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Electron Injection in Dye Sensitised Solar Cells.

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Submitted for the Degree of Doctor of Philosophy

April 2009

Except where specific reference is made, the material contained in this thesis is the result of my own work. This dissertation has not been submitted in whole or in part of a degree at this or any other university, and does not exceed 100 000 words in length.

S E Koops

April 2009

Acknowledgements.

Finishing this thesis marks a decade since I first joined IC, luckily for me in that time 3 years have been spent in the basement office well out of the way of aging, harmful, natural sunlight. In that time I have made many friends and I would like to take this opportunity to thank the people who have made completing my PhD such an enjoyable experience, from the humble beginnings in the romantically lit basement office with Saghar, Siva, Saif, Li and Chris, through the second year and the advent of Henry, Simon, Nurlan, Andrea, Safa, Tracey, Tracy, Ana and Rui, and finishing with the welcome additions of Piers, Assaf, Brian, Rick, Adrian, Harry and Joe. Not forgetting of course the constants from the experience, Marcos, Simon Turner and of course my former shadow Brett.

I would also like to thank my supervisor, Prof James Durrant, who has always provided me with support, advice and access to a great working knowledge of all things solar; and my “extracurricular” friends. Stine, Polly, Mel and Margie – without you guys I think I would be at least twice the person I am today, and in no good way. Ali, Andrea, JP, Gabe and Cam who have always been on hand to provide distraction from productive pursuits, and of course James – you showed me this was achievable.

Lastly, I would like to thank the people who made this possible; Emma and Steve who have given me a great place to squat, my father and Inge who have provided respite from work when required and my grandmother and Annette who have been a constant source of support and will be, well somewhat relieved I expect, to see this day finally arrive. I would also like to thank John for helping me pull it all together and finish it in time, I think without you I would still be writing now! Lastly, but by no means least I would like to thank my mother for her constant support and guidance throughout the whole experience.

Abstract.

In this thesis, the dynamics and quantum yields of electron injection occurring in liquid and solid state dye sensitised solar cells (DSSCs) based on titanium dioxide (TiO_2) anodes sensitised with Ru – polypyridyl or organic dyes have been measured. The electron injection process is investigated through both experimental and modelling studies. A transient emission technique based on time correlated single photon counting (TCSPC) has been developed to measure the kinetics and yields of injection occurring in both films and devices. Other processes occurring in the device are probed using a range of experimental techniques, including transient absorption spectroscopy and transient photovoltage.

Initially the principles of the TCSPC measurement technique are introduced and the procedure for measuring the injection in samples is outlined. Comparison of appropriate control sample measurements, which show transient emission decay dynamics in the absence of electron injection, with the TiO_2 sample traces enables the quantification of injection occurring in each experimental sample. TCSPC emission decays associated with each sample are then fitted using stretch exponential functions constrained by two degrees of freedom. This TCSPC technique for measuring electron injection dynamics is validated by showing agreement with previously published kinetics for an analogous system as measured by a well established ultrafast transient absorption technique. The fits to the TCSPC decay dynamics are also shown to be accurately replicated by Monte Carlo integrations based on a previously published model of the active dye / TiO_2 interface in the DSSCs. The technique is extended to probing DSSCs employing a range of different sensitisers and measuring the kinetics under different operating conditions occurring within the DSSCs where injection is found to only depend strongly on the concentration of potential determining additives.

The first results chapter describes the TCSPC technique and gives examples of the data analysis procedures associated with each transient emission decay measurement. The agreement between injection kinetics measured using TCSPC with those measured using ultrafast transient absorption technique is highlighted. The model of

the active dye / TiO₂ DSSC interface is introduced and Monte Carlo integrations based on this physical model are shown to agree well with the experimental data.

The second results chapter extends the measurement of injection kinetics to different Ru – polypyridyl based sensitisers. Injection kinetics are measured for a structure – function dye series and the observed variations in the kinetics and yields are explained with reference to the dye / TiO₂ interface. The measurements are extended to completely solid state DSSCs and successful fitting of the TCSPC data with integrations based on the physical model show dispersive injection kinetics observed in solid state DSSCs are controlled by the same parameters as the liquid cells.

The third chapter looks at a variety of factors which may affect injection in complete, operating DSSCs. The factors addressed include presence of the commonly used iodide / triiodide redox couple, residual effects of acid versus base film synthesis procedures, effect of increasing the Fermi level in the DSSC and changing the concentration of potential determining ions in the redox electrolyte. The major controlling factor is found to be the concentration of the potential determining, commonly used *tert* – butyl pyridine device additive and implications of this on DSSC performance are discussed.

The last chapter compares device parameters for DSSCs based on successful organic sensitiser with DSSCs based on the commonly used Ru – polypyridyl N719. Features which control the performance of organic dyes in general are outlined and the reduced performance of DSSCs employing these dyes is explained.

List of Publications.

- (1) Koops, S. E.; O'Regan, B. C.; Barnes, P. R. F.; Durrant, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 10.
- (2) Koops, S. E.; Durrant, J. R. *Inorganica Chimica Acta* **2008**, *361*, 663-670.
- (3) Kroeze, J. E.; Hirata, N.; Koops, S.; Nazeeruddin, M. K.; Schmidt-Mende, L.; Gratzel, M.; Durrant, J. R. *Journal of the American Chemical Society* **2006**, *128*, 16376-16383.
- (4) Barnes, P. R. F.; Anderson, A. Y.; Koops, S. E.; Durrant, J. R.; O'Regan, B. C. *Journal of Physical Chemistry C* **2009**, *113*, 1126-1136.
- (5) Nazeeruddin, M. K.; Wang, Q.; Cevey, L.; Aranyos, V.; Liska, P.; Figgemeier, E.; Klein, C.; Hirata, N.; Koops, S.; Haque, S. A.; Durrant, J. R.; Hagfeldt, A.; Lever, A. B. P.; Gratzel, M. *Inorganic Chemistry* **2006**, *45*, 787-797.

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1 Introduction

This thesis focuses on dye sensitised nanocrystalline solar cells (DSSCs). These solar cells have the potential to be a lower cost alternative to conventional inorganic solar cells due to their lower materials and processing costs. The thesis focuses upon the initial photoinduced charge separation step and compares this process in different DSSC systems under different operating conditions.

1.1 *Why Choose Solar Energy?*

In 2006, a UK government commissioned report into global climate change described climate change as the “greatest market failure the world has ever seen”.¹ To date the world has already warmed by half a degree and if the CO₂ emissions which cause this effect remain at current levels the report concluded there is a 77 – 99% chance of it warming a further 2 degrees. Furthermore if emissions increase further, there is a chance of warming by a further 5 degrees. Therefore in order to prevent the more extreme climate change scenarios being realised, significant cuts in CO₂ emissions must be achieved, such as 25% by 2050.¹ This has led to alternative energy technologies being sought which do not produce CO₂ as a by product. One such green technology is based on solar power which relies on harvesting energy from the sun; it is a potential replacement for the still heavily used fossil fuels.² This work looks in detail at one subset of solar applications - solar photovoltaic devices; these are currently used in both industrial and private application and although at present these are almost exclusively fabricated from conventional, inorganic materials potentially more cost effective thinner film devices are now becoming available.³

1.2 *Solar Cells.*

Solar photovoltaic devices can be broadly classified into three main groups - conventional inorganic based devices; dye sensitised solar cells (DSSCs) and organic polymer (or small molecule) based devices. Silicon solar cells, a subset of inorganic devices, were the first to be discovered and commercialised.⁴ The devices use built-in

electric fields formed between the electron (n-type Si) and hole (p-type Si) transporting Si materials to separate photo-generated charge carriers. Such devices are most commonly fabricated from highly pure Si wafers, although high fabrication costs are a significant limitation to commercialisation. Currently there are three main classifications of silicon devices. These are crystalline silicon wafers, thin film transfer silicon and amorphous silicon. These have certified efficiencies of $24.7\% \pm 0.5$ ⁵, $16.6\% \pm 0.4$ ⁶, and $9.5\% \pm 0.3$ respectively.^{7 8}

More recently, alternative inorganic based solar cells have also become commercialised. These include thin film devices based on CuInGaSe₂ (CIGS). In the laboratory they have reached certified efficiencies of $18.8\% \pm 0.6$ for cells,⁹ $16.6\% \pm 0.5$ for mini-modules,¹⁰ with suppliers offering up to 25 years guarantee.^{11 12}

In spite of these advancements in conventional inorganic solar cells, such devices still remain relatively expensive for mass usage and there is an economic drive to develop low cost alternatives. The most promising of these are dye sensitised solar cells (DSSCs) and organic cells, fabricated from cheaper, less pure material(s).¹³ DSSCs have reached certified efficiencies of $10.4\% \pm 0.3$ for cells and $7.9\% \pm 0.3$ for mini-modules.¹⁴ Organic, polymeric cells have reached efficiencies of $5.15\% \pm 0.3$.¹⁵ Both device types benefit from lightweight materials and low cost fabrication methods.

1.3 Dye Sensitised Solar Cells (DSSCs).

DSSCs first came to worldwide attention following a seminal report in 1991 by O'Regan et al of a $\sim 6\%$ DSSC based on sensitised TiO₂.¹⁶ To date they obtain maximum certified efficiencies of $10.4\% \pm 0.3$ and uncertified efficiencies of $>11\%$, and there are many ongoing research efforts to improve these efficiencies further.¹⁷

1.3.1 Generic Structure.

DSSCs consist of fluorine doped tin oxide (FTO) anodes coated with nanoparticles of wide-band gap semiconductors, such as TiO₂. The nanoparticles are sintered together

to form a continuous network to facilitate charge transport.¹⁸ Earlier designs used single crystal, flat semiconducting metal oxides but current generation in the resulting devices was limited by the small oxide surface area (SA) available for sensitizer coverage.¹⁹ This led to the flat electrodes being replaced with nanocrystalline, mesoporous films to increase the ratio of the surface area to the geometrical area of the electrode – this ratio being known as the roughness factor. The mesoporous semiconductor films are then coated with sensitizer dye before addition of the redox electrolyte; this forms a large interpenetrating heterojunction with the semiconductor. Optimally nanocrystalline films with a roughness factor of over 1000 are used¹⁸ because strong light absorption can be achieved using only a monolayer of adsorbed dye molecules which are chemically attached to the semiconductor by one or more anchoring groups. Following illumination the dye monolayer absorbs the incident light to form an excited state which subsequently dissociates into photogenerated charge; all charge is therefore generated at the interface. This is an inherent advantage over both Si - based and polymeric devices where excitons can be formed throughout the material and may need to diffuse to the interface before being separated into working charges. The DSSC is completed by addition of a platinum counter electrode.

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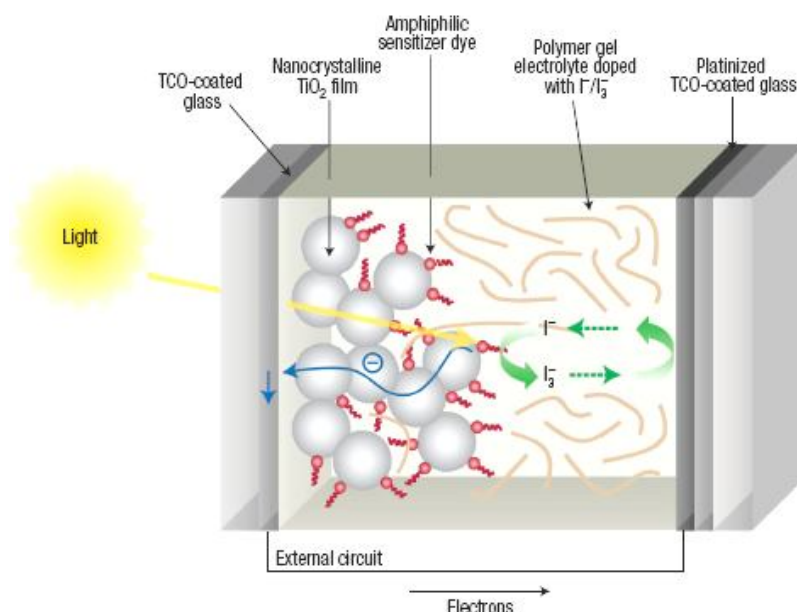


Figure 1.3.1 Typical dye sensitised solar cell (DSSC)²⁰ employing amphiphilic sensitizer dye anchored to a mesoporous TiO_2 semiconducting photoanode. The surrounding media is a polymer gel electrolyte, although commonly this is in liquid form. Overall, there is no net chemical change in the device during operation; this allows the device to run continuously for many electrolyte redox cycles.

1.3.1.1 Materials commonly used in Dye Sensitised Solar Cells.

The breakthrough ~ 6% device reported by O'Regan et al used a mesoporous TiO₂ coating on the FTO anode. This efficiency was quickly improved by replacing the trimeric ruthenium complex, RuL₂(μ-(CN)Ru(CN)L'₂)₂, where L is 2,2'-bipyridine-4,4'-dicarboxylic acid, and L' is 2,2'-bipyridine dye used with cis – di (thiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II), (N3) ²¹ leading to the most efficient devices employing TiO₂ / N3 in combination with a liquid based iodide / triiodide redox electrolyte. However, in the last ~ 15 years there have been numerous attempts to improve this system further by using different materials for each cell component. The more commonly tried materials are introduced here.

1.3.1.1.1 Anodes Commonly used in DSSCs.

Commonly tried materials for coating the FTO anode have almost exclusively consisted of transition metal oxides – including ZnO, Nb₂O₅, ZrO₂, SnO₂, In₂O₅, ^{22, 23, 24} and for each a range of morphologies has been looked at. ²⁵ However, the most successful anode material remains the mesoporous nanocrystalline TiO₂ films. All devices used in this work are based on these films accordingly.

1.3.1.1.2 Dyes Commonly used in DSSCs..

There have been many different dyes used for DSSC application over the last 15 years. However, they most typically fall into one of two groups – organic or organometallic. Organometallic dyes contain a metal in the structure and are usually Ru – bipyridyl structures. These type of dyes make the most successful DSSCs, ¹⁷ and both the N3 dye and its double deprotonated analogue, N719, belong in this group. Organic dyes do not contain a metal and this makes them potentially both cheaper and easier to fabricate. They also absorb visible light more strongly than the Ru – based alternatives. However, they are not as efficient and improving the maximum ~ 8% efficiencies achieved in DSSCs based on these dyes is an active ongoing research area. ²⁶⁻²⁸

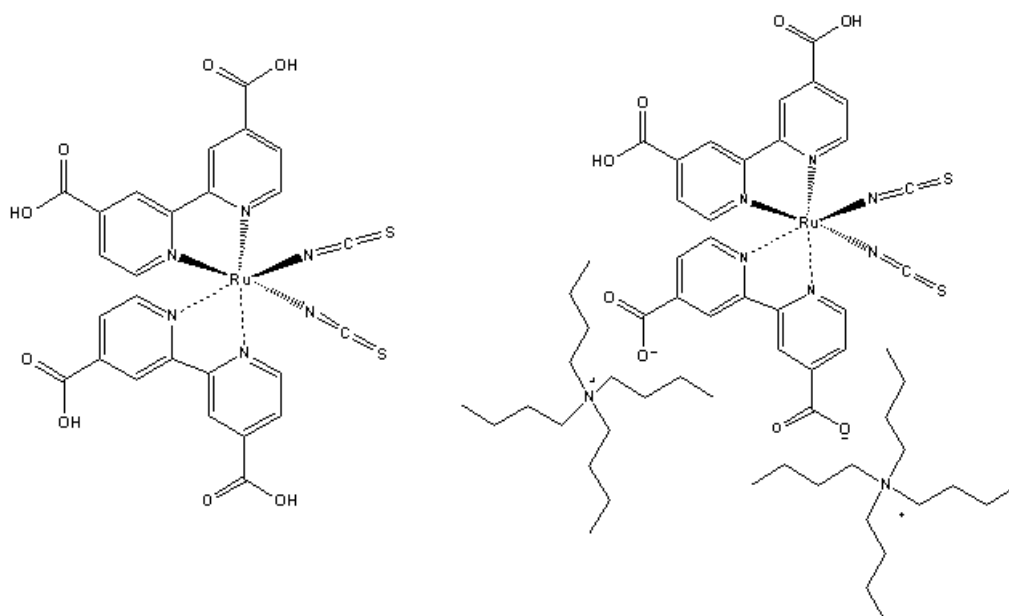


Figure 1.4.1 Chemical structure of the ubiquitous N3 dye (left) and its tetrabutyl ammonium salt, N719. Both dyes attach to TiO₂ through two COOH groups. N3 differs from N719 by protonation of the two carboxylic acid groups not used for attachment to TiO₂.

1.3.1.1.3 Electrolytes / Hole Transporting Materials Commonly used in DSCs.

DSSCs commonly employ either liquid electrolyte or a solid state hole conductor.²⁹⁻
³² The liquid electrolytes are routinely based on the iodide / triiodide redox couple and these are used in the most successful DSSCs.^{17,21} However, they require sealing and have potentially limited stabilities accordingly. The solid state hole conductor replacement is most commonly spiro – OMeTAD.²⁹ However, the maximum efficiencies of the resulting devices is only ~ 4%,³³ although this is hoped to improve dramatically as materials are increasingly synthesised specifically for solid state DSSC application.³⁴

At present therefore the optimised DSSC configuration remains largely unchanged from the TiO₂ / N3 / iodide – triiodide system.²¹ New approaches to address this include using dye mixture co – sensitisers,³⁵ or stacking two TiO₂ surfaces, each sensitised with a different dye.³⁶ However, in this work all systems studied are of the less sophisticated, one dye type.

1.3.2 Mode of Operation in Dye Sensitised Solar Cells.

Illuminating DSSCs provides the driving force for forward, useful operation. However, even in the dark current is generated upon initial contact between TiO_2 and redox electrolyte. Electrons flow from the TiO_2 anode to the redox couple – this is in the reverse direction to the useful working current and is driven by the mismatch in electrochemical potential between the TiO_2 and the redox couple. This initial charge transfer stops flowing when there is a common Fermi level throughout the DSSC.³⁷ This current does not operate in illuminated devices and is therefore beyond the scope of this work.

The forward processes which occur in illuminated DSSCs with liquid electrolytes are well understood.³⁸ They can be summarised as a series of steps which begin with the initial light absorption by the dye chromophore.

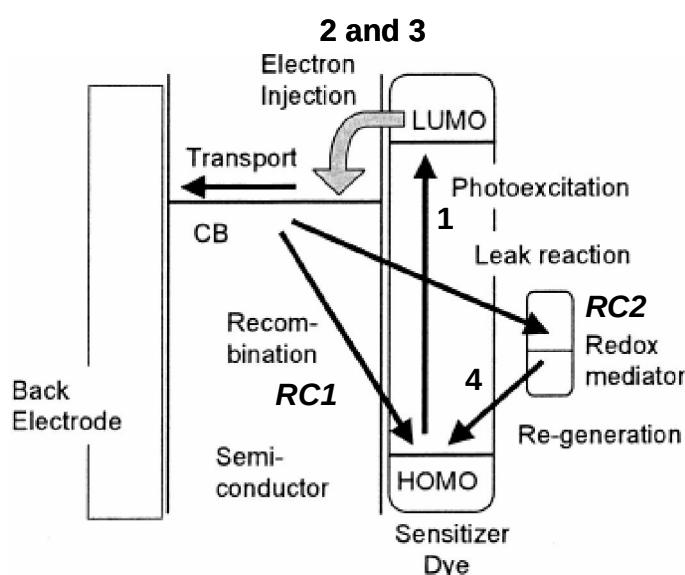


Figure 1.3.2.1: The processes occurring in an illuminated DSSC²².

- 1 Sensitiser absorbs incident light and promotes an electron from the dye ground state - highest molecular orbital (HOMO) configuration - to the first excited state – lowest molecular orbital configuration (LUMO). In the benchmark N3 / N719 sensitisers this involves a metal to ligand electron transfer (MLCT) with the electron transitioning from the metal HOMO to the LUMO π^* of the diimine directly attached to the TiO_2 surface.³⁹

- 2 Electron injection (EI) occurs from the dye LUMO to the acceptor states in the TiO_2 . Dye LUMOs are discrete, localised molecular states and acceptor states are unoccupied, highly delocalised electronic levels in the TiO_2 . Acceptor states can be conduction band (CB) or intra-band states. The injected electron flux correlates to the measurable photocurrent density (I_{SC}) produced by the device.³⁸
- 3 Following EI, the electron relaxes to lowest CB energy level and may be subsequently trapped in intra-band states on ultrafast timescales.⁴⁰ The build – up of injected electrons raises the quasi fermi level of the TiO_2 which determines the maximum device voltage – referred to as the open circuit photovoltage (V_{OC}) because it occurs when there is no current drawn from the device.³⁸
- 4 The residual hole located on the oxidised sensitizer is reduced by donation of an electron from the redox couple in the electrolyte.
- 5 Transport of the injected electron to the FTO anode and of the oxidised redox species, I_3^- , to the platinum counter electrode where the redox couple is regenerated.

Alongside these forward operations there are also three predominant loss mechanisms which run in parallel. These are radiative decay of the dye and recombination between electrons in the TiO_2 and either the dye cation (*RC1*) or the oxidised species in the redox electrolyte, I_3^- , (*RC2*). The extent to which these mechanisms occur largely determines the efficiency of the resulting device.

1.3.2.1 Optimising Forward Operation in Dye Sensitised Solar Cells.

Efficient cell performance requires all the underlying forward steps to be running close or at ideal performance with all loss mechanisms minimised. Devices which achieve this all fulfil certain key criteria, including:

- 1 Electron injection occurs with $\sim$ unity quantum yield. This requires the rate of electron injection to be faster than any other excited state decay pathways.
- 2 The donating electronic excited state of the sensitiser is well matched to the conduction band of the TiO_2 which minimises energy losses during the electron injection process. Furthermore the sensitiser absorbs efficiently over AM 1.5 solar spectrum wavelengths, whilst still retaining a sufficiently large band gap to ensure good photovoltage in the device.³⁹
- 3 D/D^+ redox potential of the sensitiser is high enough to ensure regeneration via the electrolyte is faster than recombination with injected electrons in the TiO_2 , *RC1*. Electrolyte ions can help to reduce the *RC1* rates by screening the injected charges from the residual holes.⁴¹
- 4 Electron transport through the TiO_2 and away from the interface is fast to prevent recombination with either the dye cation or the oxidised electrolyte species.
- 5 The dye can withstand 10^8 cycles, giving it a potential lifetime of approximately 20 years.¹⁸

The benchmark N3 and N719 / TiO_2 systems coated in iodide / triiodide redox electrolyte are energetically and spatially geared to fulfil these criteria. In these dyes electron injection involves transfer between the ligand attached to the TiO_2 and the TiO_2 surface,³⁹ and is accordingly fast. Following injection, *RC1* pathways are activated - however, these involve coupling between the TiO_2 and the residual positive charge which is delocalised over the metal centre and the NCS ligands some distance away from the TiO_2 surface.³⁹ This large spatial separation significantly retards the *RC1* rate which has led to the fabrication of other sensitisers which specifically focus on further retarding *RC1*.⁴²

[Conversely, no organic dye sensitisers to date comprehensively address all the points. The most efficient liquid state DSSCs based on organic sensitisers achieve

efficiencies $\sim 8\%$,²⁷ some $>3\%$ less efficient than systems based on metal polypyridyl sensitisers. This failing may stem, at least in part, from the shorter excited state lifetimes of organic dyes which mean electron injection must be even faster to compete with excited state decay to ground.⁴³ Alternatively they may arise from organic dye catalysing $RC2$ ⁴⁴ which can lead to higher recombination rates and lower voltages accordingly.^{26,45-49}

1.3.2.2 Measuring Efficiencies in Dye Sensitised Solar Cells.

To date, many different DSSCs configurations have been tried – some which satisfy the criteria required for successful operation and some which do not. It is necessary therefore to adopt a standardised definition for the efficiency (η_{eff}), thus enabling rigorous comparison. The universally accepted definition is based on the product of the short circuit current density (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (ff) and the inverse of the intensity of the incident light (I_s).¹⁸ The more efficient DSSCs typically exhibit values of $\sim 17\text{mA cm}^{-2}$, $\sim 820\text{mV}$ and 0.75 respectively.

1.3.2.2.1 Optimising Short Circuit Currents in Dye Sensitised Solar Cells.

Efficiencies in DSSCs are therefore directly proportional to the short circuit current. This is determined by the efficiencies of initial light absorption and subsequent electron injection and collection of the injected charge. All DSSCs used in this study employ the same TiO_2 anode in order to focus on differences in injection in different dye systems or under different operating conditions. The process is compared for each dye by reference to the rate and the yield. Particular focus is placed on the correlation between injection and device currents, with higher currents being observed when the yield of injection is close to or $\sim$ unity.

1.4 Electron Transfer at Dye / TiO_2 Interface.

Homogenous electron transfer theory is typically used to describe electron transfer between two discrete, molecular states, typically in solution.^{50,51} Systems where the

donor and acceptor states strongly interact are termed adiabatic and systems with less interaction are referred to as non – adiabatic. Both types of electron transfer can be described using a free energy diagram, as shown in Figure 1.5.1., based on parabolic free energy surfaces for both reactant and product as a function of nuclear arrangement.⁵¹ These parabolic free energy surfaces represent a one dimension profile of a many dimensional surface which itself arises due to the multi-nuclear fluctuations possible in both the reactant and donor system, including vibrational fluctuations and corresponding orientational contributions from the surrounding media.

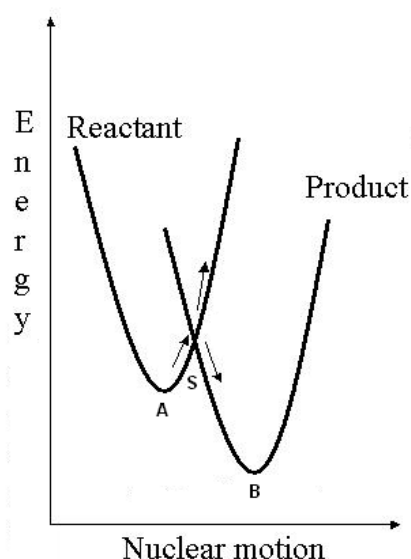


Figure 1.5.1. One dimensional parabolic profile of reactant and product states as a function of nuclear co-ordination of all atoms in the system. In DSSCs, the donor / reactant surface represents the dye excited state and the acceptor / product surface one conduction band / intra-band state in the TiO_2 film

Figure 1.5.1. shows the equilibrium configurations for both reactant and product states, A and B respectively, which arise when the surrounding solvent exerts maximum stabilising force on the state. Also shown is the electron transfer transition state, S, which occurs at the cross-over between the energy surfaces of the reactant and product state. This resonance is necessary in order for the system to satisfy both the Born-Oppenheimer approximation and conservation of energy law. The transfer process occurs when thermally aided nuclear fluctuations contort the system from the stabilised reactant state, A, to the resonant crossing state, S, and this can be calculated using Boltzmann statistics. Once at the transition point, S, the probability of the

electron transferring to the product surface is then determined by the extent of electronic coupling. In non-adiabatic systems, such as thermalized injection, the weaker coupling may cause the transition time from reactant to product surface to be longer than either the nuclear relaxation time or the time it takes the system to reach S. This may result in a lower electron transmission probability accordingly.

It is possible to extend Figure 1.5.1. to also include the effect of free energy change for the transfer, ΔG^0 , on the electron transfer process, as shown in Figure 1.5.2. The free energy change is often compared to the reorganisation energy, λ , which is defined as energy required to distort the equilibrium nuclear geometry of the reactant state (donor) into the equilibrium geometry of the product state (acceptor) without electron transfer. It can be seen that transfer is quickest when $\Delta G^0 = \lambda$.

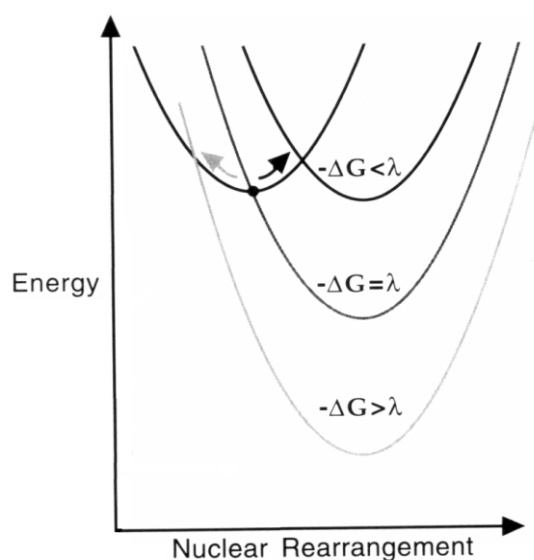


Figure 1.5.2 Parabolic potential energy surfaces of reactants and products versus nuclear configuration of all atoms in the system.⁵² For determination of the overall electron transfer rate in DSSCs, it is necessary to integrate over all available TiO_2 acceptor states as discussed further in the text.

This extended picture shown in Figure 1.5.2. can be used to describe each individual, non-adiabatic electron injection process in a DSSC., Consideration is given to the nature of the process – the coupling of a discrete molecular state in the triplet excited state dye to one of a manifold of acceptor product states. by considering the overall

system rate as an integration of the individual processes over all available conduction band / intra-band states in the TiO₂ film. It is noted that the manifold acceptor states will ensure that, wherever possible, injection will proceed to states λ below the dye excited state energy.

The overall rate is therefore determined by the collective rate of each one electron transfer process, itself determined by:

1. Nuclear motion under thermal fluctuation (necessary to reach resonance position).
2. Electronic coupling – largely determined by the distance of the donor excited dye state (LUMO) from the TiO₂ acceptor surface. In all cases where the dye is chemically bound to the TiO₂ there is some degree of coupling and the extent of it is determined by both the binding mode and the structural organisation of the dye on the TiO₂ surface. However, when dyes aggregate some of the dyes are not attached and the injection kinetics can be orders of magnitude slower accordingly.⁵³ Such retardation can also occur upon insertion of non conjugated bridging ligands or removal of the anchoring group.^{54 55} Conversely, it is possible to accelerate the injection kinetics by increasing the electronic coupling. To date the most strongly coupled system studied is alizarin / TiO₂ system which shows an electron transfer halftime of only 6fs.⁵⁶
3. Free energy change for the transfer, ΔG^0 . In DSSCs ΔG^0 is determined by the reduction potential of the dye excited state relative to the energy of the TiO₂ acceptor states. The energy of the dye and the density of the acceptor states must therefore both be considered.

