

Measurement of Ultrafast Photoinduced Electron Transfer from Chemically Anchored Ru-Dye Molecules into Empty Electronic States in a Colloidal Anatase TiO₂ Film

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Electron transfer from the excited electronic singlet state of chemisorbed ruthenium(II) *cis*-di(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylate) into empty electronic states in a colloidal anatase TiO₂ film was measured as a transient absorption signal of the injected hot electrons with a rise time <25 fs. Optical absorption of the anchored dye molecules led to the excited singlet state of the dye with a small admixture of charge transfer states. The electron transfer reaction reported here did not involve redistribution of vibrational excitation energy and was thus completely different from the well-known Marcus–Levich–Jortner–Gerischer type of electron transfer in the case of weak electronic interaction. It was also not a direct optical charge transfer transition from the donor to the acceptor level but rather an electron transfer reaction with an ultrashort but finite reaction time.

Introduction

Electron transfer from the excited electronic state of dye molecules adsorbed on the surface of a solid functioning as electrode is a process of considerable practical and theoretical importance.¹ Various aspects of this process have been utilized and studied since the end of the last century. Most recently this process has been applied in a solar cell.² There is considerable controversy and confusion in the literature on the time scale and the nature of the primary light-driven electron transfer process of Ru-dyes chemisorbed on a colloidal TiO₂ electrode.^{3–5} We report here the first measurement of the rise time of one of the product states in this light-driven reaction, i.e. the electrons injected into TiO₂, with femtosecond time resolution. The light-driven electron transfer process with <25 fs rise time represents a new type of electron transfer mechanism that is different from the well-known Marcus–Levich–Gerischer–Jortner type of electron transfer mechanism for molecules with weak electronic interaction.

Experimental Section

The dye in this investigation was ruthenium(II) *cis*-di(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate) (N3).² It was synthesized at FHI, Berlin, and was also purchased from Solaronix, Lausanne, to allow for a comparison. Absolute ethanol and other chemicals were purchased with the highest commercially available quality. Water was triply distilled in quartz vessels. Dye solutions were purged with five cycles of the well-known pump and freeze method. Stationary absorption spectra were measured with Shimadzu UV-2102 PC (250–900 nm) and Bruins Instr. Omega 20 (400–1700 nm) spectrometers. TiO₂ layers of different thickness (1–4 μ) were prepared from anatase colloids as described in the literature.² They were either a gift from EPFL Lausanne or were prepared in HMI, Berlin. For preparing the dye coverage, the layers were heated in ambient atmosphere to 440 °C for 30 min, afterward cooled to

80 °C under argon, and then dipped for 15 min into a 5×10^{-5} M ethanolic solution of N3. The N3 dye molecules anchor on the TiO₂ surface via the –COOH groups, most likely in the form of carboxylate.³ The dye-covered TiO₂ electrode was rinsed several times with pure ethanol, dried under argon, and afterward transferred into the ultrahigh-vacuum (UHV) chamber with a base pressure of 1×10^{-10} mbar, where most of the time-resolved measurements were performed. The sample was attached to the cold finger of a He cryostat (Oxford Instr.). Some of the measurements were carried out with the sample immersed in a solvent. Pump and probe pulses for transient absorption measurements were generated with a repetitive femtosecond-laser system (Coherent Instr.).⁶ Excitation of the dye occurred with 5 nJ pulses of 75–150 fs half-width (fwhm) at 407, 540, 550, and 600 nm with a 200 kHz repetition rate. The pump beam was chopped with a mechanical chopper whose phase was locked and controlled by a lock-in amplifier. Recording the amplitude and phase of the signals allowed for the identification of absorption and bleaching signals, respectively, that were directly correlated to the action of the preceding pump pulse. Only the latter signals with a completely reversible behavior at the repetition rate of 200 kHz were considered in this Letter. In contrast, with the system immersed in a solvent environment also a slow accumulation of product states was observed in addition to the above type of signals. The origin, chemical nature and kinetic behavior of such product states produced via side reactions are still to be clarified but are not the topic of this letter. They did not occur with the electrode mounted in UHV. The probe pulse in the visible spectrum was derived from a white light continuum. Probe pulses in the near-infrared were generated from the idler of the OPA (Coherent Instr.). Focusing of the beam into a pinhole after the sample reduced stray light. Precise alignment of the different laser beams on the sample was achieved by simulating the optical path into the UHV chamber in a parallel set-up. Temporal walk-off was minimized by setting the appropriate optical delay for each different wavelength. All signals were measured as difference signals with a reference beam.

