

Intermolecular charge transport in dye monolayers

by Davide Moia

Thesis submitted
for the degree of Doctor of Philosophy

Department of Physics, Imperial College London
United Kingdom, May 2015

This thesis reports the work that I carried out during the period between November 2011 and May 2015 under the supervision of Dr. Piers R. F. Barnes and Prof. Jenny Nelson in the departments of Physics at Imperial College London. I declare that, except where specific reference is made in the text to the work of others, this thesis is the result of my own work. In particular, calculations of reorganization energy values presented in Chapter 4 were performed by Dr. Valérie Vaissier at Imperial College London; simulations reported in Chapter 5 were performed using codes developed by Dr. Valérie Vaissier and Anna Szumska; solar cell devices fabrication and characterization presented in Chapter 6 and Chapter 7 was done in collaboration with Dr. Tomas Leijtens and Prof. Henry Snaith at Oxford University. Some of the materials investigated were provided by external collaborators: the dyes A2, A5, TT-1, TT-35 were synthesized by Dr. Ismael López-Duarte in Prof. Tomás Torres' group from Universidad Autónoma de Madrid; the dye N820 was provided by Prof. Mohammad K. Nazeeruddin from EPFL; the dye MP-13 was synthesized by Dr. Miquel Planells in Prof. Neil Robertson's group in University of Edinburgh.

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Davide Moia

*“... ma certe cose in fondo restano dentro
ed anche se la mia testa è presa dal mondo,
non può sparire il movimento che dentro me
ogni giorno ricorda che: sei stato con me.”*

Piano b

Abstract

This thesis reports the experimental investigation of intermolecular charge transport in dye monolayers anchored to the surface of nanocrystalline oxides. I use electrochemistry and transient spectroscopy to measure diffusion of holes within dye monolayers and interpret my observations on the basis of the non-adiabatic Marcus theory of charge transfer.

I observe thermally activated hole diffusion for dyes used in dye sensitized solar cells (DSSCs) anchored to TiO_2 and immersed in an inert acetonitrile based electrolyte. The corresponding values of reorganization energy of charge transfer between the dyes range between 700 and 1500 meV. Assuming negligible contribution from energetic disorder, this shows agreement with previously reported calculations of reorganization energy. Low outer sphere and low inner sphere reorganization energies correlate with delocalization of the HOMO and with rigid molecular structures showing extended conjugation.

I show that hole diffusion in the monolayer can be controlled both at the μm and at the nm scale by varying the fraction of TiO_2 surface covered with dyes. I present the effect of decreasing the dye surface coverage and consequently stopping hole diffusion on photo-electrochemical device structures. First, I observe a slowdown of the photo-induced recombination reaction of holes in the dye monolayer to electrons in the TiO_2 when decreasing the dye loading. This result is consistent with the hypothesis that hole diffusion in the dye monolayer contributes to faster recombination. Second, I show that hole transport in the dye monolayer is responsible for increased dye regeneration efficiency in solid state DSSCs. I quantify improved regeneration yield by between 50% and 5% depending on the degree of the pore filling by the hole transporting material spiro OMeTAD. Finally I demonstrate that effective photo-conversion can occur in solar cell structures where dye monolayers function as the only hole transport phase.

Acknowledgements

A thought to those people that have accompanied me through the years of my PhD. Each of you has shown me unique talents that inspired me and fed my enthusiasm. I would like to thank you all for this.

To Piers Barnes and Jenny Nelson. For giving me the opportunity to do this PhD. For the recipe you used to supervise me based on listening and trust. Working with you has made my PhD the exciting experience I was hoping for. And also:

To Piers. For finding interesting questions and observations about any situation and for being one of the two people in the world willing to pay for Snap Out's album.

To Jenny. For your endless will to help and the way you value the human side of being a scientist. Thank you for replying to my first email back in 2011.

To Valérie Vaissier. It has been a pleasure to be in the 'hole hopping team' with you. You have given me a great example of dedication and orderliness, along with data and extremely useful comments on my work, including this thesis.

To Brian O'Regan. For your invaluable inputs and your help on the TAS rig.

To Alex Perevedentsev. Ever since the trip to Bergün I knew it would be great. I was right. Going through the PhD with you made the difference.

To Chris Emmott. You have been a constant source of inspiration throughout these years. The Rwanda project is an experience I will never forget.

To Michelle Vezie. For all the smiles and enthusiasm you have been bringing to the office on every morning, even when you wake up 4 hours earlier than I do.

To Jason Röhr. For the contagious passion you put in everything you do.

To Xingyuan Shi. For our interesting discussions but also for inviting me to have a break when you felt I needed one.

Thanks to Aurélien Leguy, for organizing an incredible ski trip. To Florian Steiner, for your positive attitude and for changing our lives by teaching us commando bimbola. To Sheridan Few, for the jamming. To Jizhong Yao, for teaching me the most useful words in chinese. To Sachetan Tuladhar, Thomas Kirchartz, Andrew Telford, Anne Guilbert, Dorota Niedzialek, Sam Foster, George Dibb and all the other present and past members of Jenny Nelson's group.

To Themis, Michael, Katharina, Milan, Phil, Viktoryia, Nicola, Giuliana and everyone else whom I shared office H1101 with during these years. For the lunch breaks and for not chopping off my fingers when I played drums on my desk.

To the students I had the chance to supervise:

To Anna Szumska. For your outstanding work and the passion you have put in the project. Supervising you has been one of the most enjoyable things I have done in my PhD. To Andrew Wadsworth. For your valuable contribution to my experimental work.

To the colleagues from the Department of Chemistry. In particular to Xiaoe Li and Chunhung Jasper Law, for your constant assistance in the lab and for your patience showing me the world of chemistry. To the other members of the NMD group: Stoichko, Ute, Ernest, Florent, Florian, Yimeng, Scot, Andy, Luke, Maddy, Dan, Ching Hong, Cameron, Joe, Anna, Steph, Miquel, Michael, Elisa, Hendrik. For your help in the lab and the good time during breaks, at conferences, in Snowdonia, playing basketball, or just having a beer in h bar.

A special thought to Stuart Irving. Thanks for your smiles and for making many of my days in the lab so enjoyable. I wish there had been more of those.

To Carolyn, Bhavna, Juraci, Anna and Loli for taking care of all kind of beaurocratic matters for me.

To Tomas Leijtens, Nakita Noel, Henry Snaith, Alasdair Campbell, Neil Robertson, Shogo Mori, Marco Sampietro and all the collaborators who gave me access to their facilities, provided me with materials or shared their points of view on my work.

To Prof. Anders Hagfeldt and Prof. James Durrant for committing to read this thesis.

To EPSRC for funding my PhD.

To the RSD group, in particular: to Ben, for your good taste about movies and cordon bleu. To Marketa, for the artistic pancakes. To Marie, for organizing the best parties where, apparently, I met half of the people I know. To Ilan, for not shooting a missile to my office... yet.

To those who helped me clearing my mind after long hours of work. To Julian Grimm and Chris Newman, members of Snap Out. To Baris, Mestre Poncianinho and Professor Polvo for the capoeira lessons.

To the many people I shared a flat with during these years. In particular to Lewis, Vina, Tommy, Tom and Steph.

Un grazie di cuore ai miei amici. In particolare ad Oggi, Marco ed Aurora. Per il sostegno, anche se a distanza, ed il grande affetto e stima che mi trasmettete. A Paula. Per il tuo sostegno nei primi anni di questo dottorato. A Richard e Serenella. Per i momenti passati insieme durante questi anni a Londra. Siete stati la mia little Italy con cui ho potuto sentirmi a casa nei giorni difficili ed in quelli di gioia.

Alla mia famiglia:

A mio fratello Ale, per riempire ogni giorno della mia vita con qualcosa che mi stupisce. A Mieke, per la tua ospitalità. Ai miei cugini/e e zii/e, in particolare a Marco, Alessandra e zio Piero. Ai miei genitori, per tutto il vostro affetto e i vostri consigli. Se mi convinco di avere anche solo una briciola della vostra tenacia e forza di volontà allora mi sento di poter puntare in alto. Grazie.

Contents

Acknowledgements	5
List of Figures.....	13
List of Tables	15
List of Symbols and Acronyms	16
Chapter 1 Introduction.....	18
1.1 Charge transport as key towards efficient solar energy conversion ..	18
1.1.1 Solar cells: basic principles	19
1.1.2 Using dye molecules in solar cells	21
1.1.3 Liquid junction and solid state dye sensitized solar cells.....	22
1.2 Conduction in dye monolayers: motivation.....	25
1.2.1 Charge transfer phenomena in dye sensitized solar cells	25
1.2.2 Relevance to the study of molecular electronics	26
1.2.3 Other applications	26
1.3 Scope and outline of the thesis	27
Chapter 2 Hole transport between dyes: background.....	30
2.1 Charge transport in molecular semiconductors	30
2.1.1 Electronic states in organic and inorganic semiconductors.....	30
2.1.2 Free charges in a solid: from nearly-free electrons to polarons...	32
2.1.3 Hopping transport and non adiabatic Marcus theory	34
2.1.4 From electron transfer to electrical conduction.....	40
2.1.5 The effect of disorder on charge transport	41
2.2 Measuring charge transport in dye monolayers	42
2.2.1 Dye monolayers on nanocrystalline oxides	43

2.2.2	Spectro-electrochemical techniques	46
2.2.3	Transient absorption spectroscopy	50
2.2.4	Transient anisotropy spectroscopy.....	52
2.3	Previous studies of charge transport in dye monolayers	55
2.3.1	First demonstrations of hole transport in dye monolayers.....	55
2.3.2	Following electrochemical studies.....	56
2.3.3	Spectroscopic studies on inter-dye hole transport.....	65
2.4	Hole transfer and recombination processes in dye sensitized TiO ₂ based devices.....	66
2.4.1	Charge recombination in dye sensitized nanocrystals	66
2.4.2	Previous evidence of inter-dye hopping in solid state DSSCs.....	71
2.5	Summary and open questions.....	77
Chapter 3	Method	79
3.1	Materials.....	79
3.2	Sample preparation	81
3.2.1	Samples for electrochemical and spectroscopic measurements.	81
3.2.2	Solid state dye sensitized solar cells	82
3.3	Characterization techniques	83
3.3.1	Dye loading measurement	83
3.3.2	Cyclic voltammetry	83
3.3.3	Spectroelectrochemistry.....	84
3.3.4	Transient absorption spectroscopy	84
3.3.5	Transient absorption anisotropy	86
3.3.6	Electrical bias dependent spectroscopy	87
3.3.7	Electrical and photovoltaic characterization of solar cells	88
3.3.8	Other thin film characterization techniques	88
3.4	Calculations.....	89

3.4.1	Random walk	89
3.4.2	Transient absorption anisotropy simulations	90
Chapter 4 The reorganization energy of hole hopping		
	between dyes anchored to surfaces	91
4.1	Introduction	91
4.2	Method	93
4.3	Determining the charge diffusion coefficient with cyclic voltammetry	94
4.3.1	The semi-infinite slab approximation	95
4.3.2	Accounting for series resistance	97
4.3.3	Ambipolar diffusion.....	99
4.3.4	The effect of site blocking on diffusion	101
4.3.5	The relation between D_{app} and the charge transfer rate	103
4.4	Measurement of reorganization energy	104
4.4.1	Results	104
4.4.2	Chemical structure and calculated reorganization energy	108
4.4.3	Comparing measured and calculated reorganization energies .	109
4.4.4	Hole diffusion: effect of chemical structure, monolayer configuration and relevance to organic thin films	110
4.5	Summary	112
Chapter 5 Hole transport in dye sensitized nanocrystals and		
	its role on charge recombination	113
5.1	Introduction	113
5.2	Method	114
5.3	Results and discussion.....	115
5.3.1	Dye loading uniformity.....	115
5.3.2	Study of hole percolation at different scales.....	117
5.3.3	Hole diffusion and electron-hole recombination rate	121

5.3.4	Dynamics of transient absorption anisotropy decay	125
5.4	Summary	128
Chapter 6 Hole transport between dyes in solid state dye sensitized solar cells		130
6.1	Introduction	130
6.2	Method	131
6.3	Results and discussion.....	135
6.3.1	Inter-dye hole transport in ambient conditions.....	135
6.3.2	Dye regeneration dependence on pore filling and dye loading..	136
6.3.3	The role of the additives LiTFSI and tBP on regeneration.....	139
6.3.4	Inter-dye hopping and device performance	143
6.3.5	Hole diffusion as a probe of the surrounding environment: hole transporting material film formation	144
6.4	Summary	150
Chapter 7 Dye monolayers used as hole transport medium in DSSCs: the ‘dry cell’		152
7.1	Introduction	152
7.2	Method	152
7.3	Results and discussion.....	154
7.4	Summary	157
Chapter 8 Future work		159
8.1	Stability.....	159
8.2	Modelling charge transport and electron-hole recombination in dye sensitized nanocrystals.....	159
8.3	Solvent dependence of charge diffusion in dye monolayers	159
8.4	Quasi 2D SAMFETs and electrochemical transistors.....	162

Conclusions.....	164
Bibliography	172
Appendix A.....	181
Appendix B.....	182

List of Figures

Figure 1.1. Energetics o solar cells.	200
Figure 1.2. Structure of liquid junction DSSCs	222
Figure 1.3. Structure of solid state DSSCs.....	233
Figure 1.4. Working principle of a DSSC.....	244
Figure 1.5. Charge transfer processes in DSSCs	255
Figure 2.1. The polaron binding energy.....	32
Figure 2.2. Free energy of weakly coupled molecules	35
Figure 2.3. The relocation energy	36
Figure 2.4. Free energy for self-exchange reactions.....	38
Figure 2.5. Estimate of relocation energy.....	39
Figure 2.6. Weak and strong coupling regimes	40
Figure 2.7. SEM of a nanocrystalline TiO ₂ film.....	45
Figure 2.8. Anchoring groups and TiO ₂ 101 surface.....	465
Figure 2.9. Experimental setup for CV measurement of dyed TiO ₂ nanocrystals ...	46
Figure 2.10. Signals obtained from basic electrochemical measurements.....	48
Figure 2.11. Electrochemical cell for electrochemistry in solution	49
Figure 2.12. Schematics of a (μ s) transient absorption spectroscopy setup.	51
Figure 2.13. Chemical structure of the sensitizers studied in references ^[64] and ^[65] . 55	
Figure 2.14. Chemical structure of the sensitizers reviewed in this section.....	58
Figure 2.15. Charge generation and recombination in a dye sensitized TiO ₂	67
Figure 2.16. Transport-reaction model for electron-hole recombination	69
Figure 2.17. HTMs in solid state DSSCs.	72
Figure 3.1. Structures of dye molecules investigated in Chapter 4	80
Figure 3.2. Baseline correction performed for TAS measurements.....	85
Figure 3.3. Changes in $\Delta OD(t)$ during a TAS experiment due to degradation.....	866
Figure 4.1. CV measurements of hole transport between dyes on TiO ₂	922
Figure 4.2. Example of CV performed on a A2 dye sensitized TiO ₂ film	944
Figure 4.3. Validity of the semi-infinite slab approximation.....	966
Figure 4.4. CV current density peak dependence on scan rate.....	967
Figure 4.5. Series resistance in electrochemical cells	988
Figure 4.6. Compensating for the effect of series resistance.....	99

Figure 4.7. Influence of ambipolar diffusion on the determination of D_{app}	1011
Figure 4.8. Temperature dependent CV profiles	104
Figure 4.9. Temperature dependent values of D_{app}	105
Figure 4.10. Comparing λ_{meas} and λ_{calc}	108
Figure 5.1. Sets of photographs displaying time evolution of dyeing TiO ₂ films	116
Figure 5.2. Absorbance spectra for TiO ₂ films dyed with D131 and D131:DCA	116
Figure 5.3. Evidence for hole percolation threshold in CV experiments	1177
Figure 5.4. Evidence for hole percolation threshold in transient absorption anisotropy experiments.....	119
Figure 5.5. Bias dependent transient absorption measurements	123
Figure 5.6. Hole lifetime as a function of dye loading and electron density	124
Figure 5.7. Particle size dependence of transient anisotropy decay	125
Figure 5.8. Effect of TiCl ₄ treatment on transient anisotropy decay.....	1266
Figure 5.9. Simulation of transient anisotropy decays.....	128
Figure 6.1. Solar cell devices with varying pore filling and dye loading.....	130
Figure 6.2. Transient absorption anisotropy on D131:DCA sensitized TiO ₂ films in ambient condition.	135
Figure 6.3. μ s time scale kinetics of dye regeneration in solid state DSSCs.....	136
Figure 6.4. Regeneration efficiency as a function of pore filling and dye loading ...	139
Figure 6.5. Effect of LiTFSI and tBP on the transient anisotropy decay	140
Figure 6.6. Effect of LiTfI and tBP on regeneration yield.....	141
Figure 6.7. Effect of LiTFSI and tBP on the time dependent regeneration yield.....	142
Figure 6.8. j_{sc} in solid state DSSCs as a function of pore filling and dye loading....	143
Figure 6.9. Regeneration efficiency and HTM film formation.....	146
Figure 6.10. TAS decay on HTM free D131 sensitized TiO ₂ films	150
Figure 7.1. Structure of ‘dry cells’	153
Figure 7.2. j - V and IPCE measurements on ‘dry cells’	155
Figure 7.3. Cyclability of a dry cell and best performing device.....	156
Figure 8.1. The elephant in the laboratory: solvent dependence of hole diffusion..	161
Figure 8.2. Quasi 2D SAMFETs.....	163

List of Tables

Table 2.1. Previously reported values of D_{app} and percolation threshold for hole hopping in dye monolayers	59
Table 4.1. Dyeing conditions used in Chapter 4	93
Table 4.2. Charge transfer parameters determined from temperature dependence cyclic voltammetry	107
Table 5.1. Values of stretched exponential parameters after fitting to photo-induced dye cation decays for different dye loading conditions	121
Table 6.1. Values of the extinction coefficients used in the analysis of transient absorption spectroscopy data	132
Table 6.2. Hole diffusion length in HTM free D131 sensitized TiO_2 films	150
Table 8.1. Values of hole D_{app} from reference ^[64] for different solvents used in the electrolyte solution.....	160
Table 8.2. Charge transfer parameters for Z907 sensitized TiO_2 in different electrolytes	162

List of Symbols and Acronyms

A	Absorbance
a	Intermolecular distance
c_0	Dye concentration on films (cm^{-3})
c_h	Holes concentration (cm^{-3})
D	Diffusion coefficient ($\text{cm}^{-2} \text{s}^{-1}$)
D_{app}	Apparent Diffusion coefficient ($\text{cm}^{-2} \text{s}^{-1}$)
D_{ch}	Chemical Diffusion coefficient ($\text{cm}^{-2} \text{s}^{-1}$)
D_{2D}	2 dimensional Diffusion coefficient ($\text{cm}^{-2} \text{s}^{-1}$)
$DSSC$	Dye sensitized solar cell
d	Film Thickness (cm)
E	Electron energy (eV), electrochemical potential (V)
EQE	External Quantum Efficiency
$\vec{E}$	Electric Field
F	Faraday constant (C mol^{-1})
H	Hamiltonian
HTM	Hole Transporting Material
$\hbar$	Reduced Plank constant (J s)
k	Boltzmann constant (J K^{-1})
$IPCE$	Incident Photon to Converted Electron Efficiency
J	Electronic coupling (eV)
J_{eff}	Effective electronic coupling (eV)
LHE	Light Harvesting Efficiency
L	Hole Diffusion Length (cm)
N	Nucleation centers density (cm^{-2})
OD	Optical Density
P	HTM island perimeter (cm)
P'	HTM island perimeter per unit surface area (cm^{-1})
p	Hole density (cm^{-3})
p_{TiO_2}	Porosity TiO_2 film
Q	Reaction coordinates
Q'	Charge per unit area (C cm^{-2})

q	Elementary charge (C)
R	Ideal gas constant (J mol ⁻¹ K ⁻¹)
r	Anisotropy
T_{opt}	Optical Transmission
T	Temperature (K)
t_d	Diffusion time (s)
$t_{50\%}$	Half lifetime (s)
Γ	Charge transfer rate (s ⁻¹)
ΔG_0	Free Energy difference (eV)
α	Stretching parameter
α_g	Geometric factor for monolayer dimensionality
ε	Extinction coefficient (M ⁻¹ cm ⁻¹)
η_{coll}	Charge Collection Efficiency
η_{inj}	Electron Injection Efficiency
η_{reg}	Dye Regeneration Efficiency
λ	Wavelength (nm)
λ_{calc}	Calculated Reorganization Energy (eV)
λ_i	Inner sphere reorganization energy (eV)
λ_o	Outer sphere reorganization energy (eV)
λ_{meas}	Measured Reorganization Energy (eV)
ψ	Wavefunction (cm ^{-3/2})
ϕ	Electron wavefunction (cm ^{-3/2})
ρ	Density (g cm ⁻³)
θ	Dye surface coverage
$\langle \tau \rangle$	Mean relaxation time (s)
X	Nuclear wavefunction (cm ^{-3/2})

Chapter 1 Introduction

1.1 Charge transport as key towards efficient solar energy conversion

In electronic devices electrons are used to do something which, though they do not realize it, makes a difference in our daily life. Electrons exposed to sunlight, can take the energy of a photon and postpone its conversion in heat by driving a chemical reaction in a battery; they are given energy and injected in an LED where the release of that energy illuminates a room at night or the screen of a mobile phone; they represent bits in computers; they are pushed back and forth within an antenna to let us talk to someone on the other side of the planet.

Today, all of this is possible because the scientific community has learnt about the behavior of electrons in materials in the solid state. One important feature of all of the “electron manipulation” examples listed above is that, in order to complete their “task”, electrons must move. Understanding electron transport in semiconductors has been, and still is, a critical factor to develop numerous electronic and optoelectronic systems. In particular, as I will present in this introductory chapter, the transport of charge carriers (electrons and holes) is an essential step in the process of converting sunlight into chemical and electrochemical energy in solar cells.

Some classes of solar energy conversion devices employ organic semiconductors for light harvesting and electrical conduction. In particular, dye molecules can be used to sensitize and modify the optoelectronic properties of oxide films and nanostructures. This thesis describes the conduction properties of dye monolayers anchored to nanocrystalline oxides. In my research I have developed new experimental methods to characterize the process of charge transfer between dyes on a surface, I have applied this process to new device concepts and I have clarified its role in already existing optoelectronic devices.

The next sections provide an introduction to solar cells and specifically to dye sensitized solar cells. The motivation for my research and its relevance to the field of solar energy conversion, storage and molecular electronics is then outlined.

1.1.1 Solar cells: basic principles

In this section I give a brief overview of the steps involved in the conversion of light into electrochemical energy. Detailed description of the physics of solar cells has been discussed elsewhere.^{[1],[2],[3]}

The presence of an energy bandgap in semiconducting materials is the crucial electronic property that enables the fabrication of solar cells. In these devices, electromagnetic energy is converted into electrochemical energy. The bandgap of a semiconductor “divides” populations of electrons which are more energetic (because for example they absorbed one photon’s energy) and electrons that are less so. Under solar illumination the populations are changed from their equilibrium in the dark to a new quasi equilibrium, because it takes a relatively long time for the electrons to lose the energy from the absorbed photons. This allows some of this energy to be recovered from the material by collecting charges from the excited populations. Extracting charges is therefore a critical factor in the optimization of solar cells efficiency. Consequently the charge transport properties of the semiconductors from which the device is made have great influence in all solar energy conversion systems.

In a solar cell, photo-conversion occurs through a number of steps. These are illustrated in Figure 1.1 and consist of the following:

- a) Photon absorption and hot state relaxation: photons with different energy are absorbed depending on the absorption spectrum of the device. The excited state which is generated in this case relaxes to an energy value which is approximately equivalent to the bandgap of the absorber.
- b) Energy diffusion and charge separation: for the energy of the excited state to be extracted to the external circuit, the exciton needs to be separated into free charges (electron and hole). The separation of the electron hole pair can occur because of the finite temperature in the device, or can be driven by a difference in chemical and/or electrostatic potential in different parts of the device. In some architectures, diffusion of the excited state is needed to reach a charge separating interface.
- c) Charge transport and collection: once separated, charges travel across the device to reach the contacts where they are extracted. A gradient in

work function (chemical potential) within the device is needed in order to drive the transport of electrons and holes to the respective contacts.

The photovoltaic response of the device is described by its photocurrent and photovoltage. In particular, the photocurrent density j is a function of the applied voltage V , i.e. $j = j(V)$. The working condition which maximizes the product $j \times V$ is called maximum power point (MPP), and it is used to calculate the device photoconversion efficiency.

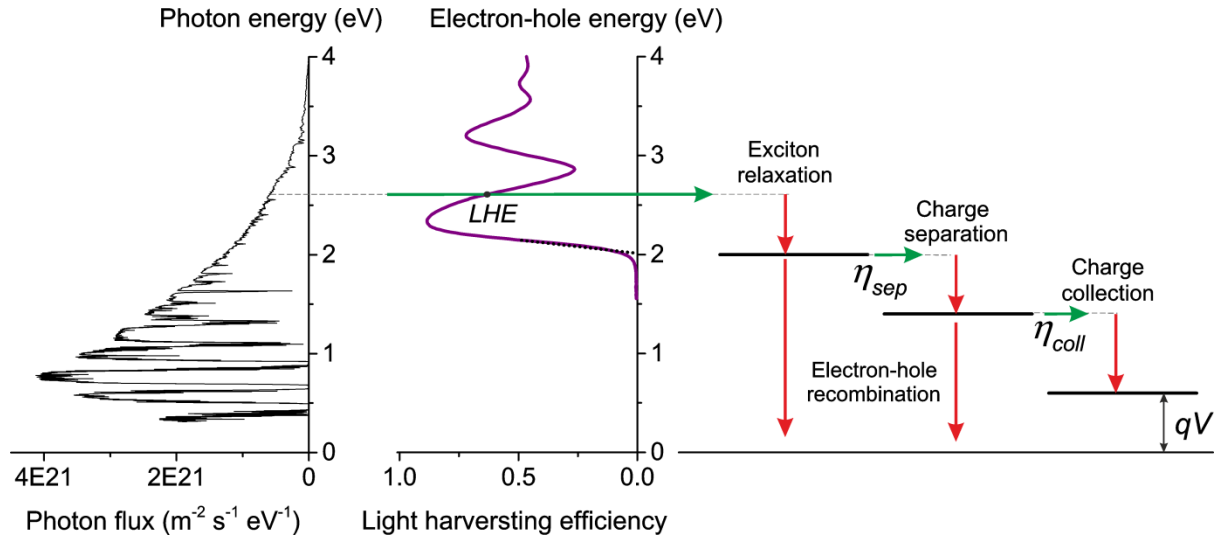


Figure 1.1. Conversion of photons' energy into available electrochemical energy. Inspired by figure 4 in reference ^[4].