1.4.1.1 Effect of Dye Energetics on the Rates of Electron Injection.

Changing the energy of the initial donor dye excited state, whilst keeping the density of TiO₂ acceptor states fixed, significantly modulates ΔG^0 and the electron transfer kinetics accordingly. This is most obviously seen by comparing the rates of electron

injection from the initially populated singlet and triplet dye excited states.⁵⁷⁻⁶¹ These injection pathways are both active in the Ru – based systems because the strong spin-orbit coupling from the Ru (Re) accelerates the rate of intersystem crossing to ~ 75 fs,⁶² which enables it to compete with femtosecond injection occurring from the singlet Franck Condon state.^{59,63-67} This process reduces the energy of the initial dye excited state by ~ 300 mV. Following intersystem crossing, injection can only occur via the thermalized, triplet excited state, observed typically on a picosecond timescale, hence it can be described using extended non – adiabatic Marcus theory.⁶² As a result of these two competing injection mechanisms the injection dynamics have often been reported to be biphasic with the ratio between the two injection processes varying with experimental conditions.^{61,68-71} In the efficient N3 / TiO₂ system, red shifting the incident light has been suggested to both reduce the ratio of singlet : triplet injection and retard the slower, triple injection rate constant concurrently.⁷²

1.4.1.2 Effect of Density of TiO₂ Acceptor States on the Rate of Electron Injection.

The density of acceptor states in the TiO₂ anode determines the number of available acceptor states for the electron injection process. In the original single crystal, planar structures all the acceptor states were assumed to be confined to the conduction band and follow an ideal, parabolic distribution.²³ However, the mesoporous films commonly used today also have additional electron acceptor states below the conduction band edge.⁷³ These states are located in the classically forbidden intra-band region and are referred to as intra-band states. They are distinct from conduction band or valence band states and can be located at either the surface or in the bulk of the oxide - some have observed the density of intra-band states to increase with increasing particle size,⁷⁴ suggesting these states are mainly located at the oxide surface, although other studies have previously observed no such dependence.⁷⁵ The chemical nature of some of these states has also been elucidated (e.g. TiOH states 1.3~1.5 eV below conduction band edge).⁷⁶ These states are therefore both chemically and energetically distinct from the classical conduction band acceptor states, and unsurprisingly do not show the same parabolic distribution. Instead, measurements of the electron density in mesoporous films have shown the states form an exponential

distribution⁷⁷ and this is largely responsible for the determining the measured injection kinetics.

Furthermore, in the mesoporous TiO₂ films it has also been observed that the density of TiO₂ acceptor states at a given energy is also sensitive to the TiO₂ surface charge. The distribution has a Nernstein dependence on the effective pH,⁷³ whereby increasing the proton concentration reduces the energy of the TiO₂ acceptor states onset; and in non-aqueous, aprotic solvents these positive shifts also occur through inclusion of potential determining ions, such as Na⁺, Li⁺ and Mg²⁺.⁷⁸ It is also sensitive to the presence of basic additives, such as *tert*-butyl pyridine (TBP), which shift the band edge onset, and the density of acceptor states accordingly, upwards.^{79,80} These upwards modulations retard the electron injection kinetics,^{79,80} whilst the downwards ones accelerate it.⁸¹

1.4.2 Factors Affecting the Yields of Electron Transfer in Dye Sensitised Solar Cells.

The kinetics of the electron injection process are, therefore, very sensitive to changes in ΔG^0 . However, yields are less dependent because in order to remain high they require only that the rate of the electron injection is faster than the rate of any competing dye excited state decay mechanism. The limiting electron injection rate which will ensure high yields is therefore determined by the rates of the other decay processes. This in turn is determined by the stability of the dye excited state. Dyes with longer lived excited electronic states have longer lifetimes giving them more available time to complete the transfer process. This means they can be successful in producing currents in even under weakly coupled conditions with smaller electron transfer driving forces.

1.5 Motivation and aim of PhD Study.

There has been much interest in understanding the electron injection process in DSSCs. Many factors which affect the rate and the yield have been identified.

However, almost all of these injection studies have used isolated photoactive layers of dye sensitised TiO₂ coated in inert solvent. This is a consequence of the routinely used electron injection measurement techniques which are based on the labour intensive, costly transient absorption spectroscopies. These techniques require transparent samples for measurement and relatively high laser fluencies which makes complete device work difficult.

This study begins by demonstrating an alternative technique for electron injection measurements based on time resolved single photon counting (TCSPC). This new technique is shown to be capable of resolving electron injection half-times down to 60 ps resolution, providing a much cheaper and experimentally easier approach to monitor such dynamics compared to more widely used femtosecond transient absorption spectroscopy. This emission method also allows routine monitoring of the injection process in complete DSSCs at a much reduced cost and on a shorter timeframe. The thesis is made up of four results chapters and these address the following points.

1. The alternative emission based technique is introduced and used with non – injecting reference films to determine injection kinetics and quantum yields for the TiO₂ / N719 system under different solvent environments. The results are then validated by comparison with previous transient absorption measurements on the same system. The kinetics are found to be well described by a simple inhomogenous broadening model of the TiO₂ acceptor states.⁷⁷
2. The TCSPC technique is used to probe a range of different dyes. These include a new Ru – based dye which aims to improve on the N719 performance and a structure – function series of dyes for application in solid state DSSCs. The technique is then extended to measuring the injection in solid state systems using spiro – OMeTAD.
3. The measurements are extended to complete operating cells. Different operating conditions are tested to see what effect they have on the injection

kinetics in the complete cells. Furthermore, it is unambiguously shown that reducing the injection kinetics to a level where they do not successfully compete with excited state decay causes the short circuit current in the device to decrease.

4. The final results chapter uses the new technique to measure and compare injection kinetics in a successful organic sensitiser to those occurring in the benchmark N719. This work is complemented by probing other processes occurring in the two cells by means of transient absorption and transient photovoltage techniques. The fundamental differences between this dye and the benchmark N719 system are then highlighted and used to explain why organic sensitisers always typically produce less efficient DSSCs.

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2 Experimental Methods.

This chapter begins with a description of the sample preparations used in the work. It then goes on to describe the general experimental techniques used for the functional analysis of these samples. For experimental techniques specific to a given study please refer to the experimental section within the relevant chapter.

2.1 Sample Preparation.

All solvents and additives were purchased from Aldrich and were HPLC grade; they were used without further purification unless otherwise stated. The dye was purchased from Dyesol and used as received. All chemicals were research grade, purchased from Sigma – Aldrich.

2.1.1 Preparation of Nanocrystalline TiO₂ Films.

TiO₂ paste, consisting of 10-15 nm-sized anatase particles, was prepared via a sol-gel route, as described previously.¹ The peptisation steps employed either 0.1 M nitric acid (acid film) or 0.1 M ammonia (basic film) to ensure electrostatic stabilization of the deagglomerated TiO₂ particles.² The paste was deposited onto TCO-coated glass substrates obtained from Hartford Glass, USA (15 Ωcm^{-2} F-doped SnO₂). Prior to deposition, the 2.5 cm x 7.5. cm glass slide was sonicated in a beaker containing ethanol and then heated to between 400 and 500 °C for 15 – 20 minutes to ensure the surface of the slide was entirely clean and achieved good contact with the TiO₂ when deposited. The clean glass slide was then carefully placed onto a flat surface, with the conducting side exposed. Both edges were firmly fixed with strips of Scotch Magic Tape™ while allowing a separation of 1 cm as shown in Figure 2.1.1. One layer of scotch tape was used throughout and this typically produced 4 μm thick films. Then a sufficient amount (0.2ml) of TiO₂ paste was introduced onto one of the un – taped ends of the glass slides and was quickly and evenly spread down the length of the glass slide using a glass rod or a Pasteur pipette. This technique is commonly referred to as “doctor blading”.

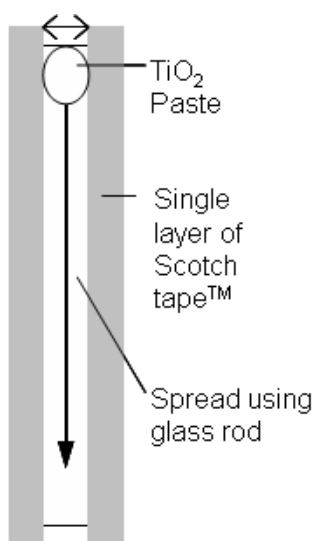


Figure 2.1.1.: Pictorial representation of the doctor blading procedure used to make the TiO_2 and ZrO_2 films. The thickness of film using this method was $4\text{ nm} \pm 1\text{ nm}$.

Following the deposition, the scotch tape was carefully removed and the paste was air dried. Upon drying the paste becomes transparent. The transparent film is then sintered at 450°C to remove any carbowax leaving the TiO_2 behind. Where indicated a TiCl_4 treatment was then applied by soaking in a 50 mM TiCl_4 solution for 30 min at 70°C , followed by a water rinse and heating at 450°C for half an hour. The treatment is typically thought to deposit a layer of TiO_2 $1\text{--}2\text{ nm}$ thick on the surface of the porous film.³ The films are stored at $\sim 120^\circ\text{C}$ prior to sensitisation so as to minimise absorption of atmospheric water.

2.1.2 Preparation of Dye Sensitising Solution.

Many different dyes were used in this thesis, requiring different conditions for effective preparation of dye sensitized TiO_2 films. These conditions include different additives aiding sensitization and different lengths of sensitizing time. However, the procedure for preparing the stock solution of each dye is essentially the same; each of the sensitisers was received as a solid dye stock and all were dissolved to 0.3 mM concentration in a $1:1$ acetonitrile:*tert*-butyl alcohol solvent system. During this initial stock solution preparation the dye solutions were sonicated and heated to ensure all

dye was completely dissolved. They were all resonicated for one hour immediately prior to use.

2.1.3 Dye Sensitisation Procedure.

Prior to sensitisation TiO₂ films were cut into ~2 cm x 1.5 cm pieces. Sensitising was then achieved by immersion in the dye solutions, in the dark. The time of immersion depends on the required optical density (OD) for the given sample. Ideally the samples for time correlated single photon counting studies will have optical densities of ~0.3; for TAS samples and complete devices ODs of ~1 were used. However, the time required for this to be achieved depends on the dye being used. Typically N719 device samples were adsorbed to the TiO₂ film by immersion overnight in a 0.3 mM solution in acetonitrile:*tert*-butanol (1:1). Following removal from the sensitizer solution they were then immersed in isopropanol for ~10 seconds before being dried over nitrogen and coated with the appropriate solvent or electrolyte solution and sealed with a thin glass slide to prevent exposure to air.

2.1.4 Fabrication of Dye Sensitised Solar Cells.

This work used both dye sensitised TiO₂ films prepared as per Sections 2.1.1. – 2.1.3. and complete devices. Films for device use had any excess dye scratched off the surface leaving 1 cm² of dye sensitised TiO₂ in the centre of the 1.5 cm x 2 cm glass piece. This is the standard area over which cells are characterised in this thesis.

Devices typically employed a ‘standard’ electrolyte A, consisting of 0.6 M tetrabutyl ammonium iodide, 0.5M *tert* – butyl pyridine, 0.1 M lithium iodide and 100 mM iodine in 3 – methoxypropionitrile, unless otherwise stated. Transparent counter electrodes were prepared by chemically depositing platinum from 0.05 M hexachloroplatinic acid in 2-propanol on to a second slide of conducting glass. Sandwich cells (1 cm²) were then prepared by sealing together the TiO₂ coated electrode with the counter electrode using a transparent film of Surlyn 1472 polymer (DuPont Ltd.) at 110 °C. The electrolyte was then introduced through holes drilled in

the counter electrode, which were sealed immediately with microscope cover slides and additional strips of Surllyn to avoid leakage.

2.2 *Functional Characterisation.*

This work used a number of different techniques to characterise both the dye sensitised films and complete devices. These measurement methods are introduced here along with the corresponding data analysis techniques where appropriate.

2.2.1 Time – Correlated Single Photon Counting Measurements (TCSPC) ⁴

Electron injection dynamics were monitored using time-correlated single photon counting (TCSPC), employing a Jobin Yvon IBH Fluorocube laser system. The apparatus employed 467 nm excitation (1 MHz repetition rate, $80\mu\text{Wcm}^{-2}$ average intensity, instrument response 250 ps FWHM), with a 695 nm high pass filter for emission detection. Samples generally consisted of either dye-sensitized films or complete devices employing inert solvent or standard redox electrolyte A; where other electrolytes have been used this is noted in the relevant section. Control, non-injecting samples employed either ZrO_2 or Al_2O_3 films, both of which have conduction band edges which are sufficiently high enough to prevent any injection from the excited state dye. ⁵ All the control emission decays were collected under aerobic conditions and therefore represent the upper limit for the rate of excited state decay occurring in a sealed, anaerobic device.

Considerable care was taken to ensure that the absolute magnitude of emission decays, as well as the dynamics, could be compared between different samples where appropriate. Dye loadings were monitored by UV / visible absorption spectra as per Section 2.3. and sensitising times optimised to obtain as close as matched optical densities as at the excitation wavelength (467 nm) as possible. Any residual variations in film optical density were taken account in numerical normalisations prior to data analysis. In all cases, non-scattering films were employed to avoid complications associated with light scatter. Care was taken to ensure uniform sensitisation across the

sample (this was found to be particularly an issue for ZrO₂ control films). Employing these strategies, emission intensities between different samples of the same sensitizer dye : film type were found to be reproducible to within $\pm 15\%$ - with this residual uncertainty being the main source of error in experimental determination of injection half times.

Data Analysis All emission decay traces were normalised where appropriate for number of photons absorbed at the 467nm excitation wavelength. Control data on non-injecting substrates were in all cases well fitted by a sum of two exponentials. Data collected with the electron accepting TiO₂ films were fitted by both (1) an iterative least squares optimised reconvolution of the Gaussian instrument response function (IRF) with a sum of three exponential decays and (2) convolution of the Gaussian IRF function with a single stretch exponential:

$$Int = A_0 e^{-(t/\tau)^\beta}$$

Where β is the stretch parameter ($\beta = 1$ corresponding to a monoexponential decay). The amplitude A_0 of the stretch exponential was set to the deconvoluted amplitude of the control non-injecting emission trace. It is noted that procedure (2), employing a stretched exponential with an initial amplitude fixed to that observed for the non-injecting control, enables fits to the experimental data to be undertaken with only 2 free fitting parameters, thereby greatly increasing the reliability and validity of the fitting procedure.

Decay dynamics were quantified by quoting half-times ($t_{50\%}$) for the injection process. This half-time is defined as being the time at which the amplitude of the deconvoluted fit decays to half the initial amplitude of the control (non-injecting) data. It was found that sensitivity was lost below a 60ps threshold; decays which could be qualitatively described as quicker yielding the same $t_{50\%}$ values. The main source of uncertainty limiting this time resolution was the $\pm 15\%$ uncertainty in the amplitudes of the emission decay relative to the control ZrO₂. Electron injection yields, ϕ , were approximated from the reduction in area between the deconvoluted ZrO₂ control and TiO₂ traces. This involved calculating the definite integrals of the deconvoluted functions between ordinate values of 0 and 100 ns to ensure the functions had fully

decayed. Any difference in the integrated areas was then attributed to electron injection, this process is illustrated in Figure 2.1.2.

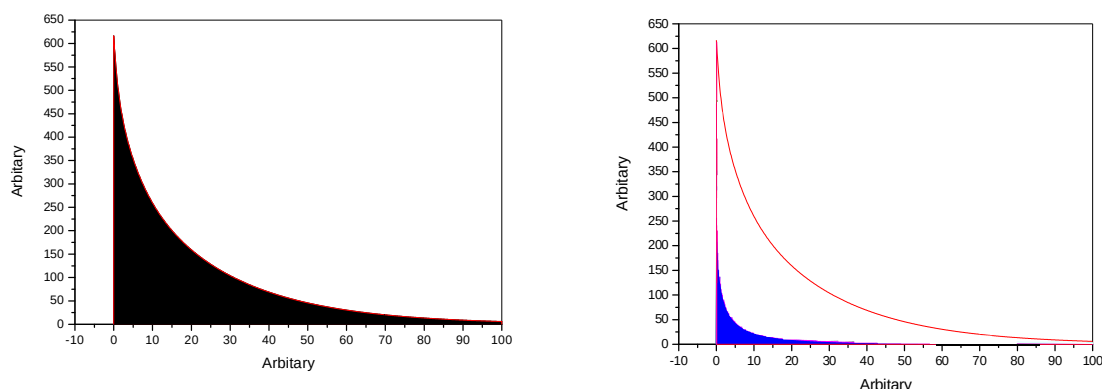


Figure 2.1.2. Typical procedure to determine the quantum yield of electron injection within TiO_2 / N719 systems. The area under the deconvoluted fit, is determined for both the control ZrO_2 (black, method (1)) and the TiO_2 (blue, method (2)) with the numerical percentage difference being attributed to electron injection.

2.2.2 Photovoltage Decays.

Photocurrent and photovoltage transients were generally taken with the use of a pump pulse generated by an array of 1 W red light emitting diodes (LEDs) controlled by a fast solid-state switch. White bias light was supplied by an array of white 1 W LEDs with the light intensity modulated by varying the current supplied to the LEDs and calibrated using a silicon cell. The pulse was incident on the substrate electrode side of the cell and pulse lengths of 10-100 μs were used with rise and fall times of $\leq 1 \mu\text{s}$. Pulse intensity was adjusted to maintain the amplitude of the transient photovoltage below 5 mV. Transients were measured using National Instruments USB-6211 multifunction data acquisition box interfaced to a PC. No signal averaging was required, the photovoltage decays were single exponential, and the time constant, τ_n , was determined by fitting.

The quantity of charge stored within the cell under open circuit conditions was determined by integrating the total current extracted from the cell immediately following switching the light off. This assumes that the recombination current in the cell is insignificant relative to the charge extraction current which appeared to be

valid in this case, Thus electron concentration, n , in the cell as a function of light intensity and photovoltage could be determined.³

2.2.3 Device Characterisation.

Device current-voltage characteristics were determined by illuminating with a 150 W Xenon lamp (Sciencetech model SS150W solar simulator), equipped with an IR filter (water filter) and an AM1.5 filter (Sciencetech). Beam intensity was calibrated using an externally calibrated silicon photodiode with a spectral response modified to approximately match the absorption profile of the N719 dye. For further calibration details, see Barnes et al.³ Current and voltage was measured and controlled using a Keithley 2400 source meter. Due to the use of relatively thin, and non-scattering, TiO₂ films (to facilitate transient spectroscopic studies and avoid electron collection limitations on device short circuit current), devices in this work yielded only modest photocurrent densities. Typically standard devices, employing electrolyte A, produced efficiencies of $\sim 4\%$, with a short circuit current density of 11 mAcm^{-2} . Typical device internal quantum efficiencies (or ‘absorbed photon to current efficiencies’) were determined to be $\sim 86\%$, indicative of efficient electron injection.

2.3 Steady State Measurements.

All transient measurements used in this thesis were complemented by the corresponding steady state technique.

2.3.1 Steady State Absorption.

All steady state absorption spectra of films and solutions were obtained using a Shimadzu UV-1601 spectrometer. Spectra were recorded with the medium scan mode with a detection bandwidth of 2nm. Solution film spectra were measured in quartz cuvettes and each spectrum was corrected for solvent and cuvette absorption. Film spectrum were corrected for both TiO₂ / ZrO₂ and substrate absorption.

2.3.2 Steady State Fluorescence.

All steady state fluorescence spectra were obtained using a *Spex FluroMax* fluorimeter, interfaced to an IBM compatible computer running *DMF3000F* control software. All spectra were recorded with entrance and exit slits set to give a resolution of 5nm, an interval of 1nm and an integration time of 1s. The excitation wavelengths used were 530nm and 467nm, and fluorescence spectra were recorded from 650 - 850nm.

2.4 References.

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Measuring Electron Transfer Rates in N719 Sensitised TiO₂ Films and Devices.

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3 Measuring Electron Transfer Rates in N719 Sensitised TiO₂ Films and Devices.

The purpose of this chapter is to introduce an alternative technique to the commonly used transient absorption spectroscopy (TAS) for measuring the rate of electron injection in dye sensitised films and devices. The technique is based on transient emission – more specifically time correlated single photon counting (TCSPC).¹ The technique is used to measure the kinetics of the injection process in nanocrystalline films sensitised with the Ru – based N719 dye, as this is most typically employed in the technological development of dye sensitised solar cells. The results are then validated by comparison with dynamics measured for the same system using ultrafast TAS.² Once validated, the chapter concludes by showing the dispersive TCSPC injection dynamics can be well represented by a previously published model of the inhomogenous dye / TiO₂ surface based on non – adiabatic Marcus electron transfer theory.³

3.1 Introduction.

Light induced electron transfer from sensitizer dye to TiO_2 film is fundamental to dye sensitised solar cell operation. In this work we have measured the rates and yields of electron transfer from typical Ru – based polypyridyl sensitizer dye to nanocrystalline, mesoporous TiO_2 film ⁴⁻⁸ and modelled this process using an extended non – adiabatic Marcus based theory introduced in Section 1.4. The rates and the yield of this process are important because they affect device photocurrent, with high currents requiring efficient charge separation. Previous measurements have shown injection in these systems to be commonly biphasic, as mentioned in Section 1.4. with regards to N719; dynamics which arise due to the ultrafast intersystem crossing ($\sim 75\text{fs}$) from the initially populated singlet state into a low energy triplet state, which competes with femtosecond injection from the singlet Franck Condon state. ^{6,9-14} Following intersystem crossing, thermalized injection can occur from the triplet excited state on a picosecond timescale. ⁹ The energetics and kinetics associated with electron transfer in such Ru / TiO_2 systems is shown in Figure 3.1.

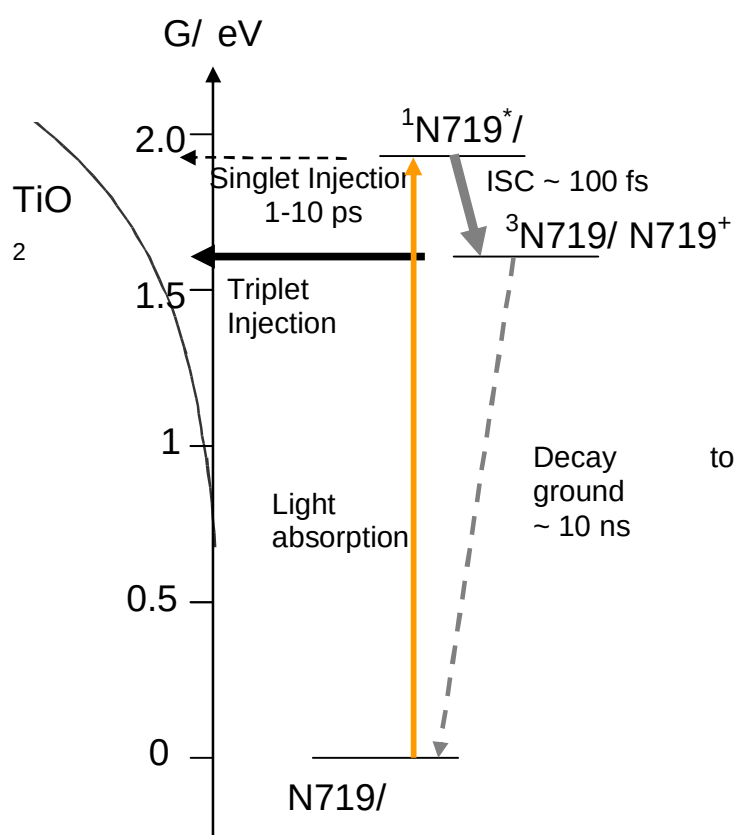


Figure 3.1. Energetics and kinetics of electron injection in a ‘standard’ Ru based DSSC. Energies are given as free energies relative to the dye ground state.

The ratio between the two competing injection pathways is sensitive to many factors. These include replacement of N3 by N719 which has been reported to decrease the proportion of singlet injection occurring, assigned to interfacial pH effects on the TiO₂ conduction band;^{15,16} excitation wavelength,^{7,16-19} solvent choice,^{20,21} inclusion of cationic potential determining ions,^{22,23} TiO₂ Fermi level energy^{23,24} and bridging components positioned between the dye and the empty accepting orbitals on the TiO₂ surface.^{17,25} This high sensitivity means that electron injection must be considered separately for all different experimental conditions.²⁶

Historically, typical electron injection measurements have focused on isolated photoactive dye sensitised films coated in inert solvent because they are the simplest experimentally accessible system. The measured dynamics in these simple systems were found to almost always contain some <100 fs component^{5-7,9,11,12,14,18,24,27-30} associated with injection from the initially populated singlet state. In the case of N3 coated in inert solvent the ratio of singlet injection was found to be as high as 50 to 60%^{12,28} and required measurement techniques with very short time responses accordingly. This led to ultrafast pump / probe laser spectroscopies, such as transient absorption spectroscopy (TAS) techniques becoming the common method for measuring the injection process. However, such studies are both labour intensive and costly, and use relatively high light fluencies, complicating studies of complete device due to charge carrier accumulation. Other less demanding injection measurement techniques are desirable. An alternative technique used in these earlier studies of electron injection was time correlated single photon counting based (TCSPC) measurements of transient emission dynamics. However, the early TCSPC systems used had much longer time responses and it was not possible to quantify how much injection occurred within the resolution of the system. These drawbacks led to reports of nanosecond injection measurements, observations which were subsequently discounted by TAS studies with femtosecond resolution as originating from a small proportion of non – injecting dyes.³¹⁻³³

More recently, measurements have also been extended to complete cells² and ultrafast transient absorption measurements (spinning the devices during the measurements to avoid charge carrier accumulation) have showed injection in a complete, optimised device based on N719 and redox active electrolyte containing

optimum concentrations of additives to be 150 ± 50 ps, more than an order of magnitude slower than for films coated in inert solvent.² The retardation was attributed to additives in the electrolyte (e.g.: *tert* – butyl pyridine, tBP) modulating the surface charge of the TiO₂ film and raising the conduction band energetics,²³ as per the known Nernstein dependence of the TiO₂ distribution of acceptor states on pH discussed further in Section 1.4. It was concluded that these slower injection dynamics benefited device operation because they were correlated with a reduction in the recombination losses in the device. This temporal link between injection and recombination means that optimum electron injection dynamics occur only just fast enough to out compete excited state decay to ground thereby ensuring almost unity charge injection yield whilst minimising recombination; devices with these dynamics are referred to as having minimal “kinetic redundancy”.²

The dynamics for these Ru – based / TiO₂ systems employing either coating have also been shown to be well described using a simple model of the inhomogenous dye / TiO₂ interface based on an extended version of the non – adiabatic Marcus electron transfer theory³⁴ as introduced in Section 1.4. Application of this theory gives rise to a generic equation for calculating the rate of transfer between each dye and each TiO₂ particle (3.1) under all conditions.³⁵

$$k_{inj} = A \int V^2 g(E) [1-f(E)] \exp \{ -(-E_m - E + \lambda)^2 / 4\lambda k_B T \} dE \quad (3.1)$$

Where V is the electronic coupling between dye donor and each TiO₂ acceptor state and can be calculated from the matrix coupling of the donor dye and acceptor TiO₂ electronic wavefunctions, and is sensitive to both orientation and distance between donor and acceptor accordingly. E_m is the energy of the dye excited state corresponding to the lowest unoccupied molecular orbital (LUMO) and E is the electrochemical potential energy for the TiO₂ acceptor states. The continuum of TiO₂ acceptor states is described by $g(E)$ and inclusion of the fermi occupancy factor, $f(E)$, ensures that injection will only proceed to unfilled acceptor states. The reorganisation energy, λ , indicates how distorted the geometries of the reactant dye excited state and product dye cation state are from one another and the exponential prefix ensures that activationless injection occurs to TiO₂ acceptor states λ in energy below the dye

excited state; therefore raising the Fermi level to within this λ retards the overall transfer kinetics.

The model assumes the distribution of the density of acceptor states in the TiO₂ anode, $g(E)$,^{36,37} for each one electron process is similar to the measured density of states in TiO₂ particle ensembles in the mesoporous anodic films. Previous measurements have shown that electron density in these films increases approximately exponentially with negative applied potential, (3.2).³⁸

$$[e^-] \propto \exp\{-E_F / E_0\} \quad (3.2)$$

Furthermore, the measurements have also shown that the exponent of the density of states, E_0 , is significantly larger than $k_B T$, with values ranging from 60 – 100 meV.^{39,40} This is consistent with an exponentially increasing density of states, (3.3), with a tail of intraband states below the conduction band edge. These states are typically assigned to Ti³⁺.³⁸

$$g(E) \propto \exp\{-E / E_0\} \quad (3.3)$$

This exponential distribution of TiO₂ acceptor states for each one electron process occurring at a single TiO₂ particle is then further extended to include secondary effects occurring in the bulk dye / TiO₂ film. These effects are assumed to arise from local energetic inhomogeneities in the density of acceptor states for each one electron injection process which in turn may cause dynamic variations in the integrated electronic coupling V ³⁸ and potentially modulate both the kinetics and yields of electron injection processes within TiO₂ and ZnO systems;^{16,23,41,42} this may account for the observed dispersive nature of the measured injection dynamics. The model assumes that the energetic inhomogeneities follow a Gaussian probability distribution, with FWHM Δ and mean 0, of energy offsets of acceptor states, $g(E)$, from the modal acceptor state, g_0 . This is pictorially represented in Figure 3.7.