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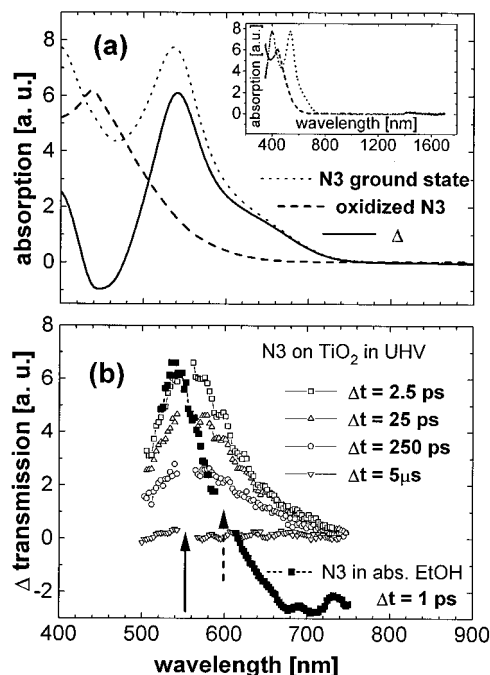


Figure 1. (a) Stationary absorption spectrum of the N3 dye (dotted curve), of the oxidized N3 dye (dashed curve), both in absolute ethanol, and of the corresponding difference curve Δ (solid curve). Up to 1800 nm there was no additional spectral feature (inset). (b) Transient transmission signal due to N3 dye molecules anchored to the colloidal TiO₂ electrode mounted in ultrahigh vacuum. The parameter is the time delay between pump pulse and probe pulses. Identical spectra were recorded with the N3-covered electrode immersed in absolute ethanol. In the latter case a residual signal remained at 5 μ s delay time (short negative delay with respect to the pump pulse). The absorption spectrum of the excited triplet state of N3 is shown for comparison (solid squares); it was measured with the N3 dye molecules in absolute alcohol.

Experimental Results

The UV–visible absorption spectrum of a 10^{-4} M solution of the ground state dye N3 in absolute ethanol was measured between 400 and 1800 nm (dotted curve in Figure 1a). The TiO₂ electrode absorbs strongly at wavelengths shorter than 400 nm. Oxidation of the dye N3 was achieved in the dark employing three different oxidation agents, Br₂, NaOCl, and MnO₂, with absolute ethanol and water as solvents, where appropriate. All the important features of the spectrum of the oxidized form of the N3 dye (dashed curve in Figure 1a) and of Ru-*tris*(bipyridyl) were found to be independent of the preparation method. Where available complete agreement was achieved with data in the literature. No further absorption was detected for the oxidized state of the dye N3 to the red of both the curves shown in Figure 1a. Recently, a transient absorption signal was reported to occur to the red of the spectra⁵ shown in Figure 1a around 750 nm for the same TiO₂ electrode with the N3 dye anchored to its surface in a solvent environment, and its rise time was ascribed by the authors to the oxidized form of the N3 dye. It is clear from Figure 1a,b that this assignment is erroneous. A signal in this spectral range can only be related to the excited, so-called, triplet state of the N3 dye, and its rise time is obviously not related to the speed of the electron injection reaction. Figure 1b gives transient bleaching spectra of the N3 dye on the electrode mounted in UHV at different delay times. In spite of an extremely careful search, no further transient signals of the adsorbed N3 dye species were detected to the red of the spectra shown in Figure 1b. With the available time resolution, transient absorption of the excited state of the N3 dye could not be detected. This indicated a lifetime shorter than 25 fs for the excited state of the anchored N3 dye, since

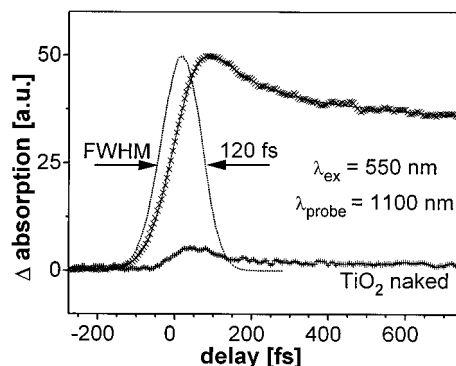


Figure 2. Transient absorption signal detected at 1100 nm for the N3-covered colloidal TiO₂ electrode mounted in ultrahigh vacuum. This signal is due to light absorption by the injected electrons. The instrumental function is shown with 120 fs half-width. For comparison the much smaller signal recorded at the naked electrode (without N3 dye molecules) under identical experimental conditions is also shown.

