the edge of the $TiO_2$ conduction band, as exemplified by the alizarin system; *Second*, the chromophore excited state that is well inside the conduction band, as seen with catechol; *Third*, a new state near the band edge that appears due to direct photoexcitation from the chromophore to the semiconductor, also seen with catechol.

Experimental and theoretical work shows that catechol and alizarin both rapidly inject the photoexcited electron into the $TiO_2$ conduction band. The injection is promoted by the strong chromophore-semiconductor coupling, which is also required for the state of the third type to be optically active. Injection near the bottom of the conduction band is preferred, since electrons injected high in the band rapidly relax to the bottom. Higher voltages are expected with Gratzel cells driven by photoexcitation into the states of the first and third kind.



The real-time *ab initio* non-adiabatic molecular dynamics simulation of the photoinduced ET in the Gratzel solar cell from the alizarin and isonicotinic acid chromophores to the $TiO_2$ surface indicates that the electron acceptor states are localized within the first 3-4 layers of the surface with about 20% of the acceptor state density due to a single Ti atom. The simulation predicts a complex non-single-exponential time dependence of the ET process.

The ET from the isonicotinic acid to $TiO_2$ occurs on a 30 fs time by the nonadiabatic mechanism at low temperatures and within 5 fs by the adiabatic mechanism at room temperature. The ET from the alizarin chromophore to $TiO_2$ occurs by the adiabatic mechanism at all temperatures, with a larger nonadiabatic contribution at low temperatures. The different behavior of the alizarin and isonicotinic acid electorn donor arise to the difference in the chromophore-semiconductor binding, which occurs either through the carboxylic acid group with an extra carbon atom, or directly through the OH oxygens.

The results of the real-time non-adiabatic molecular dynamics simulation agree with the ultrafast experimental data and provide a detailed atomistic picture of the ET process.

1. W. Stier, O. V. Prezhdo *J. Phys. Chem*. B **106** 8047 (2002)
2. W. Stier, O. V. Prezhdo *Isr. J. Chem.* **42** 213 (2003)
3. W. Stier, O. V. Prezhdo *J. Mol. Struct.-Theochem* **630** 33 (2003)
4. W. Stier, W. R. Duncan, O. V. Prezhdo *Adv. Mater*. **16** 240 (2004)
5. W. R. Duncan, O. V. Prezhdo *J. Phys. Chem.* B in review