As shown in Figure 1.1, each of the processes listed above is associated with losses (red arrows) which compromise the photocurrent and/or the photovoltage of the device. The incomplete light harvesting and the processes indicated by red arrows related to electron hole recombination result in each of these processes having less than unity quantum efficiency (LHE , η_{sep} , η_{coll}). The product of all the quantum efficiencies represents the incident photon to converted electron efficiency (IPCE) or external quantum efficiency (EQE) of the device. The photocurrent extracted from the device can be calculated from integration of the solar cell IPCE multiplied by the incident photon flux over the relevant photon energy range. The photovoltage of the device is limited by the bandgap of the absorber and reduced by the energetic loss occurring during the processes of charge separation and charge collection.

The process of photo-conversion can be implemented using different classes of semiconductors. In the next section I present the specific case of dye molecules and their role in dye sensitized solar cells.

1.1.2 Using dye molecules in solar cells

At a first glance, dyes are compounds used to color a host phase. Their color is related to the parts of the visible light spectrum they absorb and the parts they reflect or transmit.

Some dyes can anchor themselves chemically to surfaces due to the presence of specific chemical groups in their structure, spontaneously forming monolayers. The self-assembly of monolayers enables highly controlled structures to be attained with strikingly low effort in the processing steps.^[5] The first demonstration of dye sensitization of semiconductors as a strategy for photo-conversion was reported 1968 by Gerischer *et al.* In their work, light absorption by the dye molecules was followed by a charge transfer reaction at the dye/semiconductor interface which enabled the separation of the charges. This represented the first step towards the concept of dye sensitized solar cell (DSSC).

In some solar cell architectures interpenetration of electron and hole transport materials can be desired in order to extract energetic charge carriers from the bulk of the device to the external circuit. In the case of DSSCs, a stable interpenetrated heterojunction can be achieved by infiltrating a mesoporous oxide film with a liquid or solid state phase. Sensitization of the oxide with dye molecules radically changes the light absorption properties of the system. As a result, in a DSSC, different materials are used to carry out the different steps occurring during photo-conversion.^[6] Light absorption is implemented by dye molecules, whereas charge transport and collection occur in two different phases for electrons and holes. This 'strategy' implies that design of each material can in principle be optimized for one specific property.

The drawbacks of this approach are however that a larger number of interfaces are involved. For example, this introduces energy losses because non negligible driving forces are needed to transfer charges between phases. It also introduces processing limitations in that the different components must be combined through compatible processes. Despite these limitations, today the DSSC concept represents one of the most promising alternative solar energy conversion

technologies based on low cost, low toxicity materials. In particular, molecular materials have the advantage of offering solution processing routes to the fabrication of electronic devices.^{[7],[8]} DSSCs and other solution processed organic based solar cell technologies^{[9],[10],[11]} have been proposed as renewable energy source to tackle the increasing world energy demand while complying with climate change mitigation.^{[12],[13],[14]} In addition, despite the lower efficiency compared to inorganic PV,^[15] printed solar cells remain a competitive direction for solar energy in terms of energy payback time.^[16]

1.1.3 Liquid junction and solid state dye sensitized solar cells

DSSCs are generally classified as liquid junction or solid state, depending on the physical state of the hole transporting material.

In the liquid junction DSSCs, dye absorbers sensitize a nanoparticulate film of titanium dioxide which is then infiltrated with a liquid solvent containing a redox couple. In Figure 1.2 the architecture of the device is shown (a) as well as the flow of charges under operating conditions (b).

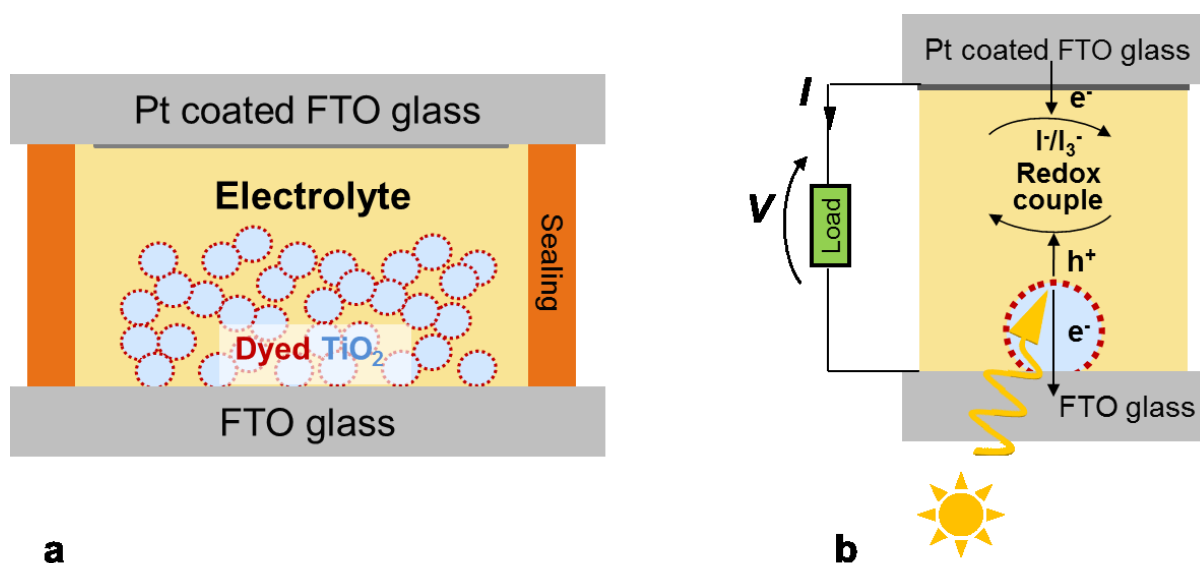


Figure 1.2. (a) Architecture of a liquid junction dye sensitized solar cell (DSSC). (b) Basic principle of solar power conversion in a liquid junction DSSC.

Commercialization of DSSCs has faced some important issues. Above all, the use of a liquid electrolyte raises the problem of good sealing of the cell. This introduces limitations on the upscaling of DSSCs production and can limit the lifetime of the device. To overcome this issue, the solid state DSSC concept has been

presented, where the liquid electrolyte is replaced by a solid state hole transporting material, typically an organic semiconductor deposited from solution on top of the mesostructure.^[17]

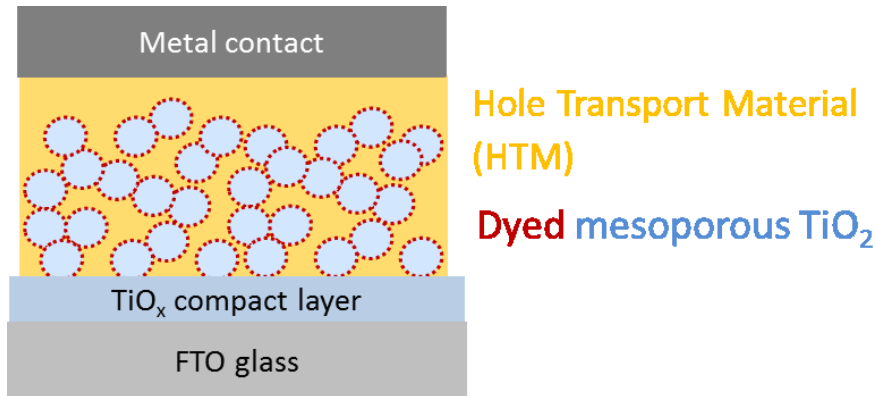


Figure 1.3. Architecture of a solid state dye sensitized solar cell.

In this architecture (shown in Figure 1.3), the photogenerated holes remaining on the dye molecules following electron injection into the TiO_2 are transferred to the solid state hole transporting material (HTM). This process is referred to as regeneration of the photo-oxidized dye. The holes are then transported through the HTM phase towards the counter electrode which is typically deposited via evaporation.

For both liquid junction and solid state dye sensitized solar cells, the steps that have to successfully occur in order to convert the photons' energy into electrochemical energy are:

- a) light absorption by the dye molecules on the surface of the TiO_2 .
- b) Injection of photoexcited electrons in the TiO_2 conduction band.
- c) Hole transfer from the dye to a hole transporting material (HTM).
- d) Charge collection to the respective contacts through the TiO_2 nanocrystalline film and the HTM.

Each of the processes b-d is in kinetic competition with electron hole recombination pathways. In Figure 1.4 all these processes are displayed considering a simplified energy band diagram of the device. As a consequence, the IPCE can be expressed as the product of the efficiency for each of the processes, such that:

$$IPCE(\lambda) = LHE(\lambda)\eta_{inj}(\lambda)\eta_{reg}\eta_{coll} \cdot \quad \text{Eq. 1.1}$$

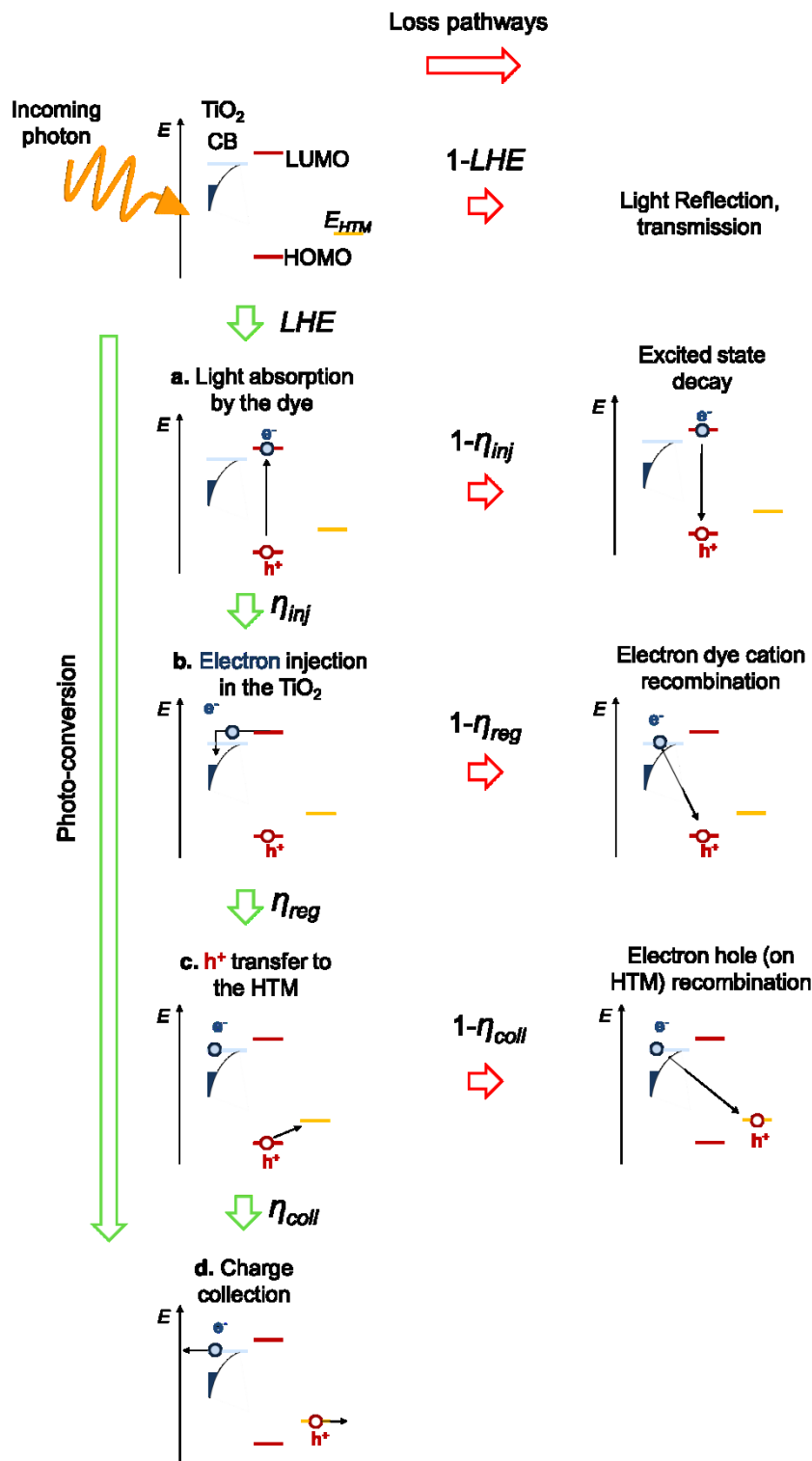


Figure 1.4. Working principle of a dye sensitized solar cell under illumination. Green arrows show all processes which contribute to the extraction of energy to the external circuit; red arrows indicate competing loss mechanisms that lead to relaxation of the excited state within the cell. The electronic energy levels of the different components (TiO_2 , dyes and hole transporting material) are shown, including partially filled trap states in the TiO_2 .

The $IPCE(\lambda)$ is in general a function of the wavelength of the photon. $LHE(\lambda)$, $\eta_{inj}(\lambda)$, η_{reg} , η_{coll} , are respectively the light harvesting (process a in Figure 1.4), electron injection (b), dye regeneration (c) and charge collection (d) efficiencies. Note that the $IPCE$ also depends on other conditions (e.g. the voltage applied to the device, the light intensity).

1.2 Conduction in dye monolayers: motivation

1.2.1 Charge transfer phenomena in dye sensitized solar cells

For DSSCs, the optimization of interfacial charge transfer processes at the dye sensitized interface is considered to be the key to the effective photo-conversion of the device. With reference to Figure 1.5, processes (ii) and (iii) represent historically the main focus for understanding the working principle of the cell.^[18] Processes (ii) include charge generation and charge separation at the TiO_2 /dye/HTM interface, while processes illustrated in (iii) refer to electron hole recombination pathways. The investigation of (ii) and (iii) envisages a 1D description of the interface TiO_2 /dye/HTM. Most studies on charge transfer in DSSCs have adopted such a 1D model and do not include the possibility for charges to move laterally in the monolayer of dyes (process i).

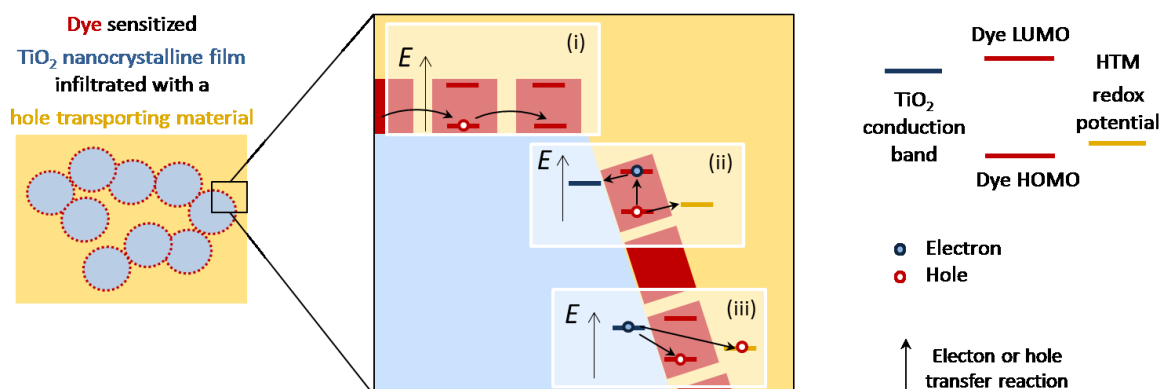


Figure 1.5. The structure of the active layer of a DSSC is shown. The charge transfer processes occurring in this class of devices are outlined in simplified energy level diagrams. (i) Hole hopping between dyes; (ii) photoinduced electron and hole transfers; (iii) electron hole recombination reactions.

Efficient lateral transport of holes in the monolayer of dyes used in DSSCs has been demonstrated in several studies (see section 2.3). This observation raises the question of what role this phenomenon has on the working principle of the

device. Some studies have already suggested its relevance to the charge dynamics and power conversion efficiency of solar cell devices.^{[19],[20],[21],[22]} However, no quantitative study has been carried out. To date it is still unclear whether hole transport between dyes is a beneficial or harmful process to the performance of dye sensitized solar cells and other photo-electrochemical systems.

1.2.2 Relevance to the study of molecular electronics

Dyes anchored to nanocrystals show unique properties: the dyes form a continuous phase on a quasi 2D surface; the dyes chemically bind to the surface, therefore the degree of order in the monolayer can be partly controlled; it is possible to expose the monolayer to different chemical, dielectric and electrostatic environments. These factors make dye monolayers useful model systems to study charge transport under controllable and constrained conditions. They also allow the use of less conventional techniques for the determination of charge diffusion coefficient and mobility between semiconducting molecules. In this thesis I will present electrochemical^{[23],[24]} and spectroscopic^[25] studies on the charge transport properties of dye molecules as a function of their chemical structure. These techniques enable new perspectives to be accessed regarding the influence of molecular configuration and surrounding environment on the charge diffusion performance. This is generally not easily achievable when measuring mobility with more standard techniques like time of flight (ToF) or space charge limited current (SCLC), where current is measured in a thin film cast from solution. Ultimately, the investigation of surface bound conjugated species can become a new platform to investigate charge transport and to define new molecular design rules for organic semiconductors.

1.2.3 Other applications

Dye molecules' multi-functionality (binding to surfaces, light absorption, transport of charges, driving of reactions) makes them suitable for several other photo-electrochemical systems. Below, few examples of application of inter-dye charge transfer are given.

Charge transport in dye monolayers has been explored as a means to introduce a conductive phase in insulating mesostructures. This is relevant to the field of lithium ion batteries, where lithium ions interact with insulating LiFePO_4

nanocrystals to convert electrical energy into chemical energy and vice versa. In commercial devices the resistive mesostructure is doped in order to increase its conductivity so that charges can be transported to the surface of the crystal and drive intercalation or ejection of lithium ions. Doping however results in a drop of the energy density achievable. Dye sensitization of the mesostructure was demonstrated to be an effective solution for maintaining the desired undoped composition of the LiFePO_4 crystal while increasing conductivity using the conductive molecular coating to deliver the charges driving the reaction.^{[26],[27]}

Lateral transport of charges on the surface of a mesostructure has also been used to exchange electrons between different surface bound species. This is a promising technique for solar fuel production where the suitable catalysts for a certain reaction might not show strong light absorption. Also, many relevant reactions of this type require multiple electrons. These are unlikely to be accumulated on the same catalyst based on the low probability that one catalyst absorbs two photons in a sufficiently fast timescale. Rather, the same reaction can be driven by multiple electrons that have accumulated on the catalyst via charge transfer from neighboring light absorbing dyes showing electrical conductivity.^{[28],[25],[29]}

Finally, electrical conduction in molecular monolayers has been reported for self-assembled monolayer field effect transistors (SAMFETs). These devices show potential for the design of transparent circuit and sensing applications. Notably, mobility as high as $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been measured in SAMFETs using oligothiophene based molecules.^{[30],[31]}

1.3 Scope and outline of the thesis

In this thesis I present experimental studies of charge transport in dye monolayers anchored to nanocrystalline TiO_2 . I discuss the measurement of parameters describing charge transport between dyes such as the charge diffusion coefficient, the reorganization energy of electron transfer and the effective electronic coupling. I report the investigation of hole transport between dyes as a function of the TiO_2 surface fraction covered with dyes. I present evidence showing that charge transport in dye monolayers plays a role in existing photo-electrochemical devices. In particular I focus on how this process can lead to improved photo-conversion efficiency of dye based solar panels. Finally I demonstrate the possibility of

designing new optoelectronic architectures where molecular conductive coatings are used as charge transport phases.

In Chapter 2, I present background concepts to the study of intermolecular charge transport in dye monolayers. Basic principles of organic semiconductor physics and charge transport are discussed. An overview of the techniques used to characterize the process of charge transport in dye monolayer is given. This is followed by a literature review of previous studies on the subject.

Chapter 3 describes the materials and experimental techniques used in the thesis as well as the procedure followed to fabricate dye sensitized samples and solar cell devices. It also presents the method used in the calculations presented in Chapter 5.

Chapter 4 illustrates a method to measure the reorganization energy of charge transfer between dyes sensitizing the surface of oxide nanocrystals. First, I assess the validity of one of the electrochemical techniques used in this field to evaluate apparent diffusion coefficient of charges diffusing in the dye monolayer. Secondly, I present experimental results on the reorganization energy of charge transfer between dyes for different classes of materials. These are compared to values obtained from quantum chemical calculations performed by former PhD student Valérie Vaissier.

In Chapter 5 I discuss the dependence of hole diffusion in dye monolayers measured at different length and time scales on the TiO_2 surface fraction covered with dyes. The effect of the diffusion of photo-generated holes within the monolayer on their recombination to injected electrons in the TiO_2 is presented. Further experimental analysis of the transient anisotropy decay related to dye cations in these systems is discussed along with calculated anisotropy profiles obtained via Monte Carlo simulations.

Chapter 6 illustrates the role of hole transfer between dyes sensitizing the surface of TiO_2 in solid state dye sensitized solar cell. The dye regeneration yield is quantified. The degree to which this process is assisted by hole transport in the dye monolayer is evaluated under different experimental conditions.

In Chapter 7, I introduce the concept of the 'dry cell'. Solar cells using the dye monolayer as hole transport phase are presented. This type of device is proposed as an example which exploits charge transport in dye monolayer in new photo-electrochemical devices.

Chapter 8 shows some of the open questions and future directions for this subject of research, given the results reported in the literature and in this thesis.

In the Conclusions chapter I summarize the findings of my work and provide an outlook on the field of intermolecular charge transport in dye monolayers.

Chapter 2 Hole transport between dyes:

background

In this chapter I give an introduction to the theory of electron transfer and charge transport in semiconductors. I then describe some of the techniques used to characterize charge transport in dye monolayers anchored to nanocrystalline oxides, followed by a literature review on the subject. Finally I give an overview on other charge transfer mechanisms at the dye TiO₂ interface immersed in inert electrolytes or within a solid state DSSC architecture relevant to the study of hole transfer between dyes.

2.1 Charge transport in molecular semiconductors

2.1.1 Electronic states in organic and inorganic semiconductors

Both inorganic and organic materials can show semiconducting properties. The former class typically refers to non-molecular solids, whereas the latter includes conjugated small molecules and polymers. Below I give a brief introduction to their electronic properties. More detailed description can be found elsewhere.^{[32],[33]}

The electronic properties of semiconductors are based on the interaction of the valence electrons of the atoms which the material is made of. This interaction results in the formation of a spectrum of electronic states which extend within the solid to a different extent depending on the nature of the chemical bonds and the order of its microstructure. The density of states of the material $g(E)$ (eV⁻¹ cm⁻³) is defined as:

$$g(E) = \frac{dn}{dE} \quad \text{Eq. 2.1}$$

where n is the volume concentration of states (cm⁻³) and E is energy (eV).

For inorganic crystalline materials, electronic states can be calculated considering a periodic lattice. In this case, the states' wavefunction extends to the whole solid. Energetically, they are described by energy bands, separated by energy gaps. In a semiconductor, at 0 K, electronic states in each band are either all filled or all empty. Among all bands showing completely filled states, the one with highest energy is called valence band (VB), whereas the lowest energy empty band is called

conduction band (CB). The energy gap of a semiconductor is referred to as the energy difference between the lowest energy state of the conduction band and the highest energy state of the valence band.

Molecular solids are made of elementary components (molecules) which show relatively weak interaction among each other. In particular, no chemical bond is formed between molecules. As a result, the electronic properties of the solid can be predicted to a large extent on the basis of the properties of a single molecule. This property also underlies some of the advantages of dealing with organic semiconductors: the design of a new material with particular properties translates into molecular design; molecular solids can be solution processed, as solvation of molecules can occur without breaking any chemical bonds.

In a molecule, atomic orbitals can undergo hybridization to different levels, giving rise to molecular orbitals. For carbon atoms, which constitute a large fraction of molecular solids, the four valence electrons $2s^2 2p^2$ can hybridize to three different degrees: sp^3 , sp^2 , sp^1 . These involve the “mixing” of 4, 3, or 2 valence electrons’ orbitals, leaving respectively 0, 1 or 2 p-orbitals unperturbed. Interaction between hybridized orbitals of neighboring atoms gives rise to bonding (occupied) σ and anti-bonding (unoccupied) σ^* bonds. The overlap between p-orbitals of neighboring atoms results in the formation of π type electronic orbitals. Due to the lower degree of electronic interaction between p-orbitals compared to hybridized orbitals, the bonding and anti-bonding π and π^* orbitals are characterized by a less pronounced splitting. Organic molecules that show hybridization sp^2 (where each carbon atom shows one unperturbed p orbital) are relevant to electronic applications and are called π -conjugated molecules. In these compounds the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are respectively the π and the π^* orbitals of the molecule.

Given the relatively low number of atoms in the molecules, the electronic states of an organic semiconductor are in principle described by a discrete set of values. Several sources of non-homogeneity in the solid can however give rise to perturbation of each molecule’s energy levels. This results in broadening of the density of states of the molecular semiconductor, which resemble the energy bands of inorganic crystalline semiconductors. However, each of the electronic states in a molecular material generally shows high degree of localization as I discuss in the next sections.

2.1.2 Free charges in a solid: from nearly-free electrons to polarons

The presence of electrons in the conduction band of a semiconductor enables electrical conduction. Similarly, conduction can be attained when electrons are missing in the valence band of the material. These concepts of excess electron in the CB and missing electron in the VB will be referred to as free electron and free hole or simply electron and hole. Electrons in a crystal can be described by a nearly free electron model, where the presence of the atoms is considered as a perturbation to the case of electrons in vacuum. However this model is only a good description of the physical system for some metals and semiconductors.

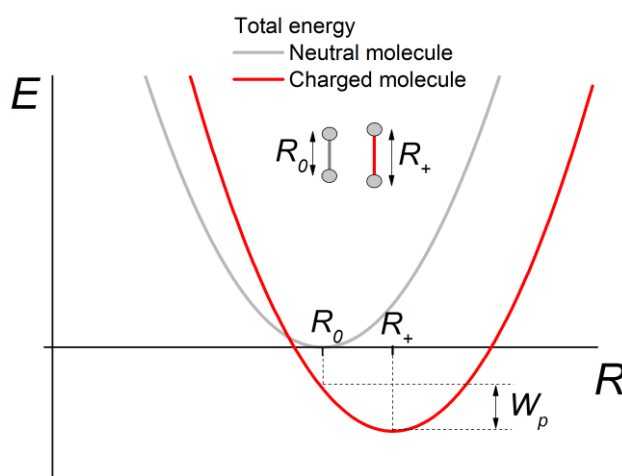


Figure 2.1. Energy of a molecule in the presence of a charge as a function of a configurational parameter R .