the latter was about the shortest time constant that could be extracted from a trustworthy deconvolution fit with the instrument function of about 100 fs half-width. This was found under ultrahigh vacuum conditions, where the transient signals behaved completely reversibly at a repetition rate of 200 kHz, and also with the dye-covered electrode immersed into ethanol with 0.3 M LiCl, where this applied to the signals that showed a genuine transient bleach or absorption behavior generated by the preceding pump pulse as indicated by the phase of the lock-in signal. The slowly accumulating signals observed in addition in the solvent environment did not show this clear relationship to the preceding pump pulse and were of a more complicated origin. They appear to stem from side reactions and are not the topic of this Letter. For a sufficiently short lifetime of the excited state of the anchored N3 dye, the spectra in Figure 1b are expected to mirror the difference between the two spectra in Figure 1a. The rise time of one product state of electron transfer, i.e. the injected electrons, was measured as a transient absorption signal in the near-infrared (Figure 2). This signal was 10–20 times weaker than the transient absorption signal from the adsorbed N3 dye (Figure 1b). Transient absorption signals were measured at the naked and at the N3-covered colloidal anatase TiO₂ electrode. The samples were exposed to excitation pulses of different wavelengths, and the transient absorption signals were measured at different wavelengths. The electron absorption signal increased when the detection wavelength was shifted from the visible range to 1100 nm, in qualitative agreement with published stationary spectra.^{7,8} Stationary absorption spectra of electrons in TiO₂ have been reported for the rutile single crystal⁷ and for the colloidal anatase electrode.⁸ They showed a maximum in the near-infrared at around 1200 nm with their origin ascribed to absorption by trapped electrons or polaron states at the conduction band edge. For the present investigation these stationary spectra served only as a source of inspiration. The origin of the signals reported is expected to be quite different, since it is ascribed to absorption of hot electrons with an experimental rise time <25 fs at 1100 nm. The transient absorption signal measured at 1100 nm at the naked TiO₂ electrode increased strongly when the excitation wavelength reached the absorption edge of the TiO₂ electrode at $\lambda < 400$ nm. In contrast, the amplitude of the transient absorption signal measured at 1100 nm at the N3 dye-covered electrode followed the absorption curve of the N3 dye (Figure 1a). The dye-covered electrode gave a 10–20 times stronger signal than the naked electrode (Figure 2) for the excitation wavelength within the absorption spectrum of the N3 dye. Both the signals shown in Figure 2 were measured in ultrahigh

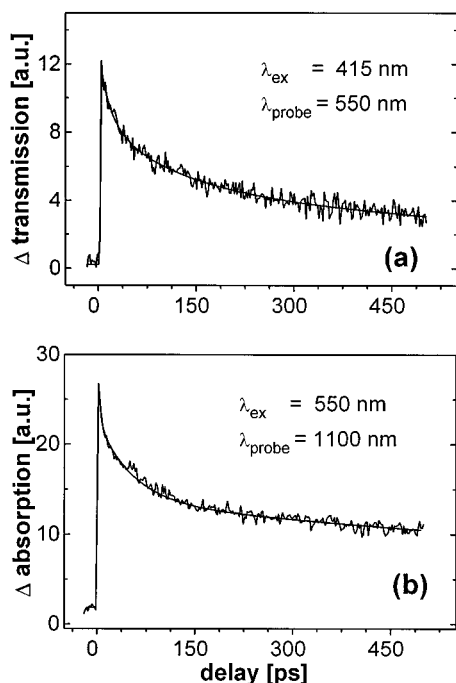


Figure 3. (a) Time dependent decrease in the transient transmission, i.e. time dependent recovery of all the ground state chemisorbed N3 molecules. The dye-covered TiO₂ electrode was mounted in ultrahigh vacuum. (b) Time dependent decrease in the transient absorption signal due to the disappearance, i.e. recombination, of the electrons that were injected into the colloidal TiO₂ electrode from excited N3 dye molecules. For the rise time and initial decay, compare Figure 2. The dye-covered TiO₂ electrode was mounted in ultrahigh vacuum.

vacuum with the sample mounted on top of the cold finger of a He-cryostat. The half-width (fwhmh) of the cross-correlation signal of pump and probe pulses was 120 fs in this experiment. Rise time and amplitude of the dye-sensitized transient absorption signal were found to be identical at room temperature and at 26 K. The calculated least-squares deviation fit of the convolution simulation to the experimental data points gave an apparent rise time <25 fs. This transient absorption signal with a rise time faster than 25 fs is assigned to the intraband absorption of the injected hot electrons. This fast rise time of the product state of the electron injection reaction from the excited singlet state of the N3 dye anchored on the surface of the colloidal anatase TiO₂ electrode is the central experimental result reported in this Letter. The fit to the curve in Figure 2 required also the introduction of two decay components whose qualitative significance is briefly sketched next.

