

# The Excitation Wavelength and Solvent Dependence of the Kinetics of Electron Injection in $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ Sensitized Nanocrystalline $\text{TiO}_2$ Films

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Ultrafast transient absorption spectroscopy has been employed to monitor the kinetics of photoinduced electron injection from  $\text{Ru}(2,2\text{-bipyridyl-4,4'-dicarboxylate})_2(\text{NCS})_2$  ( $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ ) into nanocrystalline  $\text{TiO}_2$  films. This process found to exhibit nonexponential kinetics on the femtosecond/picosecond timescales. A multiexponential analysis yielded lifetimes of <100 fs, 1.3 ps and 13 ps with relative amplitudes of 0.35, 0.22, 0.43 ( $\pm 0.06$ ) respectively. These kinetics were found to be independent of excitation wavelength, and to whether the film was immersed in organic solvent or exposed to air.

## Introduction

The injection of electrons from a sensitizer dye into nanocrystalline  $\text{TiO}_2$  [1–7] is the primary charge separation step in a new class of dye sensitized photovoltaic devices [8]. An appreciation of the parameters controlling the kinetics of this reaction is likely to be important for development of this technology.

Several studies of the kinetics of electron injection have employed organic sensitizer dyes including coumarin [1], perylene [2] and fluorescein

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[5] dyes; these studies have all reported sub-picosecond injection rates. In addition, attention has also focussed upon ruthenium bipyridyl dyes, as this class of dyes has yielded the most efficient sensitizer dyes for photovoltaic cells to date [8]. In particular, solar cells employing the sensitizer dye  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  have achieved energy conversion efficiencies of  $\sim 10\%$ . Meyer *et al.* [9], employing transient photoluminescence measurements to study electron injection in a  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  sensitized photoelectrochemical cell have reported distribution of injection rates with a maximum amplitude at  $\sim 10^9 \text{ s}^{-1}$ . Willig *et al.* [4] has reported an injection time of  $< 25 \text{ fs}$  from this dye into  $\text{TiO}_2$  electrodes under ultrahigh vacuum, although we have subsequently reported that this particular study may have been distorted by degradation of the sensitizer dye [7]. Most recently, Lian, Nozik and co-workers [6] have reported a sub-50 fs rate of electron injection from infrared transient absorption studies of  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  sensitized films exposed to air. Our own studies [3] have reported that electron injection in  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  sensitized films covered with an inert solution (50/50 propylene carbonate/ethylene carbonate) is at least biphasic, with injection times of  $< 150 \text{ fs}$  and  $\sim 1.2 \text{ ps}$ . For this system, the subsequent charge recombination exhibits nonexponential kinetics which are strongly dependent upon the application of an external bias potential to the film [10].

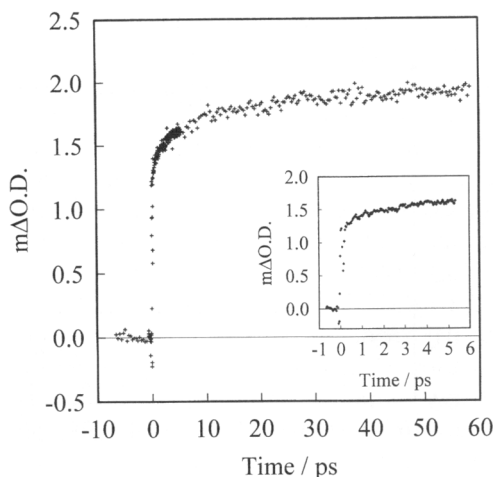
We have recently extended our previous studies of electron injection to consideration of the parameters which control the rate of electron injection. As part of this study, we present here the results of our consideration of the influence of the dye solvent environment and excitation wavelength upon the injection kinetics.

## Materials and methods

Nanocrystalline  $\text{TiO}_2$  films coated with a 10% monolayer of  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  were prepared as previously [3]. Transient absorption data were collected at room temperature using apparatus described in detail elsewhere, with a 100–250 fs instrument response, a 1 kHz repetition rate, excitation pulse energies of 10–35 nJ ( $0.35\text{--}0.7 \text{ mJ cm}^{-2}$ ) depending upon excitation wavelength, a white light probe pulse, and multichannel detector. Transient spectra were collected between 700 and 800 nm on several different timescales. The spectra obtained were indistinguishable from those reported previously [3]. For ease of presentation, transient data are only shown here at a single wavelength (760 nm).

