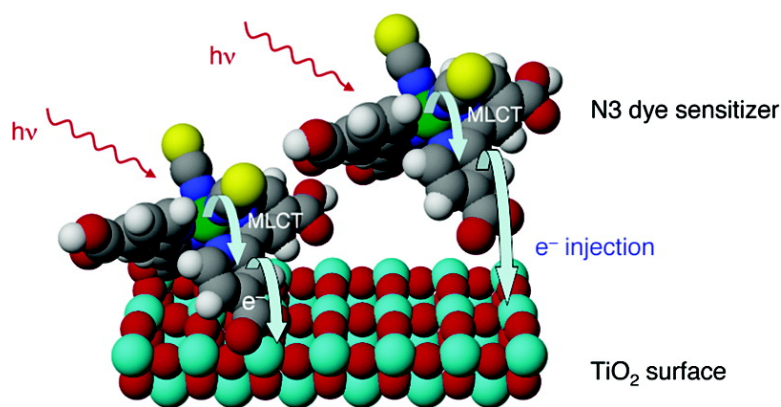Communication

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Rationale for Kinetic Heterogeneity of Ultrafast Light-Induced Electron Transfer from Ru(II) Complex Sensitizers to Nanocrystalline TiO₂

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The conversion of light into electricity in dye-sensitized solar cells (DSC) is initiated by the charge injection from an electronically excited dye molecule into the conduction band of a wide band gap oxide semiconductor.[1,2] Because of their successful use in such devices, Ru(II) polypyridyl complex dyes adsorbed on nanocrystalline titanium dioxide films have been regarded as model systems for the experimental study of the ultrafast dynamics of interfacial light-induced electron transfer (ET). Yet, the complex kinetic behavior observed for the charge injection process in this case has prevented the development of a satisfying kinetic model and has led to often contradicting conclusions. One of the most successful sensitizers used up to now for DSC is the **N3** ruthenium(II) complex (Ru^{II}(dcbpyH₂)₂(NCS)₂), which is known to inject an electron into TiO₂ with practically unit quantum efficiency.[3] The kinetics of ET from **N3** have been under study for the past decade.[2–8] In a widely referred to study, in particular, Benkö et al. reported the charge injection process to take place with a biphasic kinetics.[5] The first ultrafast component was estimated to have a rise time of 28 fs and the second multiexponential part to occur within the 1−50 ps time range. This behavior was rationalized in terms of a two-state mechanism, the fast and slow components being attributed to the injection from the singlet and triplet excited states of the ruthenium complex, respectively. Although several other studies confirm the presence of the slower component, its relative contribution ranges from <5 to 65%, and the time constants vary from 0.7 to 100 ps, with a marked nonexponential behavior and dependence upon experimental conditions.[4–9] This discrepancy actually questions the proposed interpretation. In other published works, the kinetic heterogeneity of the charge injection was attributed to dye molecules adsorbed on energetically diverse sites or in various spatial configurations at the surface of the nanocrystalline titania films.[9] Here, we show that the slow component of electron injection arises from sensitizer molecules that are loosely attached onto the surface or are present in an aggregated form. A monophasic ET with a rise time shorter than 20 fs is observed when the formation of aggregates is prevented and the sensitizer is adsorbed as a monolayer on the surface of TiO₂ nanocrystals.

Kinetic measurements employed a commercially available **N3** dye (Solaronix, Switzerland) and also home-synthesized **N3** and its doubly deprotonated derivative (Bu₄N)₂[Ru(dcbpyH)₂(NCS)₂] (**N719**).[9] Ruthenium complexes were adsorbed onto nanocrystalline titanium dioxide films from 0.3 mM **N3** solutions in ethanol or 0.5 mM **N719** solutions in acetonitrile/*tert*-butyl alcohol (1:1) solvent mixture for 12 h.[3,10] Dyed samples displayed typically an OD of 1.5 at $\lambda = 534$ nm. They were covered with a film of the redox-inactive ionic liquid (1-ethyl-2-methylimidazoliumbis(trifluoromethylsulfonyl)imide).[11] The femtosecond pump−probe spectrometer employed to measure the kinetics of charge injection to the semiconductor was described earlier.[12] Pump wavelength was tuned at 535 nm to excite the dye in its MLCT band, and the probe was
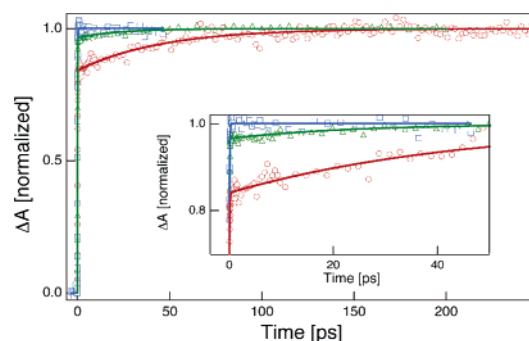

Figure 1. Transient absorbance measured at 860 nm upon ultrashort laser pulse excitation at 535 nm of commercial **N3** (○), homemade **N3** (△), and **N719** (□) adsorbed on transparent nanocrystalline TiO₂ films. Traces were fitted with an analytical convolution function of a Gaussian instrument response and one or two exponential rises. The insert displays the same data at a shorter time scale.

set at 860 nm, where, according to earlier studies, formation of the oxidized state of **N3** is expected to yield a positive transient absorbance signal with a minimal contribution (<15%) of the MLCT excited state.[4]