Excitation of the excited electronic state of the N3 dye by the laser pulse is instantaneous. Subsequent electron injection into the TiO₂ electrode was faster than 25 fs, as shown in Figure 2. Recombination between injected electrons and the oxidized form of N3 dye molecules should lead to a similar time behavior of experimental signals that monitor the disappearance of the two product states, injected electrons and oxidized dye molecules. Figure 3 gives two corresponding experimental curves measured at the same electrode under identical conditions. The qualitative similarity of the two decay curves in Figure 3 is obvious. Least-squares deviation fits gave the following rate constants and relative initial amplitudes (in parentheses): $6.3 \times 10^{10} \text{ s}^{-1}$ (30%), $9.6 \times 10^9 \text{ s}^{-1}$ (30%), and $1.1 \times 10^9 \text{ s}^{-1}$ (40%) for the upper curve (recovery of ground state dye population) and $4.1 \times 10^{11} \text{ s}^{-1}$ (50%), $1.9 \times 10^{11} \text{ s}^{-1}$ (20%), and $6.3 \times 10^8 \text{ s}^{-1}$ (30%) for the lower curve (disappearance of the injected electrons). The multiexponential fit to the data is phenomenological. Moreover, the rate constants in the fit varied

somewhat when the signals were recorded in different time windows. However, there was the qualitative trend that the initial decay of the injected electron population (lower curve in Figure 3) was systematically faster than the initial recovery of the ground state dye population (upper curve in Figure 3). This difference was tentatively ascribed to a higher absorption cross section for hot electrons compared to electrons at the bottom of the conduction band in TiO₂. This point will be taken up in the Discussion section below. The slow decay components became longer at 26 K compared to room temperature, indicating the involvement of shallow traps in the slow part of the signals. In ultrahigh vacuum these signals disappeared within 5 μs showing complete reversibility for the injection and recombination cycle under ultrahigh-vacuum conditions (curve with negative delay in Figure 1b). The recombination cycle was not yet completed after 5 μs when the electrode was immersed in the solvent environment, where the phase of the lock-in signal appeared to indicate the occurrence of side reactions, as mentioned above.

Discussion

This Letter gives the first report of the ultrafast temperature independent rise time <25 fs for one of the product states of the dye-sensitized heterogeneous electron transfer reaction from the excited electronic singlet state of chemisorbed ruthenium-(II) *cis*-di(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate), the so-called N3 dye, into empty electronic states at the surface of a colloidal anatase TiO₂ film. The rise time for the absorption signal of hot electrons injected by the excited singlet state of the dye was measured in the near-infrared at 1100 nm. Absorption of the excited state of the N3 dye anchored to TiO₂ was detected neither in UHV nor in solution. The absence of this signal was caused by extremely fast electron transfer, <25 fs, compared to the instrumental function in the range of 100 fs. Temperature independence between 295 and 20 K of the reaction speed was explained by the many electronic acceptor levels at different energies in the conduction band of TiO₂ that are accessible from the donor orbital of the excited dye state.¹ Previous attempts at measuring the speed of this electron injection reaction for the Ru-dyes chemisorbed on TiO₂ had failed for various reasons. In most cases the measured signals were not due to dye molecules anchored directly to the surface of the colloidal anatase electrode. Such a nonideal situation can arise in the experimental system, particularly in a solvent environment, due to problems with the preparation and due to exposure of the system to intense laser pulses. It was shown in this paper that the N3 dye anchored via the -COO- group to TiO₂, whether in a solvent environment or in UHV, did not yield a detectable transient absorption signal of the excited electronic states, singlet or triplet, when the half-width of the instrumental function was 100 fs or longer. Such a signal could not arise since electron transfer was faster than 25 fs. A transient signal described in the literature for the spectral range around 750 nm⁵ was either spurious or due to the absorption of the excited triplet state of dye molecules. According to the experimental results in this Letter (Figures 1, 2) absorption of the dye's triplet state must be ascribed to dye species that were not anchored to sites that allow for electron injection into the TiO₂ electrode, i.e. dye species in a solvent environment or dye species adsorbed on dead spots, if they exist, on the electrode surface. Obviously, an apparent experimental rise time for the absorption signal of the excited dye state cannot give any information on the speed of the electron transfer reaction taking place from that state. Luminescence decay of the reactant state turned out to be an inappropriate probe for the reaction, since