More commonly, the presence of a free electron in a solid results in a significant distortion of the surrounding structure. This breaks the symmetry of the system and varies the energy of the occupied electronic state leading to localization of the charge. The electron and the structural distortion move together in these solids. The electron and the lattice distortion form a quasi-particle called polaron.^{[34],[35]} Depending on the spatial extent of the distortion compared with the lattice constant of the crystal, polarons are divided into large or small polarons.

In the case of organic semiconductors, excess or missing electrons (electrons or holes) always have significant effect on their structure. In the simplest case, the distortion of the molecule can be summarized through the use of a single bond length (see for example the case of ethene, C_2H_4).^[36]

To calculate the energy of a molecular system, the Born-Oppenheimer approximation is generally assumed. According to this approximation, the wavefunction of the molecule (ψ) can be written as the product of an electronic component $\Phi(R;r)$ and a nuclear component $X(R)$. The former is a function of the electrons coordinates r and is parameterized by the value of the nuclear coordinates R . The latter is considered to be a function of the nuclear coordinates only and is calculated considering the averaged potential of the electronic cloud. Note that in general R should include the coordinates of the molecule and of the surrounding medium. The validity of the Born-Oppenheimer approximation is related to the difference in masses between electrons and nuclei, which results in significantly different timescales in their motion. Therefore, $X(R)$ can be calculated by using a potential energy profile that accounts for both nuclei-nuclei interaction and for an approximated electron-nuclei interaction. Such energy, expressed as a function of all nuclear coordinates, is called potential energy surface (PES). Figure 2.1 shows the PES of a molecule as a function of a configurational parameter R , in this case the relevant bond length. The total energy of such molecule in the neutral case (grey line) and when an excess (positive) charge carrier is added to its structure (red line) are displayed. For the neutral state, the energy minimum corresponds to a particular bond length R_0 . The energy for other values of R is approximated to a parabola, considering a simple elastic force field describing nuclear interaction. The interaction between the charge and the nuclei can be linearized for a first order treatment of the problem. The formation of an energetic well where the energy minimum of the charged molecule is displaced to a new value $R = R_+$ is expected. The energy involved in the relaxation from $R = R_0$ to $R = R_+$ on this parabola is referred to as polaron binding energy (W_p).^[37]

The polaron binding energy is relevant to the rate at which transfer of the charge occurs between molecules. Let us consider for example two identical molecules, one of them in the neutral state and one in the charged state. Transfer of the charge from the charged molecule to the neighboring neutral molecule is expected to be hindered by an activation energy barrier originating from the 'self-trapping' phenomenon described above. Such an activation energy can be calculated by considering the distortion in configuration of the two molecules which results in both molecules having the same nuclear configuration (i.e. the same value of R). It can be shown that the lowest energy cost associated with a distortion that

satisfies this condition corresponds to $E_{act} = \frac{1}{2} W_p$. An introduction to the theory of charge transfer in these systems is given in the next section.

2.1.3 Hopping transport and non adiabatic Marcus theory

As introduced in the previous section, small polarons are subjected to spatial and energetic self-trapping. Such effect hinders facile displacement of the charge within the solid. This is the case for most molecular semiconductors where the molecular orbitals corresponding to electrons or holes do not extend significantly to neighboring molecules and the polaron transfer step involves substantial reorganization of the molecular structure. The process of polaron transfer occurs in this case via thermally activated tunnelling, also called ‘polaron hopping’. In this thesis any reference to transfer, hopping or diffusion of charges (electrons or holes) is in fact a reference to polaron hopping. The commonly accepted formulation of the charge transfer rate between weakly coupled redox centers is non-adiabatic Marcus theory, which is introduced below.

Let us consider the electron transfer reaction between a weakly coupled electron donor D and electron acceptor A described by:



It is possible to approximate the free energy G of the system considering diabatic states. This corresponds to the assumption that the electron wavefunction is localized on either the donor or the acceptor and no influence on its form and energy comes from the neighboring molecule. If entropic terms are negligible, the PES represents the free energy of the system as a function of nuclear coordinates. The PES is in general different depending on whether the electron sits on the donor or on the acceptor molecule. However these two surfaces (for the electron in the donor or acceptor molecule) can intersect for particular values of the nuclear coordinates set. At these intersection points, the energies and the nuclear coordinates of the reactants and of the products are the same. Let us consider an effective reaction coordinate Q , linear combination of the coordinates in the system R . Q is defined such that, for a certain value of $Q = Q_i$ the two potential energy surfaces intersect at the lowest energy. This state is important because it is the lowest energy state at which the energies of the two PESs have the same value. This condition is called transition state. For simple molecules (e.g. diatomic molecules) Q can be directly

related to one of the molecule's bonds length and the energy of the system can be approximated with the elastic (parabolic) potential energy related to the displacement $Q - Q_1$, where Q_1 refers to the minimum potential energy configuration of the reactants, as shown in Figure 2.2.

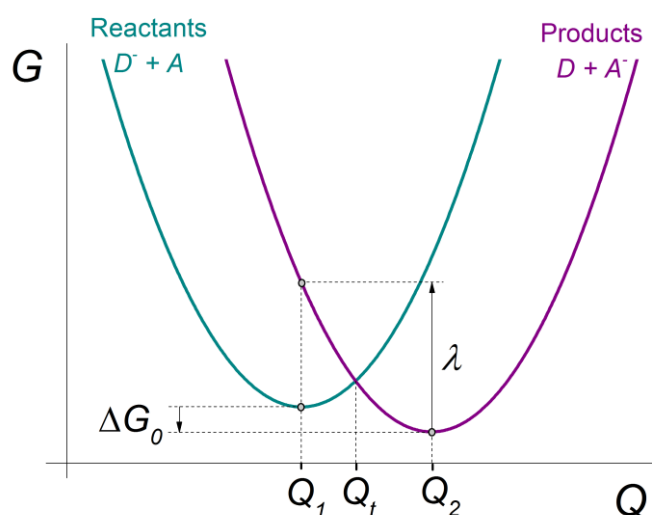
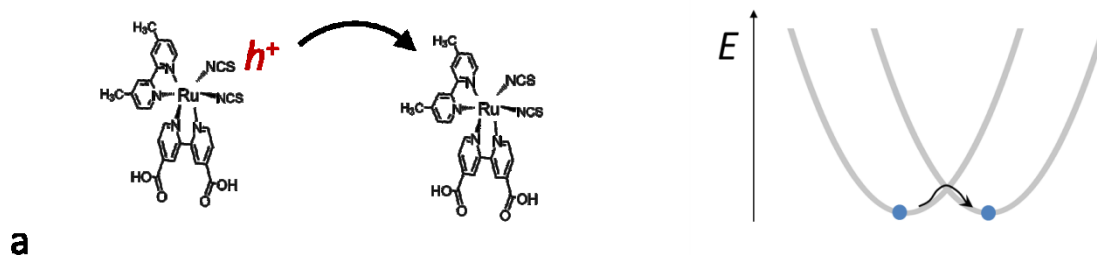


Figure 2.2. Free energy, G , of an electron donor and acceptor system illustrated as a function of an effective reaction coordinate, Q .

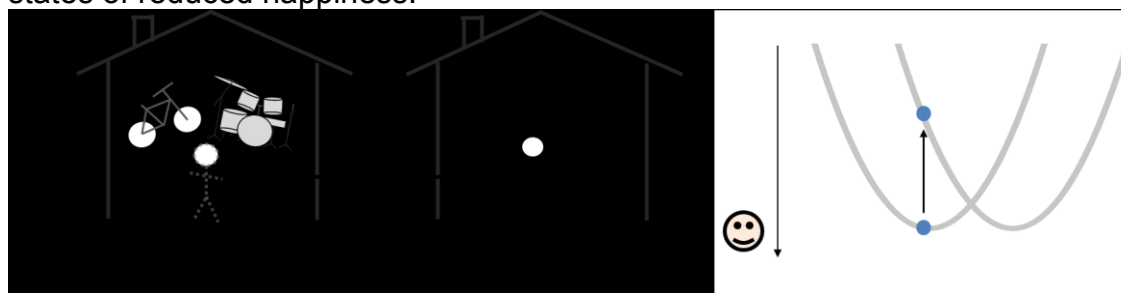
The parabola related to the products can be approximated to have the same curvature if one assumes that the oxidation state of the molecules does not significantly influence the elastic constants of their bonds. If A is a different molecule from D , the potential energy surface corresponding to the products is in general shifted in energy because a contribution to free energy can come from different values of the electronic states' energies involved in the charge exchange. This is expressed by the term ΔG_0 in Figure 2.2. Note that this parameter also influences the value of Q_t . To express the “stiffness” of the system as well as the difference in configuration related to the equilibrium states of reactants and products, another parameter called reorganization energy λ is normally used. λ is a measure of the energy involved in the rearrangement of the molecular structures and of the environment upon charge transfer. It is defined as the energy involved in the process of varying Q from the reactants' equilibrium state to the products equilibrium state without charge transfer to occur (following the reactants' parabola). It can be shown that, for the case of two identical molecules, the reorganization energy of charge transfer is twice the polaron binding energy of each molecule (see previous section).



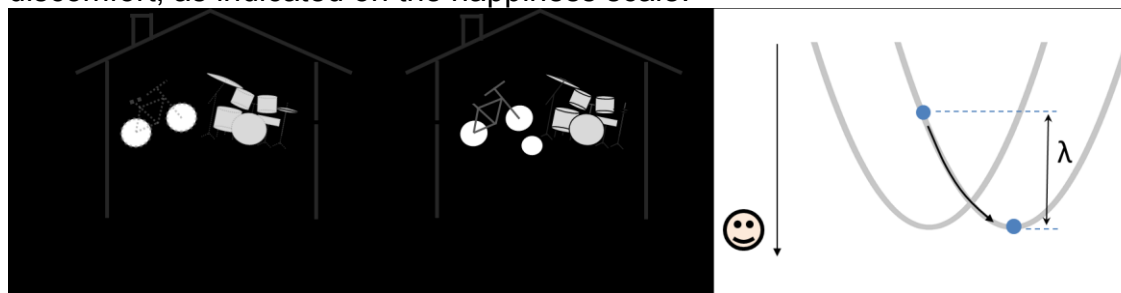
Charge transfer between two molecules involves transition through an energetically unfavorable configuration.



The process of moving house, including one's goods, involves the transition through states of reduced happiness.



To understand the concept of 'relocation energy' consider the case where the person moves to his new place without all his possessions. Clearly, this results in extreme discomfort, as indicated on the happiness scale.



Once however all the goods are moved to the new place, the state of happiness of the person is expected to recover its original level, provided that the new place is similar to the old one. The degree of happiness involved in this relaxation is the relocation energy of this particular transfer process. Note that if the new house is better or worse than the old house, the final degree of happiness is different from the starting point. However, the degree of happiness involved in the relaxation due to the transfer of goods from one place to the other would still be the same.

Figure 2.3. Schematics illustrating the concept of relocation energy of moving house in analogy to the reorganization energy of charge transfer.

λ can also be seen as the energy relaxation involved in the transition from a state in the products' parabola corresponding to $Q = Q_1$, to $Q = Q_2$. The latter process would be physically attained upon optical excitation of the reactants. This is not however the only way charge transfer can occur. When the mode referred to Q is populated with enough phonons, the system can reach the transition state $Q = Q_t$. If transition from the reactants to the products' parabola is possible, then the charge is transferred from D to A. The activation energy E_{act} associated with this process is the difference between the energy of the relaxed state on the reactants' parabola and the energy of the transition state. E_{act} can be calculated as:

$$E_{act} = \frac{(\lambda + \Delta G_0)^2}{4\lambda}. \quad \text{Eq. 2.3}$$

To familiarize with the concept of thermally activated transfer and of reorganization energy I propose the illustration in Figure 2.3. The activation barrier related to moving house can be related to a 'relocation energy' analogous to the reorganization energy required for an electron to transfer between molecules.

In practise, the rate at which charge transfer occurs between molecules is an important figure of merit as well as an experimentally observable quantity. The calculation of the charge transfer rate under the above assumption was carried out by Marcus in 1956. In the case of weakly interacting (non-adiabatic) energy surfaces, the presence of the neighboring molecule can be treated as a perturbation. The transfer rate can therefore be expressed by means of Fermi golden rule:

$$\Gamma_{1,2} = \frac{2\pi}{\hbar} |\langle \psi_1 | H | \psi_2 \rangle|^2 \delta(E_1 - E_2), \quad \text{Eq. 2.4}$$

where ψ_1 and ψ_2 are the wavefunctions of the diabatic states referred to reactants and products. This equation expresses the energy conservation principle, as the rate is non-zero only under the condition $E_1 = E_2$. Under the Born-Oppenheimer approximation the matrix element of the perturbation can be written as follows:

$$\langle \psi_1 | H | \psi_2 \rangle = \langle \phi_1 | H_e | \phi_2 \rangle \langle \chi_1 | \chi_2 \rangle = J_{1,2} \langle \chi_1 | \chi_2 \rangle, \quad \text{Eq. 2.5}$$

where H_e is the electron Hamiltonian (including electron-electron and electron-nuclei interaction). $J_{1,2}$ is defined as the transfer integral or electronic coupling of charge transfer and it is related to the overlap between the electron orbitals of the donor and the acceptor. $\langle \chi_1 | \chi_2 \rangle$ accounts for the Franck Condon principle which

states that electronic transitions occur under constant value of the nuclear coordinates. By calculating the Franck Condon factor for all the iso-energetic couples of nuclear wavefunctions describing the system in state 1 and state 2, the contribution from nuclear tunnelling can also be considered. Under the high temperature limit, an analytical formula for the rate is found, which is commonly referred to as Marcus' formulation of non-adiabatic charge transfer rate:^[38]

$$\Gamma_{1,2} = \frac{2\pi}{\hbar} \frac{|J_{1,2}|^2}{\sqrt{4\pi\lambda kT}} e^{-\frac{(\lambda + \Delta G_0)^2}{4\lambda kT}}. \quad \text{Eq. 2.6}$$

For the case of a self-exchange reaction, that is when donor and acceptor are the same species, in the same configuration and type of environment, the potential energy surfaces of the states 1 and 2 are now energetically aligned ($\Delta G_0 = 0$), as shown in Figure 2.4.

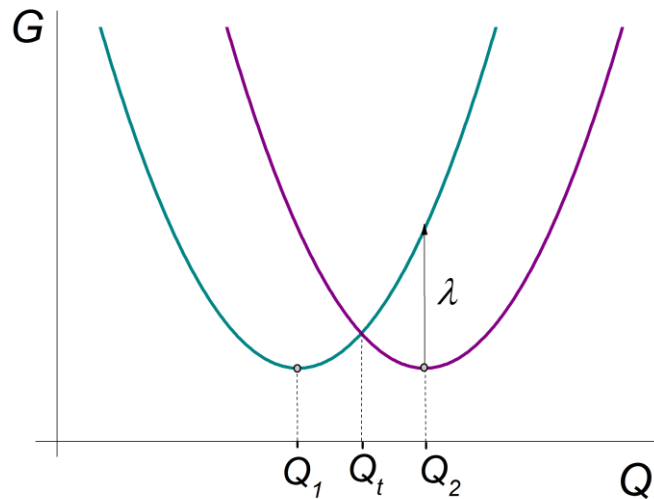


Figure 2.4. Free energy for a self-exchange reaction and acceptor system illustrated as a function of an effective reaction coordinate.

Marcus' formula becomes:

$$\Gamma_{1,2} = \frac{2\pi}{\hbar} \frac{|J_{1,2}|^2}{\sqrt{4\pi\lambda kT}} e^{-\frac{\lambda}{4kT}}. \quad \text{Eq. 2.7}$$

Thus the reaction rate should be temperature dependent, with an experimentally measureable thermal activation energy corresponding to $E_{act} = \lambda/4$ in this case. This expression is relevant to all the cases where charge transport in a single phase semiconductor with negligible contribution from energetic disorder is considered. The effect of disorder is briefly discussed in the next section.

To extend the illustrative analogy above, a temperature dependence could be expected for the relocation energy of moving house. A first order analysis of data related to the frequency of moving house in the United States, coupled with the relevant temperature data is shown in Figure 2.5.

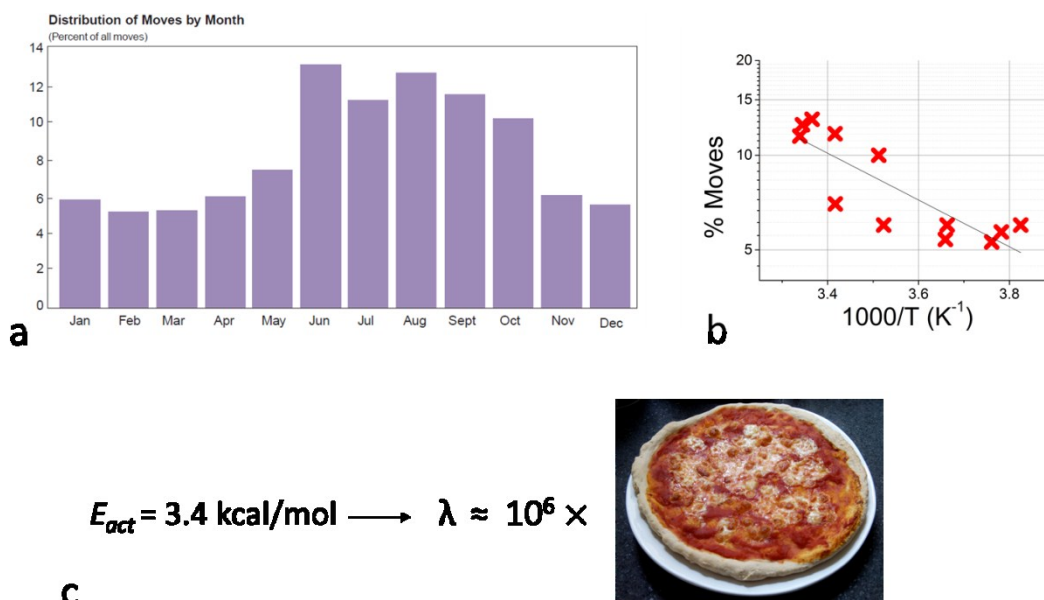


Figure 2.5. (a) Data on the seasonality of moving house in the United States (in 1993). Taken from reference ^[39]. (b) Approximated Arrhenius plot obtained by coupling data in (a) with averaged temperature data in the relevant country. (c) Estimate of relocation energy on the basis of the activation energy extracted from the fit shown in (b) and considering an average human heat capacity of 3470 J kg⁻¹ K⁻¹, and an average weight of the person moving of 60 kilograms.

The non-adiabatic approximation relies on the weak interaction of the electronic states. This implies that the system is unlikely to change its state (from 1 to 2) even when it reaches the crossing point. The electronic coupling J is responsible for breaking the degeneracy of the states at the transition point. Figure 2.6 shows the PESs related to the adiabatic states of a molecular pair showing two different degrees of electronic coupling. When the interaction between the states is strong (strong coupling regime) the probability of charge transfer at the transition point tends to 1, as the system is able to follow the low energy PES. From the comparison between the value of the electronic coupling and the reorganization energy, it is possible to define the charge transfer regime as illustrated in Figure 2.6.

In a dye monolayer, the dyes' position is defined by the available anchoring sites on the surface of the oxide scaffold. This typically results in relatively long distance (typically between 0.5 and 1.5 nm) which is expected to give rise to low

values of electronic coupling. In this thesis, charge transfer between dyes adsorbed on TiO₂ is considered to follow non-adiabatic Marcus theory in the high temperature limit. However, some dyes have a tendency to aggregate. In this case it may be plausible to expect charge transfer to be occasionally mediated by strong coupling interaction. Transfer between “islands” of strongly coupled dyes would be expected to limit the observed transport properties, justifying the use of non-adiabatic theory.

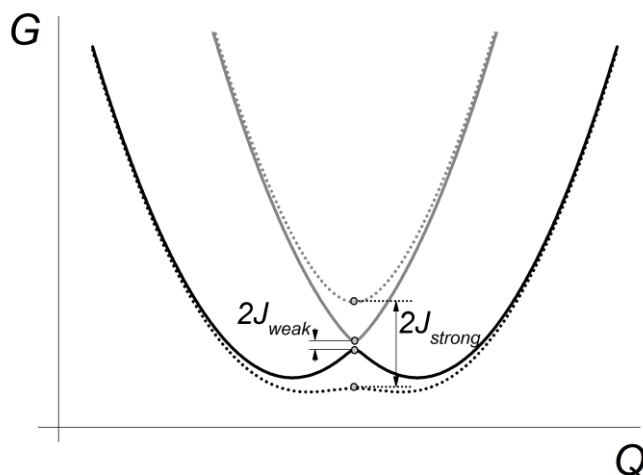


Figure 2.6. Potential energy surfaces referred to the adiabatic states of a pair of identical molecules. The cases of weak and strong coupling regimes are shown. The solid lines represent the adiabatic states for a case of weak coupling ($J = \lambda/30$), while the dotted lines show a case of strong coupling ($J = \lambda/3$).

2.1.4 From electron transfer to electrical conduction

In the previous section I showed how the charge transfer rate between molecules is related to nanoscale parameters. Efficient transfer of charges at the nanoscale results in macroscopic electrical conduction. The charge carrier mobility of a semiconducting material is a commonly used parameter to evaluate its charge transport properties. The mobility of a carrier is in general a tensor which relates the velocity of the carrier to the applied electric field. In isotropic systems, the mobility is

simply defined by the ratio $\mu = \frac{|\vec{v}|}{|\vec{E}|}$.

Let us first consider what happens when applying an external field to an inorganic crystal at a finite temperature. According to the semi-classical treatment of the problem, the field induces acceleration of the charge carriers following a modified version of Newton’s law. However, scattering events with nuclear vibrations result in

randomization of the carrier's velocity. By defining a mean scattering time τ and assuming that the average charge velocity following the scattering event is 0, it can be shown that the mobility of the electron can be approximated to a constant, field independent value defined as $\mu = \frac{|\langle \vec{v}(t) \rangle|}{|\vec{E}|} = \frac{q\tau}{m^*}$ (where m^* is the effective mass of the charge carrier^[32]). This model is referred to as band-like transport and gives a first order description of electron transport in many metals and inorganic semiconductors.

When dealing with hopping transport in molecular semiconductors, incoherent transfer of carriers between sites is expected. This means that after each charge transfer process, relaxation of the system is assumed. A simplified version of carrier mobility can be expressed by using non-adiabatic Marcus rate for charge transfer for identical molecules arranged in a regular 1D lattice. ΔG_0 between redox sites can be related to the electric field as $\Delta G_0 = q|\vec{E}|a$, where a is the intermolecular distance.

Under the assumption of low field ($\Delta G_0 \ll kT$ and $\Delta G_0 \ll \lambda$), the net current can be calculated as difference between forward and backwards fluxes. The resulting expression for the mobility is:

$$\mu = \frac{2\pi}{\hbar} \frac{|J|^2}{\sqrt{4\pi\lambda kT}} e^{-\frac{\lambda}{4kT}} \frac{qa^2}{kT}. \quad \text{Eq. 2.8}$$

By applying Einstein's relation one can express the diffusion coefficient of the charge as:

$$D = \frac{2\pi}{\hbar} \frac{|J|^2}{\sqrt{4\pi\lambda kT}} e^{-\frac{\lambda}{4kT}} a^2. \quad \text{Eq. 2.9}$$

This result is consistent with what would be expected for random walk in a 1D lattice where the transfer rate between neighboring sites is given by Eq. 2.7. Eq. 2.8 and Eq. 2.9 emphasize the importance of the electronic coupling and the reorganization energy values to the effectiveness of electrical conduction in molecular semiconductors.

2.1.5 The effect of disorder on charge transport

Even for materials where band states allow band-like transport, the presence of trap states can dominate electron dynamics. Dispersive transport characteristics

have been observed in transient photo-electrical measurements in inorganic and organic semiconductors, suggesting a broad distribution of time constants in the movements of charges. The broadening of the distribution is believed to arise from the disordered nature of solids. Scher and Montroll proposed a multiple trapping model to describe such behavior, and succeeded at fitting the transient photocurrent decays showing long tails.^[40]

For the case of hopping transport in disordered semiconductor, electrons undergo thermally activated tunnelling between localized states that lie below the band edge. A transport energy was introduced by Grünewald and Thomas^[41] as the most likely value of electronic energy level for transport to happen. The transport energy for an exponential density of states was analytically expressed by Shapiro and Adler.^[42]

One of the reference models for charge transport in organic semiconductors is the Gaussian Disorder Model (GDM) developed by Bässler.^[43] By carrying out Monte-Carlo simulation, an analytical expression for the mobility was found as function of both the configurational and the energetic disorder in the system. These were parameterized by assuming a Gaussian density of states with width σ and inter-site coupling parameter also drawn from a Gaussian distribution with standard deviation Σ . The latter is related to the spread in the relative distance between molecules and influences the value of the electronic coupling. The transfer between sites was defined on the basis of Miller-Abrahams rate.^[44] This model does not account for energetic barrier for downwards hops, which also implies lack of acceleration in the presence of electric field. The expression for the mobility found by Bässler shows a temperature dependence following T^2 . This is in contrast with the dependence outlined by non adiabatic Marcus rate, where thermally activated (T^1) behavior is observed.

2.2 Measuring charge transport in dye monolayers

In the previous section I gave a basic introduction to the theoretical background on charge hopping in molecular semiconductors. This section focuses on charge transport within monolayers of dyes anchored to the surface of nanocrystalline oxides. The system will be briefly introduced. An introduction to electrochemical and spectroscopic methods to evaluate charge transport in dye monolayers is then given.

2.2.1 Dye monolayers on nanocrystalline oxides

Sensitization of an oxide's surface with dyes can be attained via chemisorption of the molecules. This is implemented by anchoring groups that are included in their chemical structure and which react with the surface of the oxide. The most common anchoring group for dyes used in DSSCs is the carboxylic acid group (COOH), which is found to provide sufficiently strong binding to the surface of various oxides. Other groups have also been investigated in the field.^{[45],[46]} For DSSCs applications, electron acceptor character of the anchoring group is generally desirable as it results in efficient photo-induced electron injection in semiconducting scaffolds.^[6] As for charge transport within the monolayer, the choice of the anchoring group has implications on the conformation of dyes on the surface as well as their degrees of freedom.

In this thesis I present results obtained from the investigation of metal complexes and organic dyes. The former are commonly used for their redox stability over multiple oxidation states; the latter represents a potentially inexpensive alternative. Although the extinction coefficient of organic dyes is often higher than for the case of metal complexes, these dyes are generally less stable in their non-neutral state.