Recorded signals (Figure 1) show that the amplitude of the slow component varies significantly, depending on the initial solution used to adsorb the dye on the TiO₂ surface. Fitting these data with an analytical convolution of a Gaussian instrument response and one or more exponential rises[13] indicates that the amplitude portion of the slow phase is 16% (45 ps) for the commercial **N3**, only 4% (24 ps) for our own preparation of **N3**, while it is totally absent for the **N719** derivative. This result apparently rules out that a two-state mechanism is generally operative, or that the heterogeneous nature of the adsorption sites produces multiphase growth kinetics. Because the slow part disappears for certain dye preparations, it cannot be an intrinsic property of the sensitizer or a surface property of the mesoscopic anatase particles, **N719** differing from **N3** only by the protonation of the two carboxylic groups that are not in contact with the surface.[14]

Laser transient absorbance spectroscopy experiments of **N3** derivatives on TiO₂ in the presence of large concentrations of iodide recently showed that reductive quenching of **N3** derivatives occurs when these dyes aggregate at the surface. The rate of the reduction reaction of the excited state of the complex is large enough to compete with the slow component of electron injection.[15] The reductive quenching channel was actually suppressed when adsorbing the sensitizer from a very dilute solution prevented the formation of aggregates. On the basis of this observation, dye-loaded films were prepared from an ethanolic solution of the commercial **N3** sensitizer diluted 20 times (1.5×10^{-5} M). Strikingly, under these conditions, no slow growth component was observed anymore (Figure 2), suggesting that the dye uptake from the dilute solution resulted in lower surface coverage preventing aggregation. Films
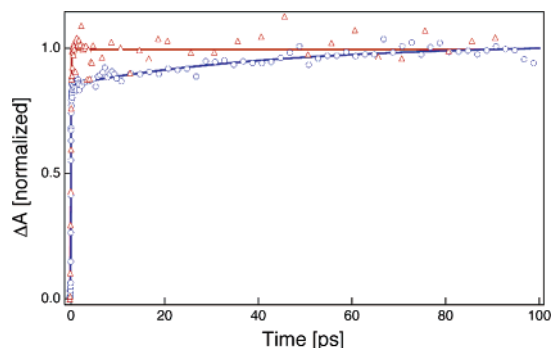
Figure 2. Transient absorbance signals measured at 860 nm upon excitation at 535 nm of the commercial **N3** dye adsorbed on TiO_2 films from 3×10^{-4} M (○) and 1.5×10^{-5} M (△) solutions in ethanol.

dyed in the dilute solution displayed an optical density of only 0.35 at 534 nm, instead of 1.5 for those prepared using the higher sensitizer concentration.

These findings suggest that the slow component in the electron injection arises from the aggregated state of the dye. Sensitizer molecules that are not in direct contact with the anatase surface experience weaker electronic coupling with the empty Ti(3d) states manifold of the TiO_2 conduction band than those anchored directly to surface Ti^{4+} ions.[12] The exponential damping of the electronic coupling matrix element with the distance reduces in a large extent the ET rate for these aggregated sensitizer molecules. Intermolecular charge transfer and exciton migration within the dye aggregate could also converge in yielding a broad spreading of injection rates. These results would also be consistent with the two-state mechanism proposed by Sundström et al., provided this mechanism is specifically involved in systems comprising aggregated dye molecules.

Previous X-ray analysis of a single crystal of **N3** showed the interaction between the sensitizer molecules to be due to hydrogen bonding.[16] Similarly, H-bonding induces dye aggregation in solution and in the adsorbed state. However, due to the deprotonation of two carboxylic groups, **N719** is less prone to undergo aggregation. The different results obtained for the two preparations of **N3** may be attributed to the presence of chemical impurities or to variations in their water content, although the UV−vis absorption spectra of solutions of the two dyes are very similar. Other factors that could affect dye aggregation in solution are the method used to dissolve the solid dye into ethanol, that is, via sonication or stirring, and the crystallinity of the initial powder.

The absence of the slow part of the injection process from **N719** affords a handle for the estimation of the rate of ET from the dye directly adsorbed on the surface. The trace shown in Figure 3 indicates that the reaction is completed within the femtosecond laser excitation pulse. Fitted data provide a cross-correlation time of 57 fs that is consistent with the instrument response measured by Kerr gating in a thin glass window. This temporal resolution does not allow accurate determination of the rate of this process, but its time constant can be estimated as being definitely shorter than 20 fs (see simulation results displayed in Figure 3). An ET process with a rate of such a magnitude can be rationalized in terms of a strong electronic coupling and of the large density of acceptor states in the semiconductor. Since nuclear motion in the molecule and its environment takes place within a time frame of at least 20 fs, the observed charge injection dynamics is probably beyond the scope
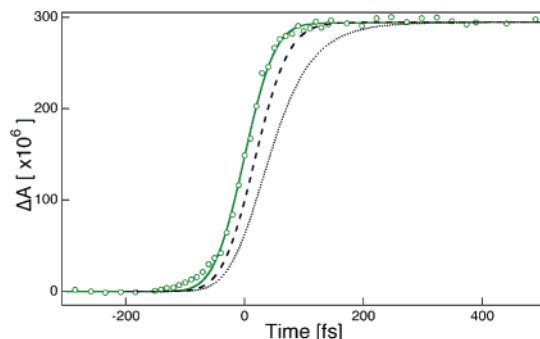

Figure 3. Transient absorption signal for **N719** adsorbed on nanocrystalline titania (○) (pump wavelength = 535 nm, probe = 860 nm). Fitted instrument response is 57 fs (—). Simulated exponential rises with time constants of 20 fs (- - -) and 50 fs (···) and convoluted with the same instrument response are shown.

of vibration-mediated ET models. The process rate is then likely to be limited only by the electron dephasing in the solid.[17] This is certainly not true for charge injection from dye aggregates, whose dynamics in the picosecond time scale should indeed be sensitive to various environmental parameters.[6−8]

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