Incorporating the revised description of the density of states leads to a new equation describing each microscopic injection rate to energy offset $d_{i,}$, equation 3.4. It does

not look typical because the exponential nature of $g(E)$ enables the nuclear overlap term (Franck Condon factor) and the integration over all available acceptor states to be included in the $k(0)$ term.³

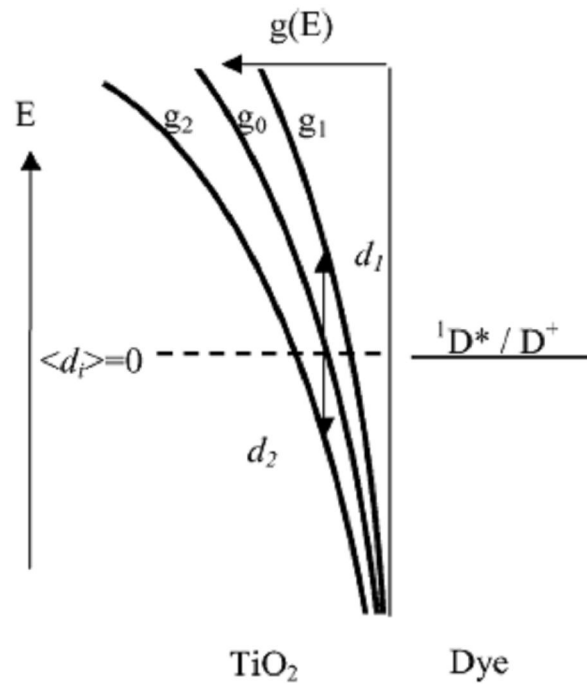


Figure 3.7. Simplified physical model of electron transfer TiO_2 acceptor states at the TiO_2 / dye interface. The distribution in the variation of the density of TiO_2 acceptor states about its modal $g(0)$ leads to a series of acceptor states, $g(E)_i$, the ensemble of which follow a Gaussian function with FWHM Δ and mean 0.³

$$k(d_i) = k(0) V^2(d_i) / V^2(0) = k(0) \exp \{2d_i / E_0\} \quad (3.4)$$

The measured ensemble injection kinetics are then assumed to be an average over the sum of all individual one electron processes; shown by N_e in equation 3.5. In this work all of the fits to the data have been based on this model and follow the detailed experimental procedure outlined in section 3.2.

$$N_e = N^{-1} \sum_{i=1}^N \exp \{-k(d_i) t\} \quad (3.5)$$

It is noted that there are alternative descriptions of the dye / TiO_2 interface which have been commonly used to explain electron injection dynamics in alternative Ru - based systems.^{41,43} One such alternative models the density of acceptor states, $g(E)$, as a convolution of the classical, parabolic density of states in the semiconductor

conduction band with a gaussian distribution of acceptor states which extend into the band gap. The intraband states are attributed to inhomogeneities in the crystal structure. However, the simple physical description of the dye / TiO₂ interface presented here has already been shown to well describe previous TAS based measurements of electron injection in N719 systems and is therefore employed later in this chapter to the TCSPC based measurements of the same experimental systems and the parameters extracted from it are compared for the two measurement methods.

The rates and yields of the electron injection process in Ru – based N719 DSSCs coated in either inert solvent or redox electrolyte have therefore been successfully probed using transient absorption techniques with the results also being well represented by a simple inhomogenous model of the N719 / TiO₂ surface based on equation 3.5. However, due to the costly and time consuming nature of TAS alternative measurement techniques are still desirable. Additionally, these cumbersome TAS based measurements on complete cells have already shown that in kinetically optimised DSSCs electron injection occurs only one or two orders of magnitude faster than the rate of excited state decay to ground. In the case of the commonly used N719 sensitizer which has an excited state lifetime in degassed solution of 40ns this means injection dynamics as slow as 1ns should provide a near unity yield of electron injection;⁴⁴ it therefore follows that for complete, kinetically optimised DSSCs sensitised with Ru – polypyridyl dyes the relevant timescale for studies of charge injection is likely to be on the order of 100's of picoseconds to nanoseconds - orders of magnitude slower than the ultrafast electron injection typical of the films coated in inert solvent. This shift to longer timescales together with the advent of fully commercial TCSPC instruments which can be used with appropriate control samples to accurately measure injection dynamics down to 60ps,¹ opens up the potential for studying electron injection in complete DSSCs using transient emission measurement techniques which are both relatively low cost and easy to perform. This chapter focuses on using one such TCSPC based technique to measure the rate of injection in similar N719 / TiO₂ systems.

Fully commercial TCSPC systems typically have instrument responses of ~ 250ps and by proper use of non - injecting control samples, collecting emission decays for matched numbers of adsorbed photons, and using a stretched exponential fitting

procedure to minimise the number of free fitting parameters, it is possible to make reliable evaluation of the proportion of electron injection occurring on timescales faster than the instrument response - enabling the reliable determination of injection halftimes down to 60ps.¹ The technique is highly sensitive and can be used to measure dynamics even in samples with very low luminescence quantum yields, ϕ_{lum} , such as N3 where $\phi_{\text{lum}} = 0.0004$ ^{44,45}. Typically the procedure, developed as part of this thesis study, involves:

1. Measuring transient emission decay profiles with matched numbers of absorbed photons for TiO₂ and ZrO₂ sensitised with N719. ZrO₂ films are used as control samples because ZrO₂ exhibits similar dye binding properties to TiO₂ but has a conduction band edge $\sim 1\text{eV}$ more negative than TiO₂, thus preventing electron injection from the dye excited state.⁴⁶
2. Performing the TCSPC data analysis procedure outlined in Section 2.2.1. Following deconvolution from the instrument response and correction for any difference in optical densities, sample amplitudes can be directly compared.
3. Equating the loss in emission in TiO₂ samples relative to the control to electron transfer from the photoexcited dye to the TiO₂; this assumes the only difference between the TiO₂ and ZrO₂ samples is injection. The decrease in amplitude of the TiO₂ trace relative to ZrO₂ at any given time indicates the extent of injection occurring in that timeframe. Losses in initial TiO₂ amplitude indicate injection which is occurring faster than the instrument response.

In this chapter the dynamic emission TCSPC based technique is applied to TiO₂ films sensitised with N719 and coated with either inert solvent or a typical redox electrolyte. The measured dynamics are then compared to the previous TAS measured dynamics and modelled using the same simple description of the dye / TiO₂ interface found to well describe the TAS measured dynamics.

3.2 *Experimental Methods.*

Electron injection dynamics have been measured for TiO₂ / N719 films and control ZrO₂ / N719 films employing either inert solvent or standard redox electrolyte A. All sample preparation and experimental procedures are outlined in Section 2.

Electron injection dynamics were quantified with reference to the time it takes for the amplitude of the deconvoluted fit to decay to half the initial amplitude of the control (non-injecting) data, $t_{50\%}$. This is similar to the analysis of the previously measured TAS dynamics and requires deconvolution from the relatively long 250ps FWHM of the TCSPC instrument; this was done following the data analysis procedure outlined in Section 2.2.1. Best fits to the deconvoluted data were then simulated using numeric Monte Carlo integrations (MCS) based on the simple inhomogenous model, see Figure 3.7. and equation 3.5. Producing accurate MCS of this data is made easier by the direct link between the MCS and the original deconvoluted stretch exponential fit parameters introduced in Section 2.2.1; the k_0 value used in the MCS to represent the rate of injection to the state with the mean reaction free energy relates to the stretch exponential τ - value and higher values of τ reflects lower values of k_0 and the Δ/E_0 ratio used in the MCS to determine the FWHM of the gaussian used to represent the disorder associated with each system relates to the β -value of the stretch exponential and larger β -values are simulated by larger Δ/E_0 ratios. Optimum values for both parameters are then found by assuming an initial energy co-efficient E_0 value somewhere between the physically reasonable 60 and 200meV limits and then trying iterative combinations of the two parameters. The results of these fits are presented in the discussion section.

3.3 *Results.*

N719 Films Coated with Inert Solvent.

Initial emission studies focused on the simplest experimental system, N719 sensitised TiO₂ films covered in inert organic solvent (50:50 PC : EC); this minimises any modulation of the TiO₂ V_{fb} by atmospheric water.²⁰ The steady state absorption and emission energy of TiO₂ and the absorption energy of ZrO₂, which shows

indistinguishable spectra to Al_2O_3 , are shown in Figure 3.2. The sample amplitudes have been normalised for ease of comparison.

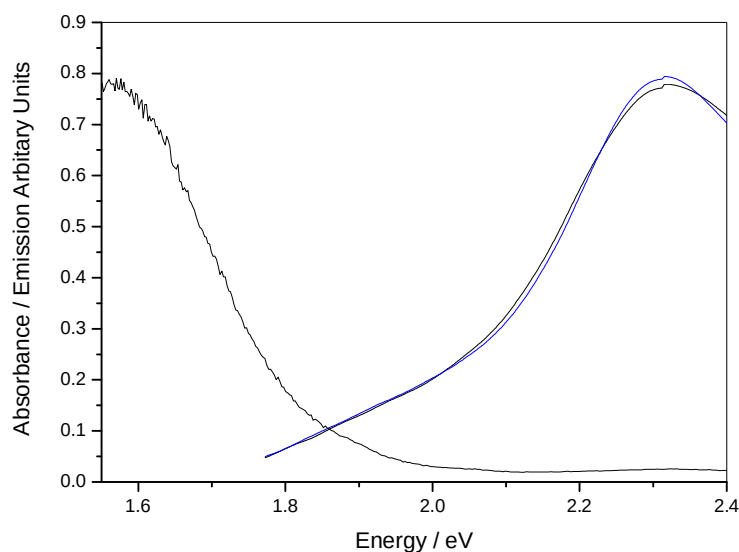


Figure 3.2 Energy profiles for absorption and emission of the N719 / TiO_2 (black). Also shown for comparison is the absorption profile of N719 / ZrO_2 (blue). The emission properties agree well with the measured solution absorption of N3 – the protonated analogue.⁴⁵

The peaks in the absorption profiles of N719 sensitised TiO_2 and ZrO_2 are identical and in good agreement with the solution measurements.⁴⁵ This indicates that attachment of the dye to either semiconductor does not alter the dye HOMO and LUMO orbitals thus enabling direct comparison between non – injecting control and experimental TiO_2 sample decays.

Figures 3.3. and 3.4. show the steady state and time resolved emission traces of the control, non-injecting N719 / ZrO_2 film and the N719 / TiO_2 sample respectively. Both figures show the emission decay dynamics on TiO_2 film are quenched relative to the ZrO_2 control film, consistent with efficient electron injection from the dye excited state. Steady state (Figure 3.3) measurements are more difficult because it is harder to keep all the experimental conditions the same; dynamic (Figure 3.4) measurements are preferable for quantifying emission losses.

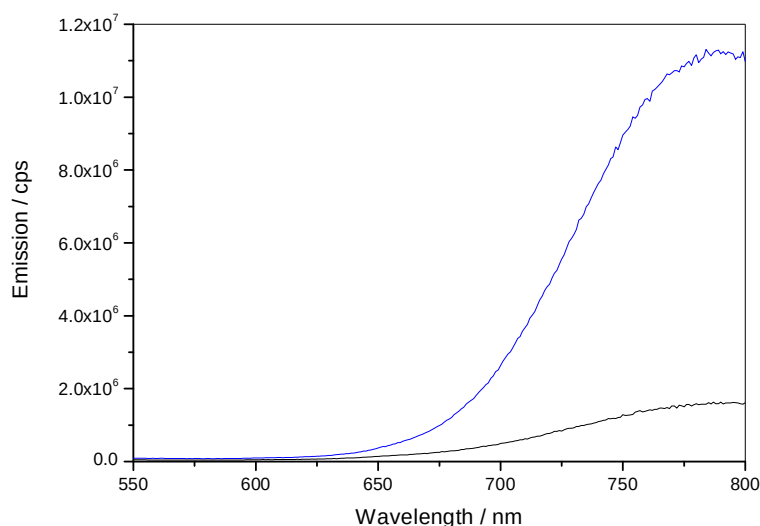


Figure 3.3 Steady state fluorescence spectra of N719 / TiO₂ (black) and N719 / ZrO₂ (blue).

Also shown in Figure 3.4. are the most accurate stretch exponential fits to the deconvoluted data. These have been used to determine the <60ps instrument response limited injection half time, $t_{50\%}$. This agrees with the previous TAS based measurement of the same system which determined $t_{50\%}$ at 8ps $\pm$ 2 for these films.²

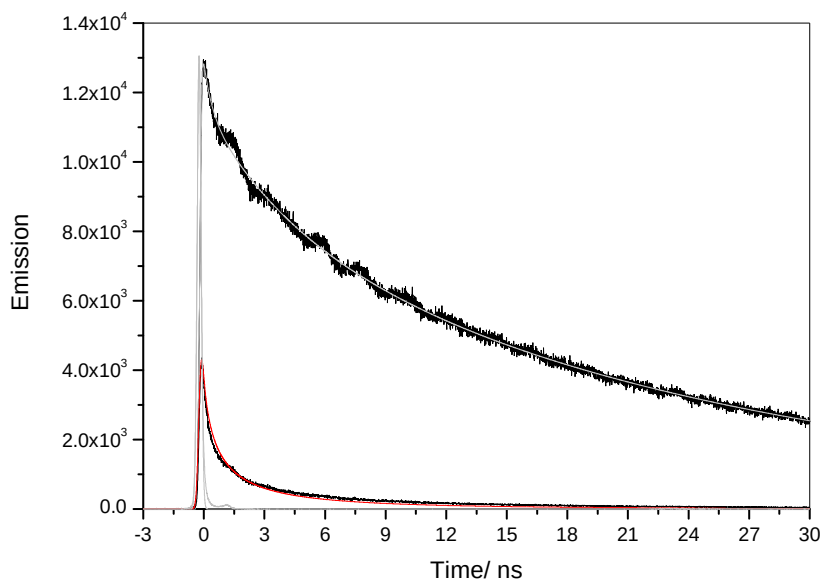


Figure 3.4. TCSPC traces of N719 / TiO₂ and N719 / ZrO₂ films covered in PC:EC. Also shown are lines of best fit (ZrO₂ light grey, TiO₂ data red). The control data are indistinguishable from that which we have previously reported and indistinguishable from Al₂O₃ control data.²

N719 Films Coated with Standard Redox Electrolyte A.

We turn now to emission studies on N719 sensitised TiO_2 coated in standard redox electrolyte A. These systems have previously shown injection rates, $t_{50\%}$, of 150 ± 50 ps measured by pump / probe transient absorption spectroscopy.² This timescale is within the TCSPC's working range thus enabling direct comparison of absolute results from the TCSPC system to the earlier TAS data. Both steady state and transient data was collected for the system and typical transient emission data is shown in Figure 3.5.

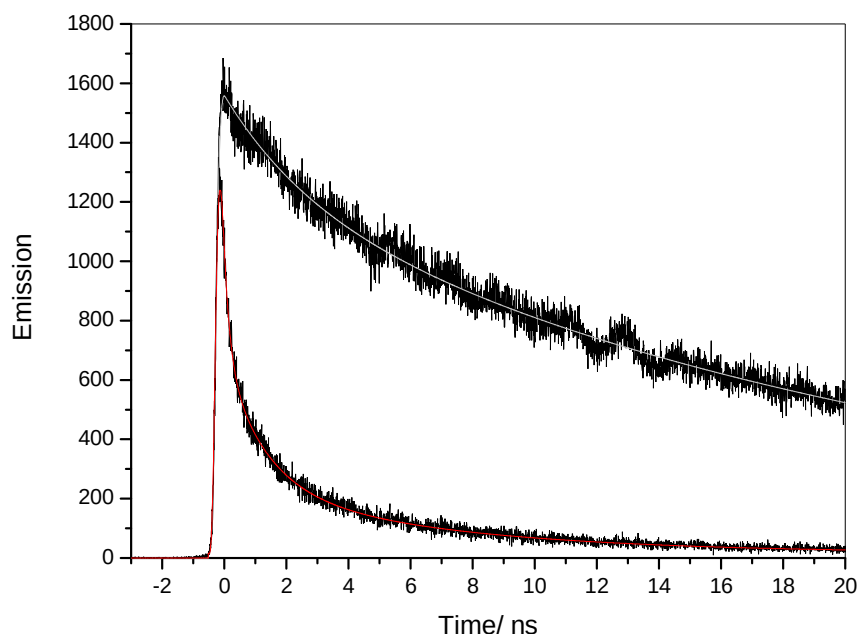


Figure 3.5. TCSPC traces of N719 / TiO_2 covered in redox electrolyte and N719 / ZrO_2 film covered in PC:EC. Also shown are lines of best fit (ZrO_2 data light grey, TiO_2 data black). The samples were excited at 467nm and the excited state luminescent decay monitored at all wavelengths above 695nm.

It can be seen that replacement of the inert solvent by the redox electrolyte has caused the initial amplitude of the TiO_2 trace to increase and the decay dynamics are less accelerated. These observations both indicate that, as expected, injection in these systems has been slowed down; using the fitting procedure detailed previously, $t_{50\%}$ for the system has been determined as $120\text{ps} \pm 30$ ps.

3.4 Discussion.

The electron injection dynamics in TiO₂ / N719 based systems under inert solvent or redox electrolyte coatings have been successfully measured using TCSPC. Halftimes for the injection process, $t_{50\%}$, have been extracted from the TCSPC emission decay traces and are in excellent agreement with those extracted from the previous TAS based measurements on the same systems.² Both the TCSPC based and the TAS based measurements are shown in Table 3.1.

Sample	Electron Injection Halftime ($t_{50\%}$) / ps	
	TCSPC	TAS
N719 / TiO ₂ / Inert Solvent	<60	8 ± 2
N719 / TiO ₂ / 0.1M Li ⁺ / 0.5M tBP	120 ± 30	150 ± 50

Table 3.1: Comparison of electron injection halftimes, $t_{50\%}$, measured by TCSPC and TAS⁷⁹.

It can be seen in Table 3.1. that under redox electrolyte coatings containing 0.5M TBP the injection dynamics as measured by either TAS or TCSPC are slowed to halftimes of 120 – 150 ps. However, samples in the absence of TBP (not shown) showed no such effects. Initially, these slower dynamics were surprising as prior to the TAS based measurements the influence of any of the commonly used electrolyte additives upon the efficiency of electron injection in complete DSSCs, and their correlation with device performance, had received only limited attention to date.^{2,42,47} It had been commonly assumed that the process would occur predominantly <100fs, similarly to the dynamics under inert solvent^{6,10-12}. However, the TAS studies showed that addition of the redox electrolyte containing TBP additive retarded the electron injection dynamics.² The retardation was tentatively attributed to the TBP additive acting as a base and deprotonating the TiO₂ surface relative to the sample coated in inert solvent.² This deprotonation coupled with the well known Nernstein dependence of the TiO₂ conduction band in nanocrystalline films on pH⁴⁸ was suggested to cause the TiO₂ conduction band to shift to more negative potentials thus reducing the density of acceptor states available for electron injection. It was concluded from these

arguments that in complete DSSCs the slower injection times arise because the majority of electron injection comes from the triplet excited state, populated through the ultrafast ISC from the initially populated singlet state; the retarded halftimes seen with the TCSPC measured samples support this. Furthermore, the TCSPC measured $t_{50\%}$ was also found to be reproducible across samples with a wide range of dye loading (< monolayer to multiple monolayers) and insensitive to sonicating the sensitizing solution prior to sensitisation. This consistency suggests that any dye aggregation induced by high dye loadings did not significantly impact the dynamics; this is important in light of previous studies which have highlighted the potential importance of dye aggregation upon the observed injection dynamics.⁴⁹

Another similarity between the injection dynamics measured by TAS or TCSPC comes from the multiphasic timescale. The dispersive dynamics measured using TAS have already been shown to be well represented by numeric Monte Carlo integrations (MCS) based on the same simple inhomogeneous model of the TiO_2 / dye interface, shown in Figure 3.7. This model is applied here to the best fits to the deconvoluted TCSPC emission data and Figure 3.8. shows a typical best fit for the N719 / TiO_2 sample coated in inert solvent.

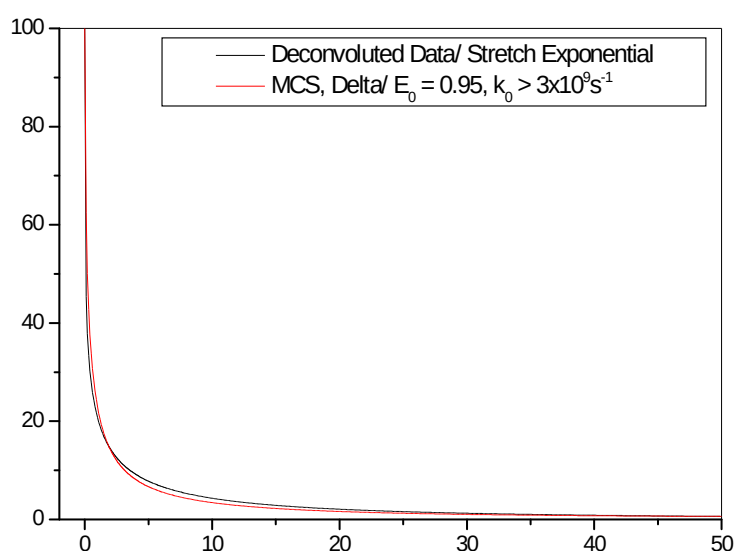


Figure 3.8. Optimised MCS integrations with the deconvoluted data taken from Figure 3.4, the optimised parameters for the decay are indicated on the figure.

The MCS based on the simple inhomogeneous model of the TiO_2 / dye interface provided good fits to the deconvoluted emission traces under both solvent

environments. The two free integration fitting parameters represent the dispersion of the overall kinetics about the mean injection, given by the ratio of Δ/E_0 ; and the injection kinetics with mean reaction free energy, given by k_0 . Using an E_0 value of 100meV, typical of experimental observations,³⁸ under inert solvent coating the system has an energetic disorder of ~ 220 meV and a calculated k_0 parameter of $> 3 \times 10^9 \text{ s}^{-1}$. The k_0 is expressed as an upper limit because even after deconvolution from the instrument response the emission trace decays too quickly to accurately quote an absolute value. The system under redox electrolyte coating had an energetic disorder of ~ 242 meV and a mean free rate of electron injection, k_0 , of $\sim 0.85 \times 10^9 \text{ s}^{-1}$. These parameters are shown alongside the previously calculated numerical Monte Carlo integration parameters used to well describe the TAS measured injection kinetics in Table 3.2.

System	MCS Parameter			
	$k_0 / \times 10^9 \text{ s}^{-1}$		Δ/E_0	
	TAS	TCSPC	TAS	TCSPC
TiO ₂ : N719: PC:EC	5	>3	1.9	2.23
TiO ₂ : N719: Redox Electrolyte	0.8	0.85	3.7	2.42

Table 3.2 Optimum MCS parameters of fits to the TiO₂ / N719 systems measured using TAS² or TCSPC techniques.

It can be seen in Table 3.2. that the TCSPC based MCS parameters for both systems are similar to those extracted from the TAS based measurements. In both systems it can be seen that addition of the redox electrolyte leads to a decrease in the mean free rate of electron injection, k_0 . This is attributed as previously to electrolyte additives modulating the TiO₂ acceptor states upwards thus reducing the density of acceptor states available for the electron transfer process. Table 3.2. also shows that for a physically reasonable E_0 value of 100meV³⁸, the observed injection dynamics for all systems are consistent with values of Δ of ~ 250 meV. This level of energetic disorder is of a feasible magnitude, being of the same order as the energetic distribution of chlorine radical pairs in photosynthetic reaction centres.³⁸

It can be concluded from the similar injection dynamics and MCS parameters that TCSPC is a useful alternative to TAS for measuring electron injection in DSSCs. However, although the technique is more robust there remain certain experimental conditions which could lead to artificially long injection halftime, $t_{50\%}$. These factors include:

1. Scatter in the TCSPC traces. If scatter from the 467nm excitation source can reach the detector array, then it can cause artificially high amplitudes for the traces. This in turn leads to artificially high fitting t_0 values, and an apparently longer half-time for injection.
2. Jitter in the TCSPC electronics. This has been observed as shifting the measured IRF peak up to 42ps from the recorded t_0 of the control sample, the live sample, or both. This is accounted for by realigning the traces prior to deconvolution procedures.

However, in this work these issues were negated by expanding the excitation beam to a 80mm diameter, greatly improving the reproducibility of the technique, and using non – scattering thin TiO₂ films. Furthermore, data reproducibility was found to be maintained across different batches of N719; different dye loadings on the films and with and without sonication of the dye prior to sensitisation. As such the protocol for measuring any sample by TCSPC did not need to involve sonicating the dye prior to sensitisation and dye coverages as close to one monolayer were routinely employed.

3.5 Conclusion.

This chapter has demonstrated that TCSPC can be used to accurately measure injection halftimes in dye sensitised nanocrystalline TiO₂ films, as validated by the agreement with previous TAS based measurements. The technique is limited by the instrument response of the TCSPC system however, the use of a non – injecting control film, together with collection of data with matched densities of absorbed photons, allows determination of the proportion of charge injection occurring within this instrument response. This, combined with the use of a stretch exponential fitting

function with only two variable parameters, allows injection half times to be determined with an effective time resolution of ~ 60 ps. It has also been shown that the deconvoluted emission decay traces can be routinely generated by a Monte Carlo integration based on a previously published physical model of the interface.³ This enables indirect determination of both the mean free rate of electron injection from dye to metal oxide and the extent of dispersion of one electron injection processes occurring within the dye / TiO₂ systems. The ease of use, and low cost, of this experimental approach suggests that this approach may be an attractive alternative to the more widely used ultrafast pump probe based spectroscopies.

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Transient Emission Studies of Dye Sensitised Films of Technological Interest.

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4 Transient Emission Studies of Dye Sensitised Films of Technological Interest.

The purpose of this chapter is to extend the transient emission measurement technique outlined in Chapter 3 to other sensitised films of interest for technological application, either employing different Ru - based dyes ¹ or using molecular hole conductors – so called solid state DSSCs. ²

The chapter begins by looking at a Ru – polypyridyl sensitiser, structurally similar to N719, with an additional substituted methoxy group to increase the molar extinction coefficient. The increased coefficient is aimed at increasing device currents through increased light absorption. Injection dynamics on isolated photoactive films coated in either inert solvent or standard liquid redox electrolyte A have been measured. The dynamics for the system under both coatings are then shown to be well represented by the inhomogenous model of the TiO₂ / dye interface presented in Chapter 3.

The chapter goes on to look at the electron injection dynamics for a series of Ru – polypyridyl sensitisers also based on the N719 template. ³ Structural deviation comes from two additional hydrophobic alkyl chains of varying length on one of the bipyridine ligands. The resulting amphiphilic dyes have enhanced ground state *pK_a* promoting binding to TiO₂, increased water stability ⁴ and the chains also form a barrier to charge recombination between the redox electrolyte and the injected electrons. ³ The chains can therefore potentially retard recombination between injected electrons and oxidised electrolyte species, raising device voltages accordingly. The effect of the chains on injection has been studied herein with measurements taken on the simplest experimental systems of isolated photoactive films coated in either inert solvent or liquid redox electrolyte containing 0.1M Li and 0.5M *t*BP additive concentrations. Physical parameters associated with the dye / TiO₂ interface have been extracted from the model TiO₂ / dye interface and both experimental and extracted parameters are compared for each dye in the series.

The chapter concludes by looking at electron injection dynamics in solid state DSCs using the commonly employed hole transport material spiro - OMeTAD in place of the liquid redox electrolyte.⁵ The solid state nature of the device is commercially attractive as it does not require the same rigorous sealing processes and it is potentially more stable. This is the first example of dynamics being measured directly for this system; measurements focus on photoactive films of TiO₂ sensitised with N719 and coated with spiro – OMeTAD with and without commonly used additives in the system. It is shown that the dynamics are similar to the liquid based systems and can also be well represented by the inhomogeneous model of the TiO₂ / dye interface.

4.1 *Optimising Dyes for use in Dye Sensitised Solar Cells (DSSCs).*

Dye design for DSSC application has, to date, had only limited success, with the most efficient devices still employing the doubly deprotonated analogue of the N3 dye first used some ~15 years ago, N719^{6 7}. However, new dyes are still routinely produced and in order to produce working DSSCs these must satisfy certain parameters, including:

1. Lowest unoccupied molecular orbital (LUMO) higher in energy than the TiO₂ acceptor states under the electrolyte conditions used.
2. High enough oxidation potential to ensure rapid regeneration via the regenerating material - an electron donating / hole transporting moiety.

Furthermore, in order to improve on N719 new dyes should also address the beneficial intermolecular charge transfer properties associated with this dye. This requires forward processes to be promoted whilst loss pathways are simultaneously reduced.⁸ One common method of addressing this is to use a template N719 structure to ensure the new dye retains the beneficial charge transfer properties of N719. Structural modifications are then introduced which attempt to improve on other properties associated with N719. Properties typically focussed on include the water induced desorption of N719 from the TiO₂ surface as this makes high purity, costly electrolytes a necessity for the system; the relatively modest molar extinction coefficient of N719 – particularly in the redder part of the solar spectrum;⁴ and lastly the recombination between injected electrons and residual cationic N719 or regeneration material.⁹ It is noted that this last point has also recently been addressed by inserting physical interfacial blocking layers between the TiO₂ and dye.¹⁰

This work looks at two new dye structures, the tetrabutylammonium [Ru(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine) (4,4'-di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2'-bipyridine)(NCS)₂] dye (N945) and a series of Ru – popylpyridyl dyes which include two additional hydrophobic alkyl chains of varying length on one of

the bipyridine ligands. These aim at increasing the molar extinction coefficient and retarding the recombination process in the working device respectively.

4.1.1 Improving Light Absorption in DSSCs.

4.1.1.1 Introduction.

Light absorption is a fundamental prerequisite for DSSC function and dyes with higher molar extinction coefficients are beneficial accordingly. Organic dyes with no transition metal often have the highest coefficients,¹¹ however they have also been shown to accelerate unwanted recombination processes and thus produce less efficient devices.¹² Ru – based dyes with improved light absorption properties are therefore of great interest^{4,13} such as N945, Figure 4.1.

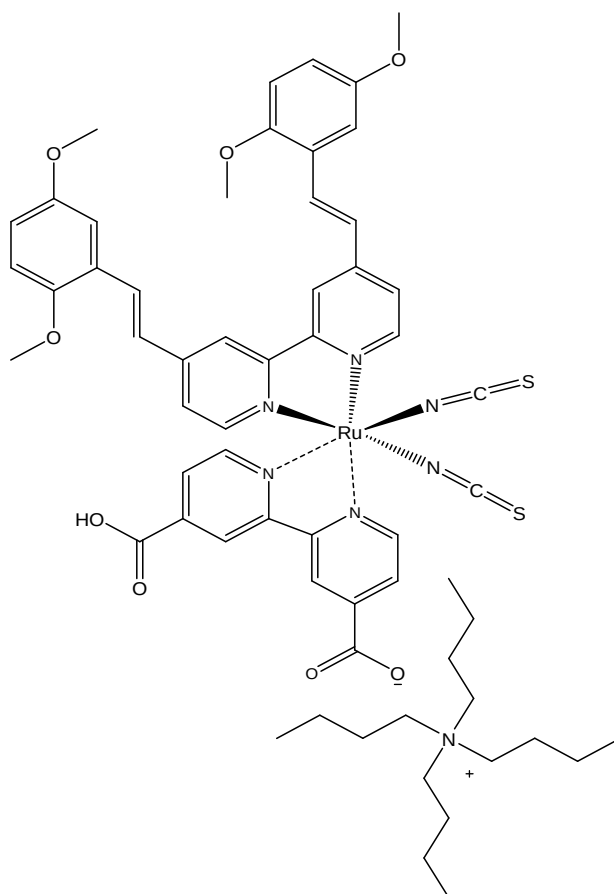


Figure 4.1 Structure of tetrabutylammonium [Ru(4,-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(4,4'-di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2'-bipyridine)(NCS)₂] (N945).