Several metal-oxides can be functionalized via chemisorption of organic molecules or metal complexes.^[47] The main focus of this thesis is on the behavior of dyes sensitizing titanium dioxide (titania or TiO₂) nanocrystals. This material shows suitable properties for photochemical devices for water splitting.^{[48],[49],[50]} Given its relatively high bandgap (3 - 3.2 eV), TiO₂ absorbs only a limited fraction of the solar spectrum. Dye sensitization has been a key factor for its success as a solar cell material. In addition, TiO₂ has the attractive potential of being fabricated in nanostructured morphologies and obtain high surface area thin films.^[51] TiO₂ shows many polymorphs of which three are commonly studied: rutile, anatase and brookite. Here, I focus on the anatase phase which is most commonly employed in dye sensitized systems, showing stability at small particle sizes.^[52] Anatase TiO₂ is a tetragonal crystal with lattice parameters $a = b = 0.373$ nm and $c = 0.937$ nm.

Due to the many stable phases of titanium-oxygen crystals showing different stoichiometry, defects are easily formed in the bulk of TiO₂. Oxygen deficiency results in reduced TiO_{2-x} compositions. The relevant point defects are oxygen

vacancies, Ti^{3+} and Ti^{4+} interstitials. Oxygen vacancies and Ti^{3+} states lead to n type doping of the semiconductor. This implies that the physical properties of the material (e.g. conductivity, density of states) are strongly related to the environment and the preparation procedure.^[53] The resulting density of states relates to these defects. The shape, the density and physical location of such states also has fundamental influence on electronic properties of the material.^{[54],[55],[56]} Studies have shown that the dependence of the electron diffusion coefficient as a function of electron density is consistent with an exponential density of states lying below the conduction band edge. This is also consistent with chemical capacitance measurements performed on TiO_2 electrodes.^[57] For this reason, most models for electron transport include such an exponential tail of states.^[58] The physical basis for such a model is however still not clear. In particular spectroscopy shows that bandgap states related to Ti^{3+} states are measured at deeper energies than the characteristic energy for the experimentally observed exponential density of states.^[59]

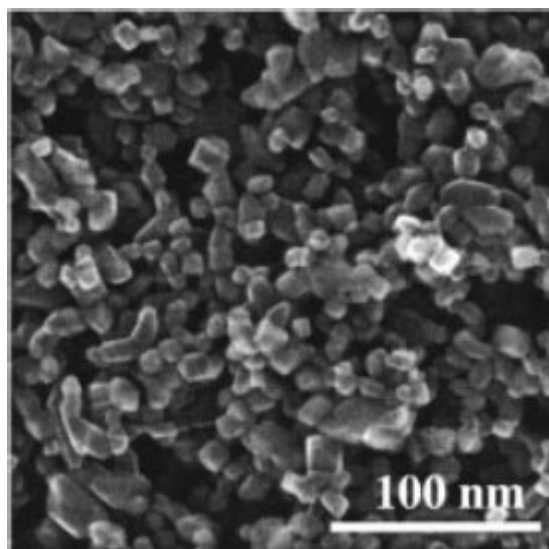


Figure 2.7: Scanning electron micrograph (SEM) of a mesoporous anatase TiO_2 film. Reprinted with permission from “Efficient Lateral Electron Transport inside a Monolayer of Aromatic Amines Anchored on Nanocrystalline Metal Oxide Films” P. Bonhôte, E. Gogniat, S. Tingry, C. Barbe, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, *J. Phys. Chem. B* 1998, 5647, 1498. Copyright 1998 American Chemical Society.

Figure 2.7 shows a scanning electron micrograph of a nanocrystalline anatase TiO_2 film. The size of the nanoparticles is in the order of 10 to 20 nm. This size generally results in efficient dye sensitized solar cells. In the micrograph it is possible

to notice different shapes for the crystals. In some cases particles' edges and facets are resolved.

The use of nanoparticulate anatase TiO_2 could raise the question of quantum confinement effects. Bulk bandgaps have been observed for particle size >2 nm.^{[60],[61]} Since the particle sizes used in most devices are greater than this value, quantum confinement is unlikely to play an important role in device behavior. On the other hand, the size of the particles has implications on the charge transport properties of the material. Nanocrystalline TiO_2 immersed in electrolytes is generally analysed with the assumption that ions surrounding the semiconductor provide enough screening to ensure field free transport of carriers. This is because charge depletion in the particle would account for variations in the electrostatic potential which are below the thermal energy at room temperature.^[62]

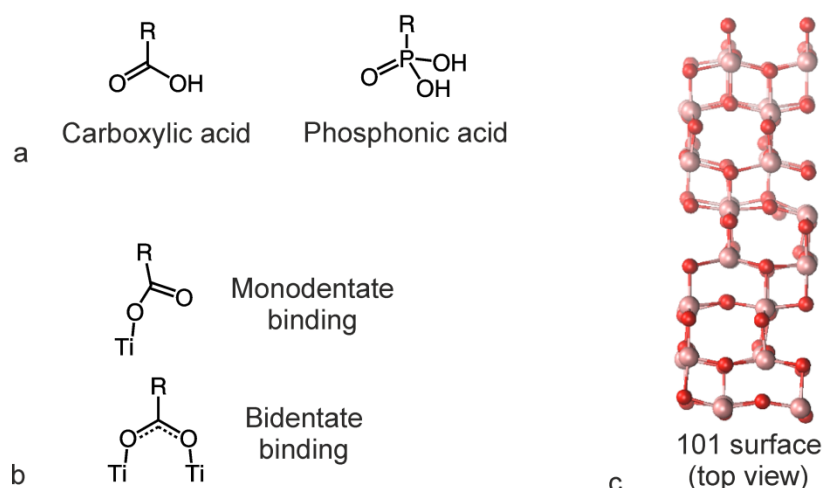


Figure 2.8. (a) Chemical structures of common anchoring groups for dyes. (b) Binding modes of carboxylic acid to titanium atoms on TiO_2 surface. (c) 101 TiO_2 surface, color scheme: red oxygen atoms, pink titanium atoms (courtesy of Valérie Vaissier).

Figure 2.8 shows the chemical structures of the most commonly used anchoring groups in dyes for DSSCs: the carboxylic acid and the phosphonic acid groups. It also displays possible binding mechanisms of COOH to titanium atoms on TiO_2 , where either one or both of the oxygens in the group chemically bind to the metal. Figure 2.8c illustrates the structure of TiO_2 anatase surface corresponding to the 101 plane. The 101 surface shows the lowest surface energy and it is therefore the most stable, as one can also observe in naturally grown crystals.^[63] It is also representative of the mesoporous films considered in this thesis.

2.2.2 Spectro-electrochemical techniques

Charge transport in dye monolayers sensitizing the surface of nanocrystalline oxides can be measured using electrochemical and spectro-electrochemical techniques. Figure 2.9 shows the architecture of an electrochemical cell in a three electrode configuration which can be used to implement such measurement. Here, I discuss briefly some details of this experimental setup.

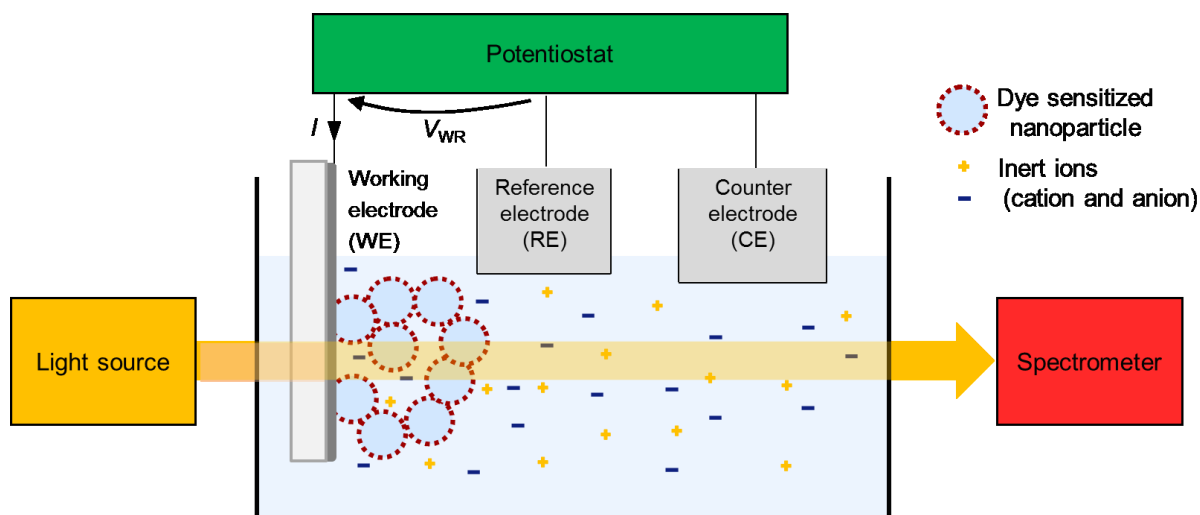


Figure 2.9. Electrochemical cell using a dye sensitized nanocrystalline film deposited on a conductive substrate as working electrode. Optical transmission measurements of the film is performed simultaneously to the electrochemical measurement.

The electrochemical cell is filled with an inert electrolyte, where ions are free to move, but do not participate in any redox reaction. The three electrodes are referred to as the working, reference and counter electrodes and are connected to a potentiostat which performs the electrical measurement. The working electrode (WE) is directly involved in the electrochemical process under study. The rate of electrons exchanged at its interface (the current) or its chemical potential (the voltage) constitute the measured signal. Current flowing through the WE is driven via the counter electrode (CE) and the electrolyte. The reference electrode (RE) is so called because it provides a standard chemical potential which is used as reference during the measurement. By referring the voltage at the WE to the RE, it is possible to translate the applied potential into an equivalent chemical potential. When used in potentiostatic mode, a potentiostat ensures a defined voltage between the WE and the RE (V_{WR}) and measures the current flowing through the WE. This is implemented

via a feedback loop which compares V_{WR} to the set potential and drives the current needed to zero the difference between the two values through the CE. No current flows through the RE.

In order to measure charge transport in dye monolayers, a dye sensitized nanocrystalline film is deposited on a conductive substrate and used as the working electrode of the electrochemical cell. Under these conditions, the measured current is related to charges being injected into the nanocrystalline scaffold or into sensitizing molecules which are in contact with the conductive substrate. In all cases discussed in this chapter, the electrochemical potential spanned by the WE is such that only limited charge injection into the oxide scaffold occurs. The measured current is therefore related to charges transferred to dyes in contact with the conductive substrate and which then “jump” between the rest of the dyes anchored to the surface of the oxide.

Let us consider the electrochemical characterization of a redox reaction involving the dyes anchored to the oxide’s surface. The reaction is described by a formal redox potential E_0 which refers to the dye under these specific conditions (anchoring scheme, surface interaction, electrolyte used). When applying an electrochemical potential E at the WE of the cell, if equilibrium is established between the electrode surface and the dyes at the interface, then the ratio between the concentration of the dyes in the oxidized state (c_{ox}) and in the reduced state (c_{red}) follows the Nernst equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{c_{ox}}{c_{red}} . \quad \text{Eq. 2.10}$$

Variations in the electrochemical potential applied at the electrode result in variations of the ratio c_{ox}/c_{red} . For this to happen, charges are being exchanged at the interface between the WE and the dyes.

When applying a step potential going from $E_1 < E_0 - kT$ to $E_2 > E_0 + kT$ at $t = 0$, c_{ox}/c_{red} changes from a value close to 0 to a value tending to 1. Holes are therefore injected into the dyes in contact with the conductive substrate. The measurement of the resulting current is commonly referred to as chronoamperometry. When the integrated current (i.e. the total charge) is monitored, the technique is called chronocoulometry.

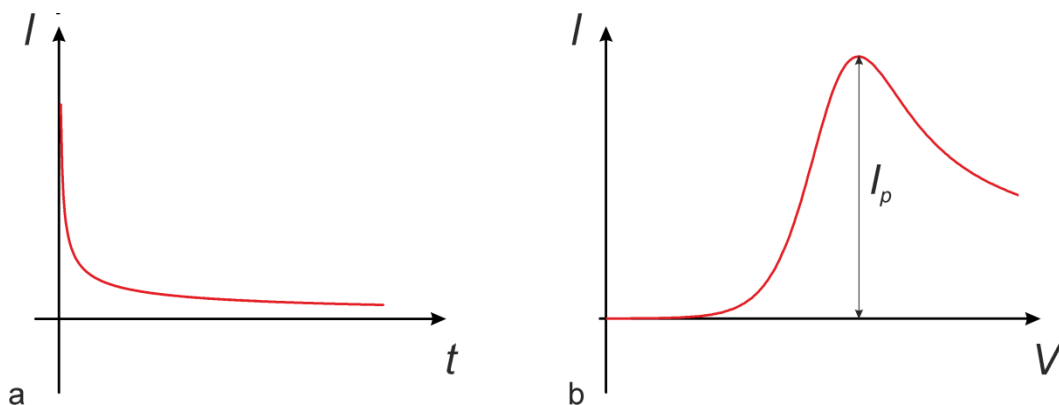


Figure 2.10. Signals obtained from basic electrochemical measurements (simulated curves). (a) applied step potential and measured current for chronoamperometry; (b) current-voltage profile in a linear-sweep voltammogram;

If the holes are able to move in the monolayer, the oxidation of the dyes can extend to the entire monolayer. The resulting current measured at the WE of the cell as a function of time is shown in Figure 2.10a. The current profile follows the Cottrell equation

$$I = \frac{nFAc_0\sqrt{D_{app}}}{\sqrt{\pi t}}, \quad \text{Eq. 2.11}$$

where A is the area of the electrode, c_0 the concentration of dyes in the film undergoing the reaction and D_{app} is the apparent diffusion coefficient of the holes in the dye monolayer. The apparent diffusion coefficient differs from the two dimensional diffusion coefficient of the holes in the monolayer in that the surface of the nanocrystal is not planar (more on this in Chapter 4). The Cottrell equation is derived from the solution to the 1D diffusion model, for the case of step potential applied to the electrode as described above. For this particular measurement (dye sensitized film of finite thickness), the equation is valid for $t \ll d^2/D_{app}$ (see section 4.3.1). When plotting the total charge transferred from the WE to the analyte against the square root of time a lineal profile is expected, the slope of which can be used to extract the value of D_{app} .

Figure 2.10b shows a linear-sweep voltammetry measurement. The applied potential is a ramp and the measured current is the result of holes injected and diffusing in the monolayer. No analytical solution can be found for such profile. However, the current peak of the linear sweep is related to D_{app} , c_0 and the scan rate defined as $v = dV/dt$ as shown by the Randles-Sevcik equation:^[23]

$$I_p = 0.4463nFAc_0\sqrt{\frac{nFvD_{app}}{RT}}. \quad \text{Eq. 2.12}$$

Once again, there is a simple relation between the measured current and the apparent diffusion coefficient of the species. To obtain a cyclic voltammogram, a sequence of two voltage ramps with opposite scan rates is applied to the WE.

These electrochemical measurement techniques can be coupled to optical transmission measurements as shown in Figure 2.9 to obtain a spectroelectrochemical measurement. Spectroelectrochemistry is a tool to optically ascertain what species are involved in the reaction driven by the applied potential. By resolving the variation in optical absorption of the sample in time while performing a chronoamperometry or cyclic voltammetry measurement, information on D_{app} can be extracted.

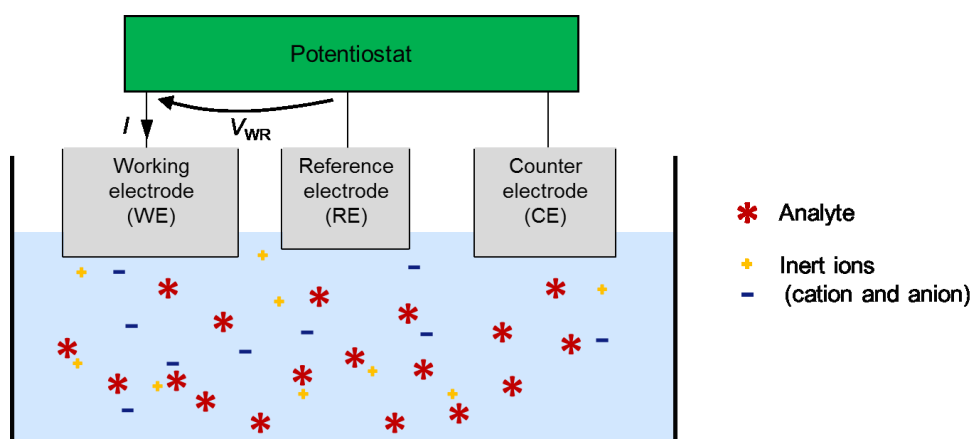


Figure 2.11. Structure of an electrochemical cell in a three-electrode configuration where the analyte is dissolved in the electrolyte.

Note that the techniques described above are more commonly applied to the case where the analyte is dissolved in solution as shown in Figure 2.11. The working electrode is in this case a metal surface immersed in the solution. Analogous models can be used to describe this system. However, normal diffusion in the three dimensions is expected in this case, so that the diffusion coefficient of the molecules in solution should be considered instead of the apparent diffusion coefficient of the charges hopping between fixed molecules.

2.2.3 Transient absorption spectroscopy

Transient absorption spectroscopy (TAS) is a tool to analyse the kinetic properties of a system. The measurement consists of monitoring variations in the optical transmission (T_{opt}) of the sample upon the application of an external perturbation. The time resolved variation in the optical transmission is the main outcome of the measurement. By defining the optical density of the sample OD as $OD = -\log_{10}(T_{opt})$, the result of the TAS measurement can also be expressed as transient variation in optical density $\Delta OD(t)$. The technique is suitable to the analysis of charge transfer processes between different species, however it can also be used to indirectly gather information on the charge transport properties of semiconductors.

The perturbation in a TAS experiment can be of diverse nature (optical, electrical, magnetic etc.). Here, I focus on optical “pumping”. The use of laser pulses is a convenient means to investigate the charge dynamics in semiconducting systems at different time scales. In Figure 2.12 the principle of and the main components involved in a μs TAS measurement are shown. A probe beam is passed through the sample to monitor its optical transmission (T_{opt}). By using a monochromator the relevant wavelength can be selected. After the monochromator, the probe beam is focused on a photodetector. The photocurrent flowing in the photodetector is converted into voltage via a trans-impedance amplifier. The circuit ensures a linear relation between T_{opt} and the measured background voltage V_{BG} .

When the perturbation is applied to the sample (e.g. laser pulse), its optical transmission at the probed wavelength can be described as the sum of the “relaxed state” transmission T_{opt} and the variation in transmission $\Delta T_{opt}(t)$ induced by the perturbation. As a result, the measured voltage becomes the sum of V_{BG} and a time dependent signal $V(t)$. In principle, the optoelectronic detection of the optical signal provides the same linear relation between $\Delta T_{opt}(t)$ and $V(t)$ as for the case of T_{opt} and V_{BG} . However, $\Delta T_{opt}(t)$ is the result of electronic transitions in the sample which can occur within relatively slow (ms-s) to ultra-fast (<ns) time scales. The time width of the laser pulse provides a first limitation to the time scales of the phenomena that can be probed. In addition, the system performing the optoelectronic detection of $\Delta T_{opt}(t)$ and its electronic amplification has a certain bandwidth which further limits the time response of the system. For the setup which I refer to in this thesis, the shortest time scale that can be resolved is in the order of few hundreds of

nanoseconds, much longer than the pulse width of the laser used (~6 ns). The resulting signal $V(t)$ can therefore be approximated as the convolution of $\Delta T_{opt}(t)$ with the optoelectronic response of the circuit to a $\Delta T_{opt, \delta}(t) = \delta(t)$, where $\delta(t)$ is the Dirac delta function.

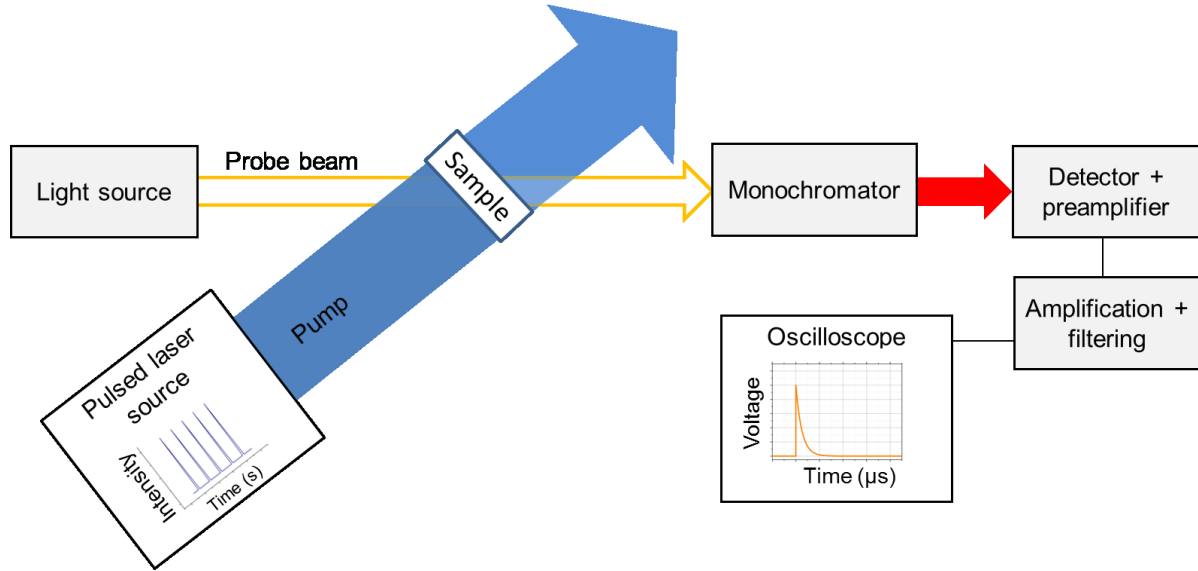


Figure 2.12. Schematics of a (μ s) transient absorption spectroscopy setup.

Based on the description above, for the time scales accessible by the TAS system, the measured electronic signal is interpreted as a relative variation in transmission or in a variation in optical density, ΔOD , using the following expressions:

$$\frac{\Delta T_{opt}(t)}{T_{opt}} = \frac{\Delta V(t)}{V_{BG}}. \quad \text{Eq. 2.13}$$

$$\Delta OD(t) = -\log\left(1 + \frac{\Delta T_{opt}(t)}{T_{opt}}\right) \approx -\frac{\Delta T_{opt}(t)}{2.3T_{opt}}. \quad \text{Eq. 2.14}$$

Note that the approximation in Eq. 2.14 is valid for $\Delta T_{opt}(t) \ll T_{opt}$.

The TAS measurements which are presented in this thesis are meant to describe the evolution of optically induced excited states. In all cases, I assume that the excitations and the electron transfer reactions under study do not vary the properties of the system. That is, upon complete relaxation of the optically induced excited states, the system is assumed to be in the same state as before the excitation. On this basis, better signal to noise ratios are achieved by pumping the system with a series of laser pulses at a certain repetition rate and averaging the transient absorption signal over a number of “experiments”.

2.2.4 Transient anisotropy spectroscopy

Transfer of charges (or in general of excited states) between identical molecules does not result in a transient absorption signal. Standard TAS measurements are therefore not directly useful to the investigation of charge transport in dye monolayers. On the other hand, transfer of charges between identical molecules can result in a change of the polarization of the excited state due to the difference in the molecules' orientation. Polarization spectroscopy is therefore a suitable strategy to characterize charge transport in molecular systems. A brief introduction to the subject is given below.

In spectroscopy, anisotropy is defined as a dimensionless quantity which represents a ratiometric measure of, for example, the difference of a system's optical transmission of light beams with different optical polarization directions. This implies that, in the case of the independent evolution of individual excited states, measurements of anisotropy are concentration independent.

The rate of absorption of photons by a dye is related to the scalar product of the electric field $\vec{E}$ of the photon and the dipole moment of the electronic transition of the dye corresponding to the photon's wavelength. For linearly polarized light, the scalar product between the two vectors determines the prefactor of the transition rate, described for example with Fermi's golden rule:

$$W_{1,2} = \frac{2\pi}{\hbar} \left| \vec{E} \cdot \langle \psi_1 | q\vec{r} | \psi_2 \rangle \right|^2 \delta(E_1 - E_2) \quad \text{Eq. 2.15}$$

where $\vec{\mu}_{1,2} = \langle \psi_1 | q\vec{r} | \psi_2 \rangle$ is the transition dipole moment.

Since dyes anchored on the surface of a nanocrystal are expected to be arranged with different orientations, excitation of the system with polarized light results in a selected population of dyes having a specific orientation to reach the excited state. Such population selection is a function of the angle ϑ between the two vectors $\vec{E}$ and $\vec{\mu}_{1,2}$.

$$\left| \vec{E} \cdot \vec{\mu}_{1,2} \right|^2 = \left| \vec{E} \right| \left| \vec{\mu}_{1,2} \right| \cos^2 \vartheta. \quad \text{Eq. 2.16}$$

To explain the effect of an anisotropic perturbation let us consider some simple cases first. If the system under study is a monolayer of dyes arranged on a flat surface forming a perfectly ordered crystal, each dye is excited with equal

probability since all dyes have the same value of ϑ . Dyes in the excited state can fluoresce and this can for example happen as the transition between the same electronic states involved in the absorption (state 2 and state 1 in Eq. 2.16). By measuring the fluorescence signal through a polarizer oriented parallel or perpendicular to the excitation's polarization, the fluorescence anisotropy can be defined as:

$$r = \frac{I_{//} - I_{\perp}}{I_{//} + 2I_{\perp}}. \quad \text{Eq. 2.17}$$

Where $I_{//} = I_0 \cos^2 \vartheta \cos^2 \vartheta$ is the fluorescence signal measured for parallel orientation and $I_{\perp} = I_0 \cos^2 \vartheta \sin^2 \vartheta$ the one measured for the perpendicular case (I_0 is an intensity prefactor). In the case of a perfectly ordered monolayer, depending on the value of ϑ , the anisotropy of the fluorescence signal ranges between 1 (for $\vartheta = 0$) and -1/2 (for ϑ tending to 90°).

