

Abstract Submitted
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Electronic Coupling–Decoupling-Dependent Single-Molecule Interfacial Electron Transfer Dynamics in Electrostatically Attached Porphyrin on TiO₂ Nanoparticles¹ B. DHITAL, V. GOVIND RAO, H. P. LU, Bowling Green State University — Interfacial electron transfer (ET) is of crucial importance in a multitude of chemical and physical applications including solar energy conversion and photocatalytic reactions. Extensive ensemble-averaged studies have indicated complex dynamics involving various regulating parameters for interfacial ET. To characterize the role of electronic coupling in inhomogeneous and complex ET mechanism, we applied photon-stamping spectroscopy to study the interfacial ET dynamics of single cationic dyes electrostatically attached on the surface of TiO₂ nanoparticles (NPs). By changing the surface charge on the TiO₂ NP, positive or negative, we were able to change the coupling between dye and TiO₂ NP. The interfacial ET activity of individual molecules altered depending on the electronic coupling strength between dye and TiO₂ NP. Our data showed high ET activity of cationic dyes attached on negatively charged TiO₂ NP surface compared to positively charged TiO₂ NP surface. The observed difference in ET activity attributed to the change in purely electronic coupling factor via electrostatic interaction. Thus, our real-time single molecule experiment revealed the significant changes in ET activity with electronic coupling for electrostatically attached dyes on TiO₂ surface. [*J. Phys. Chem. C* **2016**, *120*, 12313]

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