N945 uses the N719 template with the aim of retaining the beneficial intermolecular charge transfer properties associated with this dye. It retains the two carboxylic acid groups in the 4,4'-position of a 2,2'-bipyridine ligand to link the dye to the TiO₂ surface and the two thiocyanato ligands to localise the dye cation.¹³ Structurally N945 differs from N719 through replacement of one of the 2,2'-bipyridine ligands with a 4,4'-di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2'-bipyridine ligand. The substituted methoxy group on the new N945 ligand extends the π - conjugation leading to a 40% increase in molar extinction coefficient. This increase should theoretically result in higher maximum photocurrent fluxes,¹³ leading to detailed device studies being undertaken at EPFL.¹⁴

It is not clear, however, whether extending the π - conjugation causes the LUMO to shift away from the anchoring 2,2'-bipyridine ligand, where the N719 LUMO is localised,⁷ towards the replacement 4,4'-di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2'-bipyridine ligand. Such a shift would be accompanied by a change in the injection dynamics as increasing the distance of the LUMO from the TiO₂ surface will reduce the electronic coupling between excited – state wavefunction and conduction band manifold of TiO₂ acceptor states. This provides the motivation for this work; electron injection dynamics have been measured for N945, and compared to the N719 sensitiser, using the transient emission techniques outlined in Chapter 3. The findings are then discussed with reference to LUMO location.

4.1.1.2 Experimental Methods.

Time correlated single photon counting has been used to measure electron injection dynamics for ZrO₂ and TiO₂ films sensitised with N945 and coated in either inert solvent or standard redox electrolyte A. Sample preparation and experimental procedures are outlined in Chapter 2. Briefly, N945 dye was obtained from EPFL and used as received. Control ZrO₂ and TiO₂ films were immersed in 0.3mM N945 solution overnight and subsequently carefully rinsed with acetonitrile before application of the coating and glass slide. Dynamics are compared with reference to the time it takes for the amplitude of the emission decay to reach half the maximum of

the control value, referred to as $t_{50\%}$ and the measured dynamics are then modelled using the simple description of the dye / TiO_2 interface outlined in Chapter 3.

4.1.1.3 Results.

N945 / TiO_2 Coated with Inert Solvent.

Initial emission studies focused on the most experimentally simple system - N945 sensitised TiO_2 films covered in inert organic solvent (50:50 PC : EC). Inclusion of the inert solvent is important to try and prevent modulation of the TiO_2 conduction band energetics by atmospheric water.¹⁵ Steady state absorption and emission maxima remain unaltered upon attachment of the dye to either semiconductor indicating the dye HOMO and LUMO orbitals remain unchanged, thus enabling direct comparison between non – injecting control and experimental TiO_2 sample decays. Steady state emission traces were quenched on TiO_2 relative to ZrO_2 , consistent with efficient electron injection. Typical dynamic emission decays are shown in Figure 4.2.

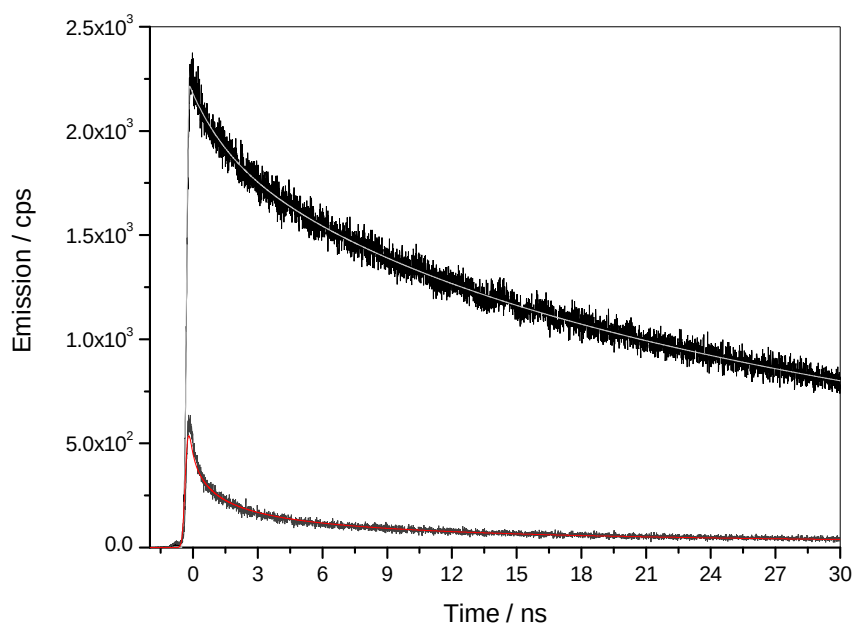


Figure 4.2: TCSPC traces of N945 / TiO_2 (black), and N945 / ZrO_2 (dark grey) covered in low vapour pressure methoxypropionitrile. Lines of best fit are produced by convolution of the instrument response with biexponential decay (ZrO_2) or a stretch exponential decay (TiO_2).

Figure 4.2. shows the N945 emission on ZrO_2 follows a biphasic decay with lifetimes (amplitudes) of 3ns (0.2) and 31ns (0.8). This compares well with the 27 ns solution dye excited state lifetime¹³. On TiO_2 the N945 emission is strongly quenched consistent with efficient electron injection and the amplitude of the trace is lower than the ZrO_2 control suggesting much of the injection occurs faster than the response of the system. The time at which the injection in the system is half completed, $t_{50\%}$, for the N945 sensitised TiO_2 film has been determined from the data analysis process outlined in Chapter 2 as <60 ps.

N945 / TiO_2 Coated with Standard Electrolyte A.

Emission studies have also been done on N945 system coated in standard redox electrolyte A. Steady state absorption and emission data was consistent with the samples coated in inert solvent showing unaltered absorption maxima and emission quenching on TiO_2 relative to ZrO_2 . Typical transient emission data for the N945 system is shown in Figure 4.3.

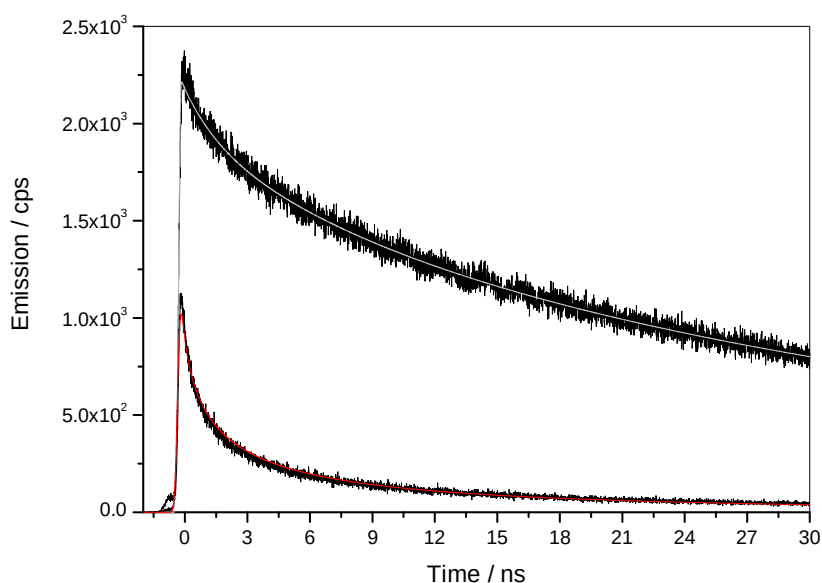


Figure 4.3 TCSPC traces of N945 / ZrO_2 covered in methoxypropionitrile, N945 / TiO_2 coated with redox electrolyte. Lines of best fit are produced by convolution of the instrument response with biexponential decay (ZrO_2) or a stretch exponential decay (TiO_2).

Figure 4.3. shows emission quenching on TiO_2 / N945 relative to the ZrO_2 control, consistent with electron injection. The quenching is reduced relative to systems coated in inert solvent corresponding to retarded injection dynamics in the presence of the

redox electrolyte. The injection kinetics for N945 / TiO₂ system show $t_{50\%} = 140\text{ps} \pm 60$ which is in good agreement with measurements on N719 under the same electrolytic conditions where $t_{50\%}$ was observed to be 150 ± 50 ps.¹⁶

4.1.1.4 Discussion.

In this work we have used time correlated single photon counting to show that electron injection in N945 systems behaves similarly to the N719 system; replacing the inert solvent coating with standard redox electrolyte A retards $t_{50\%}$ from < 60 to $140 \text{ ps} \pm 60$.¹⁶ Dynamics under both coatings are highly dispersive and are modelled here using Monte Carlo integrations based on the simple inhomogenous model of the dye / TiO₂ interface introduced in Chapter 3 and previously shown to fit well to TiO₂/N719 dynamics.¹⁷ The integrations are based on the deconvoluted stretch exponential fits to the data¹ as shown in Figure 4.4. The mean free rate of injection, k_0 , and the disorder of the accepting TiO₂ film, Δ/E_0 have been extracted from the MCS fitting parameters and are shown in Table 4.1. for the TiO₂/ N945 system.

Sample	$k_0 \times 10^{-9} \text{ s}^{-1}$	Δ/E_0
TiO ₂ : N945: Methoxy-Propionitrile	> 9	3.02
TiO ₂ : N945: Redox Electrolyte	2.1	2.42

Table 4.1 Interfacial parameters in the N945 / TiO₂ system coated in either inert solvent or redox electrolyte.

Table 4.1. shows replacing inert solvent with standard redox electrolyte A causes the mean free rate of injection to be decreased by more than a factor of four. This is in good agreement with similar studies on N719 and is similarly attributed to the inclusion of the potential determining 0.5M TBP in redox electrolyte A. The base is thought to modulate the TiO₂ conduction band edge upwards by reducing the concentration of protons on the surface; decreasing the free energy driving force for injection accordingly.¹⁶ Also shown in Table 4.1. is the energetic disorder associated with the TiO₂ acceptor states in the TiO₂ / N945 system. Employing a physically

reasonable value of 100meV for E_0 the disorder is $\sim 270\text{meV}$ under either coating.^{17,18} These values also agree well previously measured variations in TiO_2 sensitised with either N719 or Zn- porphyrin based dyes¹⁷ and is physically reasonable by comparison with variations of TiO_2 flat band potential with effective electrolyte pH.¹⁹

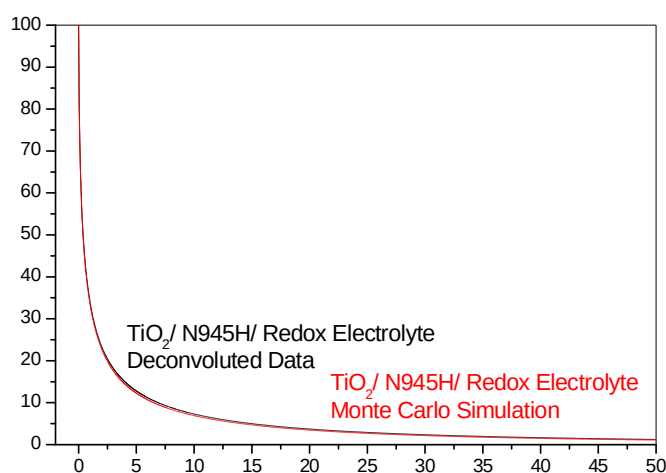


Figure 4.4 Optimised MCS integrations with deconvoluted decay traces for TiO_2 / N945 coated in redox electrolyte.

The kinetics and the model parameters have therefore been shown to be similar for both N945 and N719; injection for both systems under insert solvent is <60 ps and under standard redox electrolyte A coating N945 $t_{50\%}$ is $140\text{ps} \pm 60$, some 10 ps faster than N719. This suggests that the electronic coupling is similar; extension of the conjugated π -framework onto the replacement methoxy based ligand in N945 has not shifted the LUMO from the dcbpy ligands. This is in good agreement with a theoretical study on N945 / TiO_2 binding^{4,7} which showed protonated N945H₂ complexing to N945 / $[(\text{Ti}(\text{OH})_3)_2]$ upon binding.²⁰ The LUMO of the solution phase anionic species, N945²⁻⁴, is located on the ethenylpyridine ligands, however, interactions between N945²⁻ and the positive Ti^{4+} field lower the energy of the carboxypyridine ligand π^* sufficiently to ensure the LUMO remains on the carboxypyridine ligands binding the dye to the TiO_2 surface⁴ similarly to N719.⁷

The similarity in binding and the higher molar extinction co-efficient therefore suggest that higher currents are possible in N945 devices relative to N719.¹³ Furthermore it is also likely that the same concentrations of potential determining

electrolyte additives will minimise kinetic redundancy in N945 based devices similarly to N719 DSSCs.¹⁶

4.1.1.5 Conclusion.

N945 is a novel dye structurally similar to N719. Replacement of one of the dcbpy ligands on N719 by 4,4'-di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2'-bipyridine ligand extends the π -conjugation increasing the molar extinction coefficient whilst leaving the LUMO location unaltered on the sole remaining anchoring dcbpy ligand. Injection in N945 based systems behaves similarly to N719 systems accordingly. However, due to the increased extinction co-efficient N945 DSSCs are capable of producing higher currents, opening up the potential for use in low boiling point, robust electrolyte or thinner TiO_2 films.¹³

4.1.2 Improving Cell Voltages in DSSCs.

4.1.2.1 Introduction.

Efficiencies of dye sensitised solar cells are directly correlated with the maximum cell voltage. This is determined by the position of the quasi fermi level and is reduced by unwanted interfacial charge recombination loss mechanisms.¹⁴ Previous studies have shown that at typical DSSC operating conditions of about 1 sun, recombination between injected electrons in TiO_2 ($e^-_{\text{TiO}_2}$) and oxidised I_3^- electrolyte species (RC2)¹⁴ dominates. There are many different approaches which attempt to reduce electronic coupling between these two species accordingly. These include insertion of metal oxide blocking layers,^{10,21} energetic redox cascades for multistep hole transfer,²² and supramolecular sensitizer dyes.²³ However, alongside the effect these approaches have on recombination it has also been observed that the modifications can also affect the injection process. This work looks at injection in a series of Ru – based dyes containing alkyl chain groups which form an intramolecular blocking layer between injected electrons and oxidised electrolytic species, I_3^- ³ thus potentially reducing the recombination.

The Ru – based dyes used in this work are based on an N3 template; hydrophobic alkyl chains of varying length are directly attached to the N3 structure via one of the carboxypyridine ligands, as shown in Figure 4.5.^{9,24} Inclusion of the chains was originally aimed at improving stability to water and improving contact between dye and solid state hole transporting material in solid state DSSCs. However, it was later realised that the chains also reduce recombination between injected electrons and oxidised electrolytic species by forming an electrically insulating barrier between dye and iodide / triiodide redox electrolyte.³ This effect is further compounded by the simultaneous slowing of the regeneration until it only just out-competes recombination ensuring concentration of the triiodide species used in RC2 is minimised.³

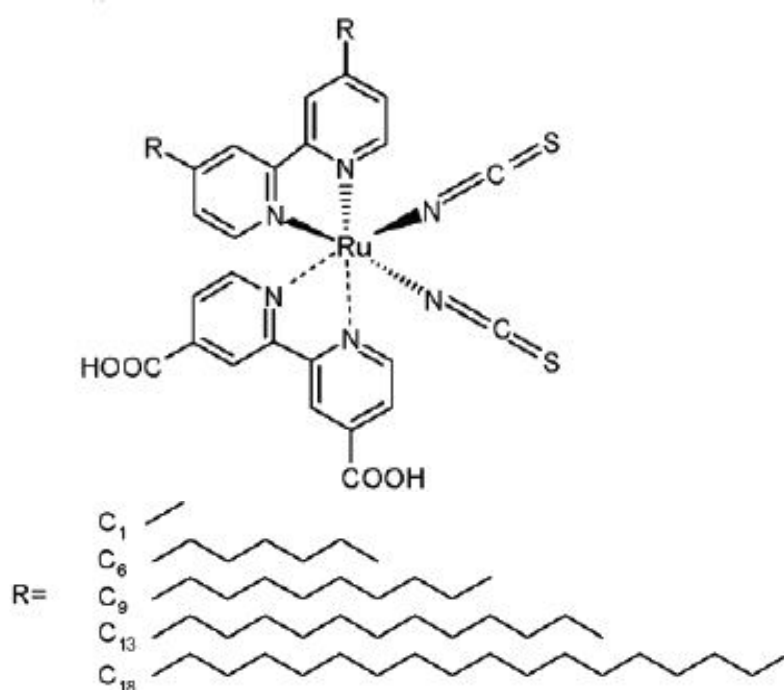


Figure 4.5 Structure of Ruthenium dye series used to minimise kinetic redundancy of the regeneration reaction.³⁴

The dyes have already been shown to improve voltages in solid state DSSCs with devices employing a dye with a 9 carbon alkyl chain, C9 (Z907), producing a ~ 25% increase in efficiency relative to the N719 based control.²⁴ Furthermore, increasing the chain length up to C13 increases solid-state device currents.⁹ This shows there is both scope to further improve on N719 performances in solid state DSSCs by changing C9 for C13 and the chains are potentially modulating the electron injection

process. This provides the motivation for this work; electron injection dynamics have been measured and compared for each dye in the series using the transient emission techniques outlined in Chapter 3. The findings are then discussed with reference to variations in driving force between each dye structure.

4.1.2.2 Experimental Methods.

Time correlated single photon counting has been used to measure electron injection dynamics for ZrO₂ and TiO₂ films sensitised with each dye in the series and coated in either inert solvent or standard redox electrolyte A as per the cells in which the currents were measured.¹³ Sample preparation and experimental procedures are outlined in Chapter 2. Briefly, the dyes were obtained from EPFL and used as received. Control ZrO₂ and TiO₂ films were immersed in 0.3mM dye solution overnight and subsequently carefully rinsed with acetonitrile before application of the coating and glass slide. Dynamics are compared with reference to the time it takes for the amplitude of the emission decay to reach half the maximum of the control value, referred to as $t_{50\%}$ and the measured dynamics are then modelled using the simple description of the dye / TiO₂ interface outlined in Chapter 3.

4.1.2.3 Results.

Dye Series / TiO₂ Coated with Inert Solvent.

Initial emission studies focused on the most experimentally simple system – alkyl chain dye sensitised TiO₂ films covered in inert organic solvent (50:50 PC : EC). Inclusion of the inert solvent prevents modulation of the TiO₂ conduction band energetics by atmospheric water.¹⁵ Steady state measurements showed unaltered absorption maxima and emission quenching on TiO₂ relative to ZrO₂. Typical transient emission decays of TiO₂ and ZrO₂ sensitised with each of the alkyl chain dyes are shown in Figure 4.6.

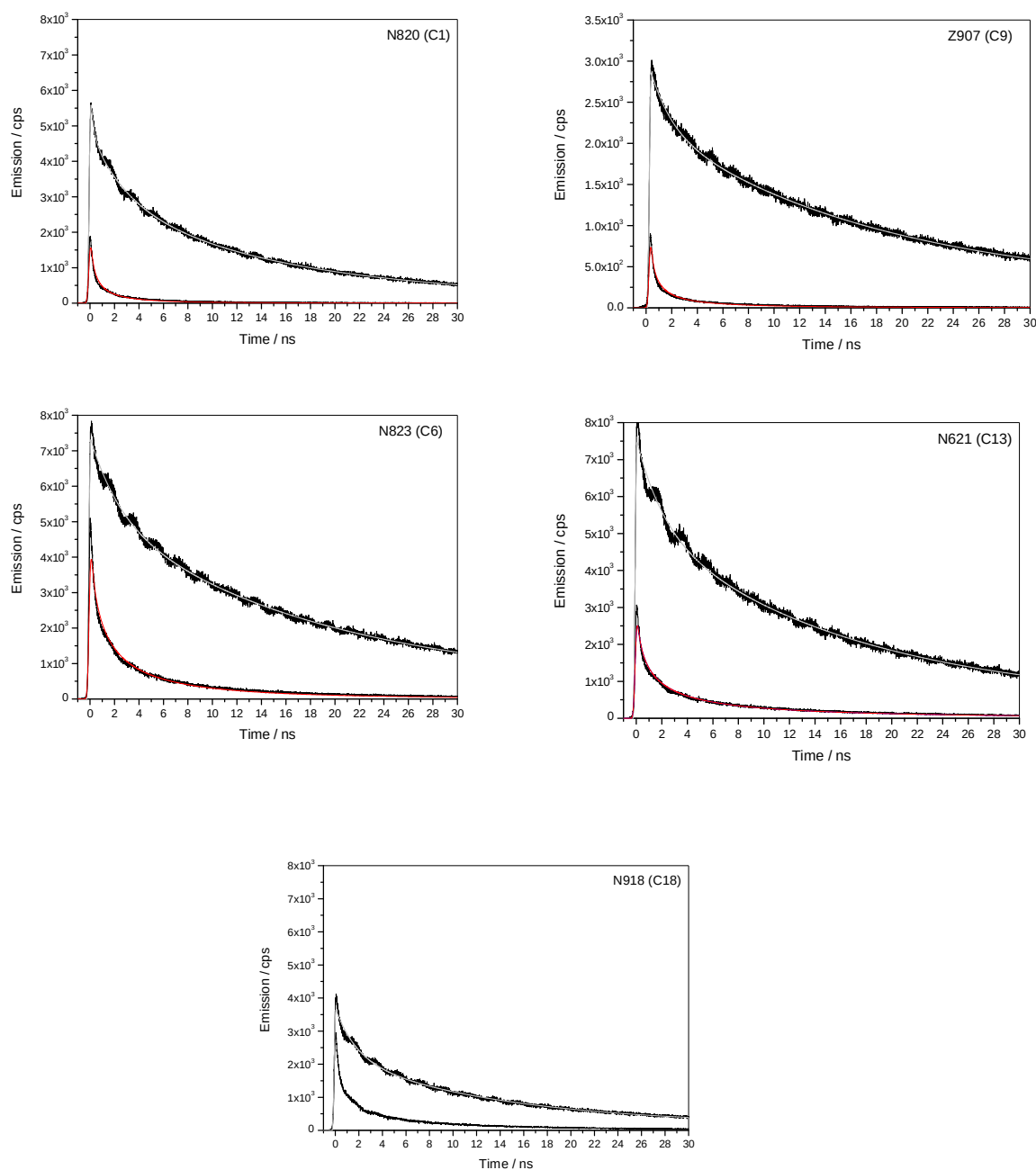


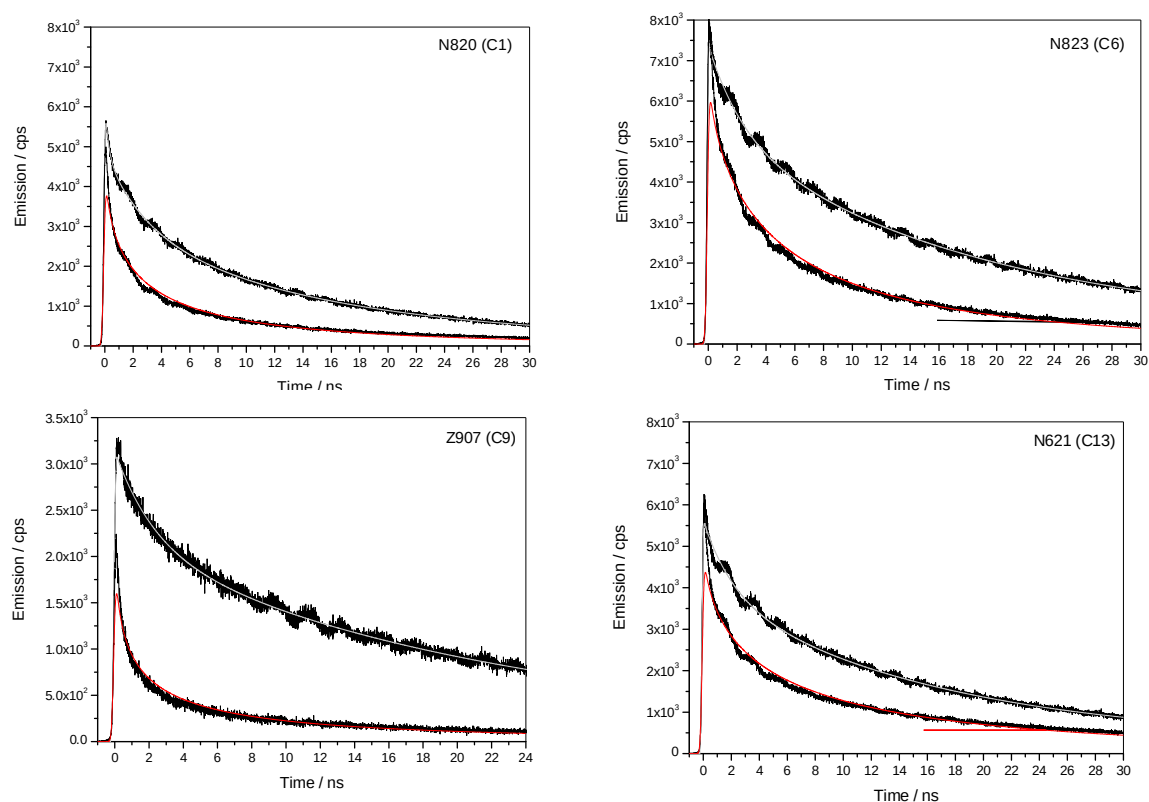
Figure 4.6 TCSPC traces of dye sensitised ZrO_2 and TiO_2 coated in inert solvent. Also shown are lines of best fit in grey and red respectively. ZrO_2 fits were generated by procedure (1), TiO_2 fits were generated by procedure (2) as outlined in Chapter 2 on page 35. Wherever necessary decays have been normalised for the number of photons absorbed at the excitation 467nm wavelength to enable direct comparison of amplitudes.

Figure 4.6. shows all TiO_2 / alkyl chain systems show quenched emission consistent with electron injection. For all dyes initial amplitudes on TiO_2 are lower than ZrO_2

controls indicating a proportion of electron injection occurring faster than the $\sim 250\text{ps}$ instrument response. The injection half – times, $t_{50\%}$, for all of these traces have been determined using procedure (2) outlined in Chapter 2 and the results are shown in Table 4.2.

Dye Series / TiO₂ Coated with Standard Redox Electrolyte A.

Injection dynamics have also been taken for the series using standard redox electrolyte A coating. The additive composition of 0.1M Li^+ and 0.5M TBP is consistent with the cell measurements³ making this system a more accurate representation of the processes occurring in the complete, operating device. Steady state and transient data were consistent with samples coated in inert solvent showing fixed absorption maxima and quenched emission on TiO₂ relative to ZrO₂ controls. Typical transient emission data of the alkyl chain dyes are shown in Figure 4.7.



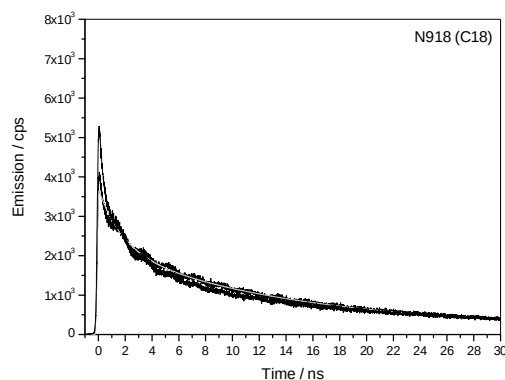


Figure 4.7. TCSPC traces of dye sensitised ZrO_2 and TiO_2 coated in redox electrolyte used previously in measured device performance.³⁴ Also shown are lines of best fit in grey and red respectively.

Figures 4.6 .and 4.7. show emission quenching of all dye / TiO_2 systems is reduced by replacing inert solvent with redox electrolyte coating. The injection half – times, $t_{50\%}$, for all systems are shown in Table 4.2.

Dye	Emission decay half-times (ps)		
	TiO_2 with solvent	TiO_2 / electrolyte A	ZrO_2 with solvent
C1	< 60	798 ± 120	4000 ± 100
C6	268 ± 100	2310 ± 170	7000 ± 750
C9	<60	206 ± 44	10000 ± 2000
C13	<60	1750 ± 150	5900 ± 500
C18	220 ± 50	2500 ± 400	3000 ± 500
N719	< 60	150 ± 50	11800 ± 500

Table 4.2 Emission decay half-times ($t_{50\%}$) for the dye series.

The emission decays of all the dyes on the control ZrO_2 films are of the same timescale as the N719 solution dye excited state decay.³ On TiO_2 all dyes except C18 show faster emission decays consistent with electron injection. Replacement of the inert solvent by redox electrolyte coating retards the dynamics in good agreement with previous studies on N719.¹⁶ It is noted that C18 with redox electrolyte coating

shows decay dynamics similar to the control ZrO_2 sample, suggesting that electron injection is not effectively competing with excited state decay. This is attributed to the collapse of the long alkyl chains, which causes inhomogeneous adsorption to the TiO_2 surface.³

4.1.2.4 Discussion.

In this work we have used time correlated single photon counting to show that electron injection in this dye series behaves similarly to the N719 system. The dynamics of the process are retarded by replacing the inert solvent coating with standard redox electrolyte A, containing 0.1M Li^+ and 0.5M TBP,¹⁶ for all dyes except C18 where the collapse of the long alkyl chains inhibits the injection process. The device data, taken from reference 3, shows that the injection dynamics correlate with the photocurrents with C13 exhibiting maximum currents in liquid devices (it is noted that liquid device data is unavailable for C9) and C9 showing maximum currents in solid state devices; both corresponding to the quickest injection kinetics.

Dynamics for all dyes under both coatings are highly dispersive and are modelled here using Monte Carlo integrations based on the same simple inhomogeneous model of the dye / TiO_2 interface used to fit well TiO_2 / N719 and TiO_2 / N945 dynamics. The details of this model are included in Chapter 3.¹⁷ The integrations are based on the deconvoluted stretch exponential fits to the data.¹ Mean free rates of injection, k_0 , and disorder of the accepting TiO_2 film, Δ/E_0 are shown for all dyes in Table 4.3. It can be seen that the mean free rate of injection across all samples is reduced by the addition of redox electrolyte. This is in good agreement with N719 and the retardation is attributed, as previously, to the 0.5M TBP modulating the conduction band edge upwards thus decreasing the free energy driving force for injection. It can also be seen that using a reasonable E_0 value, the exponent of the TiO_2 density of states, of 100 meV¹⁷ all of the dyes show $\sim 200\text{meV}$ disorder - this agrees well with variations found in both the N719 / TiO_2 system ($\sim 230\text{mV}$) and the Zn- porphyrin based dyes on TiO_2 .¹⁷

Dye	$k_0 \times 10^{-9} \text{ s}^{-1}$		Δ/E_0	
	Inert Solvent	Redox Electrolyte	Inert Solvent	Redox Electrolyte
N820 (C1)	>15	0.6	2.35	1.96
N823 (C6)	1.5	0.25	1.76	1.47
Z907 (C9)	>15	1.7	2.50	2.35
N621 (C13)	3.8	0.25	1.60	1.76
N918 (C18)	1	-	2.35	-

Table 4.3 Parameters of the MCS which showed the best fit to the deconvoluted stretch exponential function for all dye series dyes coated in inert solvent.