On the other hand one could consider dyes isotropically oriented in the three dimensions (x, y, z), as it is the case for a dye sensitized nanoparticulate film. In that case, each dye's orientation can be characterized by the value of two angles: ϑ being the angle between the dye dipole moment and the z axis, and φ the angle between the projection of the dipole moment on the x, y plane and the x axis. Excitation of the system with a polarized light source would again result in fluorescence of the dyes, assuming the nanocrystalline scaffold does not act as quencher. For z-polarized excitations, and in absence of energy transfer between neighboring dyes, the measured fluorescence would be

$$I_{//} = I_0 \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta (\cos^2 \vartheta \cos^2 \vartheta \sin \vartheta) \text{ and } I_{\perp} = I_0 \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta (\cos^2 \vartheta \sin^3 \vartheta \sin^2 \varphi). \text{ This is}$$

again, considering emission from a transition dipole moment that has the same orientation as the one involved in the light absorption. The resulting value of anisotropy using Eq. 2.17 is 0.4 which represents the maximum value achievable for non-oriented samples. Note that in cases where the orientation of the dipole moment associated with the radiative relaxation is different from the one related to the absorption (due for example to structural relaxation of the dye or to excitation to higher energy states of the dye), a value lower than 0.4 in the fluorescence anisotropy is expected.

Let us now consider the case where the excited state is able to diffuse across the surface of the nanocrystal via energy transfer between dyes. The contribution to the anisotropy of each excitation is expected to be lost in time. This is because the polarization of the excited state is gradually randomized as the exciton is exchanged between dyes with different orientations before fluorescence occurs. The dynamic behavior of the system can be probed via transient anisotropy measurements. For the particular case of dyes anchored to a perfectly spherical particle, and for normal diffusion of the excited states, the time dependent response of the fluorescence anisotropy is expected to follow a mono-exponential decay.^[64] Note that this is the same result which is expected for the fluorescence signal from dyes rotating in solution.^[65]

In the dye sensitized nanocrystalline TiO₂ systems investigated in this thesis, optical excitation of a dye results in efficient electron injection in the nanocrystalline scaffold. The remaining hole on the dye cannot be probed via fluorescence spectroscopy. However, the hole is detectable with transmission measurements. By performing transient absorption anisotropy spectroscopy, it is therefore possible to “follow” the net polarization of the photogenerated holes in time following their initial excitation with an anisotropic distribution. The concentration of excited species (holes) is no longer proportional to a detected intensity, but it is proportional to the variation in optical density of the sample at the relevant wavelengths at which the dye cation absorbs light. The transient anisotropy signal can be defined in this case as:

$$r(t) = \frac{\Delta OD_{\parallel}(t) - \Delta OD_{\perp}(t)}{\Delta OD_{\parallel}(t) + 2\Delta OD_{\perp}(t)} . \quad \text{Eq. 2.18}$$

As explained in the previous section, the absorption spectrum features of a dye cation differ from the same molecule in the neutral state. The ‘probed’ transition dipole of the cation and the ‘pumped’ transition dipole moment of the neutral molecule can be collinear or not. In the former case, once again anisotropy is expected to show a value of 0.4 at early timescales, whereas it may have lower magnitude for the case of non-collinear neutral state and cation dipoles. The decay of $r(t)$ is again expected to be exponential for normal hole diffusion on a spherical surface.

2.3 Previous studies of charge transport in dye monolayers

In this section I present a summary of the early and more recent reports on the characterization of charge transport in dye monolayers. In these studies, the techniques described in the previous sections have been applied to dye sensitized nanocrystalline oxides.

2.3.1 First demonstrations of hole transport in dye monolayers

The first observations of hole exchange between dyes sensitizing semiconducting and insulating nanocrystalline oxides were reported in the late 90s. In their work published in 1998,^[66] Bonhôte *et al.* investigated the spectroelectrochemical characteristics of semiconducting and insulating nanocrystals functionalized through solution dyeing with redox active molecules. Data for TiO₂ mesoporous films were presented.

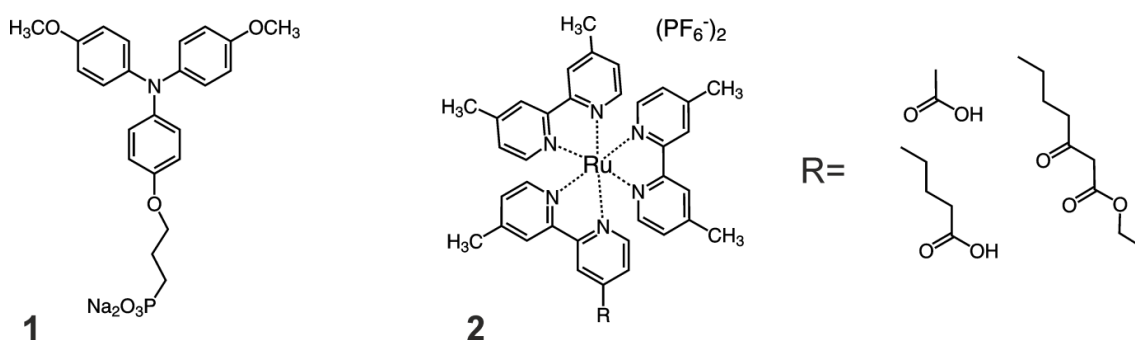


Figure 2.13. Chemical structure of the sensitizers studied in references ^[66] and ^[67].

As Bonhôte *et al.* reported "...it was striking to observe that compound 1 (a phosphonated triarylamine, structure 1 in Figure 2.13) *did exhibit reversible electrochemistry when grafted onto nanocrystalline TiO₂ layers supported by conducting glass, even though its redox potential (0.80 V) is located in a domain where the TiO₂ interface is expected to be blocking.*" The hypothesis that the TiO₂ was assisting the redox reaction was definitively ruled out by demonstrating similar effect when insulating nanocrystals (Al₂O₃ or ZrO₂) were used as scaffold.

By performing chronospectrocoulometric measurements the authors observed diffusion limited charge transfer to the molecules sensitizing the nanostructured electrode. The electrochemical response of films with different dye loadings was

assessed. When the surface coverage of the nanocrystal by the sensitizer was below about 50%, the estimated diffusion coefficient dropped by more than one order of magnitude compared to the fully covered surface case. No percolation threshold would have been expected for the apparent diffusion coefficient, had the diffusion of dyes through the electrolyte within the pores of the nanocrystal been the dominating contribution to the observed response. The possibility that the sensitizing molecules were desorbing from the nanocrystal and diffusing to the conductive substrate was therefore also ruled out. The interpretation of the result was therefore that holes could be injected into the sensitizing groups anchored to the nanocrystal from the conductive substrate, and diffuse within the molecular monolayer.

Two years before Bonhôte's publication, Heimer *et al.* reported on dyes having different anchoring groups (see structures 2 in Figure 2.13) and on their electron injection performance when anchored to mesoporous TiO₂. In their work, cyclic voltammetry measurements of dye sensitized TiO₂ films on conductive substrates were presented. The primary aim of the measurement was to compare the oxidation potential of the dyes when anchored to the oxide surface and when dissolved in solution. *"We were somewhat surprised to find quasi-reversible RuIII/II redox chemistry for the surface-anchored sensitizers"*. The integrated current obtained at slower (0.5 mV s⁻¹) scanrate conditions was used in this work to define an electro-active surface-coverage. This value was found to be higher than the amount of dyes expected to be adsorbed on the surface of the conductive oxide substrate. On the other hand it was one order of magnitude lower than the dye loading extracted spectroscopically. For the first time the following observation was reported for this class of functionalized photoelectrodes: *"in the absence of an obvious electron mediator, self-exchange electron transfer processes across the nanocrystalline TiO₂ surface(s) could account for the high electroactive surface coverage"*.^[67]

2.3.2 Following electrochemical studies

Following the above discussed work from Heimer *et al.* and Bonhôte *et al.* electrochemistry and spectroelectrochemistry of sensitized films have been applied as a new tool to investigate redox and charge transport properties of sensitizers.^{[68],[69]} The findings of the main studies which contributed to the current

understanding of the process are dealt with in this section. Figure 2.14 and Table 2.1 are a summary of the relevant structures and the results obtained in the studies reviewed below. Table 2.1 shows the chemical structure of the sensitizers and the summary of experimental conditions, measured apparent diffusion coefficient, percolation threshold when available and the corresponding reference to the publication.

Trammel *et al.* conducted the investigation on hole transport in TiO₂ nanocrystalline films sensitized with the complex [OsII(bpy)₂(4,4'-(CO₂H)₂bpy)](PF₆)₂ (structure 3). Diffusion of "surface electrons" was measured electrochemically and apparent diffusion coefficients in the order of 10⁻⁹ cm²s⁻¹ were presented. When dyeing the films with solutions having concentration ranging between 0.1 and 2 · 10⁻⁴ M, the surface coverage was controlled and varied between about 10 and 100%. A percolation threshold was observed, corresponding to coverage of 60% of the total available surface area.^[70]

Following their first observation in 1996, further contributions on the understanding of intermolecular charge transport in molecular monolayers came from the Meyer's group. In 2001, Qu *et al.* investigated the effect of the presence of protons and other cations in solution on the binding of Ruthenium complexes and their electron transfer characteristics.^[71] TiO₂ and ZrO₂ nanocrystalline electrodes were prepared and subjected to either an acid or base pretreatment in aqueous solution. IR spectroscopy showed that the different treatments resulted in different anchoring mechanism of the dye, respectively one oxygen (carboxylic acid linkage) two oxygen atoms (carboxylate linkage) per carboxylic acid groups bound to the surface. The samples were then vacuum dried and rinsed in acetonitrile before sensitization. Acid-pretreated samples showed a quasi-reversible electrochemical response during cyclic voltammetry measurements in TBAP:acetonitrile electrolyte, whereas the base-pretreated counterpart showed small to no anodic-cathodic peaks in similar conditions. Addition of the smaller cation Li⁺ to the electrolyte was found to increase the electrical signal and the reversibility of the reaction in base treated surfaces. The authors suggested that small ions could potentially increase the translational mobility of the dyes' carboxylate linkage. Also, adsorption of protons or Li⁺ ions on the semiconductor surface may be influencing the dynamics of charge transfer or of dye migration. An alternative explanation was a drop in reorganization energy of charge transfer induced by the presence of small cations.

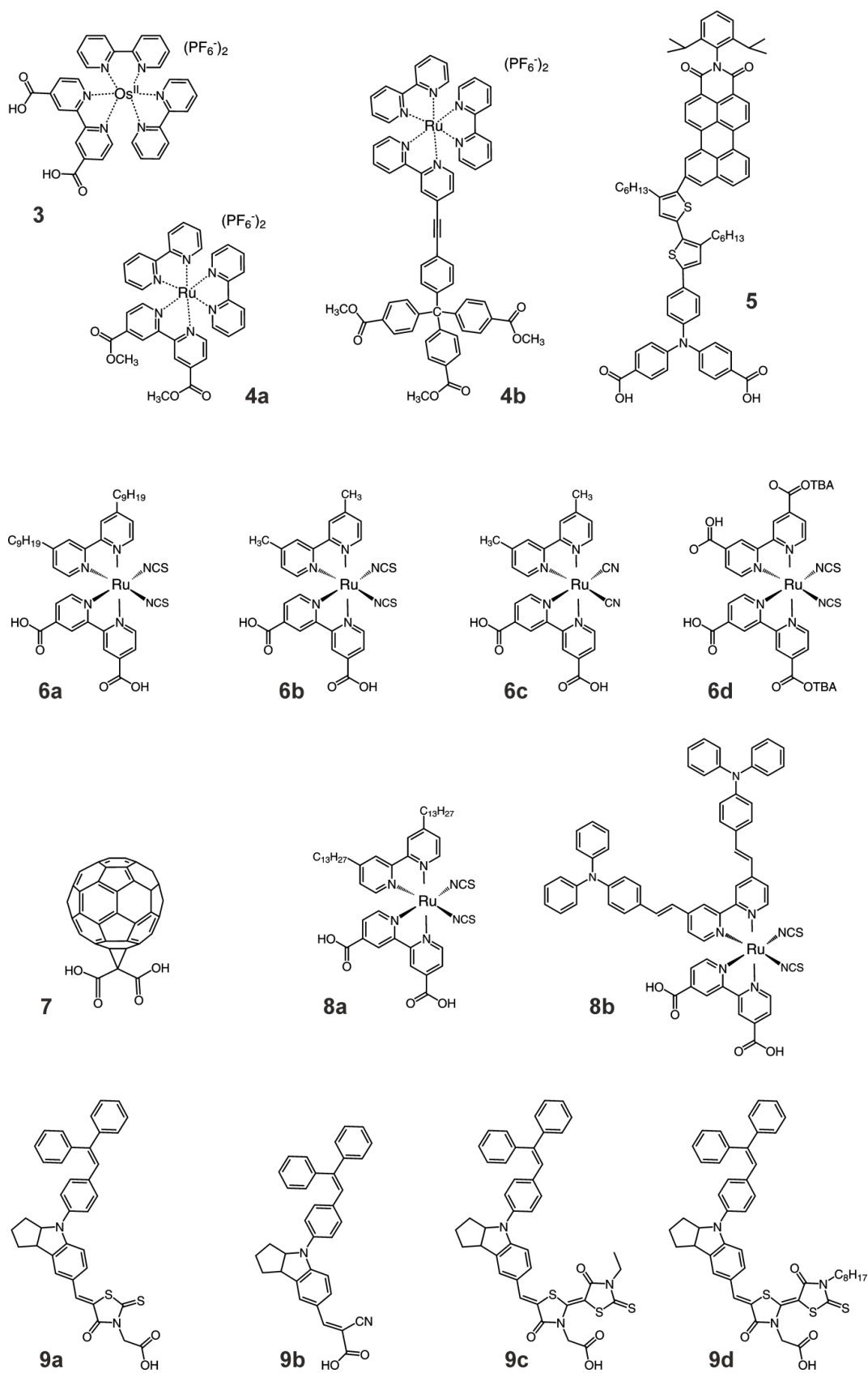


Figure 2.14. Chemical structure of the molecular sensitizers used in the studies described in this section.

Table 2.1. Experimental conditions, apparent diffusion coefficient (D_{app}) and percolation threshold (Γ_t) values reported by different studies on charge transport in molecular monolayers.

Molecule (Figure 2.14) and naocrystalline scaffold	Technique and experimental conditions	D_{app} (cm²s⁻¹) (charge carrier)	Γ_t	Ref
Phosphonated triarylamine (1)	Chronoabsorptometry in EMITFSI or EMITFSI in acn or MPN	$2 - 11 \cdot 10^{-7}$ (holes)	50%	[66]
[OsII(bpy)2(4,4'-(CO ₂ H) ₂ bpy)](PF ₆) ₂ On TiO ₂ (3)	Chronoabsorptometry in 0.1M TBAH:acn	$1.4 \cdot 10^{-9}$ (holes)	60%	[70]
RuIII/II(dcb)(bpy) ₂ on TiO ₂	Chronoamperometry in 0.1M LiClO ₄	$8 \cdot 10^{-9}$ (holes)	-	[71]
Ru(bpy) ₂ (Ad-tripod-phen) ²⁺ (4a, 4b)	Chronoabsorptometry in 0.1M TBAP	$\sim 10^{-11}$ (holes)	-	[71]
Fullerene derivatives on ZrO ₂ (7)	Chronocoulometry 1M Li ₂ NH in 1:1 EC:DMC 0.2M TBA-Tf	$\sim 10^{-8}$ (electrons)	50%	[72]
PMI-T2-TPA on TiO ₂ or on Al ₂ O ₃ (5)	Chronocoulometry in EMITFSI	$2.2 \cdot 10^{-8}$ (on TiO ₂) $3.5 \cdot 10^{-9}$ (on Al ₂ O ₃) (holes)	50%	[73]
Ruthenium 2,2'-bipyridyl-4,4'-dicarboxylic acid Complexes (6a-c)	Cyclic voltammetry in 0.1M EMITFSI in acn In EMITFSI Impedance spectroscopy in 0.1M TBAPF ₆ in acn	$2 - 11 \cdot 10^{-9}$ (holes)	50%	[24]
N621 HW456 on TiO ₂ (8a, 8b)	Cyclic voltammetry and chronoabsorptometry in 0.1M TBAP in acn	$2 - 5 \cdot 10^{-9}$ (N621) $4 \cdot 10^{-8}$ (HW456) (holes)	60%	[74]
N719 (6d)	Cyclic voltammetry in 0.1M TBAPF ₆ in acn	10^{-9} (holes)	-	[75]
D131, D102, D149, D205 on TiO ₂ (9a-d)	Cyclic voltammetry in 0.1M TBAPF ₆ in acn	$>10^{-5}$ (holes)	-	[76]

In a following study by Galoppini *et al.*, Meyer's group considered Ruthenium 2,2'-bipyridine complexes where different anchoring groups were included in the chemical structure of the dyes. Ru 4-4'-(COOH)₂-2,2-bipyridine was compared to analogous redox centers built on tripod-shaped anchoring structures (for example 4a and 4b). These were based on 1,3,5,7-tetraphenyladamantane and tetraphenylmethane connected to the ruthenium center via a phenylethynyl spacer. Chronoabsorptometry measurements gave values of apparent diffusion coefficient in the order of 10^{-11} cm²/s for all complexes anchored to nanocrystalline TiO₂, with and without the tripod anchoring group. Since surface coverage was comparable for the two cases, the authors suggested that distance from the surface of the redox centers does not have an effect on the rate of charge transfer. This also suggested that for this system the dynamics of ion adsorption/desorption on the surface of the electrode do not influence the migration of charges in the monolayer of dyes.^[77]

Investigation on the influence of ions on charge transfer between dyes has been carried out by Westermarck *et al.* by a combined approach of electrochemistry and photoelectrospectroscopy (PES).^[78] In their work, the same phosphonated triarylamine considered by Bonhôte in his pioneering paper (structure 1) was used to sensitize TiO₂ nanocrystalline films. Upon electrochemical oxidation of the dye monolayer in an inert electrolyte, the film was measured via PES to monitor variations in the binding energy of core electrons in the dyes due to their different oxidation state. Results were then compared with quantum chemical calculation of the optimized geometry for the neutral and oxidized states. These calculations highlighted a propeller like geometry for the triarylamine group where the phenyl groups are twisted out of the same plane by 50 and 40 degrees respectively for the neutral and oxidized form. Simulation of the cationic state of the molecule showed the localization of the positive hole in proximity of the Nitrogen atom. Experimentally, signals of the Nitrogen 1s orbital showed clear differences for the oxidized versus neutral population of dyes. The fraction of oxidized population could therefore be resolved. Values extracted from PES were found to be systematically lower than the ones predicted electrochemically, the latter being calculated by integrating the current measured during oxidation of the film in a chronoamperometry measurement. The mismatch was ascribed by the authors to X-ray photo-excited valence band electrons in the TiO₂ regenerating the oxidized state in the measured area. This argument was supported by the observation of color variation in the active area

exposed to the X-rays for PES measurement. Such area could be then re-oxidized electrochemically. The authors also investigated the effect of different counter ions on the fraction of electrochemically accessible dyes as well as on the rate of electron transfer. Lithium perchlorate (LiP) and Lithium triflate (LiT) salts were dissolved in anhydrous acetonitrile and used for electrochemical oxidation of the film. Due to charge compensation, one perchlorate or triflate counterion was expected to remain on the surface for each oxidized molecule. The regeneration effect described above was found to be localized and pronounced for the perchlorate case and to be slower and extend to larger area when using a triflate based salt. This was interpreted as a sign for better charge diffusion in the case of a bigger size counterion. The rational proposed was that when counterions have tendency and geometrical possibility to form strong ion pairs with the oxidized dyes, then packing within the monolayer is less favorable and charge hopping is hindered. Conversely, for the case of the bigger triflate anion, the monolayer is perturbed to a lesser extent and hole hopping is facilitated.

In 2002, Papageorgiou *et al.* reported electron transport, as opposed to hole transport, in molecular monolayers of derivatized fullerenes (see for example structure 7) sensitizing nanocrystals of Zirconium oxide. The experiments suggested that also for dyes with an electron acceptor character, intermolecular charge transport is possible. By scanning the electrochemical potential to negative values, and down to 2V vs Li, the functionalized electrode showed reversible behavior. Interpretation of the electrical signal as a single electron reaction led to the estimation of diffusion coefficients in the order of 10^{-8} cm²/s. In order to vary the amount of molecules adsorbed on the surface of the nanocrystal, different volumes of the same solution (0.2 mM concentration of fullerenes in tetrahydrofuran) was used. A percolation threshold was again observed when the loading of the film was estimated to be about 50% of the full coverage. The experiments were conducted in 0.2M tetrabutylammonium triflate in propylene carbonate or acetonitrile and 0.5M lithium imide in a 1:1 ethylene carbonate:dimethyl carbonate mixture. Surprisingly, the authors observed no significant difference in the electrochemical response of the functionalized electrodes when using these different electrolytes.

Further contribution from the Grätzel's group showed for the first time ambipolar n and p type charge transport in monolayers of a triad (PMI-T2-TPA) consisting of a triphenylamine donor, a perylenemonoimide acceptor connected

through a bithiophene bridge (structure 5). In their work, Wang *et al.* extracted apparent diffusion coefficients for hole and electron transport from spectroelectrochemistry measurements in EMITFSI of Al₂O₃ nanocrystalline films sensitized with PMI-T2-TPA. D_{app} for holes of $2.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ was estimated, whereas electrons showed about 20 times slower diffusion. The authors noted that corresponding values of charge self-exchange rate between the dyes are lower than the diffusion limited rate constant expected for the supporting electrolyte. Values of D_{app} obtained were therefore not limited by the diffusion of ions in the electrolyte. Confirmation of charge transport in the monolayer was presented by looking at the dependence of D_{app} on the concentration of redox sites in films where the inert linker HDMA was added to the dye solution. A percolation threshold around 70% surface coverage was observed for both electrons and holes.^[73]

Following this study, Wang *et al.* carried out a similar investigation on hole transport for ruthenium dyes more commonly used in dye sensitized solar cells (structures 6a-d).^[24] Particular focus was given to cis-Ru 2,2'-bipyridyl-4,4'-dicarboxylic acid 4,4'-dinonyl-2,2'-bipyridyl (NCS)₂ and cis-Ru 2,2'-bipyridyl-4,4'-dicarboxylic acid 4,4'-dimethyl-2,2'-bipyridyl (NCS)₂ which are referred to as Z907 and N820 respectively. When sensitizing TiO₂ nanocrystals and immersed in 0.1M EMITFSI dissolved in acetonitrile, these dyes showed holes apparent diffusion coefficients of 4×10^{-9} and $>10^{-8} \text{ cm}^2 \text{ s}^{-1}$ respectively. In this work, more detailed analysis of the dependence of D_{app} on the chemical structure of the dyes was conducted. Substitution of the NCS groups with CN groups in the structure of N820 led to a decrease in D_{app} by about one order of magnitude. Although the anchoring mechanism of the two versions of the dye on TiO₂ was expected to follow a similar scheme, the absence of the sulphur atoms was identified by the authors as the cause for lower molecular orbitals overlap between neighboring dyes on the surface. This translates to lower electronic coupling and transfer rate values. The central contribution of the NCS groups was emphasized using quantum chemical calculations that showed a clear localisation of the HOMO on these ligands for both N820 and Z907 dyes. ATR-FTIR spectra of the sensitized film before and after exposure to Hg²⁺ solution showed that the metal ions strongly interact with the NCS groups. This result was accompanied by an evident reduction in the electrochemical response of the dye monolayer which, according to the authors, corroborates the mediation of NCS groups in the charge exchange. The dye N3 was also

investigated. This compound showed low reversibility, no diffusion coefficient was reported. The complex is similar to N820 but presents carboxylic acid groups on both the bipyridine ligands. The anchoring mechanism of N3 is such that the two carboxylic acid groups which are in the trans position with respect to the NCS bind to the surface. The authors suggested that this anchoring scheme results in longer distance between NCS groups and less efficient charge transfer. Impedance spectroscopy was also presented by Wang *et al.* as a method to assess hole transport in these systems. A time constant was extracted from the impedance measurement of dye sensitized films using a model including a double channel transmission line. This represented diffusion of holes in the monolayer and ions in solution. The diffusion coefficient obtained by considering the film thickness as diffusion length matched the values extracted from cyclic voltammetry within a factor of 2.5.