the N3 Ru-dye molecules showed very weak luminescence and the compounds were often not completely pure. The fluorescence of the actual N3 compound is probably too weak for fluorescence up-conversion measurements with the necessary femtosecond resolution. If dye molecules also reside in the solvent compartments of the spongelike TiO₂ electrode, they can occupy various distances from the surface, and therefore show slow electron transfer, and can give rise also to transient absorption signals of the excited electronic state of the dye. Electron transfer from dye molecules excited at a greater distance from the electrode can lead to apparent slow signals for the electron transfer reaction, e.g. in the range of picoseconds or even nanoseconds, depending on the initial distance from the electrode. Such signals have been reported.^{3,4} The overall injection process involves in such cases transport of the dye to the surface or electron transfer from a larger distance corresponding to a much wider electronic tunneling barrier than for the anchored dye.

The ultrashort time constant for electron transfer <25 femtosecond measured for the above system indicates a completely different reaction mechanism than has been found hitherto for electron transfer reactions occurring from a larger reaction distance. In the latter case the redistribution of vibrational energy occurs in the dye molecules on a faster time scale than does the electron transfer reaction.⁹ The electron transfer reaction reported here does not involve vibrational relaxation and is thus completely different from the well-known Marcus–Levich–Jortner–Gerischer type of electron transfer mechanism devised for the case of weak electronic interaction. It is also not a direct optical charge transfer transition from the donor to the acceptor level. It is rather an ultrafast electron transfer reaction with a finite reaction time. The latter is controlled essentially by electron tunneling. Electron transfer occurs prior to any significant redistribution of vibrational energy in the dye's reactant state. However, the finite reaction time allows for the motion of a vibrational wave packet in the time span between the generation of the excited reactant state and the appearance of the product states. This will be discussed in more detail in conjunction with the publication of a more complete set of experimental data for this type of reaction⁹ that was recently obtained by our group utilizing the perylene chromophore in place of the N3 dye.

Reverse electron transfer of the electronic wave packet representing the initially formed hot electron in the semiconductor is considered virtually impossible, since this wave packet spreads in time and moves away from the reaction distance. After a series of elastic and inelastic scattering events, the injected electron can return to the interface; however, the wave packet representing the electron will now be completely different: it will have lost energy, changed momentum, etc. Figure 3 serves the purpose of ensuring the correct assignment of the signals utilized here as a probe for the speed of the electron injection reaction. A relevant discussion of the complicated recombination pathways would require many additional measurements. Just a few remarks concerning the nature of the signals shown in Figure 3 appear in order. The actual recombination reaction between injected electrons and oxidized dye molecules is expected to be preceded by a cascade of energy loss processes leading to the generation of phonons in the solid. This will occur in the conduction band to form a polaron state at the bottom of the conduction band from the initially hot injected electron. In addition, phonons can be generated as the electron is moving down a ladder of electronic states in the band gap of TiO₂. The overall recombination

process, in which the electronic ground state of the dye molecule is formed, will thus be composed of a complex series of consecutive reactions. They comprise not only the above mentioned energy loss mechanisms but also trapping, detrapping, and spatial motion of the wave packet prior to the actual irreversible recombination reaction. Clearly, the sequence of these events cannot be expected to follow a simple description with only one rate constant. In addition, depending on the concentration of electrons and oxidized dye molecules and on the effective mobility, i.e. spatial range of the electrons on the electrode surface, there can be contributions from geminate and nongeminate recombination events to experimental recombination signals as shown in Figure 3. The qualitative similarity between the two different signals in Figure 3 probing the concentration of injected electrons and oxidized dye molecules, the latter as deficit in the concentration of ground state dye molecules, is sufficient to ascertain the correct assignment of the signals reported in this Letter. However, a detailed investigation of the recombination reactions and possible side reactions, particularly in a solvent environment, is not the topic of this Letter.

The injection reaction is controlled by the electronic tunneling barrier, essentially determined by the anchor and spacer group, by the Franck–Condon overlap for the respective vibrational states of reactant and product, and by the escape time for the initially prepared wave packet describing the hot electron from the reaction distance of the oxidized dye molecule. Anchoring of the chromophore groups of the dye molecule via the –COO– bridge to the surface of the anatase electrode facilitates the ultrafast electron transfer time <25 fs.

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