Table 4.3. also shows different dyes exhibit different kinetics, but there is no obvious correlation between electron injection and alkyl chain length across the series. This suggests no systematic variation in either electronic coupling between dye excited state LUMO / TiO_2 surface or free energy driving force with chain length. The similarity in dynamics to N719 across the series implies that the dye excited state LUMO is localized on the binding ligand. This is in good agreement with LUMO orbital calculations for the isolated C1 dye which indicate a small energetic stabilisation on the binding dcbpy.⁷ However, electronic coupling could contribute to the discrepancies in $t_{50\%}$; single binding bi-(carboxypyridine) (dcbpy) ligand (compared to two in N719) enables greater flexibility in binding orientation and a 100 – fold retardation of injection dynamics requires only 5Å increased spatial separation.^{3,25} Alternatively, the variation in $t_{50\%}$ could come from differences in free energy driving force with the similar dye excited state oxidation potentials $E(\text{D}^+/\text{D}^*) = -0.94 \pm 0.02 \text{ V vs. SCE}$ suggesting variations in TiO_2 acceptor energies are more likely to be responsible. Furthermore, the alkyl chains have previously been shown to be capable of significantly reducing hydration of the TiO_2 surface²⁶ and modulating the conduction band edge of TiO_2 accordingly.^{3,15,27} It follows that different alkyl chain lengths could therefore create different conduction band energy levels within the TiO_2 and injection rates would vary accordingly.

In addition to these findings, it was also observed that electron injection dynamics for Z907 / TiO_2 films were strongly dependent on the batch of Z907 used. Figure 4.8.

shows typical emission decays for complete DSSCs based on two batches of the sensitizer and Table 4.4 shows the corresponding device characteristics.

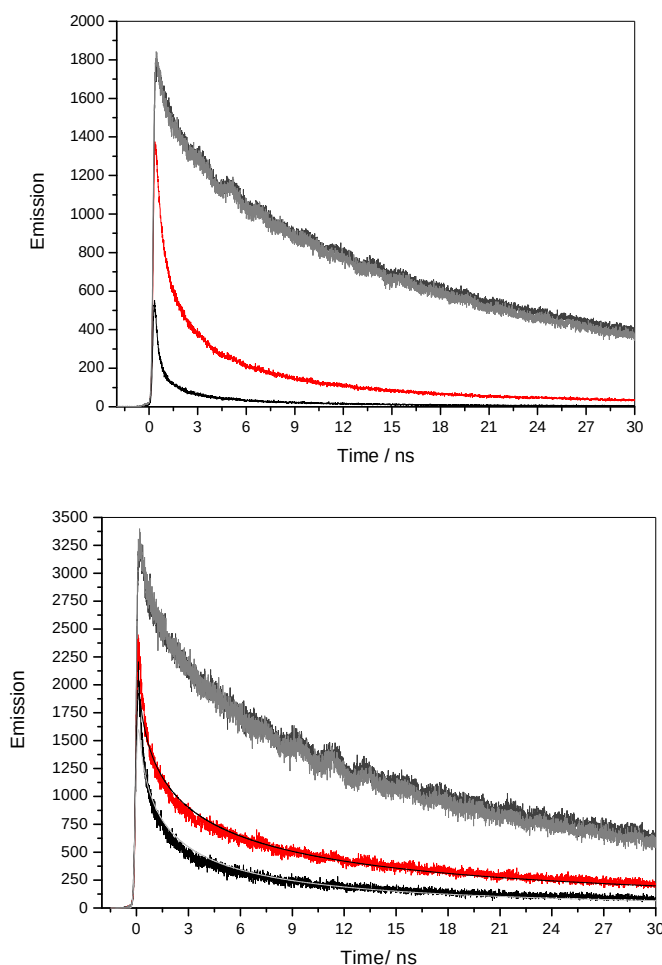


Figure 4.8: TCSPC traces of ZrO_2 sensitised with Z907 batch 1 (grey) and batch 2 (dark grey). The top data shows TiO_2 films sensitised with each batch (#1 – black, #2 – red) and coated with inert solvent. The bottom data shows complete cells made using each batch – the colour scheme is consistent. Also shown on the complete cell data are lines of best fit generated by procedure (2).

	Z907 Batch 1	Z907 Batch 2
$V_{\text{OC}} / \text{mV}$	724	677
$J_{\text{SC}} / \text{mA cm}^{-2}$	9.17	7.9
$t_{50\%} / \text{ps}$ for redox electrolyte coated films	282 ± 50	785 ± 120

Table 4.4. Different photovoltage characteristics of DSCs made using two batches of Z907.

It can be seen from Figure 4.8. and Table 4.4. that batch 1 exhibits faster injection dynamics and higher device currents. Interestingly these are also accompanied by higher voltages, which is unexpected from the well established temporal link between injection and recombination.¹⁶ This seeming contradiction is attributed to the presence of impurities in batch 2 which hinder the dye's performance. One likely source of these impurities is Na^+ as this ion is involved in the synthetic procedure and would be expected to retard the electron injection dynamics by replacing protons which lower the TiO_2 conduction band more effectively.^{19,27}

4.1.2.5 Conclusion.

The alkyl chain series form an important dye set which produces solid state devices competitive with the highest efficiency devices produced to date.²⁴ Furthermore, inclusion of the chains has also previously been demonstrated to be successful at blocking unwanted recombination between injected electrons and the oxidised species in the redox electrolyte.³ In this study we probed the effect of alkyl chain length on electron injection dynamics and found no obvious correlation with increasing chain length but different performances depending on chain length employed. This is attributed to the different dye structures shielding the TiO_2 surface from atmospheric water to different extents. This finding supports other work which has shown the injection dynamics of any system can be altered by the presence of atmospheric water¹⁵ and highlights the need to monitor the injection performance of potential new dyes under simulated operating conditions.

4.2 Electron Injection Studies on DSSCs Employing Molecular Hole Conductors.

This chapter concludes with studies on electron injection in DSSCs which employ robust, solid state alternatives to the volatile liquid electrolyte.^{5,28} These systems are not yet as efficient as the liquid based analogues,⁷ which benefit from fast ion diffusion and easy penetration into the TiO_2 pores, or the quasi – solid systems - so called because the fluidic redox active species is encapsulated within a solid framework material - which benefit from high thermal stability, negligible vapour

pressure, relatively high ionic conductivity and good stability.²⁸ However, they are in principle more stable than both these alternative systems, do not require rigorous sealing to prevent leaking of the electrolyte and are not susceptible to the potentially corrosive effects of the I^- / I_3^- redox couple, all of which make them very attractive for commercial application.

4.2.1 Introduction.

Solid state DSSCs, sDSSCs, refers to any system in which the liquid based electrolyte has been replaced by a hole transporting material (HTM). Following photoinduced electron injection from the dye into TiO_2 residual holes are injected directly from dye cation into the HTM. The holes can then move freely between electronic states in the HTM. Many different HTM materials have been tried for sDSSC application, including copper iodide,^{29,30} polypyrroles³¹ and triphenyldiammine.³² However, the most successful HTM to date is the organic molecule 2,2',7,7' - tetrakis (*N,N* - di - *p* - methoxyphenyl - amine) - 9,9' - spirobi - fluorene (spiro - OMeTAD) and sDSSCs employing this material currently produce efficiencies of $\sim 4\%$.^{24,33} The success of spiro - OMeTAD based devices comes from its small molecular size, high solubility and amorphous nature³⁴ which enables it to better wet the TiO_2 pores. However in spite of this superior wetting, pore penetration in sDSSCs is still much lower than in the liquid based systems. This is coupled with observed faster recombination rates between injected electrons and residual dye cations and leads to lower efficiency devices³⁵ which optimally employ thinner films ($\sim 2\mu m$ in sDSCs versus $\sim 10\mu m$ in liquid based systems⁵) thus requiring dyes with large molar extinction coefficient, such as N945.

Alongside the faster recombination, spiro - OMeTAD based systems also show faster regeneration than liquid analogues; both processes being up to three orders of magnitude faster in the solid system. Nanosecond hole injection into OMeTAD³⁶ is accompanied by micro - millisecond recombination between injected electrons and oxidised OMeTAD, in part due to the one electron nature of the process.⁵ However, the dynamics of the electron injection process have hitherto been assumed to be similar to the liquid based systems. This provides the motivation for this work.

Electron injection measurements have been made on the promising TiO₂ / N719 spiro – OMeTAD system both with and without the commonly used TBP and Li⁺ cell additives. The measurements are based on the TCSPC technique outlined in Chapter 3 and the results are discussed with reference to the electron injection dynamics in the more commonly used liquid based devices.

4.2.2 Experimental Methods.

Time correlated single photon counting has been used to measure electron injection dynamics for ZrO₂ and TiO₂ films sensitised with N719 and coated in spiro – OMeTAD either with or without 0.1M Li⁺ / 0.5M TBP. Briefly, samples have matched optical densities at the 467nm excitation wavelength and emission is collected for all wavelengths above 695nm. The geometry of the excitation and emission optics are fixed to enable direct comparison of amplitudes and all films are non scattering. Dynamics are compared with reference to $t_{50\%}$ and the measured dynamics are then modelled using the simple description of the dye / TiO₂ interface outlined in Chapter 3. For more experimental details please refer to Chapter 2.

4.2.3 Results.

N719 / TiO₂ Coated with Spiro – OMeTAD.

Initial emission studies focused on the most experimentally basic system – N719 sensitised TiO₂ films coated with spiro – OMeTAD without any potential determining additives. The spiro – OMeTAD coating prevents modulation of the TiO₂ conduction band energetics by atmospheric water.¹⁵ Steady state measurements were taken prior to the dynamic measurements and these showed unaltered absorption maxima and emission quenching on TiO₂ relative to the ZrO₂ control. Typical transient emission decays are shown in Figure 4.9.

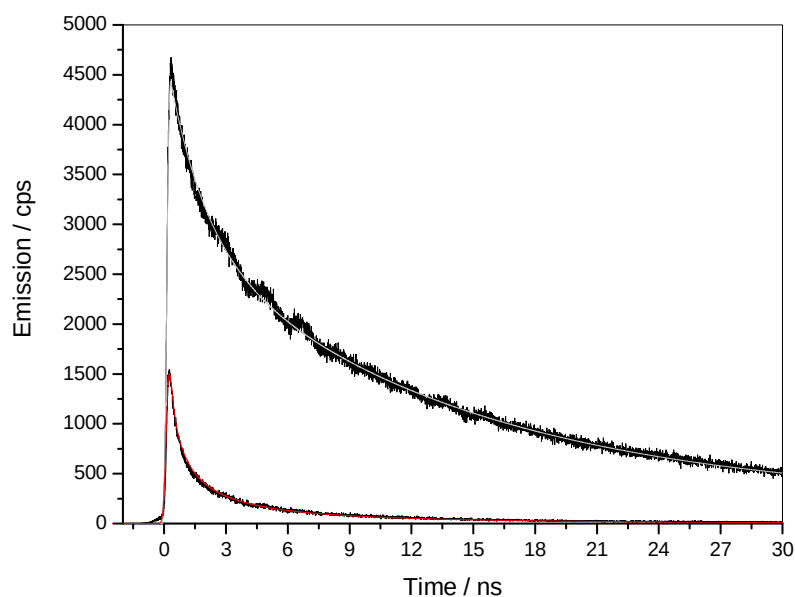


Figure 4.9: TCSPC traces of N719 / TiO₂ (dark grey), and N719 / ZrO₂ (black) coated with spiro - OMeTAD. Lines of best fit are produced by convolution of the instrument response with biexponential decay (ZrO₂) or a stretch exponential decay (TiO₂).

Figure 4.9. shows that typical emission traces for the control N719 / ZrO₂ sample give a biphasic decay with lifetime (amplitudes) of 3ns (0.3) and 30ns (0.7). This is in good agreement with the previous measurements of N719 on ZrO₂ and coated in inert solvent, refer to Chapter 3 for the supporting data, but slightly shorter than the ~50ns solution dye excited state lifetime due to the aerobic conditions employed in the measurement.³⁷ It is also noted that the absence of quenching on the ZrO₂ control shows that there is no direct electron or hole injection into the spiro - OMeTAD. On TiO₂ the emission is strongly quenched consistent with efficient electron injection; $t_{50\%}$ is <60 ps. This agrees well with the dynamics for N719 coated in liquid, inert solvents suggesting that replacement of the liquid by spiro - OMeTAD does not significantly alter the injection process.^{1,16}

N719 / TiO₂ Coated with Spiro – OMeTAD and Additives.

The N719 / spiro – OMeTAD system has also been studied with potential determining additives, 0.1M Li⁺ and 0.5M TBP as these additives are often included in the complete, operating device. Typical transient emission data are shown in Figure 5.0.

Amplitudes of all controls were normalised to allow direct comparisons between samples.

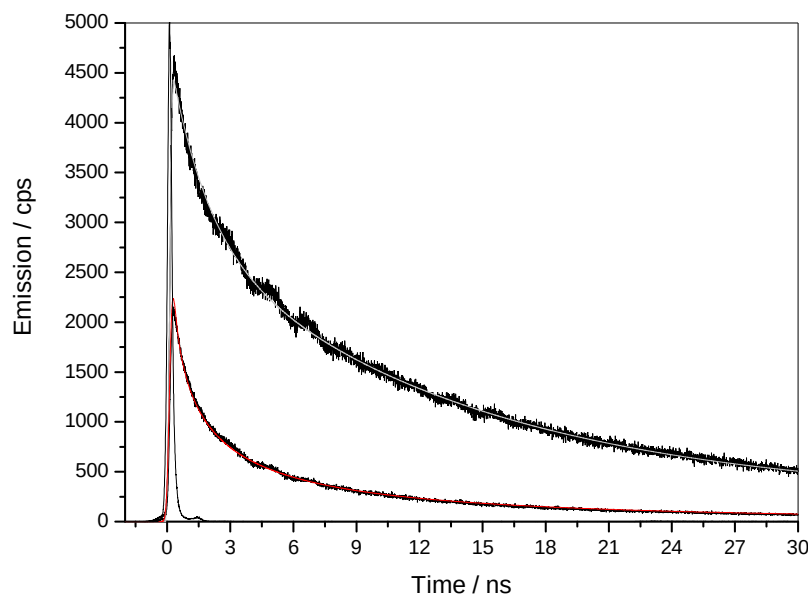


Figure 5.0 TCSPC traces of N719 / ZrO₂ (black) and N719 / TiO₂ (dark grey) coated with coated spiro – OMeTAD with potential determining additives (0.1M Li⁺ and 0.5M TBP). Lines of best fit are produced by convolution of the instrument response with biexponential decay (ZrO₂) or a stretch exponential decay (TiO₂).

It can be seen from Figures 4.9 and 5.0 that inclusion of the potential determining additives reduces the emission quenching of the TiO₂ samples relative to the ZrO₂ control. This corresponds well with previous measurements on liquid devices employing the same potential determining ions.¹⁶ Inclusion of the ions retards the injection halftime, $t_{50\%}$, to $150\text{ps} \pm 45$.

4.2.4 Discussion.

In this work we have used time correlated single photon counting to show that electron injection in solid state N719 systems is similar to the analogous liquid systems; under HTM coating alone $t_{50\%} = <60\text{ps}$, under 0.1M Li⁺ / 0.5M TBP / HTM $t_{50\%} = 148\text{ps} \pm 45$.¹⁶ The dispersive injection dynamics in the solid state system have also been fitted using the same previously published, simple inhomogeneous model of the dye / TiO₂ interface used to describe the liquid based N719 system – for more detail on this model see Chapter 3.¹⁷ Typical Monte Carlo integrations (MCS) of the

deconvoluted stretch exponential fits to the data ¹ yields MCS fitting parameters representing mean free rate of injection, k_0 , and disorder of the accepting TiO₂ film, Δ/E_0 in the solid state system, these are shown in Table 4.5.

Sample	$k_0 \times 10^{-9} \text{ s}^{-1}$	Δ/E_0
TiO ₂ / N719 / spiro – OMeTAD	>10	1.92
TiO ₂ / N719 / spiro – OMeTAD / 0.1M Li ⁺ / 0.5M TBP	1.8	2

Table 4.5 Interfacial parameters in the solid state N719 / TiO₂ system with and without potential determining additives.

Table 4.5. shows that the slower dynamics in the presence of the potential determining ions are due to a reduction in the mean free rate of injection. However, looking at the disorder parameter and using a physically reasonable value of 100meV for E_0 ^{17,18} it can be seen there is no large variation in disorder between the films. Furthermore the disorder is similar to the liquid based N719 systems where samples both with and without potential determining ions showed ~230mV disorder. In summary, both the mean free injection and the disorder parameters for both systems are similar to the liquid based analogues. It is therefore likely that both the electronic coupling and the free energy driving force are similar in both the liquid and solid state systems; and that the mode of operation of the potential determining additives is also similar with the 0.5M TBP dominating the overall effect to cause net modulation of the conduction band edge upwards thus decreasing the free energy driving force for injection. ¹⁶

4.2.5 Conclusion.

Electron injection in the most successful solid state DSSCs to date occurs similarly to the liquid based systems. Furthermore the injection is modulated similarly by the inclusion of potential determining additives. This is important because it means the same principles can be applied to solid systems for optimising the electron injection

process; and that the optimal injection rate – which occurs only just faster than excited state decay - should be achievable with the same concentration of potential determining additives as required in the liquid based system.¹⁶

4.3 *Concluding Remarks.*

The time correlated single photon counting emission technique introduced in Chapter 3 has been successfully used to study electron injection in both liquid systems employing different dyes and solid state systems. The dynamics for all the systems have been determined and all show predominantly picosecond injection. Furthermore the dynamics have all been shown to be well represented by a simple, inhomogenous model of the dye / TiO₂ interface based on non – adiabatic electron transfer theory. The success of using this low cost, low labour intensity technique highlights how easy it is to perform these measurements on a variety of different systems.

4.4 References.

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Parameters Influencing the Efficiency of Electron Injection in Dye Sensitised Solar Cells.

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5 Parameters Influencing the Efficiency of Electron Injection in Dye Sensitised Solar Cells.

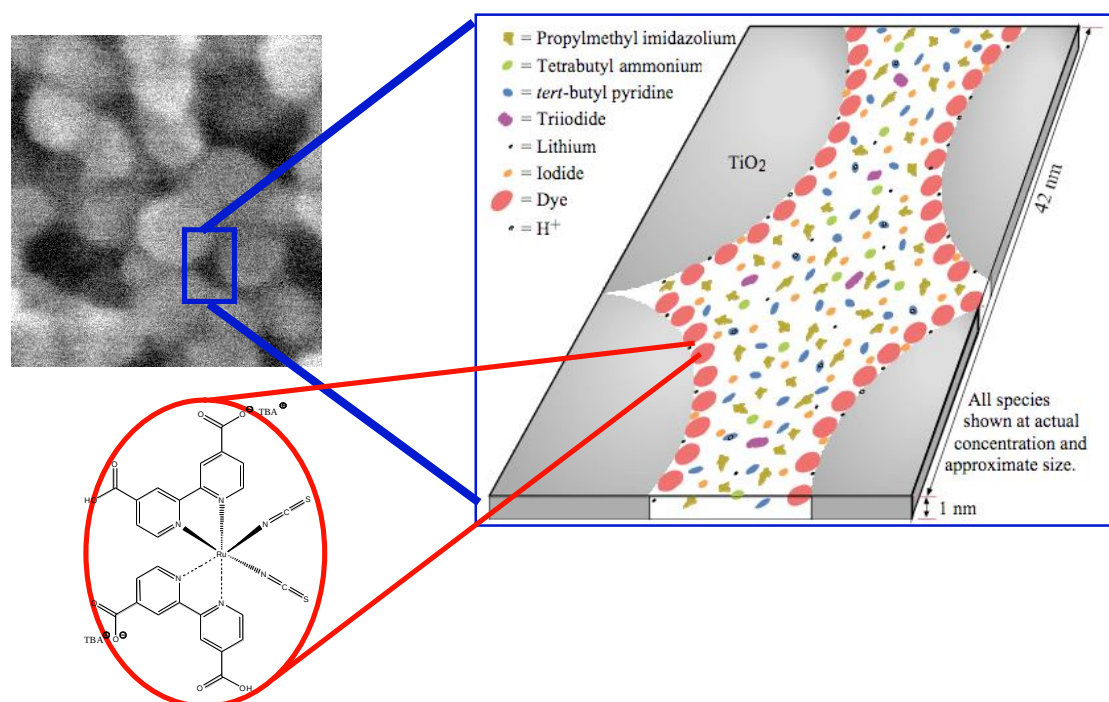
The purpose of this chapter is to extend the transient emission measurement technique outlined in Chapter 3 to complete dye sensitized nanocrystalline titanium dioxide solar cells (DSSCs) employing the ruthenium bipyridyl sensitizer dye N719.¹ The chapter looks at the influence of a range of parameters upon electron injection, including the TiO₂ film synthesis, electrolyte additives including Li⁺ ions, tBP and the I/I₂ couple and the influence of applied bias. Electron injection dynamics and quantum yields are then correlated with device performance and explained with reference to variation in the energetics of the TiO₂ conduction band and filling of available acceptor states. It is shown that the relative energetics of the dye excited state versus the titanium dioxide acceptor states is a key determinant of the dynamics of electron injection in DSSCs, and that variations in these energetics, and therefore in the kinetics and efficiency of electron injection, impact directly upon device photovoltaic efficiency.

5.1 Introduction.

Electron injection studies on TiO_2 / Ru – bipyridyl dye systems have extensively focussed on films coated in inert solvent. Under these conditions sub-picosecond injection dynamics, ²⁻⁵ orders of magnitude faster than the competing process of excited state decay to ground, are common. This has led to studies of device optimization typically focusing upon light absorption and electron collection. ¹ However, in complete DSSCs employing electrolyte additives commonly used to enhance device performance, such as t-butyl pyridine (tBP) and Li^+ , injection has been shown to be retarded onto the 100s of picoseconds timescale ⁶ opening up the possibility for electron injection to impact directly upon device photovoltaic efficiency. Indeed, electron injection has already been shown to potentially affect DSSC performance. Structure – function studies on a series of organic dyes have highlighted the need for the dye excited state to be sufficiently high in energy to enable injection to occur. Dyes which did not fulfil this requirement were observed to have lower photocurrents. ⁷⁻⁹ Improved currents in DSSCs based on the Ru black dye have also been reported to be affected by improved injection performance. ¹⁰ Similarly, dye aggregation has been suggested to reduce the efficiency of electron injection for some sensitizer dyes, thereby reducing device performance. ¹¹ However, the effect of the commonly used electrolyte additives, t-butyl pyridine (tBP) and Li^+ , which have been shown to influence electron injection dynamics by modulating the relative energetics of the dye excited state versus the TiO_2 conduction band, ¹²⁻¹⁴ upon the efficiency of electron injection in complete DSSCs, and their correlation with device performance, have received only limited attention to date. ^{6,15,16}

This study focuses on electron injection in complete, functioning DSSCs based on N719. In typical complete DSSCs based on this system electron injection dynamics are on the 100 ps timescale, ⁸ proceeding from the dye triplet state. These kinetics are slow enough to be measured using the time correlated single photon counting techniques (TCSPC) introduced in Chapter 3. Scheme 5.1 shows, to scale, the structure of the active environment in the operating DSSC, illustrating the chemical complexity of the pores of a DSSC in the presence of a typical electrolyte, and thus emphasising the importance of complete device studies of injection dynamics as

opposed to model system studies of dye sensitized films covered in inert solvent. The dynamics and yields are measured under different operating environments including the TiO₂ film synthesis, electrolyte additives including Li⁺ ions, tBP and the I⁻/I₂ couple and the influence of applied bias. Key parameters influencing injection efficiency in complete DSSCs are elucidated and related directly to device performance.



Scheme 5.1: Schematic of the chemical composition of a typical pore in a complete DSSC filled with redox electrolyte. All components are drawn approximately to scale, neglecting molecular interactions. Also shown is a HRSEM image of such a pore, and the molecular structure of the N719 sensitizer dye. This illustration neglects intermolecular complexation which is likely to further complicate the chemical composition of the pores.¹⁷

5.2 Experimental Methods.

Time correlated single photon counting has been used to measure electron injection dynamics for ZrO₂ and TiO₂ films sensitised with N719 and coated in either inert solvent or standard redox electrolyte A. Sample preparation and experimental procedures are outlined in Chapter 2. Briefly, N719 dye was obtained from EPFL and

used as received. Control ZrO₂ and TiO₂ films were immersed in 0.3mM N719 solution overnight and subsequently carefully rinsed with acetonitrile before application of the coating and glass slide. Devices employed standard redox electrolyte A unless otherwise stated.

Dynamics are compared with reference to the time it takes for the amplitude of the emission decay to reach half the maximum of the control value, referred to as $t_{50\%}$, and β values (where β refers to the stretch parameter as defined on page 35) were 0.353 ± 0.028 for all samples employing standard electrolyte A, varying only by 0.02 between zero and maximum applied negative bias. This allowed half – times between samples to be directly compared. In the tBP studies, however, β values ranged more significantly from 0.3 to 0.39 and for this reason the quantum yields of electron injection are considered in tandem with the $t_{50\%}$ values. Injection quantum yields were determined by integration of the emission decays over time, with the lower integrated areas observed for the TiO₂ films relative to the ZrO₂ control being assigned to electron injection. The non-exponential nature of the emission decay dynamics observed for the TiO₂ samples gave rise to calculated injection quantum yields which are significantly lower than those obtained from comparison of decay half-times alone.

5.3 Results.

Initial emission studies focussed on a complete DSSC using standard electrolyte A, and control data collected for a ZrO₂ control cell. The emission decay traces for the control ZrO₂ samples typically showed $t_{50\%}$ of ~ 10 ns, consistent with previous studies of the decay dynamics of the N719 triplet excited state.¹⁸ In the TiO₂ based complete DSSC the emission was strongly quenched consistent with electron injection into the TiO₂ conduction band. The injection half time, $t_{50\%}$, was 200 ± 60 ps,¹ in good agreement with previous transient absorption studies.⁶ The kinetics were found to be independent of dye loadings (for devices corresponding to approx. 10% - 100% monolayers dye coverages).

The dispersive (stretched exponential) nature of the emission decays observed in Figure 5.1 prevents the yield of electron injection being calculated from measurement of the injection half-time alone. Instead quantification of the yield of electron injection can be made easily by comparison of the integrated areas under the emission decays for the TiO₂ and ZrO₂ samples – with the magnitude of quenching of this emission area observed for the TiO₂ samples being taken as a measure of the injection yield. Injection quantum yields of ~ 0.84 were observed for these samples. This is in excellent quantitative agreement with previous measurements of the maximum internal quantum efficiency (or absorbed photon to current efficiency) for these standard devices, determined under short circuit conditions to be 0.86,¹⁹ and in good quantitative agreement with analysis of injection efficiency determined from front and back illumination external quantum efficiency data.¹⁹ These observations strongly indicate that for these ‘standard’ N719 sensitized devices; the internal quantum efficiency for photocurrent generation is primarily limited by the efficiency of electron injection.

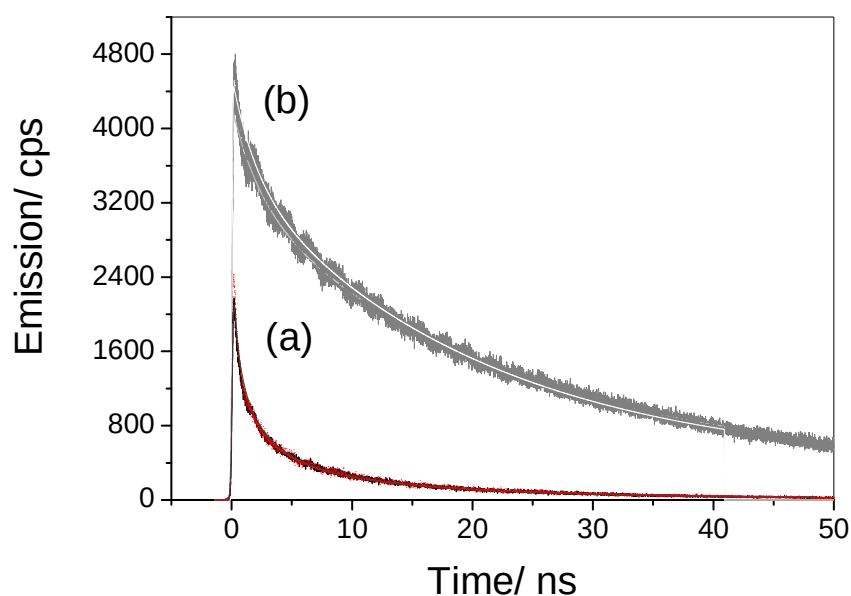


Figure 5.1: Time resolved emission decays for (a) N719 / TiO₂ (black) and (b) N719 / ZrO₂ (grey) films in electrolyte A. Also shown (a) are the corresponding data collected for an electrolyte omitting the iodide / iodine redox couple (red), which is essentially identical to that observed in the presence of electrolyte A. Smooth lines correspond to fits to the experimental data after convolution with the instrument response.

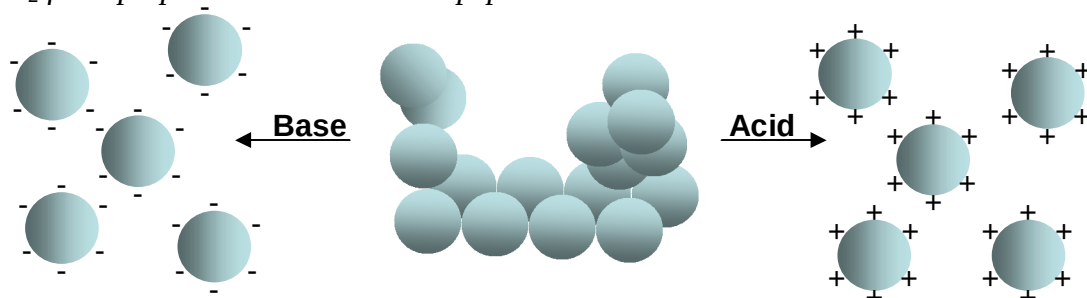
Injection dynamics in presence and absence of redox couple.