Investigation of the effect of the dye chemical structure on the hole transport performance of ruthenium complexes was also carried out by Li *et al.* In their study two ruthenium dyes with NCS ligands were compared (structures 8a and 8b). Both dyes present two carboxylic acid groups on one bipyridine ligand. In addition, the dye N621 has two tridecyl chains attached to the second bipyridine ligand, whereas HW456 has two triphenylamin groups. Density functional theory (DFT) calculations showed that the HOMO of the neutral molecules is localized on the NCS ligands in both cases. However, when in the first oxidation state, the HOMO of HW456 is spread towards the triphenylamine groups. Spectroelectrochemistry measurements were performed on dye sensitized TiO₂ films and showed a percolation threshold around 60% of full coverage conditions for both dyes. The maximum dye loading of HW456 was found to be about half as high as for N621, due to the bulky donor groups. This could in principle lead to lower interaction between the dyes and lower electronic coupling. However, the extracted diffusion coefficient for HW456 was $2.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, about 20 times larger than the one recorded for N621. The authors attributed this result to different mechanisms of hole transfer between dyes. While for N621, hole hopping occurs through the NCS ligands, similar to the mechanism Wang *et al.* reported, HW456 relies on the interaction of the TPA groups to perform hole transport between redox centers. This hypothesis was confirmed by measuring hole transport in the presence of mercury ions, which are known to form complexes with NCS groups and hinder hole transfer when this is mediated by such group. The

observed hole diffusion was quenched for N621, whereas it was somewhat faster for the case of HW456.^[74]

Further contribution in the field came from Fattori *et al.* In their work, they reported investigations of the electrochemical properties of the ruthenium complexes N719, Z907 (structure 6d and 6a) and the indolene dyes D131, D102, D205 and D149 (structure 9a-d) sensitizing FTO or TiO₂ nanocrystalline films on FTO. When adsorbed onto FTO coated glass, half-life time of 288 ms was estimated for the oxidized state of N719. Cyclic voltammetry of the same dye adsorbed on TiO₂ showed low reversibility, consistent with a degradation process occurring to the dye when in the oxidized state. The authors suggested that degradation happening at the FTO surface could explain the inactivity of the film observed after a slow oxidation scan. This was corroborated by the almost unchanged optical absorption spectrum of the film after the measurement. Degradation of the N719 monolayer at the FTO/TiO₂ interface was also described as a potentially beneficial phenomenon for DSSC devices, in that it hinders the hole surface recombination with electrons at the cathode due to migration of holes within the monolayer.^[75] The electrochemical characterization of the dye Z907 anchored to FTO and TiO₂ nanocrystal was presented in a following study. Cyclic voltammetry of Z907 sensitized films showed similar chemical degradation for the oxidized dyes as described previously for N719. The kinetics of degradation of the dye anchored to FTO substrates was two orders of magnitude slower than for N719. The investigation of the electrochemical properties of indolene organic dyes sensitizing FTO or TiO₂ (9 nm diameter) nanoparticles was presented by Fattori and coworkers in a later study. When sensitizing FTO, multiple peaks were observed in cyclic voltammetry measurements for the dyes D102, D149, D205. These were ascribed to aggregation of the molecules on the surface, leading to repulsive interaction during the formation of neighboring cations. D131 showed a single peak, which was suggested to be due to the different structure of its anchoring group. When anchored to TiO₂, oxidation of the monolayer showed a single peak for all the dyes. The observed integrated charge extracted from cyclic voltammograms had limited dependence on the scan rate values. On this basis, the authors estimated the apparent diffusion coefficient to be beyond a lower limit of about $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. This represented the approximation for the diffusion coefficient needed to explain full oxidation of the (3 μm thick) dyed TiO₂ film within the time that it takes to span a voltage of kT/q . The absorption spectrum of D149 sensitizing TiO₂ films

compared to the spectrum of the dye in solution showed a red shift and broadening. Spectroelectrochemical measurements of the dye also showed a broad absorption window for the oxidized monolayer in the near infrared. The authors suggested these observations were strong indication for presence of J-aggregates.^[76]

2.3.3 Spectroscopic studies on inter-dye hole transport

Following the electrochemical studies presented in the previous section, strong evidence for hole transfer between dyes sensitizing the surface of TiO₂ nanocrystal was presented by Ardo and Meyer in 2010.^[28] Transient absorption anisotropy related to the Z907 cation signal was measured upon laser pulsed excitation. Strikingly, decay in anisotropy was observed. The decay showed a stretched character extending from the nanosecond to the millisecond timescale. The anisotropy profile was found to be similar when the sample was immersed in acetonitrile or in 0.1M LiClO₄ dissolved in acetonitrile. Different results were obtained when investigating the dye Ru(dcb)(dtb)₂ in these two environments (dcb is 4-4'-(COOH)₂-bpy and dtb is 4-4'-di-*tert*-butyl-bpy). The presence of ions was in this case necessary for the system to show hole transfer between dyes. The authors suggested that ions might be playing a role in decreasing the work term of charge transfer in charged compounds. On the other hand the measurement of N3 sensitized TiO₂ resulted in nearly constant anisotropy. The difference between these observations for Z907 and N3 were consistent with electrochemical measurements.^[24]

In a following study, the same authors used transient anisotropy spectroscopy to analyse both hole and energy transfer between dyes on different oxide nanocrystals.^[25] Once again, the first process occurred with a strongly stretched behavior (stretching parameter values were in the order of 0.15). Strikingly, for the same dye (Ru(dtb)₂(dcb)) adsorbed on TiO₂, the energy transfer anisotropy decay measured from photoluminescence showed monoexponential character. An average correlation time, defined as the mean relaxation time of the fitted stretched exponential function, was calculated for the two processes. Values of about 2-3 μs for energy transfer and 10-17 μs for hole transfer were found. The authors suggested that the measurement of different diffusion rates for the two different excited states is evidence for the molecules being immobile on the surface, ruling out the possibility that a major contribution to the anisotropy decay could come from surface diffusion

of loosely bound adsorbants. Moreover, negligible temperature dependence was reported for the energy transfer anisotropy decay.

Finally, Ardo and Meyer reported the first demonstration of hole diffusion used to transfer charges to a catalyst cosensitizing the surface of TiO_2 . The catalyst CoTCPP was coanchored to a Z907 sensitized TiO_2 nanocrystal. Upon excitation of Z907 and electron injection, a TAS signal ascribable to the oxidation of the catalyst was detected. This result opened the possibility of using conductive monolayers for accumulating charges on catalyst to drive reactions involving more than one electron, such as direct water splitting. Following a similar approach, Brennan *et al.* have used tetra-aryl porphyrin dyes to implement accumulation of holes on a hole traps on the surface of SnO_2 .^[29] From their results, an estimated charge transfer rate of $(25 \text{ ns})^{-1}$ was extracted, which is significantly faster than the value reported for the ruthenium dye Z907.

The electrochemical and spectroscopic studies discussed here showed that lateral transfer of photo-generated holes between dyes in monolayers sensitizing oxide semiconductors is possible and can happen at a remarkable rate. In order to understand the effect of this phenomenon on the functioning of dye based devices, other competing processes have to be considered. In the next section I give an overview on the other hole transfer phenomena occurring at dye sensitized interfaces that underlie the functioning of dye-based devices.

2.4 Hole transfer and recombination processes in dye sensitized TiO_2 based devices

In this section I present previous studies related to the dynamics of photo-generated holes in dye monolayers within dye sensitized devices. First, I discuss the parameters that are commonly considered to affect the recombination of photo-generated holes in the dye monolayer to electrons in the TiO_2 scaffold. Secondly, I present the current understanding of the parameters that enable efficient hole transfer between photo-oxidized dyes and the infiltrated solid state hole transporting material in solid state DSSCs.

2.4.1 Charge recombination in dye sensitized nanocrystals

The photogeneration of holes in dye sensitized semiconducting nanocrystals involves the injection of the excited electron in the inorganic scaffold which leaves

the hole on the photo-excited dye. Charge generation is followed by charge recombination, where the hole recombines with an electron in the oxide.

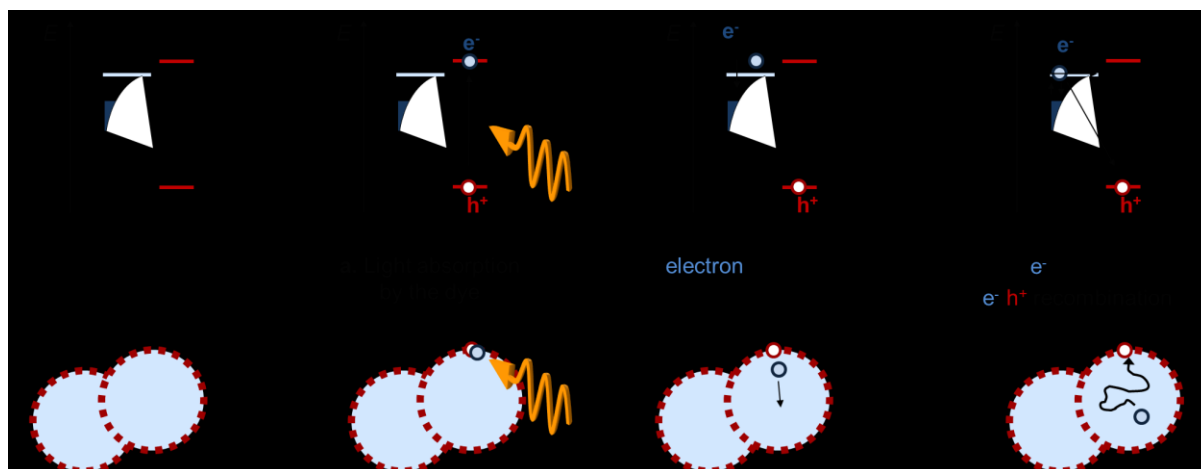


Figure 2.15. Charge generation and recombination in a dye sensitized TiO₂ nanocrystal. The simplified energy band diagrams show the HOMO and LUMO of the dye and the conduction band edge of the oxide semiconductor. It also shows the exponential density of trap states of the oxide lying below the conduction band.

Figure 2.15 describes these two processes. The energy band diagram shows the energy levels corresponding to the HOMO and the LUMO of the dye as well as the conduction band (CB) of the TiO₂. It also shows a qualitative density of states due to trap levels lying below the semiconductor CB. When performing a TAS experiment, it is possible to monitor these processes and to resolve their dynamics. This is true, provided that the different states of the dye (Dye, Dye*, Dye⁺) and the TiO₂ (TiO₂, TiO₂ + e⁻) have different spectral signatures. In most cases, dyes that are able to inject photo-excited electrons in the TiO₂ do so at very short timescales. This means that process a (Dye → Dye*) and b (Dye* → Dye⁺) occur within timescales which are fast to ultrafast and require femtosecond TAS measurements to be detected. In this thesis, process (c) is the focus of transient absorption experiments. Previous studies reported transient absorption spectroscopy measurements to investigate the relationship between electron transport in the TiO₂, dye chemical structure and surrounding environment on the electron hole recombination dynamics. Below I give an overview of some of these works.

Early study on the subject showed that photo-induced electron injection in TiO₂ from dye molecules and back electron transfer occur at remarkably different timescales.^{[79],[80],[81]} Injection was in fact observed to occur at timescales faster than

1 ps, whereas charge recombination happens with a stretched behavior which extends from nanoseconds up to tens of milliseconds.

Haque *et al.* investigated the correlation between the charge carrier concentration in the TiO₂ and the recombination rate to photo-oxidized dyes. By electrochemically controlling the position of the Fermi level in the nanocrystal between 0 and -500mV vs Ag/AgCl, the observed half lifetime ($t_{50\%}$) of the dye cation decreased by more than three orders of magnitude. Given that the position of the Fermi level in the experiment was expected to be >150mV below the estimated conduction band edge of the semiconductor, the authors suggested that holes on the dyes recombine to electrons occupying the intraband trap states in the TiO₂.^[82]

The Meyer's group showed that the electron hole recombination process in a dye sensitized TiO₂ system follows second order, equal concentration kinetics. This behavior would be expected if the generated charges are able to separate upon electron injection. The need for 2 second-order processes to describe the observed TAS decays was interpreted as a sign for interfacial heterogeneity.^[83] In a following study, Hasselmann and Meyer showed that the recombination kinetics was insensitive to the sensitizer molecular geometry, the metal (Re, Ru, or Os), the number of carboxylic groups and variations in driving force up to 960 meV. These observations were interpreted by the authors as sign for diffusion limited encounters of electrons and holes.

A possible mechanism for the electron-hole recombination was suggested by Nelson. To describe electron transport in TiO₂ a continuous-time random-walk (CTRW) model was used. Monte Carlo simulations were run considering an exponential density of trap states $g(E) \propto e^{\alpha(E_c - E)/kT}$, where α is a measure of the energetic disorder in the semiconductor and E_c the conduction band edge of the semiconductor. Each trap site could be occupied by one single electron and all traps were "filled" on the basis of the Fermi-Dirac distribution so that, for different positions of the Fermi level, the average depth of filled traps varied accordingly. The model envisaged trapping and thermally assisted detrapping of charge carriers. The waiting time associated to each trap was calculated based on its energetic depth. A waiting time distribution of the form $\psi(t) = \alpha \tau_{th} t^{-1-\alpha}$ is expected for an exponential density of states (where τ_{th} is the minimum detrapping time corresponding to states at energy $E = E_c$). The simulation of electron hole recombination in a dye sensitized TiO₂ film

produced a dispersive and Fermi level dependent recombination rate which was in good agreement with Haque's observations.^[84] In a later study, Nelson *et al.* showed that the CTRW model could reproduce the experimentally observed trend of the half lifetime as a function of electron density $t_{50\%} \propto n^{-1/\alpha}$. Importantly, this could not be explained by considering a homogeneous second order reaction model. Tunnelling of electrons between trap states or to the dye cation "target" was also considered as a possible regime for electron dye cation recombination. However the calculations showed that the tunnelling model could reproduce the experimental kinetics only for the high electron density case where the electron transfer reaction to the dye might be limiting the recombination rate. The shape of the experimental decays was instead not reproduced for the "slow recombination" cases.^[85]

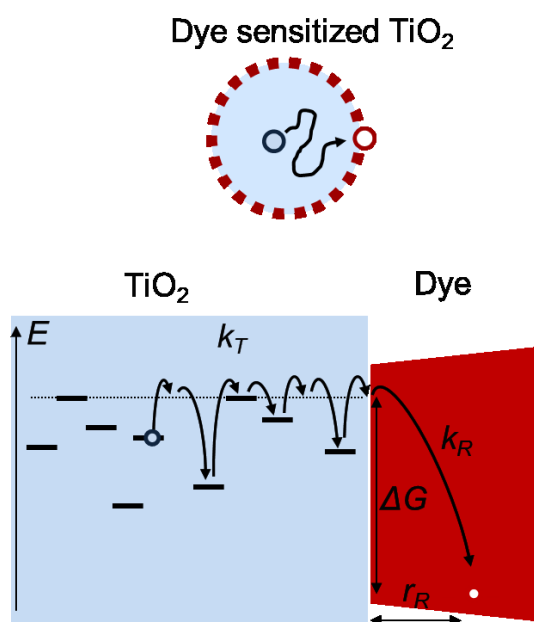


Figure 2.16. Transport-reaction model based on references ^{[84],[85],[86],[87]} to describe electron-dye cation recombination kinetics in dye sensitized nanocrystalline films.

Further studies on the different regimes of the electron hole recombination reaction were carried out by the Durrant's group. In their work, Clifford *et al.* considered dyes with diverse chemical structure sensitizing the surface of nanocrystalline TiO₂. The half lifetime $t_{50\%}$ and the stretching parameter α were obtained by fitting a stretched exponential to the recombination decay profile. These parameters were interpreted in terms of the free energy of electron hole recombination and the calculated spatial separation of the dye's HOMO from the TiO₂ surface extracted from semi-empirical calculations. Very little correlation

between $t_{50\%}$ and ΔG was observed. Conversely, $\log(t_{50\%})$ showed a linear dependence on r which suggested that the different kinetics of recombination for the different dyes could be ascribed to the contribution of (tunnelling mediated) electron transfer reaction at the interface. A tunnelling factor $\beta = 0.95 \text{ \AA}^{-1}$ was found from data collected for different dyes. This interpretation was supported by a clear correlation between the stretching parameter and $t_{50\%}$. Following the schematics shown in Figure 2.16, the observed recombination is limited by the electron transport properties of TiO_2 and by the electron transfer kinetics at the interface with the dye. When the two “rates” are very different, recombination can be described as either transport or reaction limited. In particular, the dispersive character of the decay can be compared to the TiO_2 trap distribution parameter to discriminate which regime is dominant for a particular dye TiO_2 system.^{[86],[87]} On the basis of the above model, Nelson and Chandler were able to extend the description of the electron hole recombination process to a multi-particle system to infer the interparticle transport properties of mesoporous TiO_2 . Experimental values of $t_{50\%}$ showed continuously increasing values even when the estimated number of photogenerated dye cations per particle was below 1. This suggested that facile interparticle transport of electrons occurs in mesoporous TiO_2 , as saturation of $t_{50\%}$ would be expected if the photogenerated electrons were not able to be transferred to neighboring particles at low pump intensity levels. CTRW simulations reproduced experimental data by parameterizing the necking between particles which, the authors noted, could be equivalently interpreted as interparticle barrier or scattering probability.^[88]

Modifications of the multiple trapping model have been suggested. For example, Barzykin and Tachiya presented a random flight model, where electrons were able to diffuse while occupying the inner part of a particle and were trapped at states localized on the surface of the particle. The model is in contrast with the evidence of small polaronic transport in TiO_2 , however similar shape of the electron hole recombination kinetic decay to the CTRW model were obtained.^[89] Bisquert presented a hopping model for electron transport in TiO_2 where electrons are allowed to hop between states lying below the conduction band edge using the Miller-Abrahams jump rate.^[90] At low charge density, this model is expected to give results similar to the CTRW approach.

Contribution to the understanding of electron dye cation recombination came from the Mori's group.^[91] The spectroscopic study carried out by Ogawa *et al.* raised

interesting observations on the kinetic of dye cation reduction. A comparison of dye chemical structures which differed only for the presence of alkyl side chains was drawn from TAS experiments. The slower kinetics of electron hole recombination observed for dyes with inert side groups was ascribed to a hindered hole diffusion in the monolayer. To support this argument, Ogawa *et al.* also showed slower kinetics for films sensitized with dyes and an inert coadsorbent (cheno deoxycholic acid) compared to the dye only case. As described previously, decreasing the dye loading of the film is an effective way to inhibit hole percolation in the monolayer. Analogous trends were obtained for two commonly used organic dyes.

Similar results were reported by Miguel *et al.* ^[92] In their study, electron-hole recombination in squarine based dyes sensitizing TiO₂ was found to undergo a slowdown by a factor of 2-3 upon coadsorption of DCA. In this case, the authors ascribed the variation in recombination rate to the different electronic coupling of high dye loading H-aggregated dyes to the electronic states of the TiO₂ traps/conduction band, compared to the low dye loading case. It is however not clear whether the difference in recombination rate in this work was evaluated at equal electron density conditions.

The study of electron hole recombination in these systems has provided insights into the electron transport and transfer reaction at the interface between dye molecules and TiO₂. In liquid junction DSSCs, this recombination process competes with dye regeneration, which involves hole transfer from the photo-oxidized dye to the redox couple. Dye regeneration has been demonstrated to occur at significantly faster rate than the electron hole back reaction discussed above. Such process is also believed to occur homogeneously within the pores of the dyed TiO₂, given the ability of the electrolyte to infiltrate in the pores. On the other hand, dye regeneration efficiency in solid state DSSCs has been subject of debate, given the observation of incomplete pore filling of the solid state HTM in the mesoporous film. An overview of previous studies on this issue and the potential of hole transport between dyes to optimize dye regeneration is given in the next section.

2.4.2 Previous evidence of inter-dye hopping in solid state DSSCs

The role of the HTM in a solid state DSSC is to effectively regenerate photo-oxidized dyes and to transport holes to the counter electrode of the solar cell. In Figure 2.17 shows some of the main hole transport materials which enabled the

fabrication of efficient solid state DSSCs. Figure 2.17 also shows the additives tert-Butylpyridine (tBP) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) which are normally processed on the dyed TiO₂ from the same solution as the HTM. The use of these additives in the HTM solution results in remarkable improvement in the device's performance. Their role in terms of HTM doping, TiO₂ conduction band shift and recombination blocking has been discussed in the literature and it is still subject of debate.^{[93],[94],[95],[96],[97],[98]}

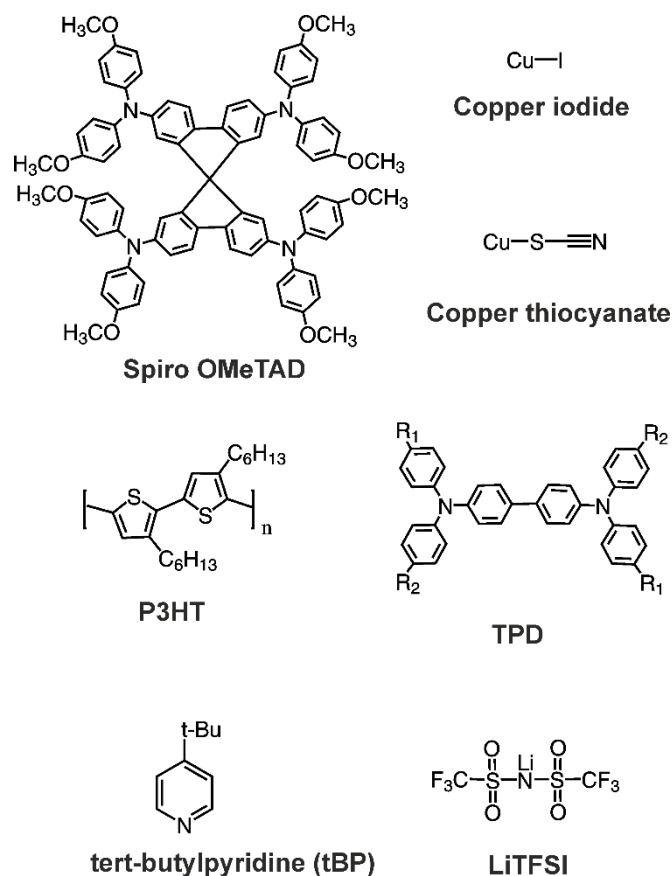


Figure 2.17. Chemical structure of some of the hole transport materials and additives used for the fabrication of solid state DSSCs.

Spiro OMeTAD is the most commonly used HTM in this class of devices. Solution processing of this small molecule results in films with low level of crystallinity. However, due to its high cost of production and its relatively low hole mobility ($\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), other HTMs have been subject of research. Inorganic p-type HTMs like CuI^[99] and CuSCN^[100] and semiconducting polymers like P3HT also proved to be suitable materials for fabricating solid state DSSCs, showing however lower performance than spiro OMeTAD.^{[101],[102]}

One of the requirements for a dye/HTM system to show efficient regeneration is the appropriate design of the energetics, in terms of the HOMOs of the two materials. For example, Haque *et al.* investigated the regeneration performance of N,N9-diphenyl-N,N9-(m-tolyl)-benzidine (TPD) based HTMs and spiro OMeTAD in mesostructures sensitized with different dyes using TAS. The results showed a trend in regeneration yield with respect to the driving force $\Delta G_{(\text{Dye-HTM})}$. The latter was calculated from electrochemical measurements of the HOMO energetic positions for the different compounds. Similar energetic inhomogeneity was found for all the systems investigated and was ascribed to fluctuations in the electrostatic environment.^[103] The results suggested that, due to disorder, a large $\Delta G_{(\text{Dye-HTM})}$ (> 0.2 eV) is necessary to obtain efficient regeneration.

A similar study was also reported by Weisspfennig *et al.* for a different set of HTMs. Spiro OMeTAD outperformed all the other HTMs studied in terms of solar cell device performance, even though it did not show the highest regeneration yield.^[104] The trend could not be explained in terms of difference in the pore filling performance as this was found to be similar for all the small molecular semiconductors tested. Kroeze *et al.* considered tri-aryl amine based polymers with different molecular weights. The measured regeneration yield under front or back illumination showed similar values and a slight decrease for HTMs with higher molecular weight.^[98] The values obtained were significantly lower than the one measured for spiro OMeTAD, even though more than 200 meV driving force was estimated for all HTMs from electrochemistry. The authors commented that the calculation of $\Delta G_{(\text{Dye-HTM})}$ may be inaccurate due to neglecting contributions from the electrostatic environment in the actual device. The short circuit current of full solid state DSSCs devices linearly correlated with the calculated regeneration yield, whereas no clear correlation was found with the hole mobility of the different HTMs.

The second central requirement for efficient regeneration is high coverage of the dye monolayer by the HTM. This enables efficient hole transfer from the dye monolayer to the HTM phase. Solution processing of the HTM on the mesostructure of TiO₂ generally results in limited infiltration of the pores. Specifically, the pore filling fraction is a quantity defined as the pore volume fraction occupied by the HTM. Pore filling and its effect on dye regeneration in solid state DSSCs has been subject of several studies.

In the earliest reports on dye regeneration in solid state DSSCs, Bach *et al.* reported femtosecond spectroscopy performed on N3 sensitized TiO₂ mesoporous films infiltrated with spiro OMeTAD.^{[17],[105]} The kinetics at 520 nm (where both the neutral dye and the HTM cation absorb) was found to be non-monoexponential. This was ascribed to non-perfect contact between the dye monolayer and the HTM phase. Hole hopping between dyes was suggested as an alternative route to regeneration.

Qualitative evaluation of the pore filling ability of different hole conductors has been carried out using SEM. This approach is however not sufficient to accurately resolve the dyed surface/HTM interface.^{[106],[107],[104],[108]}

O'Regan *et al.* presented the first quantitative analysis on the pore filling performance of HTMs in solid state DSSCs. In their work, copper thiocyanate (CuSCN, see Figure 2.17) was investigated for N3 sensitized TiO₂ mesoporous films. By measuring the weight of the device before and after the HTM deposition, knowing the volume and the porosity of the film, the pore filling fraction could be calculated. A value of 100±10% pore filling was found for 2 µm thick films. The pore filling dropped to 64% for 5.8 µm thick films.

Snaith *et al.* investigated the pore filling performance of spiro OMeTAD in K68 sensitized TiO₂ films. The pore filling fraction was calculated by comparing the thickness of a spiro OMeTAD film spin coated on the surface of a flat dyed TiO₂ compact layer and the thickness of the spiro OMeTAD capping layer formed upon spin coating of the HTM on top of the mesostructure. By assuming that a similar thickness of the wet layer is obtained in the two situations, the amount of HTM infiltrated in the pores could be estimated. A pore filling fraction of 0.6 was reached by optimizing the solution processing of the HTM in 6 µm thick films. Photoinduced absorption (PIA) was used to evaluate the regeneration performance of the devices. Difference in the PIA measurements performed under front and back illumination in 7 µm thick films suggested that the distribution of the hole conductor may be uneven along the depth of the film.^[109] Even distribution was instead expected for thinner films.

Olson *et al.* used PIA and UVvis spectroscopy to evaluate pore filling and dye regeneration in Z907 sensitized DSSCs using Spiro OMeTAD as HTM.^[110] A correction factor was suggested to account for viscosity in capillary infiltration when using Snaith's method to calculate the pore filling fraction. From the PIA

measurement at two different wavelengths, the authors presented a method to estimate the regeneration yield.

A further PIA study looking at the regeneration performance of spiro OMeTAD was reported by Cappel *et al.* The HTM was solution processed in ID28 sensitized 2 to 6 μm thick TiO_2 films.^[107] Spectra obtained for thicker films suggested that efficient regeneration occurs, as negligible trace of the oxidized dye spectrum was detected. Appropriate design of the HTM solution also resulted in indistinguishable PIA spectra when illuminating the samples from the glass or the spiro OMeTAD sides, suggesting uniform filling of the pores. The authors discussed the measured peak position of the cationic species as indication of pore filling performance. Peak shifts between spectroelectrochemistry and PIA measurements were rationalized in terms of distance between the holes in the HTM phase from the interface opening the possibility to assess the HTM morphology from the accurate deconvolution of PIA spectra.

Ding *et al.* used UVvis spectroscopy to quantify the pore filling fraction of spiro OMeTAD.^[111] By desorbing the HTM from the cell and quantifying its volume spectroscopically, the authors validated Snaith's approach for the calculation of the pore filling. Furthermore, the use of X-ray photoelectron spectroscopy (XPS) depth profilometry enabled to establish the depth profile of the HTM in the device. The results showed a flat signal for 5 μm thick films, suggesting uniform distribution of spiro OMeTAD along the depth of the device. This work was followed by a study from Melas-Kyriazi *et al.* who investigated the device performance of Z907 based solid state DSSCs as a function of pore filling.^[112] Dye regeneration by spiro OMeTAD was quantified using TAS and increased super-linearly for pore filling fractions increasing from 25 to 65%. Improved pore filling was also found to positively impact the ambipolar diffusion length of the carriers and the charge collection efficiency of the solar cells.

Docampo *et al.* introduced a non-destructive method to quantify pore filling in solid state DSSCs.^[113] By analysing the interference pattern in the reflectivity spectrum of the cell in the region where none of the components absorb, an effective refractive index can be extracted. This can be translated into a pore filling fraction, once all the refractive indices and volume fractions of the other components are known. The method was applied to D102 sensitized 2.6 μm thick TiO_2 films and to the HTM spiro OMeTAD. The authors showed that using HTM concentrations which

correspond to the formation of a HTM capping layer resulted in best performing devices. In particular, the short circuit current of the devices was found to saturate to a maximum value for pore filling fraction higher than about 60%.