## Results and discussion

We have previously demonstrated that electron injection from the photoexcited  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  results in a 100 nm red shift of a induced transient

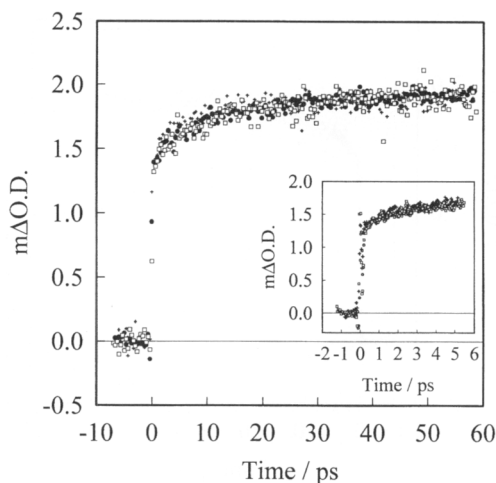


**Fig. 1.** Transient absorption data at 760 nm following excitation of  $\text{Ru(dcbpy)}_2(\text{NCS})_2$  sensitized  $\text{TiO}_2$  films at 560 nm.

absorption maximum from  $\sim 700$  nm to  $\sim 800$  nm<sup>3</sup>. This induced absorption most probably results from a ligand-to-metal charge transfer transition associated with the NCS groups (oxidative degradation of the dye, causing a loss of the NCS groups, results in loss of this induced absorption [7]). In Fig. 1 we show the kinetics of this red shift, monitored by the appearance of the induced absorption at 760 nm. These data are in agreement with those we have reported previously [3]. However the improved signal to noise and extension to longer timescales allow us to resolve additional kinetic components. A multi-exponential analysis revealed at least three exponential components with lifetimes of  $<100$  fs, 1.3 and 13 ps. It should also be noted this analysis is only intended to provide a simple quantification of the kinetics, which may result from an underlying distribution of lifetimes.

A full spectral analysis of these kinetics, allowing consideration of the contribution of excited state absorption to the signal at 760 nm (as conducted previously [3]) indicates that the relative yields electron injection associated with these components are 0.35, 0.22, 0.43 ( $\pm 0.06$ ) respectively. A slower  $\sim 100$  ps component could also be resolved with low amplitude ( $<10\%$ ), however the probe wavelength dependence of this component suggests it is not primarily associated with electron injection.

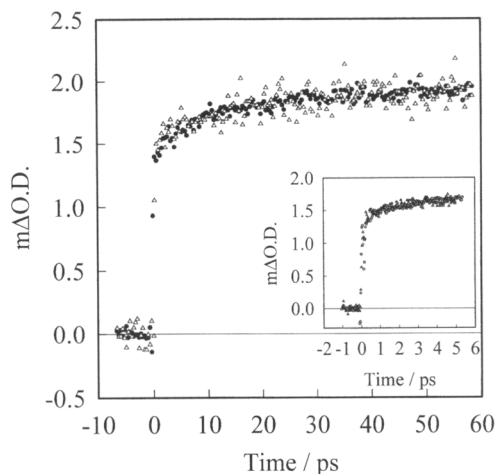
These nonexponential injection kinetics are in contrast with monoexponential kinetics recently reported for the organic sensitizer dyes coumarin [1], perylene [2] and fluorescein [5]. One possible reason for this difference is the complex manifold of electronic excited states of  $\text{RuL}_2(\text{NCS})_2$  with



**Fig. 2.** Excitation wavelength dependence. As Fig. 1 but with excitation wavelengths of 520 (+), 560 (●) and 600 (□) nm.

different kinetics resulting from electron injection from different electronic states (recent MO calculations suggest 4 different states contribute to the ground state absorption between 500 and 700 nm [11]). In order to address this possibility, we monitored the electron injection kinetics as a function of excitation wavelength. As shown in Fig. 2, we find that the kinetics of electron injection are independent of excitation wavelength. We thus conclude that the nonexponential injection kinetics are not related to the complex photophysics of this dye. This conclusion is also consistent with our recent observation of remarkably similar nonexponential injection kinetics with free base and Zinc tetracarboxyphenyl porphyrins (to be published elsewhere).

Alternatively it is possible that the nonexponential injection kinetics could be associated with a dynamic solvation of the dye by the solvent environment. Indeed, the recent study by Ellingson *et al.* [6], conducted with the same sensitizer dye but on air exposed films, reported only a single  $<50$  fs phase of electron injection. Fig. 3 therefore compares the kinetics we obtain for  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  films exposed to air and covered in 50/50 propylene carbonate/ethylene carbonate. Data were also obtained with ethanolic and water free acetonitrile electrolytes. In all cases the transient kinetics are indistinguishable from each other, indicating, solvation of the dye does not have a significant effect upon the injection kinetics. It should also be noted that the ethanol solution was not dried, and therefore contained a significant water content. This water content evidently has a negligible effect upon the kinetics of electron injection.



**Fig. 3.** Solvent dependence. As Fig. 1 but comparison of data collected for sensitized films under a propylene carbonate/ethylene carbonate solvent (●), or dried in air (Δ).

We thus conclude that the kinetics of electron injection from photoexcited  $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$  are independent of the electronic state initially populated, and the solvent environment of the sensitizer dye. Consideration of the parameters which do have a strong influence upon the rate of electron injection will be presented elsewhere.

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