The first operational parameter studied is the potential influence of the iodide / tri-iodide redox couple in quenching the sensitizer dye excited state. As illustrated in Scheme 5.1, it is possible that the redox couple could have a significant impact upon the chemical environment of the dye / TiO₂ interface. Previous studies of analogous ruthenium dyes have indicated that this redox couple can potentially quench the dye triplet excited state by either oxidative or reductive quenching and that this may be a significant factor influencing DSSC device performance.²⁰⁻²³



Data was collected and compared for samples with and without the iodide / iodine redox couple (electrolyte B, as A but with iodide anions replaced by perchlorate). Typical transient emission data for samples employing electrolytes A and B are shown in Figure 1 (electrolyte B, red trace). It is apparent that for both the TiO₂ and ZrO₂ control samples, data collected in the presence and absence of the redox couple are indistinguishable. It can be concluded that neither oxidative nor reductive quenching of the N719 dye excited state, nor the influence of the redox couple on the TiO₂ electron density in the dark, are significant factors influencing electron injection efficiency for N719 sensitized solar cells employing this electrolyte A.

TiO₂ films prepared via acid or base peptisation.



Scheme 5.2: Schematic of TiO₂ particles following acid (positive) or base (negative) peptisation.

The next operational parameter studied is the potential influence of TiO₂ film fabrication procedure upon the injection kinetics. Electron injection in dye / TiO₂

films has previously been reported to be sensitive to film preparation,²⁴ more specifically the pH of the peptisation agent used to electrostatically stabilise TiO₂ film particles.²⁵ Furthermore, model system studies of dye / TiO₂ electron injection have shown a strong dependence upon ambient pH.^{26,27}

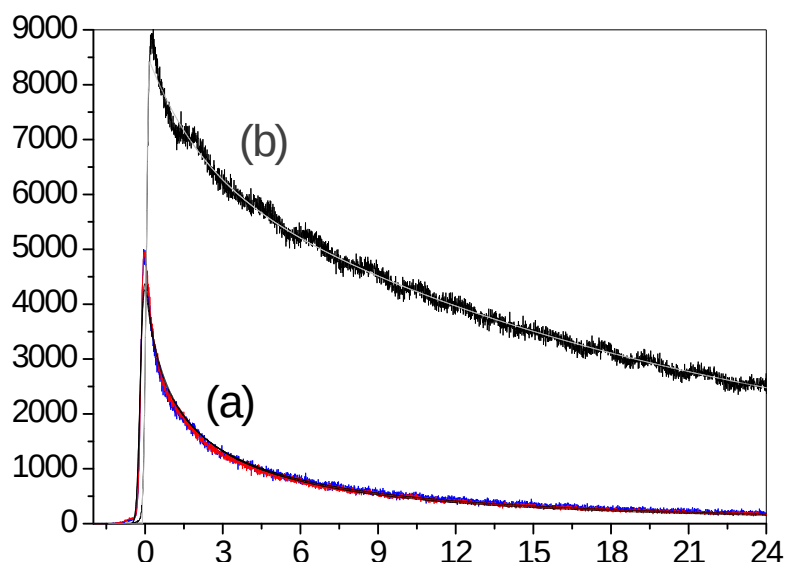


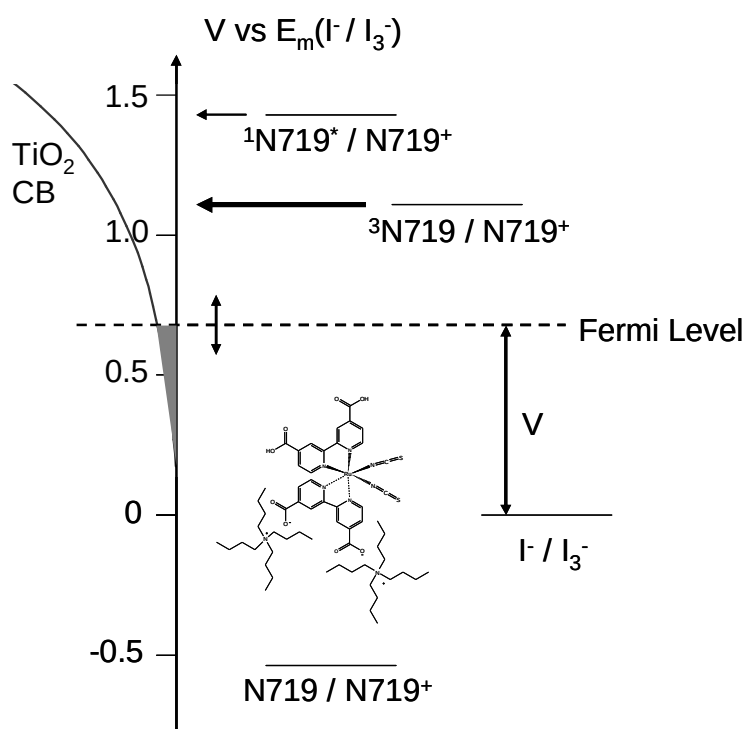
Figure 5.2: (a) Time resolved emission decays for N719 / TiO_{2Acid} (blue) and N719 / TiO_{2Base} (red) films in standard electrolyte A. Also shown are (b) the corresponding N719 / ZrO₂ control data and (smooth lines) the convoluted fits to experimental data.

Typical transient emission data of electron injection in either TiO_{2Acid} or TiO_{2Base} N719 sensitized films in electrolyte A are shown in Figure 5.2. It is apparent that the electron injection dynamics for these two film preparation procedures are indistinguishable. It is concluded that electron injection in the N719 sensitized DSSCs are unaffected by the pH of the initial peptisation used in film preparation.

Influence of applied electrical bias.

The third parameter considered is the effect of electrical bias on electron injection. In model system studies employing three electrode photoelectrochemical cells, application of an electrical bias of -700 mV relative to Ag/AgCl to N3 / TiO₂ films in the presence of a redox inactive electrolyte has been shown to retard the injection rate 25-fold (where N3 is the fully protonated analogue of N719).²⁸ This retardation was assigned to an increase in electron density within the TiO₂ CB, reducing the density of

unoccupied states available for electron injection. Solar irradiation of complete DSSCs has also been shown to result in substantial increases in electron density, depending upon irradiation intensity and cell voltage. For example, for the ‘standard’ DSSCs studied herein, charge extraction studies under simulated AM1.5 conditions determined increases in electron density, relative to the dark short circuit conditions, of $\sim 3 \times 10^{17} \text{ cm}^{-3}$ at short circuit and $\sim 3 \times 10^{18} \text{ cm}^{-3}$ at open circuit, in good agreement with previous work.²⁹ This increase in electron density, and therefore in TiO_2 Fermi Level, E_F , has been shown to accelerate interfacial charge recombination losses, with a 100 mV increase in E_F typically decreasing the recombination half time by a factor of 5. It is therefore of interest to consider the influence of applied electrical bias upon the injection dynamics in DSSCs.



Scheme 5.3: Illustration of the effect of negative bias on electron injection. The applied bias, V , raises the TiO_2 Fermi level relative to the chemical potential of the electrolyte. This results in increasing occupancy of electron acceptor states in the TiO_2 , illustrated as the shaded area in the exponentially increasing density of conduction band / trap states.

Transient emission data were collected for standard N719 / TiO_2 DSSCs employing electrolyte A under forward bias in the dark for the bias range 0 V (corresponding to

short circuit) to -1.07 V (greater than the device V_{OC} under 1 sun ~ 0.76 V). Corresponding charge extraction data indicate that this voltage range corresponds to electron densities up to $6 \times 10^{18} \text{ cm}^{-3}$, and therefore corresponds to the full range of electron densities present in devices under solar irradiation. Typical data for a device under 0 V (blue) and maximum 1.07 V negative bias (red) are shown in Figure 5.3.

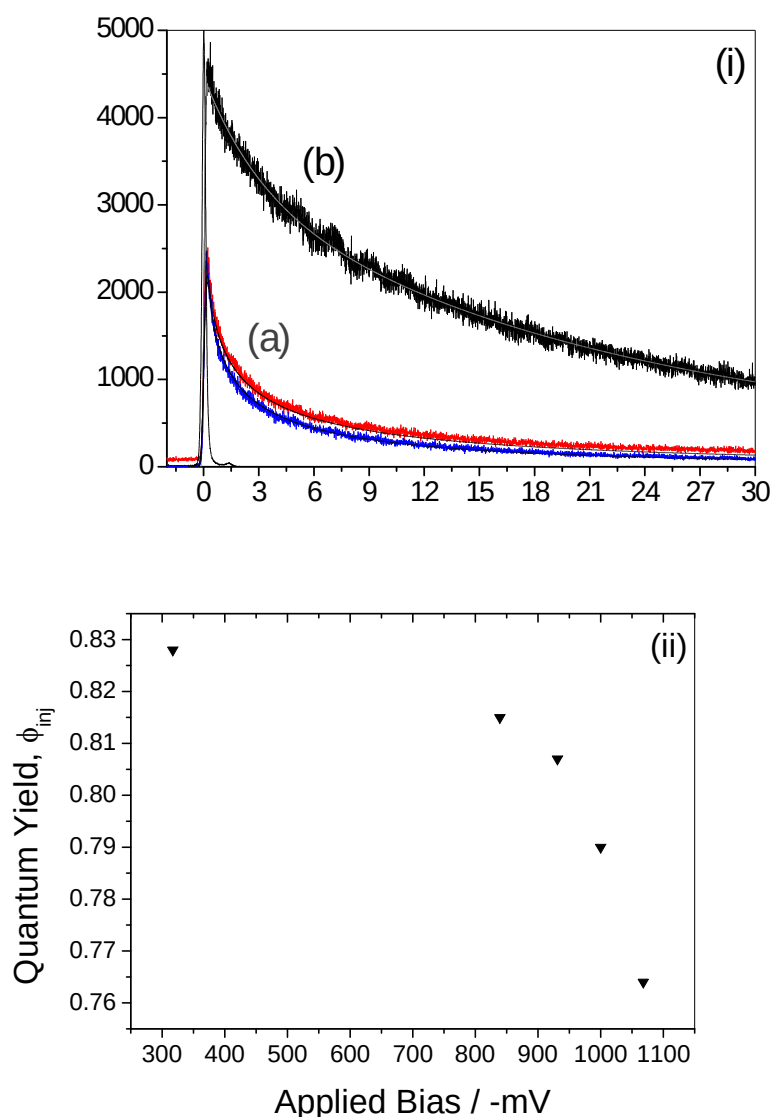
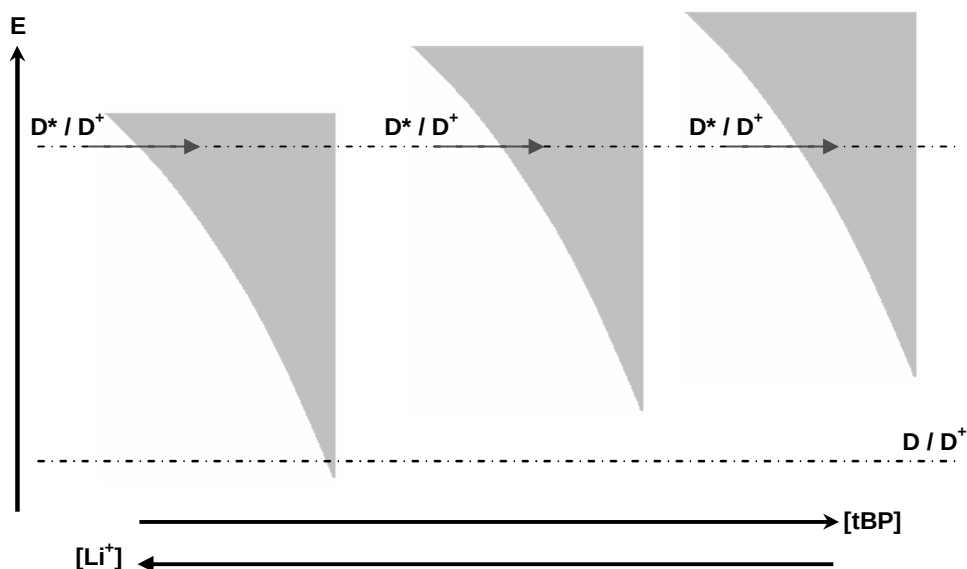


Figure 5.3: (i) (a) Time resolved emission decays for N719 / TiO_2 DSSC employing the electrolyte A under 0 V (blue) and -1.07 V (red) applied bias. (b) Control data for N719 / ZrO_2 devices. Also shown are stretch-exponential fits to the TiO_2 data (smooth lines) (ii) Plot of quantum yield for electron injection, ϕ_{inj} , determined from emission decays such as those shown in (i) versus applied bias.

Control data on the ZrO_2 device as a function of applied bias showed, as expected, no dependence upon applied bias. For the TiO_2 DSSC, the application of negative bias resulted in modest increase in electron injection halftime $t_{50\%}$, from 180 ps at 0 V to 230 ps at -1.07 V, as shown in Figure 5.3. This effect was fully reversible with variation in applied voltage. Similar, weak but measurable, dependence of injection half times upon applied voltage were observed for all such DSSCs studied. Determination of the electron injection quantum yields (from the integrated emission areas, as detailed above) indicate that the applied bias results in a modest reduction in quantum yield from 0.83 at 0 V to 0.76 at -1.07 V, as illustrated in Figure 5.3(ii).

Affect of electrolyte additives – Li^+ and tBP.



Scheme 5.4: Effect of commonly used electrolyte additives on the energetics of the density of TiO_2 conduction band acceptor states. The density of conduction band / trap states (shaded areas) is represented as an exponential distribution consistent with previous measurements.³⁰

The final operational parameter studied concerns the effect of two commonly used electrolyte additives, *tert* – butyl pyridine (tBP) and lithium cations (Li^+), on electron injection. Device optimisation is commonly achieved by including these electrolyte additives, or analogues, in the cell to modulate the maximum device short circuit current (J_{SC}) and maximum open circuit voltage (V_{OC}).^{6,31-34 35} tBP and Li^+ have been shown to affect both the kinetics and quantum yield of injection in Ru-bipyridyl

sensitized systems.^{6,14,15,36} Here injection has been measured in complete, functioning devices and changes in device J_{SC} and V_{OC} values have been quantitatively correlated with modulation of the electron injection process.

Transient emission traces were collected for complete N719 / TiO_2 DSSCs employing electrolytes based on A but using tBP and Li^+ concentrations varied over the range typically used in DSSC device optimisation studies (0 – 0.1 M Li^+ , 0 – 0.5 M tBP). Typical emission data for three different electrolyte compositions are shown in Figure 5.4.

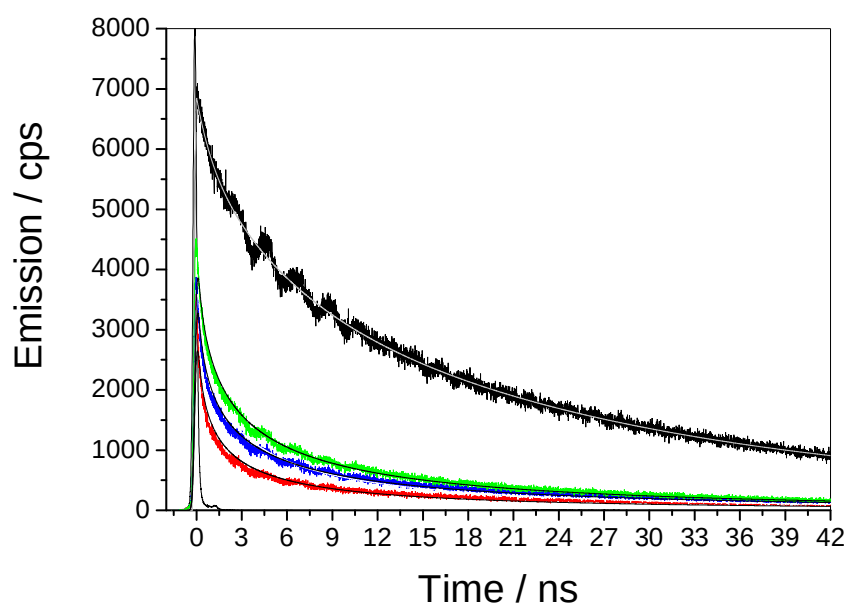


Figure 5.4: (a) Time resolved emission decays for N719 / TiO_2 films in electrolytes employing 0.1M tBP / 0.1M Li^+ (red), 0.2M tBP / 0.1M Li^+ (blue) and 0.2M tBP / 0 M Li^+ (green). Also shown is the corresponding N719 / ZrO_2 control data (black) and (smooth lines) the fits to experimental data.

It is apparent that electrolyte composition has a significant influence upon injection dynamics, with injection half-times ranging from <60 ps for 0.1 M Li^+ , 0 M tBP to $550 \text{ ps} \pm 120$ for 0 M Li^+ , 0.5 M tBP . Injection half-times, and the corresponding device performance data are summarised in Table 5.1 (devices used 4 μm , non-scattering TiO_2 films in order to facilitate TCSPC studies and therefore exhibit only modest absolute current densities due to relatively low light absorption). The variation of device performance with electrolyte composition is in good agreement with previous studies which have shown that more ‘basic’ electrolytes (low Li^+ , high tBP)

reduce J_{SC} but increase V_{OC} ,^{6,31,32,34} with optimum device efficiency being obtained at the ‘standard’ electrolyte composition of 0.1 M Li^+ , 0.5 M tBP .

Charge extraction measurements³⁷ were employed using the procedure outlined on page 38 to determine the relative TiO_2 conduction band energies for the device series studied (with the energies quoted corresponding to the open circuit voltage corresponding to a photoinduced electron density of 10^{18} cm^{-3}). As expected, the addition of tBP was observed to result in a shift of this density of states to more negative potentials, whilst addition of Li^+ shifted it less negative (towards the redox couple potential). Figure 5.5. plots the correlation between these relative conduction band energies and the injection half time. A reasonable correlation is observed, with a 100 mV shift in conduction band energetics correlating with a two fold increase in injection half-time.

Table 5.1: Device and electron injection parameters measured in complete cells employing electrolytes with varying tBP concentrations with and without the addition of 0.1M Li^+ . All devices use 0.6M I^- / 100mM I_2 . Quantum yields have been determined using the procedure outlined on page 38.

[tBP]	[Li^+]	$t_{50\%}$ / ps	J_{SC} / mA cm^{-2}	V_{OC} / mV cm^{-2}	η / %	Quantum Yield	Rel. CB Energy / V
0	0.1	< 60	11.28	565	2.55	0.97	-
0.1	0.1	70 ± 30	10.81	621	3.35	0.87	0.47
0.1	-	272 ± 79	7.40	734	3.42	0.79	0.71
0.2	0.1	185 ± 63	9.83	651	3.62	0.77	0.52
0.2	-	395 ± 96	7.32	738	3.41	0.72	0.722
0.5	0.1	202 ± 71	9.55	670	3.82	0.78	-
0.5	-	547 ± 121	6.54	762	3.04	0.70	0.75

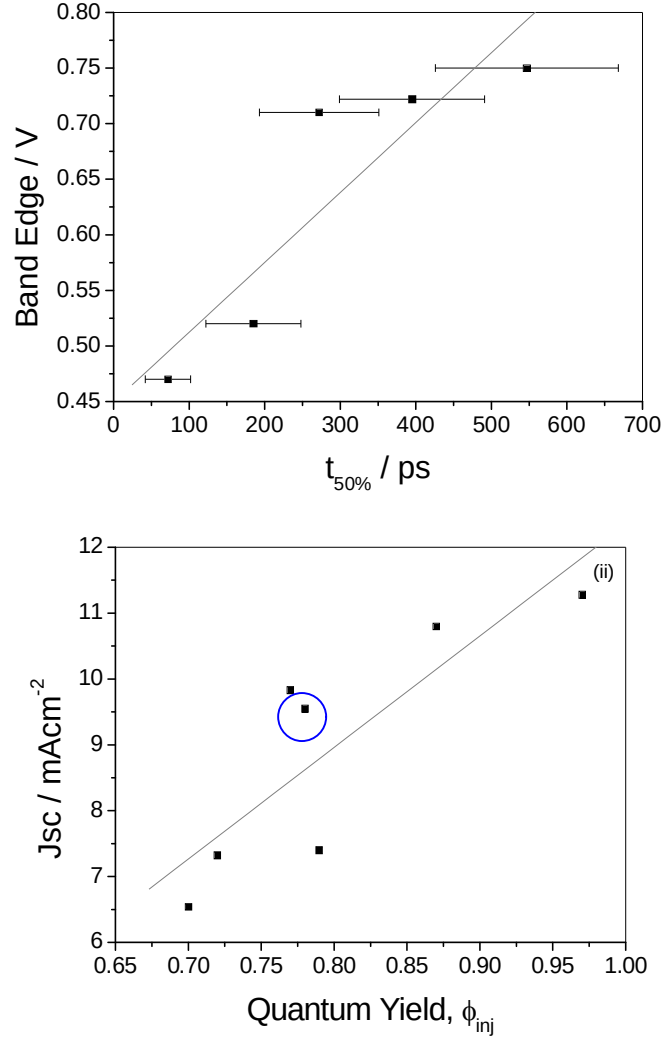


Figure 5.5: (i) Plot of the electron injection half-time determined from TCSPC data versus an estimate of the relative energies of the TiO₂ conduction band determined from charge extraction data for DSSCs fabricated with different concentrations of Li⁺ and *t*BP in the electrolyte. (ii) The corresponding plot of the electron injection yield ϕ_{inj} determined from TCSPC data versus the device short circuit currents measured under 1 sun simulated irradiation. Also shown are the linear best fits in grey. In (ii), the data point corresponding to the highest device efficiency is circled in blue. It is apparent that the device with the fastest injection dynamics, and highest injection yield, does not correspond to the device with the highest overall device efficiency.

Figure 5.5. shows the electron injection yield, ϕ_{inj} , (determined from the TCSPC data as above) varied from 0.97 for the electrolyte with the highest Lewis acidity (0.1 M Li^+ , 0 M tBP) to 0.7 for the most ‘basic’ electrolyte (0 M Li^+ , 0.5 M tBP), indicating, depending on the electrolyte employed, substantial (up to 30 %) losses of photocurrent generation due to excited state decay to ground. Figure 5.5(ii) shows a plot of injection yield versus device photocurrent, demonstrating that a linear correlation is observed, strongly indicative of electron injection losses being a key determinant of device photocurrent efficiency.

5.4 Discussion.

In this work we have used time resolved single photon counting to investigate the influence of a range of parameters upon the kinetics of electron injection in N719 sensitized solar cells. The injection half-time for a solar cell employing a ‘standard’ electrolyte A (0.1 M Li^+ , 0.5 M tBP), $t_{50\%} = 200$ ps is found to be in good agreement with previous studies of electron injection dynamics by ultrafast pump/probe transient absorption spectroscopy and studies on similar model systems outlined in Chapter 3.⁶ Similarly to the model measurements in Chapter 3, emission decay dynamics for this standard cell (and indeed in all TiO_2 samples studied) were found to be well represented by convoluting stretched exponential functions with the instrument response function. This is in good agreement with our previously proposed model for electron injection based on local inhomogeneities in the TiO_2 conduction band energy; this is discussed in more detail in Chapter 3.³⁸

Energy dependence of injection kinetics.

The primary determinant of electron injection kinetics in the studies reported in this chapter is found to be the composition of the redox electrolyte, and specifically the concentrations of the additives Li^+ and tBP in this electrolyte. The injection half time was observed to change from <60 ps for 0.1 M Li^+ / 0 M tBP to ~ 550 ps for 0 M Li^+ / 0.5 M tBP . The injection efficiency varied from 0.97 to 0.7, in excellent quantitative agreement with injection yield measurements as shown in Figure 5.6, completed on the same samples using IPCE techniques, for more information please refer to Barnes et al.¹⁹ The dependence of $t_{50\%}$ was correlated with the influence of these additives

upon the relative energetics of TiO₂ conduction band (CB) determined from charge extraction data. As discussed in both the Introduction and Chapter 3, high charge density cations, such as Li⁺, have previously been shown to be ‘potential determining ions’, adsorbing to and/or intercalating into the nanocrystalline TiO₂ film, and thereby modulating the film charge and thus the film energetics. Furthermore, it has previously been shown that addition of 0.1 M Li⁺ can induce a >1 V downward shift in the conduction band energy of unsensitized TiO₂ films and a 300 meV shift in N3 / TiO₂ films.^{28,39} Conversely, the addition of tBP has been shown raise the energy of the TiO₂ conduction band attributed to its Lewis base characteristics, either by direct co-ordination to the TiO₂ surface via lone pairs on the N moiety^{40,41} or through reducing the surface adsorbed proton concentration, as illustrated in Scheme 5.3.³²

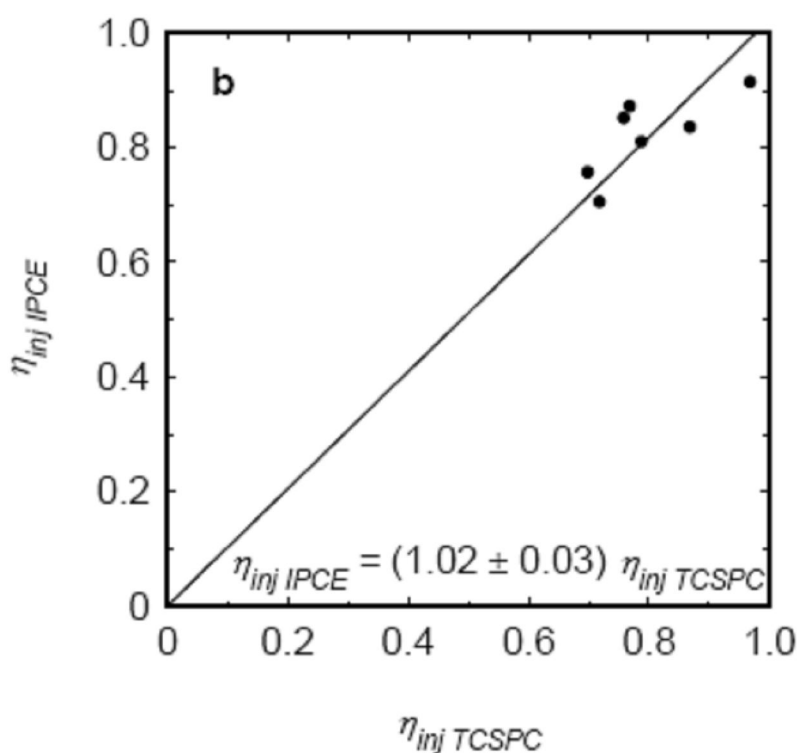


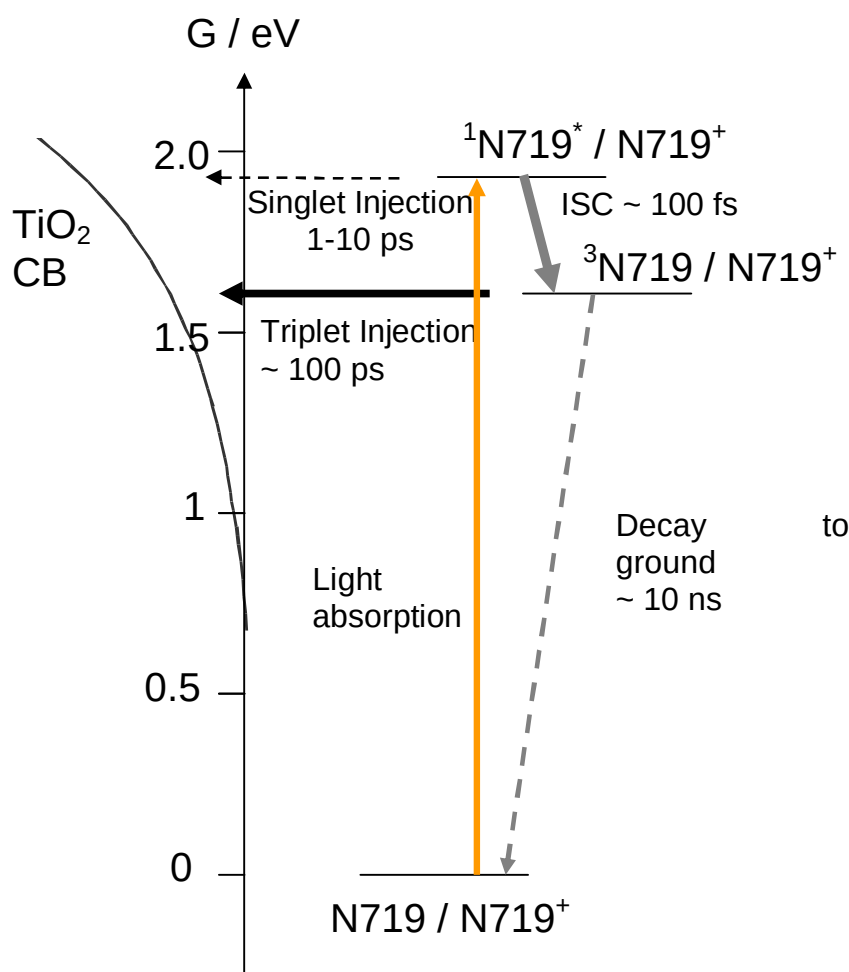
Figure 5.6: Photoluminescent injection yield ($\eta_{inj\ TCSPC}$), measured using TCSPC techniques outlined in Chapter 2, plotted against injection efficiency inferred from IPCE measurements ($\eta_{inj\ IPCE}$). Figure reproduced from Barnes et al.¹⁹

Figure 5.5(a) shows the correlation between injection half-time and the conduction band energetic and indicates that a 280 meV shift in conduction band energy results in an ~8 fold retardation of the injection kinetics. This is in agreement with previous analysis of injection kinetics in N3 sensitized TiO₂ films in three electrode

photoelectrochemical cells by ultrafast transient absorption spectroscopy, where addition of 0.1 M Li^+ ions was observed to result in a 7 fold acceleration of injection kinetics, correlated with a 300 meV shift in TiO_2 conduction band energetics.²⁸ This finding is also quantitatively similar to the dependence of injection kinetics upon the relative energetics of the dye excited state relative to the TiO_2 conduction band (referred to hereafter as $\Delta E_{\text{inj}}^{\text{rel}}$) in studies of porphyrin sensitized TiO_2 films as a function of porphyrin singlet energy, where a 300 meV shift in singlet energy resulted in an order of magnitude acceleration of injection kinetics.⁴²

As discussed in Chapter 3, the dependence of injection half-time upon the energetics of electron injection, $\Delta E_{\text{inj}}^{\text{rel}}$, can be analysed in terms of changes in the influence of $\Delta E_{\text{inj}}^{\text{rel}}$ upon the density of energetically accessible TiO_2 acceptor states. Assuming the rate constant for electron injection is proportional to the number of accessible states, $t_{50\%} \propto \exp(-E/E_0)$, a 280 meV increase in $\Delta E_{\text{inj}}^{\text{rel}}$ can be expected to result in an acceleration of the injection half-time by ~ 16 in reasonable agreement with the observed acceleration (~ 8 fold). The observed dependence of $t_{50\%}$ upon TiO_2 conduction band energy is therefore in good quantitative agreement with the simple model introduced in Chapter 3, for which the rate of electron injection is proportional to the density of energetically accessible acceptor states. This analysis is independent of whether one considers the relevant density of states determining electron injection to be the magnitude of $g(E)$ at the dye excited state oxidation energy $E_m(\text{S}^+/\text{S}^*)$, at an energy corresponding to $E_m(\text{S}^+/\text{S}^*) - \lambda$ where λ is the reorganisation energy (corresponding according to Marcus - Gerischer to the energy for activationless electron injection), or integration of the density of states up to either of these energies, as in all cases an exponential density of states will give the same relative change in injection dynamics for a given change in $\Delta E_{\text{inj}}^{\text{rel}}$. It is also noted that this analysis only considers the effect of Li^+ and *t*BP concentrations upon the relative energetics of the TiO_2 conduction band versus the dye excited state, and not other effects specific to either Li^+ or *t*BP (for example deriving from surface binding of *t*BP).