Weisspfennig *et al.* carried out a study on dye regeneration as a function of pore filling for C106 sensitized 1.7 μm thick TiO_2 films infiltrated with spiro OMeTAD using TAS.^[114] In their work, pore filling fraction greater than 25% were sufficient to achieve 100% regeneration yield. Pore filling fractions ranging between 0 and about 65% were investigated. The short circuit current of solar cells increased monotonically with pore filling. The trend was fitted to a model of hole percolation in the HTM phase. This envisaged step-like improvements in photocurrent at pore filling values which corresponded to gradual completion of spiro OMeTAD monolayers as predicted by a Monte Carlo model. This work strongly suggested that collection efficiency of this class of devices is not limited by dye regeneration. In particular, the observed high value of regeneration yield at low pore filling suggested inter-dye assisted hole transfer to the HTM.

All of these and other studies allowed the identification of some of the critical parameters for optimizing pore filling and charge transfer at the dye/HTM interface in solid state DSSCs. Despite the improved understanding on the HTM infiltration ability, the pore filling fraction cannot be directly correlated to the dyed TiO_2 surface fraction covered by the HTM. The latter is the relevant figure of merit in regard to dye regeneration and has been discussed to a lesser extent in the literature.

Electrochemical studies of TiO_2 mesostructures sensitized with the dye D131 and infiltrated with the hole conductors spiro OMeTAD and P3HT showed that, when pore filling is increased, surface coverage also increases (Fang *et al.* unpublished). This study also suggested that, for 1.8 μm thick devices under optimized pore filling conditions, surface coverage does not reach 100%. This observation implies that, in optimized solid state DSSCs, a fraction of the dyes may not be in contact with the HTM phase. Therefore, under operating conditions, a significant fraction of holes are potentially trapped on dye molecules resulting in higher recombination and suboptimal charge collection efficiency. However, this is in contrast with the high regeneration yield of solid state DSSCs observed in some of the studies mentioned above. Some studies have already argued that hole hopping between dyes could happen in solid state devices and plays a role towards improved dye

regeneration.^{[19],[20],[21],[22]} However, to my knowledge, no experimental evidence for this has been reported to date.

2.5 Summary and open questions

Charge transport between dyes anchored to the surface of nanocrystalline oxides immersed in inert electrolytes has been suggested and demonstrated. Two experimental pieces of evidence for this phenomenon were presented in the literature based on: the electrochemical response of dye sensitized mesoporous oxide films fabricated on conductive substrates; the observation of transient absorption anisotropy decays upon polarized optical excitation of dyes anchored to oxide scaffolds that allow electron injection. Also, electrochemical methods enabled the measurement of the charge diffusion coefficient. Values of apparent diffusion coefficient between 10^{-11} to over $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ were reported. The key questions arising from these observations are:

- 1) What is the electron transfer regime relevant to the observation of charge transport in dye monolayers?
- 2) What is the limiting parameter to the rate of such transfer?
- 3) What is the role of the solvent and the ions on the charge diffusion?

Electrochemical studies have also shown the presence of a percolation threshold for charge transport in dye monolayers anchored to mesoporous oxides. Control of the dye loading has been attained using different techniques which enabled control on the coverage at the film scale. The following points are still to be addressed:

- 1) Can a percolation threshold be observed for charge diffusion at the particle scale?
- 2) Is it possible to infer information on nanoscale diffusion from previously demonstrated absorption anisotropy decays?
- 3) Is charge diffusion in the monolayer at the nanoscale influencing the recombination dynamics in dye sensitized systems?

Finally, hole transport between dyes was suggested to contribute to the photo-conversion efficiency of solid state DSSCs in order to explain the high regeneration yield observed at low pore filling of the dyed mesostructure by the HTM. However, experimental evidence for this has not been reported yet. Thus:

- 1) Can hole diffusion in dye monolayers occur in ambient conditions?

- 2) If so, what role does this phenomenon have on the dye regeneration performance of solid state DSSCs?
- 3) Would enhanced hole diffusion in the dye monolayer improve the efficiency of current DSSCs?

Chapter 3 Method

In this chapter I present the experimental details for the sample fabrication, techniques and equipment used in my work. These general details are applicable to a range of experiments presented in the following results chapters. Further specific details are provided where relevant in the corresponding chapters. I also present the method used to implement Monte Carlo simulations of transient absorption anisotropy.

3.1 Materials

Dyes: dye molecules widely applied in DSSCs and that present a diverse range of chemical structures (Figure 3.1) are examined in Chapter 4. The ruthenium bipyridine complexes Z907, N719 were chosen since they represent reference dyes in the field of DSSCs. The dye N820 was also considered to compare the effect of removing the long alkyl chains from the structure of Z907. Organic indoline dyes D131 and D149 have been successfully employed as sensitizers in DSSCs, especially in thinner film devices, on account of their high extinction coefficient. Phthalocyanines (Pc) represent another important family of organic semiconductors, used as sensitizers but also as absorber and hole transport materials in organic electronic devices.^[115] A series of zinc (TT-1) and ruthenium (TT-35, A2 and A5) phthalocyanines were investigated. TT-1^[116] and TT-35^[117] complexes share the same peripheral substitution pattern based on the presence of *tert*-butyl groups and the carboxy anchoring group directly attached to the Pc ring. In the case of ruthenium phthalocyanines A2 and A5,^[118] the anchoring group is on one of the axial pyridine ligands and is therefore orthogonal to the Pc plane, the other axial pyridine ligand is bearing an electron-donor group, namely triphenylamine (A2) and methoxy (A5). This set of Pc based complexes enables the assessment of different relative molecular orientations and different metal centers. The dye zinc protoporphyrin(IX) (ZnPP) was also tested since interest in porphyrin sensitizers has been increasing after high efficiency values for liquid DSSCs were achieved using a molecule from this class.^[119] Some of these molecules have been already studied as efficient hole transporters in dye sensitized systems.^{[24],[76],[120],[75]}

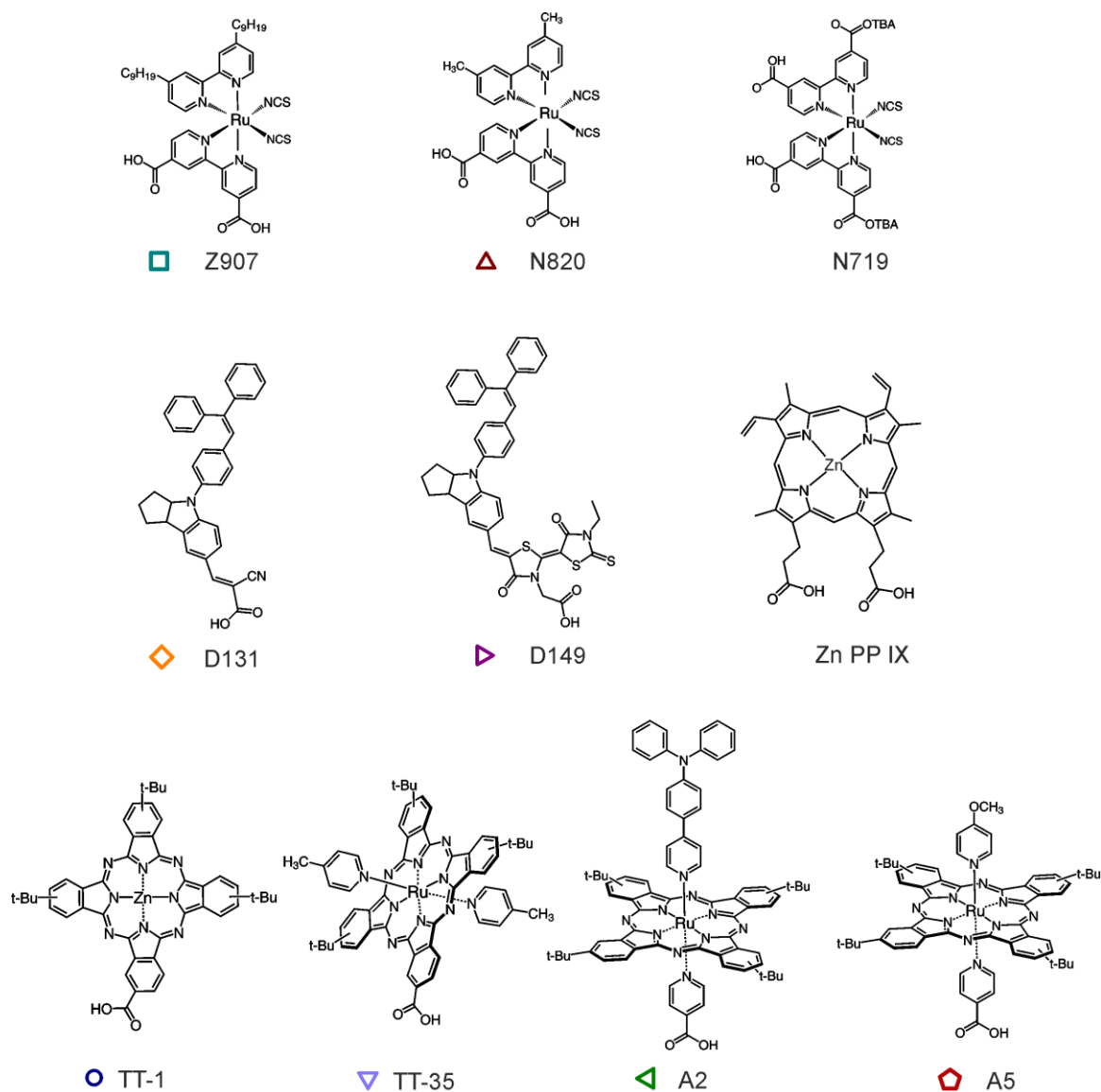


Figure 3.1. Structures of dye molecules investigated in this study. The symbols displayed below each structure are used to identify the dyes in Chapter 4.

TiO₂ pastes: the commercial TiO₂ paste DS 18NR-T was used in all experiments unless stated otherwise. In Chapter 5, some of the measurements were performed on films fabricated from the pastes DS 18NR-AO and DS 30NRD as specified in the text.

3.2 Sample preparation

3.2.1 Samples for electrochemical and spectroscopic measurements

The preparation of dye sensitized TiO_2 samples for electrochemical and spectroscopic characterization was carried out in the Chemistry department of Imperial College.

Substrate cleaning: microscope glass slides or conductive FTO glass slides (TEC-15, purchased from Pilkington) were used as substrates for the samples. The slides were cleaned with soap, rinsed with deionized water, acetone and isopropanol. They finally underwent a heating process at 450°C for 30 minutes.

TiO_2 compact layer spray pyrolysis (if applicable): a solution of 0.6 ml of titanium isopropoxide (from Sigma Aldrich) in 0.4 ml acetylacetone (Sigma Aldrich) and 9 ml of absolute ethanol were sprayed on the substrates, kept at 450°C . The spraying was carried out using a spray gun fed with compressed air. 4 phases of spraying separated by about 10 seconds were performed. 4 g of solutions were used when spraying over a surface of about 20 by 30 cm^2 . The substrates were then left sintering at the same temperature for 30 minutes. This resulted in the formation of a 50 to 100 nm thick TiO_2 compact layer.

Mesoporous TiO_2 film processing: TiO_2 paste was deposited on the FTO glass via doctor blading or spin coating. The films were sintered at 450°C for 30 minutes (10 minutes for the heating ramp) resulting in film thicknesses ranging between 2 and 7 μm . Samples were stored at 120°C and used within one day after sintering.

TiCl_4 treatment (if applicable): TiCl_4 treatment was carried out by immersing the samples in a 10.5 mg ml^{-1} titanium(IV) chloride tetrahydrofuran complex aqueous solution (Sigma Aldrich) for 30 minutes at 70°C , and by repeating a sintering step at 450°C for 30 minutes.

Dyeing: The dyeing process was performed at room temperature in the dark. The dye solution volume was high enough to guarantee limited variation in dye concentration in solution upon dye uptake on the mesostructured TiO_2 . The samples were immersed in dye solution directly from the oven where they were stored. After dyeing, the samples were rinsed for about 1 minute. The solvent used for rinsing was the same used for the dye solution.

3.2.2 Solid state dye sensitized solar cells

Solid state DSSCs have been fabricated following the method described in reference ^[94]. The device preparation was carried out in the Clarendon laboratory in the Physics department at Oxford University.

Substrate patterning and cleaning: FTO TEC15 substrates ($15 \Omega \text{ cm}^{-1}$ purchased from Pilkington) were patterned by etching with zinc powder and 2M HCl. The patterned substrates were washed with Hellmanex (2% in deionized water), deionized water, acetone and ethanol. This was followed by a 10 min oxygen plasma cleaning step to remove organic residues.

TiO₂ compact layer spray pyrolysis: a compact TiO₂ layer (between 50 and 100 nm) was deposited via spray pyrolysis at 300°C from a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt % in isopropanol) diluted at 10 vol % in ethanol. The spray gun used was fed with compressed air.

Mesoporous TiO₂ film processing: mesoporous TiO₂ films were deposited via screen printing. Dyesol 18NR-T paste was used. The TiO₂ films were heated to 450°C (temperature ramp over 2 hours) and sintered for 30 minutes in air.

TiCl₄ treatment: TiCl₄ treatment was carried out by immersing the samples in 0.015 M TiCl₄ aqueous solution for 45 minutes at 70°C, and by repeating a sintering step at 450°C for 45 minutes. The substrates were then cooled down to 70°C before immersion in dye solutions.

Hole transporting material (HTM) processing: the solution for the HTM deposition was prepared by dissolving spiro OMeTAD in chlorobenzene at different concentrations (between 5 and 136 mg/ml) at 70°C for about 20 minutes. The additives tert-butyl pyridine (tBP) and LiTFSI were added to the solution at concentrations of 65.5 mM and 23.3 mM respectively (the latter was predissolved in acetonitrile at a concentration of 170 mg ml⁻¹). Concentration of the additives was kept constant unless stated otherwise for different spiro OMeTAD concentrations in order to obtain similar conditions on the surface of the TiO₂. To be noted LiTFSI is involved in the doping of spiro OMeTAD. This process is expected to occur to a different extent for different spiro concentrations. The solution was deposited on the dyed film and spread to ensure it covered the entire surface of the sample. The substrate was then spun at 1000 rpm for 30 seconds and at 2000 rpm for 5 seconds.

150 nm of Silver was then deposited via thermal evaporation to form the counter electrode on the complete solar cells.

3.3 Characterization techniques

3.3.1 Dye loading measurement

The average volume concentration of dye molecules (c_0) attached to the TiO_2 mesoporous films upon sensitization was determined as follows. In Chapter 4 UV-vis measurements were performed on the films after sensitization. In some cases, measurements of the UV-vis spectrum of the known amount of solution used to sensitize the film before and after the dyeing process were performed.

In order to quantify the dye loading of the samples in Chapter 5 and Chapter 6, D131 dyes were desorbed from the surface of the TiO_2 by immersing the films in a known volume of 0.5 mM tetramethylammonium hydroxide (TMAOH) solution in acetonitrile. Given the volume of the TiO_2 film and the extinction coefficient of D131 in 0.5 mM TMAOH in acetonitrile, the concentration of dyes c_0 in the film was evaluated by measuring the absorbance of the resulting solution. In these chapters I refer to dye loading as the TiO_2 surface fraction covered with dyes. The dye loading was calculated by dividing c_0 by the maximum value of c_0 measured for each experiment. Note that this quantification of fractional coverage is not a robust one. In particular, it would be inaccurate in the presence of dye aggregates which could potentially form more than one layer on the surface of the TiO_2 .

3.3.2 Cyclic voltammetry

Cyclic voltammetry (CV) measurements were performed using a three-electrode cell. The FTO/dyed- TiO_2 films were used as the working electrode, a silver wire as the quasi reference electrode and a platinum electrode as counter electrode. The electrolyte composition was 0.1 molar tetra-butylammonium perchlorate (TBAP) dissolved in acetonitrile for all experiments in this thesis unless stated otherwise. The solvent was bubbled with nitrogen gas for 20 minutes before the experiment and a flow of nitrogen was kept flowing on the electrolyte throughout the experiment for the results shown in Chapter 4. Nitrogen was not used for the electrochemical analysis reported in Chapter 5.

For temperature dependent measurements a fresh sample was used for each (CV) scan to avoid uncertainty due to the degradation of films between scans. The electrochemical cell was immersed in an acetone bath where dry ice was added to vary its temperature between 230K and 300K (the freezing point of acetonitrile is 228K). The temperature inside the cell was measured by means of a thermocouple inserted in the cell through a sealed glass capillary which was dipped in the electrolyte solution. The accuracy in the temperature determination was expected to be within 1K from calibration measurements using a low temperature thermometer and a second thermocouple directly inserted in the solution.

3.3.3 Spectroelectrochemistry

In some experiments electrochemical measurements, performed as described above, were coupled with simultaneous optical UV-vis transmission measurements (see Figure 2.9). These were implemented by focusing a probe beam from a halogen lamp through the sample onto an optical fiber coupled to an Ocean Optics spectrometer. A quartz cuvette was used as the electrochemical cell.

3.3.4 Transient absorption spectroscopy

Transient spectroscopy was carried out using an extension of the setup described in reference ^[121]. A Nd:YAG pumped OPO (Opotek Opolette 355) was used as pump with wavelength 450 nm for D131 samples. Repetition rates between 10 Hz and 20Hz were used. Fluence was kept between 6 and 10 $\mu\text{J cm}^{-2}$. Samples were placed perpendicularly to the pump beam, which was directed from the laser output through a beam-guide, and slightly offset (about 30°) with respect to the main optical axis defined by the probe beam. A 100W quartz halogen lamp (Bentham IL1) driven by constant current power supply (Bentham 605) was used as probe light source in the system. Neutral density and long pass filters were used to attenuate the intensity of the probe and to limit its spectral range to wavelengths above the absorption window of the dye. After the sample, the probe beam was passed through a monochromator where the probe wavelength was selected before reaching an infrared detector. The electrical signal from the detector was amplified via a Costronics preamplifier and amplifier and recorded with an oscilloscope (Tektronix TDS 1012). The amplifier also measured the background level which was used to calculate the variation in optical density upon laser excitation, ΔOD , using the

formula $\Delta OD(t) = -\log_{10}(1 + V(t)/V_{BG}) \approx -V(t)/(V_{BG} \cdot 2.3)$ where $V(t)$ is the transient signal and V_{BG} the background level.

For all the measurements presented in this thesis a baseline $V_o(t)$ was subtracted from the measured voltage $V_{meas}(t)$ to obtain $V(t)$ before the calculation of $\Delta OD(t)$. $V_o(t)$ was measured using the same setup and by blocking the probe beam. Any contribution to photoluminescence from the sample and/or electronic interference is assumed to be corrected for under these conditions. In all cases, the measured $V_o(t)$ had the same profile to within the noise as a measurement taken while blocking the detector. This implies that only contribution from electromagnetic interference due to the laser pulsing affected the measurement. The level of $V = 0$ was then calculated by considering the average value of the calculated $V_{meas}(t) - V_o(t)$ for $t < 0$. In Figure 3.2 I show an example of this baseline correction for a D131 sensitized TiO_2 film immersed in 0.1M TBAP in acetonitrile.

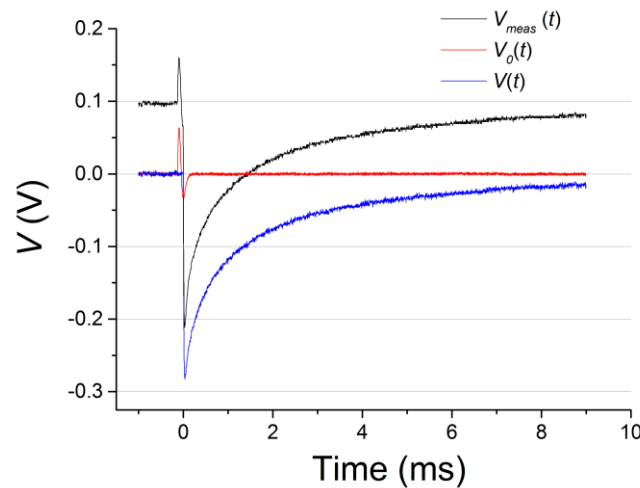


Figure 3.2. Baseline correction performed for transient absorption measurements. The voltage signal used to calculate ΔOD is obtained from the subtraction of the signal obtained when blocking the probe beam from the pump probe measurement. $V = 0$ level is then calculated by subtracting the average value of the resulting signal for $t < 0$.

Changes in the transient absorption signal were detected while the dye sensitized sample was measured for long times. In Figure 3.3 I show the changes in $\Delta OD(t)$ for 4 measurements taken during a 3 hours measurement of the sample continuously excited with a 10 Hz repetition rate $\sim 3 \mu\text{J cm}^{-2}$ fluence excitation at 450 nm. Decrease in the absorbance of the sample was also observed after the

measurement, consistent with the presence of degradation pathways of the photo-oxidized dyes.

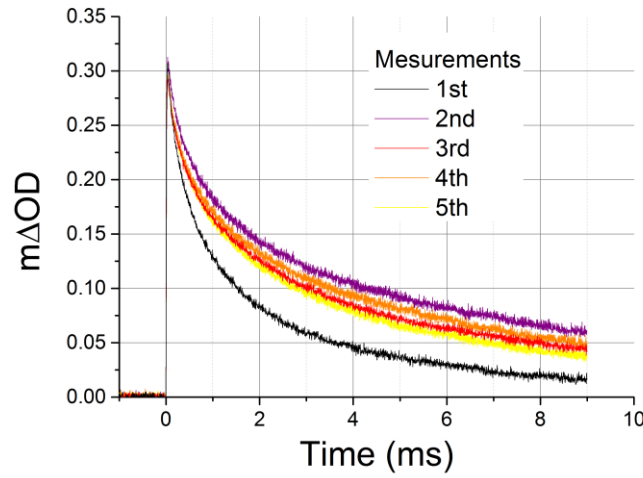


Figure 3.3. Changes in $\Delta OD(t)$ during a transient absorption spectroscopy experiment on a D131 sensitized TiO_2 film in 0.1M TBAP:acetonitrile. The measurements were taken about every hour.

3.3.5 Transient absorption anisotropy

For transient absorption anisotropy measurements, a similar setup to the one described above was used. The sample was placed at 45° with respect to the probe beam. The pump beam was passed through a Glan-Thompson polarizer (GTH10M-A from Thorlabs) before hitting the sample. The polarization of the pump was kept vertical with respect to the plane of the optical table and it was pointed towards the sample perpendicularly to the probe beam. A second polarizer (LPVIS050 from Thorlabs) was mounted before the monochromator to probe the vertical or horizontal polarization (parallel or perpendicular to the pump beam's polarization) of the transient optical signal transmitted through the sample or to measure the transient signal at the Magic angle ($\approx 54.7^\circ$). ΔOD was calculated as above for all conditions.

The transient anisotropy $r(t)$ was calculated from the measurements under vertical and horizontal polarization of the probe beam ($\Delta OD_V(t)$ and $\Delta OD_H(t)$) as:^[64]

$$r(t) = \frac{\Delta OD_V(t) - \Delta OD_H(t)}{\Delta OD_V(t) + 2\Delta OD_H(t)} \quad \text{Eq. 3.1}$$

For all the anisotropy measurements shown in this thesis, ΔOD_V has been calculated as the average of a measurement taken before the measurement of ΔOD_H and one taken after, to approximately compensate for any degradation of the

film. The ratio of the amplitudes for the two ΔOD_V measurements was >0.9 for most measurements. Laser pulse repetition rates ranging between 10 and 20 Hz have been used in this work. In those cases where incomplete relaxation of the excited states was observed within the time between pulses, the calculated anisotropy may be affected by the signal referring to residual population of charges generated by previous pulses. The analysis of the data at timescales that are sufficiently shorter than the time between pulses should give meaningful information on the variations of absorption anisotropy in the system.

3.3.6 Electrical bias dependent spectroscopy

Transient absorption and transient anisotropy spectroscopy were also carried out under controlled bias of the samples in an electrochemical cell. The cell was sealed and the electrolyte was flushed with argon for 20 minutes before the beginning of the measurements. The flow of argon was left blowing on top of the solution during all measurements to guarantee oxygen free environment. This was done to prevent electrochemically induced or photo-generated electrons to react with oxygen. The dyed TiO_2 sample was used as working electrode in a three electrode configuration similarly to the electrochemical setup described in section 3.3.2. A silver wire was used as quasi reference electrode. Its potential was measured before and after measuring every sample versus an Ag/AgCl reference electrode.

Spectroscopy measurements were carried out while applying different potential values at the working electrode as also carried out by Haque *et al.* (see reference ^[82]). For each trace, starting from a potential of 0.2V vs silver wire quasi reference electrode, the working electrode was switched to the desired potential (between 0V and -0.5V vs silver wire). The TAS measurement was performed under these conditions. The working electrode was then switched back to 0.2V at the end of the TAS measurement. The electron density in the film (n) was calculated by integrating the measured current density from the last of the three steps. The measured signal is expected to be related to the electron density in the TiO_2 during the TAS measurement. A non-zero current was recorded even after long time, suggesting a faradaic component due to electrons exchanged with the electrolyte. The reported values of charge density refer to the integrated current over a constant period of 60 seconds. The current density value at 60 seconds was subtracted to compensate for the baseline faradaic current. The potential of the silver wire was

measured before and after each measurement. Fluctuations of its potential up to 0.25V were recorder before and after an experiment. Cyclic voltammetry was also performed on the samples before and after the transient absorption measurements.

3.3.7 Electrical and photovoltaic characterization of solar cells

j-V measurements: current voltage measurements under solar-simulated AM 1.5 sunlight were performed using an ABET solar simulator calibrated to give 100 mW cm⁻², an NREL-calibrated KG5 filtered silicon reference cell and a sourcemeter (Keithley 2400, USA) for the electrical measurement. *I-V* curves were measured at a scan rate of 0.15 V s⁻¹ starting with a forward scan (increasing voltage) followed by a reverse scan.

IPCE measurements: the IPCE of solar cells was measured by illuminating the samples with a chopped monochromatic light (frequency 2 Hz). A background bias light was applied using light emitting diodes at an equivalent solar irradiance of 10% sun unless stated otherwise. For solar cells with semitransparent metal contact the measurement was performed by exposing either the FTO glass side or the metal side of the solar cells to the light sources.

Devices were masked with aperture of 0.09 cm² for all optoelectronic measurements. All measurements of *j-V* and IPCE were carried out in air.