Singlet versus triplet injection:



Scheme 5.5: Energetics and kinetics of electron injection in a ‘standard’ DSSC, focusing in particular upon comparison of triplet versus singlet injection. Energies are given as free energies relative to the dye ground state. The energy difference ΔE_{inj}^{rel} referred to in the discussion refers to the energy difference between the dye excited states and the density of acceptor states in the TiO_2 . Given the exponential shape of this density of states, assigned to the TiO_2 conduction band / trap states, and thus the difficulty of defining an absolute conduction band ‘edge’, the effect of variations in the relative value of this energy difference, rather than its absolute value are considered herein.

The analysis reported herein focuses on electron injection on the picosecond timescale, and therefore is assigned to electron injection from the N719 triplet state formed by ultrafast (~ 100 fs) intersystem crossing from the initial generated singlet

excited state, as illustrated in Scheme 5.5. Increases in photocurrent from RuL₃ (L = 4,4' - dicarboxy - 2,2' - bipyridyl) sensitized TiO₂ in an ethanol electrolyte have previously been attributed to the band edge being shifted down by the addition of acid to the electrolyte, thereby causing a shift from the singlet to the triplet injection pathway.⁴³ The dependence of injection kinetics upon the relative energetics of the dye excited state versus the TiO₂ conduction band, ΔE_{inj}^{rel} , found herein enable further analysis of the relative injection dynamics from the N719 singlet and triplet excited states. The N719 singlet and triplet excited state energies can be estimated from steady state absorption and emission data to be approximately 1.95 and 1.6 eV respectively. Employing the dependence of injection half-time upon ΔE_{inj}^{rel} found herein, the rate constant for electron injection from the singlet excited state should therefore be $\sim$ one order of magnitude faster than from the triplet state. This difference in injection rates is consistent with previous analyses of biphasic injection dynamics for N3 sensitized TiO₂ films^{44 45}, assigned to parallel pathways for electron injection from the N3 singlet and triplet states. However this one order of magnitude difference in injection rate constant is much smaller than the difference in the kinetics of the competing decay pathways from these states, this being $\sim$ 100 fs for the singlet state and $\sim$ 10 ns for the triplet state, resulting in it being much easier to achieve efficient electron injection from the triplet rather than singlet state of the N719 dye.

The analysis detailed above indicates that electron injection from the singlet excited state of ruthenium bipyridyl dyes is only likely to be observed for very favourable interfacial energetics (i.e.: very large ΔE_{inj}^{rel}), such as those present for N3 sensitized TiO₂ films in the absence of other potential determining species (due to the acidic properties of N3). For more modest values of ΔE_{inj}^{rel} , such as those observed in typical devices due to the presence of the potential determining electrolyte, singlet injection does not compete effectively with intersystem crossing to the triplet state. As mentioned in Chapter 3, intersystem crossing to the triplet state results in a loss of ΔE_{inj}^{rel} (due to the $\sim$ 300 meV lower energy of this triplet state), and thus $\sim$ ten fold retardation of the injection kinetics. However this retardation is outweighed by the five orders of magnitude increase in excited state lifetime, enabling electron injection to proceed from this triplet state with a high quantum efficiency. As a consequence, except for very large values of ΔE_{inj}^{rel} , electron injection in N719 sensitized TiO₂ films and devices is likely to be dominated by injection from the N719 triplet state,

consistent with the data reported herein. Furthermore, conditions resulting in a large value of ΔE_{inj}^{rel} , and thus significant injection for the singlet state, would necessarily result in a large free energy loss associated with the electron injection, and are therefore not likely to be compatible with efficient overall device performance.

Other materials factors influencing electron injection kinetics

In addition to the influence of Li^+ and tBP concentration in the electrolyte upon the injection kinetics, the dependence of the injection kinetics upon the TiO_2 preparation methodology, the presence of redox couple in the electrolyte and N719 dye loading were also studied. In all these cases, no significant variation of injection kinetics could be resolved. It can thus be concluded that the primary device composition factor determining the kinetics of electron injection for N719 sensitized TiO_2 solar cells is the concentration of potential determining ions in the solution.

Considering the dependence upon film preparation, the sensitivity of electron injection rates to sample preparation, and particularly to film crystallinity, has been previously highlighted.²⁴ Here two extreme cases of film fabrication have been studied, employing either acid or base peptisation, which might be expected to influence the film surface charge, and therefore ΔE_{inj}^{rel} . However, the absence of any change in injection kinetics strongly indicates that the energetics of electron injection, ΔE_{inj}^{rel} , in the complete devices were independent of the peptisation employed. This can most probably be attributed to the subsequent film treatments (sintering, dye sensitization and electrolyte addition) removing any initial difference in energetics deriving from the peptisation. Previous studies have shown that the kinetics of charge recombination, and indeed overall device performance, are dependent upon the peptisation step employed.²⁵ At present the origin of the different dependence of electron injection and recombination upon film peptisation is unclear, although it is noted that the recombination dynamics have been suggested to be particularly sensitive to intraband recombination sites on the film surface which in turn may be sensitive to the peptisation procedure.

Several reports have reported both reductive quenching of Ru-bipyridyl excited states by iodide^{21,22} and oxidative quenching by iodine²³ and considered the potential impact of these quenching pathways upon device performance. This work showed that

the transient emission dynamics observed for both the N719 / TiO₂ DSSCs and for the N719 / ZrO₂ control films were independent of the presence of the iodide / iodine redox couple in the electrolyte, at least at the concentrations studied (0.7 M iodide, 0.1 M iodine). This observation contrasts with that of a recent study by Smeigh et al.⁴⁰ However, from this study it is concluded that neither oxidative nor reductive quenching of the N719 excited states by the redox couple is a significant decay pathway for the devices studied herein, consistent with the observed efficient device operation.

Previous studies have also discussed the potential importance of dye aggregation upon the observed injection dynamics.¹¹ However, in the studies reported herein the sensitizer solution was sonicated prior to sensitization to break up any such dye aggregates and similar injection data was observed for a broad range of dye loadings, suggesting that any dye aggregation induced by high dye loadings did not significantly impact upon the observed data. This is supported by the high device internal photocurrent quantum efficiencies (~ 86 %) in electrolyte A which also strongly indicate that dye aggregation did not have a significant impact upon the data reported herein.

Injection dynamics under applied bias

Figure 5.5. shows the effect of applying negative bias to the standard N719 / TiO₂ DSSC's. It can be seen that there is a relatively small dependence of $t_{50\%}$ and ϕ_{inj} on applied bias, with the dark application of -1070 mV causing an increase in $t_{50\%}$ from $180 \text{ ps} \pm 45$ to $230 \text{ ps} \pm 60$ and a corresponding 8% decrease in ϕ_{inj} from 0.83 ± 0.04 to 0.76 ± 0.04 . Given this potential range results in a variation of electron density and TiO₂ Fermi level significantly larger than that generated by typical device operation under AM1.5 irradiation, this observation strongly suggests that the electron injection yield for such N719 sensitized DSSCs is relatively insensitive to electron density in the TiO₂ film over the operating range of the device. This is consistent with the relatively low electron densities injected into the TiO₂ film ($\sim 10^{18} \text{ cm}^{-3}$, corresponding to up to ~ 10 electrons per nanoparticle), with the high TiO₂ dielectric constant resulting in negligible electron / electron repulsion. Furthermore, the absence of a strong bias dependence of the emission dynamics indicates that thermal excitation

of injected electrons back to the dye LUMO orbitals, resulting in repopulation of the dye excited state does not appear to be a key limiting factor for device operation. This contrasts, for example, to charge separation in photosynthetic reaction centres, where thermal repopulation of singlet excited states results in the observation of ‘delayed fluorescence’.

The relatively modest bias dependence observed can most probably be assigned to a reduction in the density of unoccupied acceptor states.⁴⁶ The observed modest bias dependence may result in a small decrease in device fill factor and open circuit voltage. However, significant bias dependence was only observed for the highest applied voltages (> 0.8 V), whereas the data only indicates a loss of injection yield due the increase of electron density of ≤ 2 % under the range of typical device operation. This indicates that the bias dependent loss of injection yield does not significantly impact upon the photovoltaic performance of the DSSCs studied herein.

Correlation between injection kinetics and device performance

This study suggests that the primary factor determining the efficiency of electron injection for the N719 sensitized DSSC’s studied herein is the energy of the density of TiO_2 acceptor states relative to the dye excited state, $\Delta E_{\text{inj}}^{\text{rel}}$ and this energy difference is primarily determined by the concentration of additives such as Li^+ and tBP in the electrolyte (or alternatives such as guanadinium thiocyanate)^{31,47} Varying the concentration of these additives produces devices which show good correlation between the efficiency of electron injection, determined by the transient emission studies, and device short circuit current J_{sc} . This observation is aided by employing thin ($4 \mu\text{m}$) TiO_2 films which ensure minimal recombination losses during electron transport to, and collection by, the FTO electrode. A more detailed analysis of this dependence, including consideration of the influence of additive concentration upon the efficiency of electron collection as well as electron injection, is reported elsewhere.³⁹ Notwithstanding this consideration, the data report herein show a variation of injection efficiency between 0.7 and 0.97 for the range of additive concentrations studied, and strongly indicates that variations in electron injection efficiency is a key determinant of the variations in short circuit current density as a function of electrolyte composition.

A particularly striking observation from the results reported herein is that the electrolyte additive concentrations resulting in optimum overall device efficiency do not correspond to those yielding the fastest, and therefore most efficient, electron injection. The fastest electron injection dynamics, observed in the presence of 0.1 M Li^+ and 0 M *t*BP, yielded an injection efficiency of 97 %, and the largest device J_{sc} . However in this case, the device open circuit voltage is only 565 mV, attributed to the relatively low energy of the TiO_2 acceptor states. Under these conditions, electron injection results in a relatively large loss of free energy. Optimum device performance is obtained with the addition of 0.5 M *t*BP, raising the energy of the TiO_2 density of acceptor states by ~ 200 meV. This reduces the injection efficiency by ~ 10 %, correlated with a loss of device photocurrent. However this loss of photocurrent is more than compensated for by an increase in the TiO_2 fermi level at which the interfacial recombination flux matches the photogeneration flux, resulting in a 100 mV increase in V_{OC} and higher overall device efficiency.

This influence of electron injection upon device efficiency can be readily understood in terms of the ‘minimisation of kinetic redundancy’, as has been previously reported.⁸ Efficient device performance requires only that electron injection is fast relative to excited state decay to ground, as discussed in Chapter 3. Optimum device performance is therefore a compromise between achieving a sufficiently large energetic driving force for electron injection (ie. $\Delta E_{\text{inj}}^{\text{rel}}$) to enable electron injection to compete with excited state to ground versus raising the TiO_2 conduction band as high as possible to minimise recombination losses and thus raise cell voltage. It can be viewed as a requirement to minimise the free energy loss associated with electron injection, whilst still maintaining reasonably high quantum efficiency for this process.

5.5 Conclusion.

This work suggests that even for N719 sensitized TiO_2 based DSSC’s, the most widely studied device materials to date, electron injection is a key limitation upon device performance. Efficient electron injection requires that electron injection is fast relative to excited state decay to ground. As such it is dependent upon excited state lifetime - with for example the relatively short singlet excited lifetime of N719 (~ 100

fs) relative to its corresponding triplet state (~ 10 ns) resulting in triplet state injection being the optimum pathway for charge separation in efficient devices. The kinetics of electron injection are strongly dependent upon the relative energetics of the dye excited state relative to unoccupied TiO_2 acceptor states, and therefore to the influence of ‘potential determining’ additives in the electrolyte on the interfacial charge densities / dipoles. Optimum device performance requires optimisation of these additive concentrations such as to allow reasonably efficient electron injection whilst at the same time minimising the recombination flux at a given film Fermi level, and thereby maximising cell voltage. For the device series studied herein, this optimum device performance is found to correspond to additive concentrations yielding an injection half time of ~ 200 ps and an injection quantum yield of ~ 84 %.

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Comparing Photophysical Properties of DSSCs Based on Commonly used Organic Dyes and Benchmark Ru – Based Dye Sensitisers.

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6 Comparing Photophysical Properties of DSSCs Based on Commonly used Organic Dyes and Benchmark Ru – Based Dye Sensitisers.

The purpose of this chapter is to characterize dye sensitised TiO₂ films employing the benchmark Ru – based N719 and the successful organic NKX2677 sensitizer using the transient emission technique outlined in Chapter 3, transient absorption and transient photovoltage techniques. Differences in cell parameters including electron injection rates and yields, recombination rates and regeneration rates are then explained using the fundamental photophysical properties associated with each dye. In particular the study focuses upon the interfacial charge separation and recombination processes central to device function and identifies why NKX2677 based DSSCs show lower voltages and lower efficiencies than the Ru – based N719 analogues.

6.1 Introduction.

Sensitiser dyes commonly employed in DSSCs can be broadly classified into two separate classes – organometallic dyes which include a transition metal in the structure and organic dyes such as indoline – derived dyes^{1,2} porphyrin – based complexes,³ benzothiazole merocyanines based – dyes,⁴ oligo – ene dyes⁵ and coumarin derivatives.^{6,7} Currently the most efficient DSSCs are based on TiO_2 / Ru – bipyridyl dye systems, with efficiencies of $\sim 11\%$ being achieved with the N719 dye,⁸ and new organometallic dyes often build directly upon the N719 structure.⁹ In contrast there are many structurally discrete, successful organic dyes.^{5,6,10}, such dyes typically benefit from lower fabrication costs and higher molar extinction coefficients than Ru-bipyridyl dyes but generally produce less efficient solar cells. Improving efficiencies in DSSCs based on these organic dyes is thus an area of strong current research activity.⁷

This work looks, in part, at the interfacial electron transfer processes at the metal oxide / dye / electrolyte interface, critical to DSSC function. It compares this process in NKX2677 based systems, where NKX2677 is a coumarin based organic dye (structure shown on page 133) which has yielded device efficiencies of $\sim 8\%$, close to the highest reported for organic dye based DSSCs,¹¹ and has large molar extinction co – efficient and good thermal stability under one sun soaking,¹² with N719. The process is illustrated in Figure 6.1.

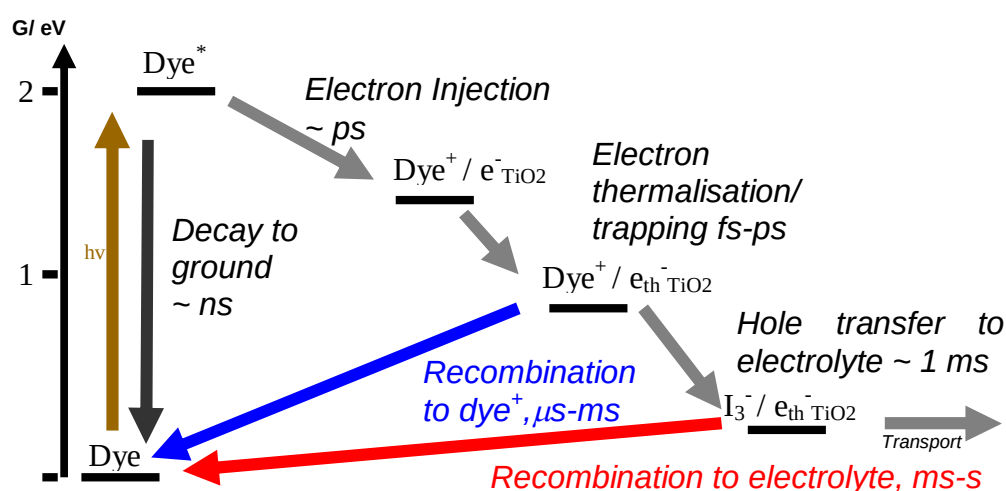


Figure 6.1: Free energy and kinetics of all states in DSSCs. Kinetics of each forward (light grey) and reverse (dark grey, blue, red) processes rely on these energies.¹³

There are several fundamental differences between the photophysics of organic sensitizer dyes such as NKX2677 compared to Ru-bipyridyl dyes such as N719, which are likely to impact upon their function in DSSCs. Visible light absorption in organic dyes is typically based upon $\pi - \pi^*$ transitions to form singlet excited states.¹¹ Intersystem crossing (ISC) to the lower energy triplet state is typically relatively slow (nanoseconds) and thus most such dyes are primarily regarded as singlet sensitizers. In contrast visible light absorption by Ru-bipyridyl dyes is typically dominated by metal – to – ligand charge transfer (MLCT) transitions.⁷ Moreover the presence of the heavy metal centre results in ultrafast intersystem crossing (~ 75 fs) to the triplet excited state, with such dyes thus typically being regarded as triplet sensitizers in solution.¹³ These differences can be expected to have a large impact upon the dye performance in DSSCs. The MLCT transfer character of the N719 dye has been suggested to be critical to the function of this dye in DSSCs. There have been several studies focusing upon achieving analogous vectorial charge transfer in organic dyes, i.e. moving the HOMO away from the TiO_2 surface, including with the NKX2677 studied herein. Similarly there have been extensive studies of singlet versus triplet electron injection from the photoexcited N719 dye into the TiO_2 electrode, with the relative importance of singlet versus triplet injection depending upon the kinetics of ISC and triplet decay to ground, the electronic coupling and relative energetics between the dye excited states and the TiO_2 acceptor states.¹⁴ The relative energetics of these states are furthermore strongly dependent upon the electrostatic charge environment of the interface, and thus the concentrations of additives such as lithium cations and of *tert* – butyl pyridine (TBP) in the electrolyte. It has recently been shown that for electrolyte compositions corresponding to optimized device efficiencies, the dominating electron injection pathway for N719 sensitized DSSC proceeds from the triplet rather than the singlet state.^{14,15} This is similar to alternative ruthenium phthalocyanine sensitized DSSCs.¹⁶ In contrast, the relatively slow ISC dynamics for organic dyes suggests that for these dyes, electron injection from the singlet state is likely to be more dominant, consistent with previous ultrafast transient absorption studies of such dyes,¹¹ although the implications of this difference for dye design and device performance have not received significant attention to date.

In addition to differences in their photophysics, a further difference between typical organic and organometallic dye function in DSSCs is that organic dyes have been

found to be more susceptible to aggregate formation. Such aggregate formation has been suggested to promote unwanted intermolecular energy transfer or non-radiative decay pathways, thus reducing the electron injection efficiency.¹⁷ Commonly both the incident – photon – to – electron conversion efficiency (IPCE) and the DSSC currents in organic based devices are improved by addition of co – adsorbers to break up these aggregates.¹⁷⁻¹⁹ Conversely, Ru – polypyridyl N719 has been shown not to form aggregates^{20,21}, and addition of co – adsorbers to Ru based DSCs only yields modest or no increase in photocurrents;²²⁻²⁵ effects which are not assigned to breaking up aggregates by the co – adsorber.^{20,24,26}

A particular concern for the development of organic dye based DSSCs is that such devices typically yield lower open circuit voltages than Ru-bipyridyl based devices, indicative of faster rate(s) of recombination between injected electrons and dye cations (*RC1*) and (or) electrolyte (*RC2*),²⁷ and / or slower regeneration dynamics (*RG*), as shown in Figure 1.^{4,18,28-31} Possible origins for such differences include:

1. Dye induced acceleration of recombination with the electrolyte (*RC2*). It has recently been shown that the sensitizer dye can strongly influence the rate constant for *RC2*, and such differences were assigned to the influence of the dye on the local concentration of oxidized redox couple (iodine) adjacent to the TiO₂ surface.^{32,33}
2. N719 based DSSCs benefit from good spatial separation between injected electrons and the dye cation, thereby reducing *RC1*.⁷ This is achieved by the electron donating thiocyanato ligands which shift the distribution of the highest occupied molecular orbital (HOMO) on the dye cation away from the reacting TiO₂ surface and reducing the recombination rate accordingly.³⁴ In contrast the residual dye cation HOMO on the NKX2677 organic dye is delocalized along the structural backbone between the binding moiety and the remainder of the dye.¹¹
3. Stabilisation of the intermediate in the dye regeneration process (*RG*). It has recently been proposed that, for Ru – polypyridyl based DSSCs, the regeneration reaction proceeds via formation of the bound dye cation –

iodide intermediate state,³⁵ enabling this regeneration reaction to compete efficiently with the unwanted recombination pathway *RC1*.

As such, organic sensitized DSSCs often employ higher concentrations of TBP to improve device voltage output,¹⁵ although this has been reported to be a concern for the long term stability of the DSSC.¹² Alternative additives and / or co – adsorbents which improve device voltages in organic DSSCs without decreasing stability are desirable.^{18,19,25}

This work uses transient absorption and emission spectroscopies to monitor the dynamics of charge separation, charge recombination and regeneration in liquid-electrolyte DSSCs employing NKX2677 and N719. These processes are compared and the influence on device photovoltaic performance is considered. The limitations of the NKX2677 with reference to the N719 dye are discussed. Furthermore, the mechanisms by which the commonly used co – adsorbent, deoxycholic acid (DCA), can affect maximum voltages and currents in organic DSSCs are investigated. The work concludes by discussing possible ways of optimising efficiencies in devices based on organic dyes.

6.2 *Experimental Methods.*

Sample preparation and experimental procedures are outlined in Chapter 2. Briefly, N719 dye was obtained from Dyesol, NKX2677 from Tokyo University and used as received. Dye was applied to the films from either a 0.3 mM solution of N719 in 1:1 mixture of tert-butyl alcohol (TBA) and acetonitrile (ACN) or from a 0.3 (0.03mM) mM solution of NKX2677 $\pm$ 40mM (4mM) deoxycholic acid co-adsorbent in a 1:1 mixture of TBA:ACN (parenthesis values relate to samples used to measure regeneration dynamics). Films were dyed for ~ 1 day to ensure complete surface coverage; the dyed films were then rinsed in TBA : ACN solution prior to cell construction to help remove aggregated dye molecules from the TiO₂ surface. The sensitizing time was varied to ensure approximately matched dye loadings. All measurements were conducted under aerobic conditions at room temperature.

For complete devices, a sealed, sandwich configuration of $\sim 1 \text{ cm}^2$ area were used. Their photovoltaic performance was characterized, as per Chapter 2. Typical NKX2677 cells produced 2.2% efficient devices ($J_{\text{SC}} = 7.75 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.697 \text{ V}$, $\text{FF} = 0.41$) which improved to 3.1% ($J_{\text{SC}} = 8.96 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.706 \text{ V}$, $\text{FF} = 0.48$) upon addition of the 40mM DCA co – sensitiser. These are similar V_{OC} but lower J_{SC} and FF than those reported previously,⁸ consistent with the non-scattering, thinner TiO_2 films, and non-optimised device configurations used in this work to facilitate the transient optical studies. Control N719 sensitized devices exhibited efficiencies of 3.4% ($J_{\text{SC}} = 10.1 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.716 \text{ V}$, $\text{FF} = 0.47$).

Time correlated single photon counting was then used to measure electron injection dynamics for ZrO_2 and TiO_2 films sensitised with N719 or NKX2677 $\pm$ DCA and coated in either inert solvent or standard redox electrolyte A. Dynamics have been compared with reference to the time it takes for the amplitude of the emission decay to reach half the maximum of the control value, referred to as $t_{50\%}$. Injection quantum yields were determined by integration of the emission decays over time, with the lower integrated areas observed for the TiO_2 films relative to the ZrO_2 control being assigned to electron injection.

Transient absorption experiments were conducted as reported previously by Kroeze et al³⁶ employing low-intensity pulses (550 nm, $\sim 40 \text{ } \mu\text{J/cm}^2/\text{pulse}$) from a nitrogen-laser-pumped dye laser (PTI GL-3300, 0.8 Hz, 600 ps pulse duration) or a Nd:YAG laser (Quantel Big Sky Ultra CFR, 1 Hz, 6 ns pulse duration) and using home-built photodiode-based optical amplification and filtering equipment. Photovoltage transients were taken as per the procedure outlined in Chapter 2.

6.3 Results.

Transient Emission Studies

Transient emission decay dynamics have been measured for N719 and NKX2677 TiO_2 and ZrO_2 films coated in either an inert solvent (3 – methoxypropionitrile) or redox electrolyte B, which has the same composition as standard electrolyte A with an additional 0.5M TBP and has been shown to produce optimum efficiency for

NKX2677 sensitized films.⁶ It is noted; however, that the 1M TBP concentration has previously been shown to result in a modest retardation of injection kinetics, and loss of injection yield for N719 sensitized devices relative to the more typically used 0.5M concentration. NKX2677 sensitized films were fabricated with and without the commonly used deoxycholic acid (DCA) co – adsorbant. Typical transient emission data are shown in Figure 6.2, including control data of N719 and NKX2677 sensitized nanocrystalline ZrO_2 film and dye sensitized TiO_2 film data.

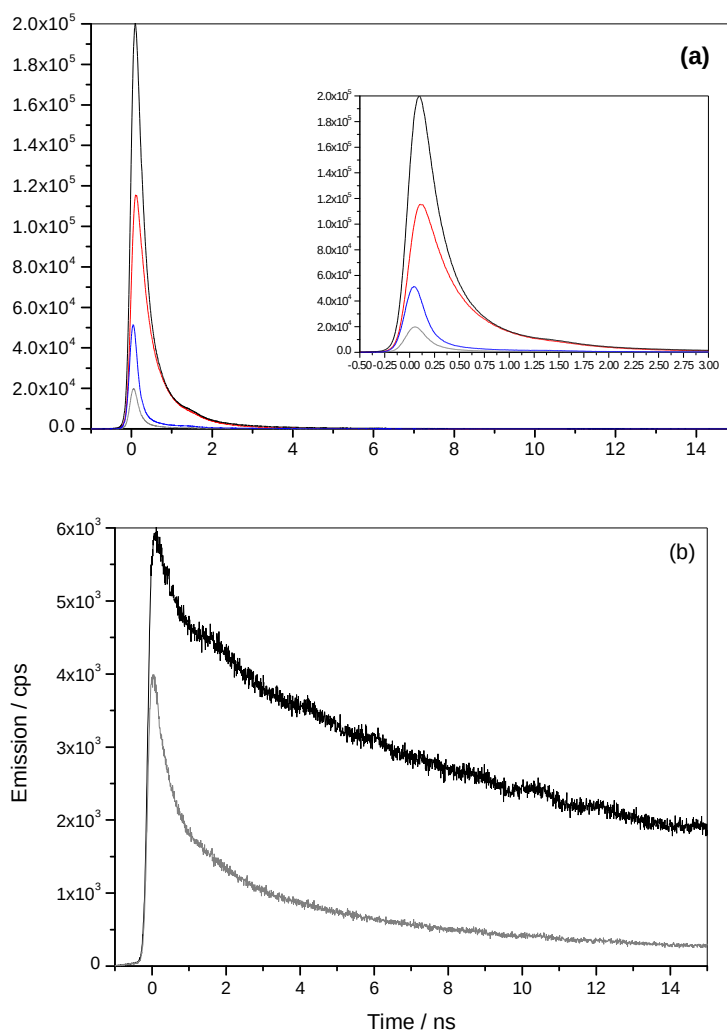


Figure 6.2: (a) Time resolved emission decays for ZrO_2 / NKX2677 films coated in inert solvent and co – sensitised with (black) and without (red) DCA; TiO_2 / NKX2677 coated in redox electrolyte containing 1M TBP and co - sensitised with (blue) and without (dark grey) DCA. (b) Time resolved emission decays for ZrO_2 / N719 coated in inert solvent (black) and TiO_2 / N719 coated in redox electrolyte containing 1M TBP (grey).

ZrO₂ films sensitised with NKX2677 show monoexponential emission decay dynamics, with an emission half time, $t_{50\%}$, of ~ 0.5 ns in good agreement with the ~ 1 ns exponential lifetime reported for the singlet excited state of this dye in solution.¹¹ In comparison, the ZrO₂ / N719 films exhibit a half time of ~ 6 ns, assigned to decay of the N719 triplet state. This ZrO₂ / N719 emission half time is ~ 2 - fold faster than the previous measurements in this thesis and this is attributed to variations in N719 and / or ZrO₂ batches.³⁷ The approximately 10 – fold slower emission decay dynamics for the N719 dye compared to NKX2677 primarily results from ultrafast ISC in N719 due to the presence of the ruthenium atom, with the resultant N719 triplet state being relatively long lived relative to the NKX2677 singlet excited state. The initial emission amplitudes for the ZrO₂/NKX2677 films are much higher than for ZrO₂/N719 films, consistent with the expected much higher radiative transition dipole for the NKX2677 singlet excited state. Omission of the co-adsorbant DCA from the NKX2677 sensitizing solution resulted, for the ZrO₂ control films in a 40% loss of emission intensity (at matched densities of adsorbed photons) but no change in emission lifetime, indicative of the presence of a $\sim 40\%$ sub-population NKX2677 dye aggregates in which the dye excited state lifetime is strongly quenched. The presence of significant dye aggregation in the absence of DCA is consistent with previous observations, this aggregation has been suggested to promote intermolecular interactions which compete with charge separation,²⁸ and / or form a layer of non – injecting dyes.²⁰ For the control ZrO₂ films, replacement of the inert solvent with redox electrolyte did not change either the emission amplitudes or decay dynamics (data not shown), consistent with the previous studies of N719 in this thesis, and indicative that the presence of redox electrolyte does not directly influence the decay dynamics of either dyes excited states.

Strong emission quenching was observed for both dyes adsorbed on TiO₂ films relative to the ZrO₂ controls, consistent with efficient electron injection from the dye excited states.³⁸ TiO₂ / N719 films covered in redox electrolyte exhibited an emission half time of $350\text{ps} \pm 70\text{ ps}$, in good agreement with previous observations at comparably high TBP concentrations.¹⁵ The TiO₂ / NKX2677 showed instrument response limited decays (estimated as $< 60\text{ ps}$ after deconvolution, please refer to Chapter 2 for details) for films prepared both with and without DCA. Such injection

dynamics are consistent with previous reports of electron injection for analogous sensitizer dyes determined by ultrafast transient absorption spectroscopy. Electron injection yields, ϕ , were estimated from analysis of the quenching of the emission areas for TiO₂ films relative to the ZrO₂ controls and are shown in Table 6.1. For the N719 sensitized films, the injection yield is estimated at $\sim 81\%$, consistent with the relatively high TBP concentration. For the TiO₂ / NKX2677 films in the presence of DCA, the injection yield is estimated at $\sim 93\%$, consistent with the high incident photon to current efficiencies ($> 90\%$, at 498nm)¹¹ reported for this dye even in the presence of 1 M TBP. In the absence of DCA, significant quenching of the emission on TiO₂ relative to ZrO₂ is still observed, corresponding to an injection yield of $\sim 74\%$ for those dyes which are not aggregated (and can therefore be monitored in our transient emission studies). Taking account of the estimate from the ZrO₂ control films, there is a $\sim 40\%$ sub-population of aggregated dyes in the absence of DCA, and assuming these dyes do not inject (consistent with their strong emission quenching), the overall estimate of injection efficiency for TiO₂ / NKX2677 films in the absence of DCA is $\sim 44\%$.

Table 6.1: Electron injection yields for typical organometallic dye based DSSC and organic based DSSCs with and without a co – adsorber determined from transient emission data.

Sample	Electron Injection Yield
TiO ₂ / N719	0.81 ± 0.04
TiO ₂ / NKX2677 – DCA	0.74 ± 0.1^a for non aggregated dyes only 0.44 ± 0.1^b of total adsorbed dyes
TiO ₂ / NKX2677 + DCA	0.93 ± 0.1

^a Determined using ZrO₂ / NKX2677 – DCA control. ^b Determined as for (a) but including consideration of 40% dye aggregates determined from comparison of ZrO₂ / NKX2677 $\pm$ DCA. This analysis assumes non-emissive NKX2677 dye aggregates present in the absence of DCA are unable to inject electrons into the TiO₂.

Transient Absorption Data:

Initial transient absorption studies of N719 and NKX2677 $\pm$ DCA sensitised TiO₂ films were completed in the absence of the redox electrolyte, and monitored on the micro- to millisecond timescales. The absorption transients, observed in the near-infrared, are assigned to photoinduced absorption of the N719 and NKX2677 dye cations, and the concomitant absorption of electrons injected into the TiO₂. This data has been previously analysed in detail for N719 sensitized films, please refer to Kroeze et al.³⁷ The transient spectrum observed for an TiO₂ / NKX2677 + DCA exhibited an absorption maxima at 990 nm, assigned to NKK2677 cation absorption. Typical absorption transients data are shown in Figure 6.3, monitored at the maxima of the N719 and NKX2677 cation absorption bands. It is apparent that, in the absence of DCA, the initial amplitude of the NKX2677 absorption transient is only $\sim 40\%$ of that observed in the presence of DCA, indicative of a reduced efficiency of electron injection, and in excellent agreement with the transient emission data reported above. However, it is noted that uncertainties about the relative dye cation extinction coefficients prevent this data being used alone to compare these injection efficiencies with N719.

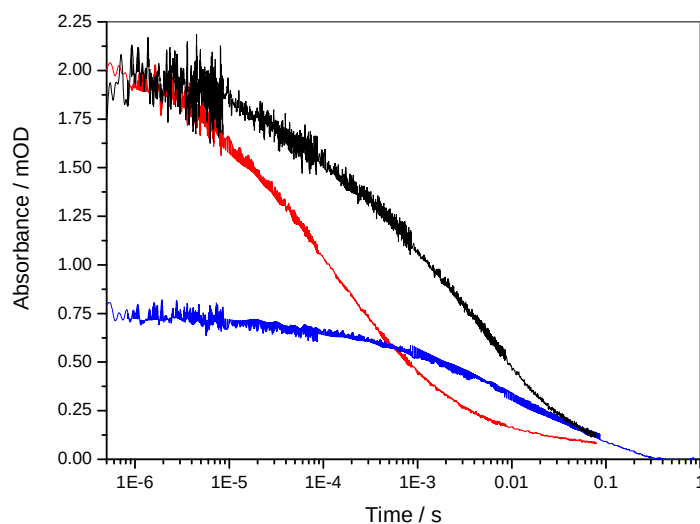


Figure 6.3: Transient absorption data for TiO₂ / N719 (red), and for TiO₂ / NKX2677 films in the presence (black) and absence (blue) of DCA, monitoring electron recombination with dye cations (*RC1*). All data were collected for films covered in inert solvent. Data for N719 films was collected at 800 nm, for NKX2677 films at 990nm for films sensitized; the N719 data is normalized to the NKX2677 data for ease of comparison.

The decay dynamics of these absorption transients is assigned to recombination of injected electrons with the dye cations, *RC1* in Figure 6.3. All the transients exhibited stretched-exponential behavior ($OD \propto \exp[-(t/\tau)^\beta]$), consistent with the recombination dynamics being primarily controlled by electron trapping / detrapping dynamics in the TiO_2 particles.³⁹ NKX2677 samples with and without DCA co – adsorbant both show recombination half-times, *tRC1*, slower than the $\sim 150\mu\text{s}$ halftime observed for N719. In the presence of DCA, the decay half-time for the NKX2677 cation was observed to be 1.5 ms, increasing in the absence of DCA to ~ 7.5 ms. These recombination half-times agree well with previous recombination measurements on similar systems.^{17,40,41} The increase in recombination half-time in the absence of DCA is analogous to other work on ruthenium phthalocyanine sensitized films;¹⁶ it could originate either from cation migration to the dye aggregates or for the influence of the DCA upon the dye orientation / energetics relative to the TiO_2 surface. The slower recombination time for NKX2677 sensitized films relative to N719 is more surprising and is discussed further below. In any case, it is apparent that the recombination pathway *RC1* is slower in NKX2677 films relative to N719 sensitized films, and therefore that this pathway is unlikely to be an important loss factor in NKX2677 sensitized devices.

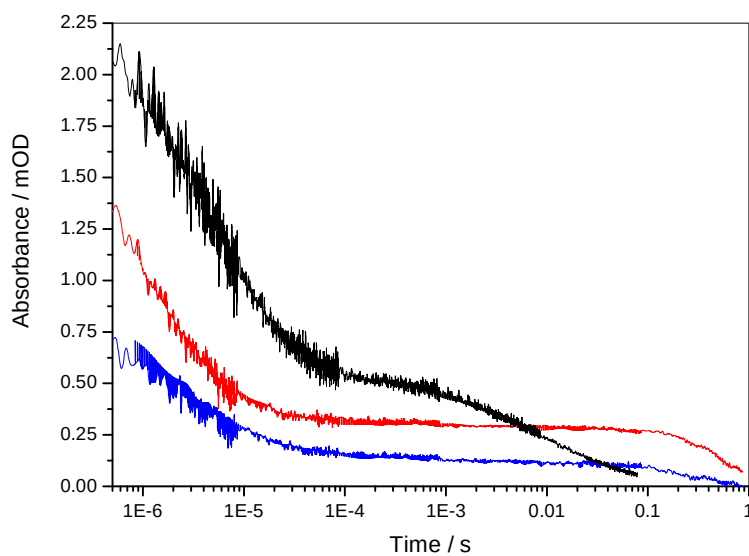


Figure 6.4: Transient absorption data as for Figure 3, but in the presence of redox electrolyte. Data for TiO_2 / N719 (red) and for TiO_2 / NKX2677 films in the presence (black) and absence (blue) of DCA. Data for N719 has not been normalized to NKX2677 data, allowing comparison of the amplitudes of the slow decay phase, assigned primarily to TiO_2 electron absorption.

Further transient absorption data were collected in the presence of redox electrolyte, as shown in Figure 6.4. These transients show two distinct decay phases. As previously,⁴² the fast phase ($\sim$ microseconds) is assigned to regeneration of the dye ground state from the dye cation by reduction by I^- , whereas the residual long-lived (millisecond lifetime) signal results primarily from the absorption of long-lived electrons in the TiO_2 .⁴³ Decay of this long-lived signal is assigned to electron recombination with the redox couple, *RC2*. Kinetic analysis of fast phase is complicated by it being on a similar timescale to the instrument response. Employing data collected in the presence of inert solvent to provide an estimate of the initial dye cation absorption amplitude, regeneration half times can be estimated at $\sim 0.5 \mu s$ for the N719 sensitized films (in good agreement with previous studies on this system) and $\sim 5 \mu s$ for NKX2677 sensitized films both $\pm$ DCA. However, this slower regeneration time for NKX2677 is matched by a comparably slower half time for the competing *RC1* recombination pathway. It thus appears likely that, as for typical N719 sensitized solar cells, kinetic competition between dye regeneration, *RG*, and dye cation / electron recombination, *RC1*, is unlikely to be a significant loss pathway in NKX2677 sensitized solar cells.

It can be seen in Figure 6.4 that the samples also exhibit a slow decay phase in the absorption dynamics, assigned to the long – lived transient species assigned to photoinduced absorption of injected electrons. Again it is apparent that the absence of DCA results in a $\sim 60\%$ reduction in the amplitude of this transient for NKX2677 sensitized films. As discussed above, this does not appear to be associated with a loss of regeneration efficiency. Rather this is assigned to a loss of electron injection. This loss of electron yield due to inefficient electron injection is in excellent quantitative agreement with the transient emission data, and the dye cation absorption data observed in the absence of redox electrolyte. Furthermore, comparison of the NKX2677 + DCA data compared to N719 also indicates higher injection yield for the NKX2677 samples compared to N719, consistent with the transient emission data presented herein.

Transient Photovoltage Analysis

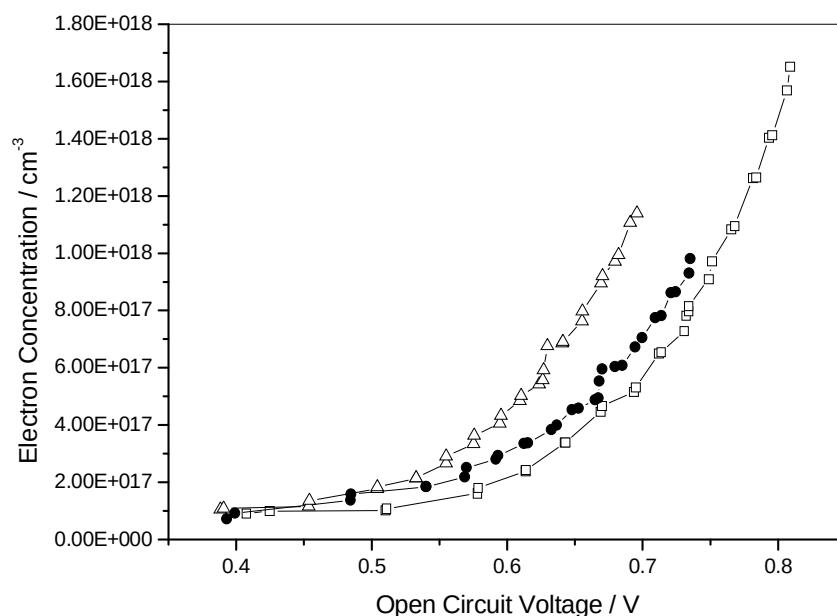


Figure 6.5: Comparison of solar cell electron concentration / cm^{-3} as a function of V_{OC} for DSSCs with NKX2677 + DCA (black spots), NKX2677 – DCA (open triangles) and N719 (open squares) determined from photovoltage and photocurrent transients.⁴⁴ For the N719 data, the TBP concentration was 0.5 M rather than 1 M.

The remaining interfacial electron transfer pathway illustrated in Figure 6.1 that is addressed herein is recombination of injected electrons with the redox couple, *RC2*. Photovoltage transients have previously been employed to analyse this reaction and have been employed here.⁴⁴ These analyses were undertaken on complete solar cells held at open circuit as a function of bias light intensity, for a more detailed experimental procedure refer to page 38. These analyses enable both the charge density present in the film as a function of open circuit voltage, and thus the recombination lifetime as a function of charge density, to be determined. Typical data from these analyses are shown in Figures 6.5 and 6.6 accordingly.

The electron concentration / cm^{-3} versus open circuit voltage data shown in Figure 6.5 is indicative of any shifts in the TiO_2 conduction band density of states between the three devices studied. It is apparent from these data that the NKX2677 sensitized DSSCs showed a lower energy TiO_2 conduction band density of states relative to the N719 – shifted by 75 mV in the absence of DCA and ~ 20 mV in the presence of DCA. However, due to the 0.5M lower TBP concentration used for the N719

sensitized DSSC the magnitude of these shifts is reduced and it is expected that for matched TBP concentrations these shifts should be increased by ~ 30 mV. The shifts in TiO_2 conduction band as a function of dye / DCA are assigned to differences in the dye dipoles and film surface hydration. These shifts result in an increased electron density in NKX2677 DSSC relative to N719 at matched open circuit voltages, and can be expected to result in a corresponding increase in recombination losses RC_2 , as discussed below.

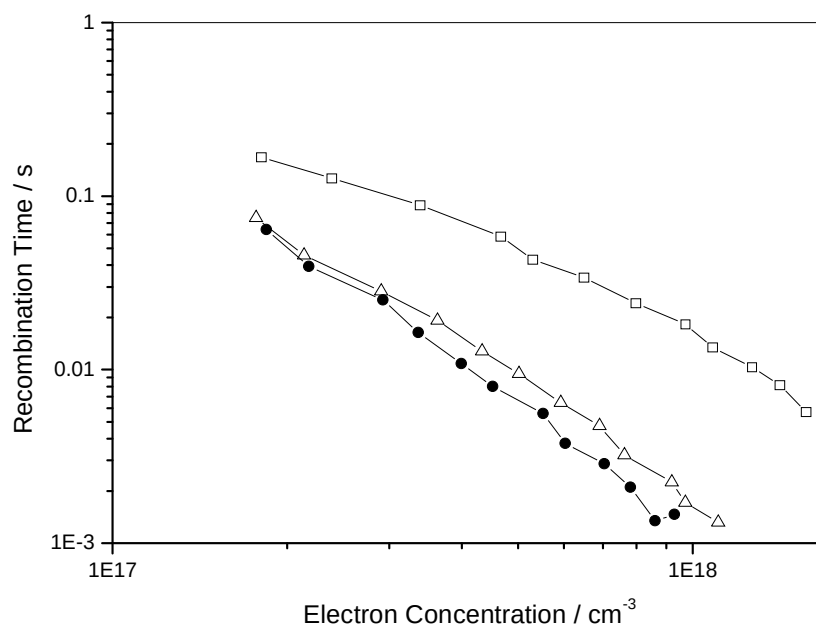


Figure 6.6: Recombination time constants as a function of electron density for DSSCs sensitized with NKX2677 + DCA (black spots), NKX2677 – DCA (open triangles) and N719 (open squares). Electron densities controlled by varying bias light intensity under open circuit conditions.⁴⁴

Figure 6.6 shows recombination time constants for RC_2 measured as a function of electron density. It is apparent that N719 sensitized devices show ~ 10 - fold slower RC_2 time constant relative to NKX2677 sensitized devices, with or without DCA co-sensitiser. An analogous acceleration of this recombination pathway has been observed in Ru – based phthalocyanines.³² The acceleration is assigned to the NKX2677 increasing the local concentration of oxidized redox couple (iodine) adjacent to the electrode surface and / or to dye specific catalysis of this two electron redox reaction. This acceleration can be expected to result in a further increase in recombination losses for NKX2677 devices relative to N719, as is discussed more quantitatively below.

6.4 Discussion.

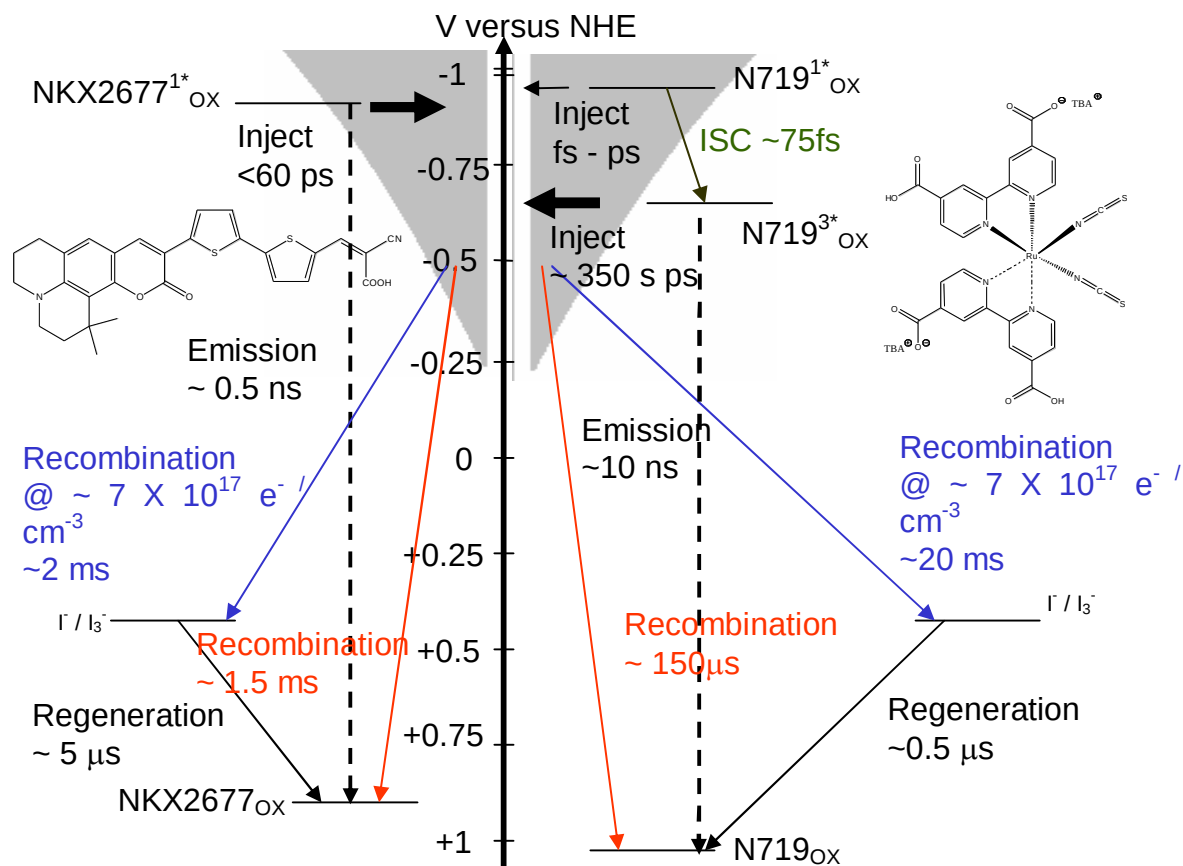


Figure 6.8: Energetics and interfacial processes occurring within DSSCs based on the typical organic dye, NKX2677 + DCA co - adsorber and the typical Ru – bipyridyl dye, N719. The TiO₂ acceptor states are shown as an exponential distribution in light grey.⁴⁵

In this study the interfacial electron transfer dynamics present in dye sensitized solar cells employing occurring two typical sensitizers: the organometallic dye N719 and the coumarin based organic dye NKX2677 have been compared. The discussion begins by considering the physical origins of the different dynamics observed for these two sensitizer dyes. It then goes on to discuss the correlation between these dynamics and device photovoltaic performance, the role of the co-adsorbant deoxycholic acid (DCA), and the implications for future device optimization.

Comparison of interfacial electron transfer dynamics.

Figure 6.8 summarizes the kinetic data reported herein for the two different sensitizer dyes, plotted as a function of redox energy. For the NKX2677 dye, only the data collected in the presence of DCA is considered. The energetics of N719 states have been reported previously.¹⁴ The ground state oxidation potential of NKX2677 has been determined previously.¹¹ From this value, the singlet excited state oxidation potential was estimated from consideration of the E_{0-0} energy determined from optical absorption and emission spectra.

In terms of electron injection, in matched redox electrolytes, it has been observed that electron injection from the NKX2677 excited singlet state exhibits a half time of < 60 ps, at least 6 fold faster than the 350 ps half-time observed for injection from the N719 triplet state. It is noted that under high TBP conditions employed herein, electron injection from the N719 singlet state is unable to compete effectively with intersystem crossing to the N719 triplet state (75 fs). Similarly, it is noted that the relatively slow timescale of intersystem crossing for NKX2677 results enables the NKX2677 triplet state to be neglected from the analyses. The observed difference in injection dynamics appears to be unlikely to be due to differences in spatial separation (and therefore) electronic coupling between the dye LUMO orbitals and the TiO_2 acceptor states. For N719, the LUMO orbitals are localised upon the dicarboxybipyridyl groups which bind the dye to the TiO_2 surface,⁴⁶ ensuring good overlap between the dye electron donor state and the TiO_2 acceptor states. In NKX2677, the LUMO orbital is preferentially localized upon the cyanoacetic acid binding moiety¹⁷ ensuring similarly strong overlap. The difference in observed injection rates is rather assigned to difference in the energetics of the states involved. As illustrated in Figure 6.8, the N719 triplet state is estimated to be 300 meV lower in energy than the NKX2677 singlet excited state. Such a 300 meV shift in relative energetics between the dye injecting state and TiO_2 conduction band has been shown in Chapter 5 to cause a 10 fold change of injection rate – with this change in rate resulting primarily from the density of TiO_2 acceptor states increasing exponentially with energy.¹⁴ On the basis of this it is therefore predicted that the higher energy of the NKX2677 singlet state will result in a ~ 10 fold increase in injection rate relative to the N719 triplet state, in excellent agreement with our experimental observations. It can thus be concluded that the faster injection rate observed for NKX2677 versus

N719, under matched electrolyte conditions, can be assigned to the higher energy of the NKX2677 singlet state compared to the N719 triplet state.

Turning to comparison of the other electron transfer processes illustrated in Figure 6.8, it can be seen that NKX2677 exhibits ~ 5 fold slower regeneration dynamics, *RG*, compared to N719 – this can most probably be assigned to the 110 meV smaller free energy driving this reaction, although uncertainty over the detailed mechanism of this reaction prevents a quantitative analysis of this dependence. NKX2677 also shows slower recombination dynamics with TiO₂ electrons, *RC1*, than N719. The origin of this beneficial effect is unknown. It appears to be unlikely to be due to an increase in the spatial separation of the dye cation HOMO from the TiO₂ surface – HOMO orbital calculations would suggest that the N719 dye cation is localized further from the surface than that of NKX2677.¹¹ Finally we find that the recombination dynamics between TiO₂ electrons and oxidized redox couple, *RC2*, is an order of magnitude faster for NKX2677 than N719. This acceleration is assigned to the NKX2677 increasing the local concentration of oxidized redox couple (iodine) adjacent to the electrode surface and / or to dye specific catalysis of this two electron redox reaction.

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Next the influence of these differences in electron transfer dynamics upon device photovoltaic performance is considered. Our observation that both regeneration (*RG*) and recombination to dye cations (*RC1*) show similar retardations for NKX2677 relative to N719 suggests that, as for N719 sensitized DSSCs, kinetic competition between *RG* and *RC1* is unlikely to be a significant loss mechanism for NKX2677 sensitised devices. Of more significance is the difference in the recombination rate constant for *RC2*. This recombination pathway limits the electron density which can be supported by the TiO₂ film before the recombination flux to the electrolyte starts to limit the efficiency of electron collection by the FTO electrode, and ultimately limits the open circuit voltage achieved by the cell. This issue is further exacerbated by the lower conduction band energy observed for NKX2677 sensitized films relative to N719, assigned to differences in interfacial surface dipoles. These two effects account for the ≥ 54mV lower open circuit voltages achieved with NKX2677 sensitized DSSC compared to N719 sensitized devices with matched electrolyte compositions.

The primary strategy employed to counter the influence of faster $RC2$ upon device open circuit voltage for NKX2677 is to modulate the electrolyte composition to raise the TiO_2 conduction band, primarily by increasing the TBP concentration. However, this strategy is limited by electron injection considerations. As is shown in Chapter 5 for N719 sensitized devices, increasing the TBP concentration reduces the rate constant for electron injection (due to a reduction in the density of energetically accessible acceptor states), and thus reduces the injection yield. For the NKX2677 dye, electron injection is favoured by the ~ 300 meV higher singlet excited state oxidation potential, as illustrated in Figure 6.8, resulting in a 10-20 fold increase in the injection rate. However this increase in injection rate is offset by a reduction in the lifetime of the injecting state – 0.5 ns for the NKX2677 singlet excited state versus ~ 6 -10 ns for N719 triplet state. As such, a faster injection rate for NKX2677 is essential for it to achieve comparable injection efficiencies compared to N719. As a consequence, the TiO_2 conduction band energetics cannot be raised substantially for NKX2677 sensitized devices without resulting in a large loss of injection efficiency and thus photocurrent. The net consequence of this is that the maximal open circuit voltages achievable with NKX2677 sensitized DSSC remain significantly below those achievable with N719 devices.

Furthermore, these injection considerations may explain the difficulties in achieving efficient DSSCs with lower optical bandgap organic sensitizer dyes. The NKX2677 sensitizer exhibits an effective optical bandgap for photocurrent generation of ~ 1.65 eV (750 nm) (one of the smallest reported for efficient organic sensitizers), but still greater than that of N719 ~ 1.55 eV (800 nm). This results in a significant loss of photocurrent generation from red / near infrared photons, limiting device J_{SC} . Reducing this bandgap requires either raising the dye ground state oxidation potential or lower the excited state potential. Raising the ground state potential will further reduce the free energy driving regeneration, and is likely to cause $RC1$, recombination to the dye cation, to become a significant loss pathway. Lowering the excited state oxidation potential reduces the free energy driving electron injection, and is therefore likely to reduce the efficiency of injection losses. In this context, the high spin orbit coupling present in N719 may be regarded as beneficial. The N719 triplet state exhibits a relatively long excited state lifetime (albeit not as long as other

organometallic dyes) combined with a sufficiently large transition dipole to allow significant light harvesting out to 800 nm.

This chapter concludes by considering the influence of the co-adsorbant DCA in enhancing the performance of NKX2677 sensitized films. The primary effect of the co-adsorbant appears to be to improve the efficiency of electron injection. This effect was observed both in transient emission studies of the quenching of the NKX2677 singlet state, and in transient absorption studies of the dye cation and injected electron yields. All three studies indicated that DCA injection yield could approximately double the injection efficiency and this increase was strongly dependent upon the sensitizing conditions employed – varying with DCA and dye concentrations and sensitizing times. This increase in injection efficiency is likely to be the primary origin of the observed increase in device photocurrent with DCA, as has been reported previously for several other organic sensitizer dyes. Consideration of our control emission data collected on ZrO_2 films $\pm$ DCA indicate the lower injection efficiency in the absence of DCA primarily results from the presence of a significant sub-population of non-emissive dyes, attributed to dye aggregates where the intermolecular interactions result in rapid quenching of photogenerated excited states.

The presence of DCA also results in a modest increase in device V_{OC} , as is also observed for other organic dye sensitized DSSCs.^{13, 35, 43, 44, 45} This increase is often attributed to increased recombination between injected electrons and either the dye cation, *RC1*, or the oxidized electrolyte species, *RC2*. The addition of DCA to organic based systems has been shown to improve the voltages¹⁹, an effect often attributed to DCA retarding recombination between injected electrons and electrolyte, *RC2*, through shielding effects.^{18,19,28} This work has shown that, at least for the NKX2677 dye studied, the presence of DCA does not retard the time constant for *RC2*. Furthermore, whilst the presence of DCA does retard *RC1*, even in the presence of DCA, the half time for this reaction is probably sufficiently slow relative to dye regeneration by the electrolyte that it does not significantly impact upon device performance. Rather the increase in cell open circuit voltage with DCA is assigned to a shift of the TiO_2 conduction band to high energies (more negative potentials). This shift is in good agreement with previous studies²⁶ – and may be attributed to the

bulkier DCA adsorbing preferentially to the TiO_2 surface via its carboxylic acid group¹⁹ thus reducing the density of protons released per unit surface area. This is similar to other work in which a coumarin based organic dye was moderated by inclusion of a side ring which increased the size of the dye and reduced the dye surface concentration / protons per surface unit area by $\sim 20\%$.⁴⁷ In both cases the proton reduction modulates the energy of the TiO_2 acceptor states upwards in a manner similar to that observed by replacing N3 with N719.⁴⁸

6.5 Conclusion.

This work has highlighted the differences in electron injection rates and yields, recombination rates and regeneration rates occurring in dye sensitised TiO_2 films employing the benchmark Ru – based N719 and the successful organic NKX2677 sensitiser. The work has shown that the lower efficiencies associated with DSSCs based on NKX2677 arise, in part, from inherently faster recombination between organic dye and oxidised electrolyte species, RC2 , and this is compounded by a reduction in the energy of the TiO_2 acceptor states. This leads to lower photovoltages in the organic based device and, whilst addition of the DCA co-sensitiser raises the energy of the TiO_2 acceptor states, it does not modulate this recombination rate and device voltages remain lower. The work emphasises the need to pay strict attention to the effect of novel organic dyes on the rate of recombination between injected electrons and the oxidised redox electrolyte species.

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Future Studies.

7 Future Studies

The work presented herein has introduced a time correlated single photon counting (TCSPC) based emission technique which can be used as a cost effective, quick alternative to TAS for successfully measuring electron injection dynamics and yields in both model film systems and complete dye sensitised solar cells.

Further studies should now be undertaken using this TCSPC technique to measure electron injection dynamics and yields in systems as a function of different fabrication parameters. These include studies on different dye / metal oxide combinations, different film thicknesses and different electrolyte systems. Furthermore, the technique should be modified to probe the photophysics associated with the injection process in these systems; potential studies include looking at the effect of varying excitation wavelength or excitation power. These applications highlight the potentially diverse application of this simple method for measuring the dynamics and / or yields of electron injection in dye sensitised systems.