3.3.8 Other thin film characterization techniques

Thickness measurements: the thickness of thin films was measured using a profilometer. An Alphastep profilometer was used in Chapter 4 and Chapter 5, while a Dektak profilometer was used in Chapter 6 and Chapter 7. All thickness measurements reported are calculated as average of at least three measurements taken on films scratched using metal tweezers.

UV-vis absorption: UV-visible measurements were performed using a Thermo Genesys 10 UV-vis spectrophotometer. The UV-vis spectrometer measures the specular optical transmission defined as the ratio between the specular transmitted light intensity *I* and the incident light intensity *I*₀, $T_{opt} = I/I_0$. T_{opt} is resolved as a function of wavelength. The optical absorbance spectrum *A* is calculated from T_{opt} as $A = -\log_{10} T_{opt}$.

Contact angle: contact angle measurements were carried out using a Krüss DSA 100 under ambient conditions. The solvent or the solution was dispensed on

the substrate under investigation and images of the drop were recorded using a camera. The drop was left for about 10 seconds on the substrate to allow stabilization of its shape. The value of the contact angle was then taken over the time before significant evaporation took place.

3.4 Calculations

Calculations were performed to simulate the transport of charge and polarization state between dyes anchored to nanoparticles during transient anisotropy measurements. Modified versions of codes written by Valérie Vaissier^[122] and Anna Szumska were used. The codes included functions written by Florian Steiner.

3.4.1 Random walk

Random walk calculations were run considering sites arranged in a square lattice. 6 square spaces of 20×20 sites were used to map the surface of a $20 \times 20 \times 20$ cube, representing a simplified single TiO_2 particle. Hopping between 8 nearest neighboring sites was considered, therefore allowing diagonal charge transfer steps. Waiting time between hops was calculated using an adaptive time step defined as:

$$t_{wait} = -\frac{\ln(R)}{\sum_i \Gamma_i}, \quad \text{Eq. 3.2}$$

where R is a random number between 0 and 1 and Γ_i is the Marcus rate calculated between the occupied site and its i -th neighbor. The value of the electronic coupling (J) was either kept constant or drawn from a gaussian distribution for each pair of sites before running the random walk and kept constant throughout the simulation. The gaussian distribution was defined for $\log(J)$ as first order approximation to the fluctuations in inter-site distances between dyes. The value of reorganization energy was kept constant for all pairs. Energetic disorder was considered by drawing energy values for each site at the beginning of the simulation from a gaussian distribution. ΔG_0 related to each charge transfer was calculated for each pair as the difference between site energies. When surface coverage < 1 was considered, the sites were randomly populated using a defined number of dyes and the charge was allowed to hop only on occupied sites.

3.4.2 Transient absorption anisotropy simulations

Before each random walk experiment, the system (cube) was rotated randomly in the 3D space to model the isotropic orientation of TiO_2 particles in mesoporous films. To simulate the photo-excitation of a dye, a facet was selected on the basis of the relative orientation of the normal vector to the facet and a vector with constant orientation representing the incoming polarized light (referred to as vertical). The probabilities of exciting a dye on a given facet was proportional to the square of the scalar product of the facet's normal vector and a unity norm excitation vector. This model assumes that the transition dipole moments of all dyes in the neutral and cationic state are oriented perpendicularly to the surface of the TiO_2 . When averaged over many runs, these conditions result in an initial anisotropy value of $r(0) = 0.4$. When running the random walk experiment, the orientation of the charged molecule's dipole moment was recorded in terms of the square of its projection onto two axes, one parallel and one perpendicular to the excitation orientation. The lifetime of the charges τ_{RW} was kept constant. The experiments yielded profiles of ΔOD_V and ΔOD_H between $t = 0$ and $t = \tau_{RW}$. The two profiles were averaged over all experiments and the results were used to calculate the simulated anisotropy decay according to Eq. 3.1.

Chapter 4 The reorganization energy of hole hopping between dyes anchored to surfaces

In this chapter¹ the use of cyclic voltammetry to measure diffusion of holes in monolayers of dyes on TiO₂ nanocrystalline films immersed in inert electrolytes is discussed. This method is extended to temperature dependent measurements. The data are analysed in terms of non-adiabatic Marcus theory of charge transfer. This enables the estimation of the reorganization energy of hole transfer and of an effective electronic coupling for dyes commonly used in the field of dye sensitized solar cells.

4.1 Introduction

Non-adiabatic Marcus theory is commonly used to express the charge transfer rate, Γ , between a weakly coupled electron donor and electron acceptor as a function of the electronic coupling, J , the reorganization energy, λ , and the difference in free energy between the equilibrium states of products and reactants, ΔG_0 . In the background section its formulation has been discussed.

In the particular case of a self-exchange reaction, such as hole hopping between two identical dye molecules anchored to a surface, $\Delta G_0 = 0$ can be assumed so long as the system shows negligible energetic disorder. Then:

$$\Gamma = \frac{2\pi}{\hbar} \frac{|J|^2}{\sqrt{4\pi\lambda k_B T}} e^{-\frac{\lambda}{4k_B T}} \quad \text{Eq. 4.1}$$

The reorganization energy λ is a measure of the energetic cost of rearranging the molecules' conformation and the surrounding medium upon the charge transfer step. Electrochemistry as well as transient absorption spectroscopy and Raman spectroscopy have been employed to experimentally determine λ for non-adiabatic charge transfer processes.^{[123],[124],[125],[126],[127]} In these studies, heterogeneous charge transfer between an electrode and molecules either in solution or anchored to the electrode surface and homogeneous charge transfer reactions between

¹ Moia, D. *et al. Chem. Sci.* 2014, 5, 281. Reproduced in part by permission of The Royal Society of Chemistry (see Appendix B)

molecules in solution have been considered. To my knowledge, no measurement of λ for charge transfer between dyes anchored to a surface has previously been reported.

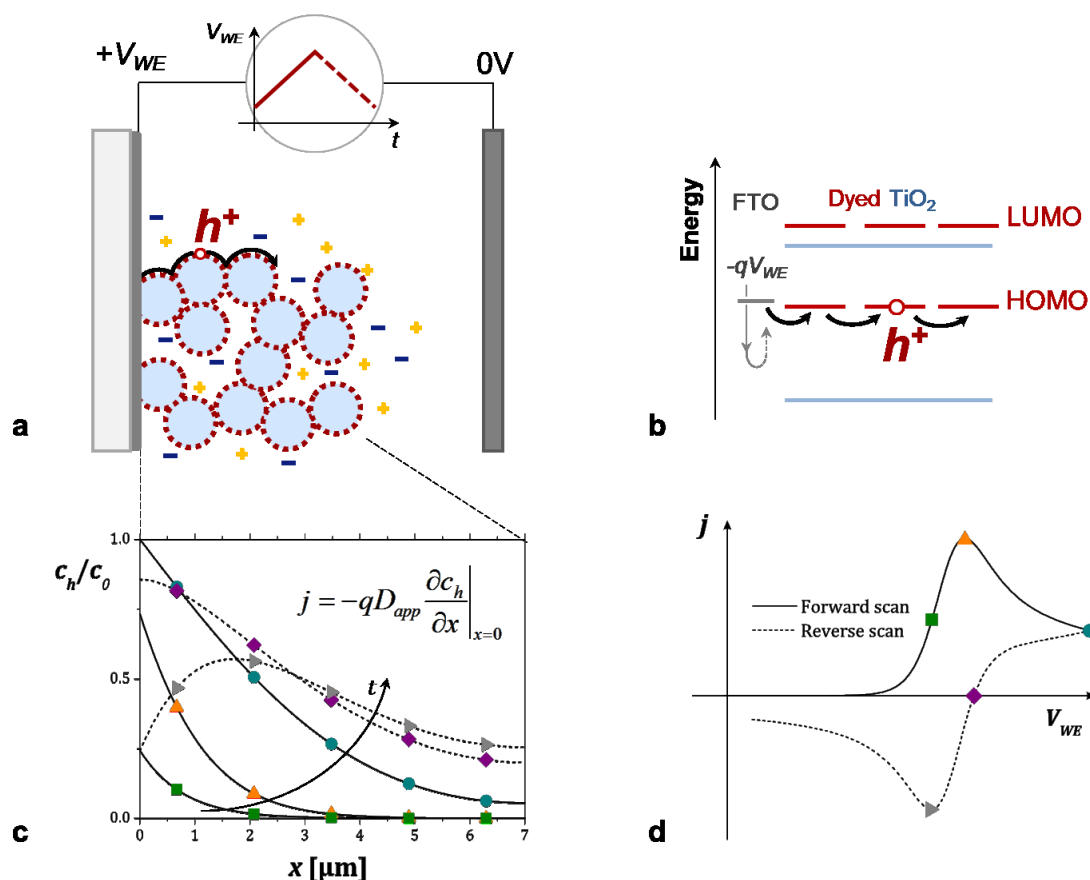


Figure 4.1. (a, b) Cyclic voltammetry measurement of dye sensitized titanium dioxide mesoporous films on FTO in an inert electrolyte. When the positive voltage ramp (V_{WE}) is applied to the sample (working electrode of the electrochemical cell), holes injected from the FTO electrode in the HOMO level of the dyes travel across the dye sensitized surface. (c) Fraction of oxidized dyes in the film (concentration of holes, c_h , divided by the total concentration of dyes, c_0) as a function of position in the film. c_h varies throughout the forward (solid lines) and the reverse (dashed lines) voltage scans following Fick's diffusion equation. The boundary conditions are set by the potential V_{WE} at the FTO electrode and the finite thickness of the film. (d) The current density j flowing across the dyes during the cyclic voltammogram is related to the gradient of c_h at the FTO/dyed-TiO₂ interface.

In the case of transport between dyes anchored to a surface, the rate Γ of intermolecular charge transfer between dyes is expected to be related to the apparent diffusion coefficient D_{app} of holes hopping across the surface of a dye sensitized film. An estimate of D_{app} can be obtained from electrochemical measurements such as cyclic voltammetry of the films (see Figure 4.1).^[24] Thus, by examining the dependence of D_{app} on temperature for a monolayer of dyes, Eq. 4.1

can be used to derive estimates for λ for thermally activated diffusion of holes across monolayers. The values of λ can then be compared to those that were obtained using computational methods by Vaissier *et al.*^[128]

The method presented here can be applied to any redox active molecule, whose oxidized state is stable within the timescale of the measurement. The molecule also needs to be able to chemically anchor to a surface.

4.2 Method

Materials: the dyes illustrated in section 3.1 have been investigated. TiO₂ has been used as scaffold for the formation of dye monolayers since it does not participate in the hole hopping process. Note that other inert insulating materials can be used.^{[66],[27]}

Sample fabrication: mesoporous TiO₂ films were fabricated following the method described in section 3.2.1. The dyeing process was performed at room temperature in the conditions described in Table 4.1. The last column represents the dyes volume concentration on the TiO₂ film after dyeing (dye loading).

Table 4.1. Dyeing conditions for the materials investigated in this work. Solvents acronyms correspond to: acetonitrile (ACN), tert-butyl alcohol (TBA), dichloromethane (DCM), ethanol (EtOH) and dimethyl sulfoxide (DMSO).

Dye	Solvent	Concentration (mM)	Dyeing time (hrs)	c_0 (10^{19} cm^{-3})
Z907	ACN:TBA 1:1	0.3	20	9.1 ± 1.4
N820	ACN:TBA 1:1	0.3	20	9.6 ± 1.5
N719	ACN:TBA 1:1	0.3	20	6.6 ± 1.2
D131	ACN:TBA 1:1	0.1	3.5	8.8 ± 1.4
D149	ACN:TBA 1:1	0.06	3.5	6.6 ± 1.0
ZnPP	DMSO	0.3	20	4.2 ± 0.7
TT-1	EtOH	0.1	20	13 ± 2
TT-35	DCM	0.1	20	4.4 ± 0.7
A2	DCM	0.1	20	7.0 ± 1.1
A5	DCM	0.1	20	2.7 ± 0.4

Dye loading measurement: quantification of the dye loading c_0 was performed as described in section 3.3.1. The intermolecular distance a was calculated from the value of c_0 . For this estimate, I considered the surface area of rigid spherical TiO₂ particles with radius of 10 nm occupying 40% of the mesoporous film volume and

assumed dyes arranged in a square periodic lattice. The inferred values of a for the dyes investigated are in the range between 1 and 2 nm.

Experimental setup: temperature dependent cyclic voltammetry (CV) measurements were performed using a three-electrode cell as described in section 3.3.2.

4.3 Determining the charge diffusion coefficient with cyclic voltammetry

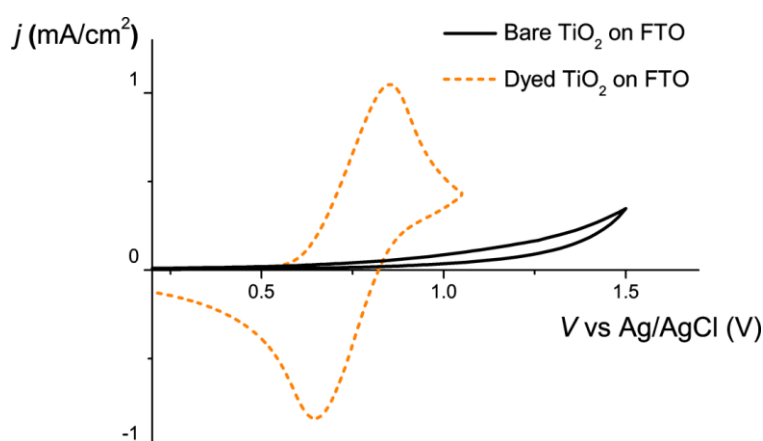


Figure 4.2. Cyclic voltammetry performed on a A2 dye sensitized TiO_2 mesoporous film deposited on FTO coated glass in 0.1M TBAP in acetonitrile. The control measurement performed on a bare TiO_2 film is also shown.

In Figure 4.2 the cyclic voltammogram of an A2 dye sensitized TiO_2 film is shown. A corresponding voltammogram of an unsensitized TiO_2 film is also shown. The voltage range spanned by the scan lies within the band gap of TiO_2 , well below its conduction band. Under these conditions the unsensitized TiO_2 behaves like an insulator. The low current density that is observed may be related to the oxidation of impurities at the FTO electrolyte interface. In contrast, when dye molecules are anchored to the TiO_2 film's surface, a significant redox response is recorded. The value of the integrated current density from the beginning of the scan up to the positive peak is in the order of 1 mC cm^{-2} (in this case at 0.1 V s^{-1} scan rate). Considering the dye loading and the thickness of the film (respectively about $7 \cdot 10^{19} \text{ cm}^{-3}$ and $7 \text{ }\mu\text{m}$), this suggests that the oxidation extends to about 10% of the molecules in the film when the current peak is reached. This result is interpreted in terms of holes hopping from dye to dye, screened by the counter-ions in the

electrolyte. The surface of the TiO₂ nanocrystals is therefore charged and discharged by the diffusion of holes from and to the FTO substrate.

4.3.1 The semi-infinite slab approximation

The apparent diffusion coefficient of holes diffusing in the monolayer of dyes can be estimated by rearranging the Randles-Sevcik equation presented in section 2.2.2.

$$D_{app} = 5.02 \frac{k_B T j_p^2}{q^3 c_0^2 \nu} . \quad \text{Eq. 4.2}$$

This equation is commonly used for cyclic voltammetry performed in solution and it is consistent with a semi-infinite 1D diffusion problem. Hole diffusion in dye monolayers can be described by a similar model where an additional boundary condition given by the finite thickness of the film is introduced:

$$\left\{ \begin{array}{l} \frac{\partial c_h(x, t)}{\partial t} = D_{app} \frac{\partial^2 c_h(x, t)}{\partial x^2} \\ c_h(0, t) = \frac{c_0}{1 + e^{\frac{q(E_0 - E(t))}{k_B T}}} \\ E(t) = E(t=0) + \nu \cdot t \\ \frac{\partial c_h(d, t)}{\partial x} = 0 \\ c_h(x, 0) = \frac{c_0}{1 + e^{\frac{q(E_0 - E(t=0))}{k_B T}}} \end{array} \right. . \quad \text{Eq. 4.3}$$

In the model, c_h is the hole concentration, c_0 is the dye concentration, E is the chemical potential at the FTO/dyed TiO₂ interface, E_0 is the formal oxidation potential of the dyes, d is the film thickness, ν is the scan rate, x is the distance from the FTO/dyed TiO₂ interface and t is time. The semi-infinite slab approximation is a reasonable treatment of the problem as far as the approximated distance travelled by the holes, L_p , calculated as $L_p = (D_{app} t_d)^{1/2}$ remains lower than the film thickness d . The term t_d can be considered as the time that the measurement takes to reach the current peak from the oxidation onset. L_p is an overestimate of the depth at which

the holes have substantially diffused to during the time t_d . Given the thickness d of the films under investigation, this condition sets a constraint on the minimum scan rate that can be used in the experiments since, as the scan rate reduces, t_d increases.

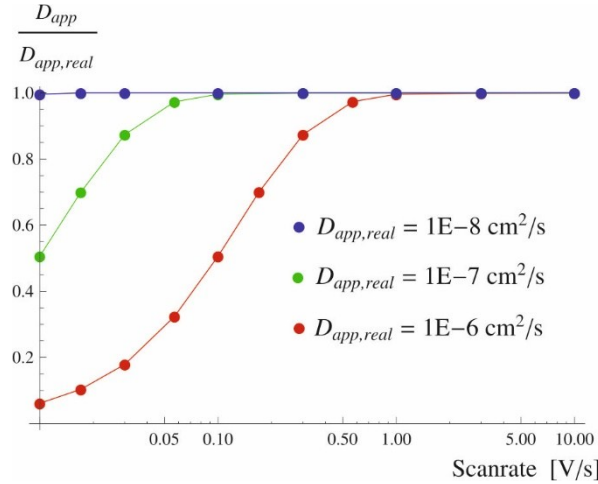


Figure 4.3. The ratio of estimated to actual D_{app} function of scan rate is shown for three different values of the actual apparent diffusion coefficient $D_{app,real}$. The data refer to the numerical solution of Eq. 4.3 for 7 μm thick films and to the case of no series resistance.

Figure 4.3 shows a comparison between the values of D_{app} and the actual apparent diffusion coefficients, $D_{app,real}$. $D_{app,real}$ correspond to the values used to find the solution $c_h(x,t)$ to the numerical version of the model expressed in Eq. 4.3 (considering a value of film thickness of $d = 7 \mu\text{m}$ and for a range of scan rates). D_{app} is calculated from substituting the peak current density resulting from the numerical solution in Eq. 4.2 (assuming the semi-infinite to hold true). Values for the scan rates between 0.1 and 1.5 V s^{-1} were adopted in this study, depending on the dye and the consequent value of D_{app} expected. Thus, under these experimental conditions, and calculating $j_p = I_p/A$, where I_p is the measured peak current and A is the projected area of the TiO_2 film, the value of D_{app} can be extracted from the cyclic voltammetry measurement using Eq. 4.2. The validity of this method is supported by the linear dependence of the measured j_p on $v^{1/2}$ for cyclic voltammograms performed on dye sensitized TiO_2 films (see Figure 4.4).

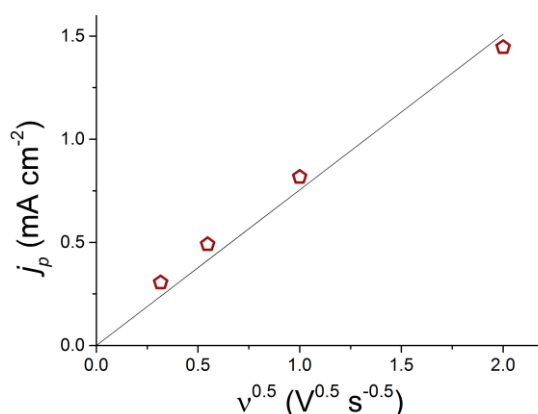


Figure 4.4. Current density peak plotted against the square root of scan rate for cyclic voltammograms performed on A5 sensitized TiO_2 films on FTO in 0.1M TBAP in acetonitrile.

4.3.2 Accounting for series resistance

Considering the design of a typical electrochemical cell, some parasitic resistances can be identified. In Figure 4.5, R_{sub} indicates the resistance due to the FTO layer (light blue) connecting the dyed TiO_2 film (red area) to the electrical contact between sample and the potentiostat lead (V_c). Resistances due to the electrolyte between the working and reference electrodes, $R_{e,1}$, and the reference and counter electrodes, $R_{e,2}$, are also illustrated. The relevant resistance for this analysis is $R_s = R_{sub} + R_{e,1}$ since it represents the resistance between the electrodes where the voltage is applied by the potentiostat. The capacitor $C_{d/e}$ represents the simplest model for the interface between the dyes and the electrolyte (a double channel transmission line would be more appropriate).

One of the signs of significant series resistance effect is the increase in the potential difference between the positive and the negative current peaks position of the CV measurement. In the case of diffusion in a semi-infinite system, no series resistance and for reversible reactions, this value approaches 59 mV at 25°C at any scan rate conditions, whereas it is higher than 59 mV when the voltage drop on R_s is playing a limiting role. This results in distortion of the shape of the CV measurement due to the variation of the scan rate actually applied to the electrode.

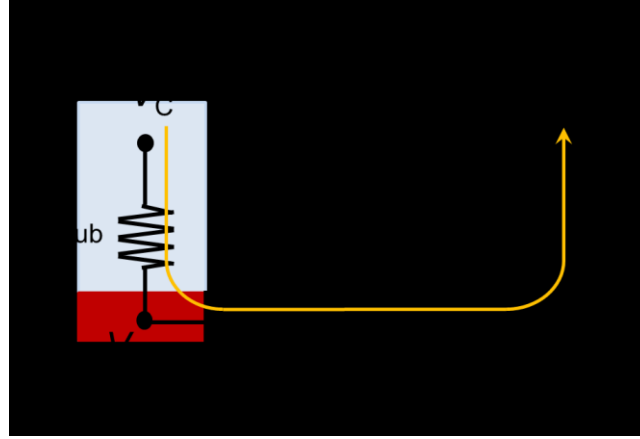


Figure 4.5. Schematics of a simplified equivalent electrical circuit representing the relevant electrical components in a three electrode cell.

When studying the diffusion problem with the model described in Eq. 4.3, one should use the time dependent scan rate to define the chemical potential at $x = 0$. Thus the boundary condition describing $E(t)$ in equation S2.1 becomes:

$$E(t) = E(t = 0) + \nu \cdot t - R_s I(t), \quad \text{Eq. 4.4}$$

where the effective scan rate ν_{eff} , defined as the derivative of $E(t)$ with respect to t , is now a function of time. By applying this correction, it is possible to draw a better interpretation of a measured CV curve.

In Figure 4.6, the CV measurement of an A2 dye sensitized film is fitted with the model Eq. 4.3 corrected for the effects of series resistance according to Eq. 4.4. The calculation of D_{app} from the current peak of the experimental data with Eq. 4.3 would give in this case $1.6 \cdot 10^{-8} \text{ cm}^2/\text{s}$, whereas the fit returns $2.2 \cdot 10^{-8} \text{ cm}^2/\text{s}$. Figure 4.6 also shows what the CV curve would look like if there were no series resistance limitations (i.e. with $R_s = 0$ and $D_{\text{app}} = 2.2 \cdot 10^{-8} \text{ cm}^2/\text{s}$). In this case Eq. 4.3 returns the same value of D_{app} that was set for the simulation. Despite the good quality of the fit in the example of Figure 4.6, several CV curves measured showed a broader peak than the numerical solution.

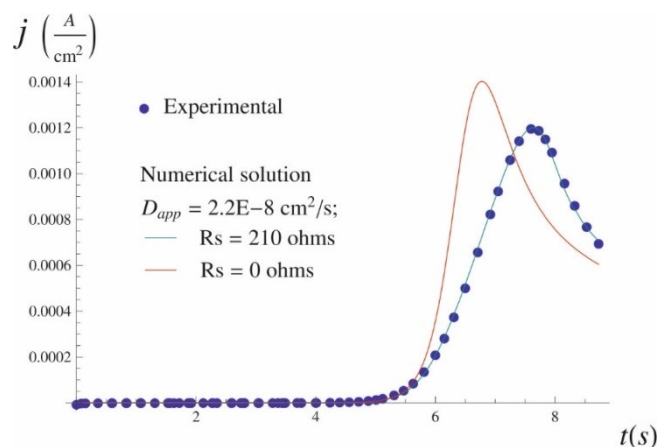


Figure 4.6. The experimental cyclic voltammogram performed on A2 dye sensitized TiO₂ film is compared to the calculated solution. By including the effect of series resistance it is possible to describe the shape of the current density function of time with the one dimensional diffusion model expressed in Eq. 4.3. The numerical solution for the same system without the effect of series resistance is also shown.

Notably, other effects can be playing a role in the determination of the shape of the CV profile. In particular limitations in terms of the interfacial kinetics can produce similar effects as described for the series resistance. Electron transfer from dyes to the FTO substrate is assumed to be fast enough to guarantee the equilibrium boundary condition at the interface. This may not be true for high scan rates. An overpotential would then be needed to drive the electron flux at the interface. This can be estimated on the basis of the Butler-Volmer equation.^[129] Linearization of this equation in proximity of the origin can be used to include the effect of the kinetics at the interface in terms of series resistance. Moreover, dyes anchored to the FTO may act as ion blocking layer. When scanning the potential at the FTO electrode, the Fermi level of the first monolayer of dyes may not shift accordingly. This could be expected if ions were to screen the potential variations only after the first monolayer of dyes. Hole injection from and to this monolayer would therefore contribute to limit the measured current.

4.3.3 Ambipolar diffusion

The diffusion phenomenon described in the previous section is an ambipolar diffusion process. This is because charges in the electrolyte must be rearranged to maintain local charge neutrality as holes diffuse across the TiO₂ surface. For this reason, Eq. 4.2 is only valid under the assumption that the transport of the holes is a more limiting factor than the transport of ions in the surrounding electrolyte. The

diffusion coefficient used in Eq. 4.2 refers in general to an ambipolar diffusion coefficient D_{amb} , which is related to the holes apparent diffusion coefficient D_{app} through the following equation:

$$D_{amb} = \frac{c_h + c_i}{\frac{c_h}{D_i} + \frac{c_i}{D_{app}}} . \quad \text{Eq. 4.5}$$

According to this relation, the value of the diffusion coefficient measured in cyclic voltammetry D_{amb} is between the values D_{app} and the diffusion coefficient of the ions in solution (D_i). In particular, D_{amb} varies depending on the concentration of the ions c_i , given a certain hole concentration c_h . A slightly different formulation of D_{amb} when considering the different dimensionalities of the monolayer and the electrolyte may be expected.

Measurements of the molar conductivity of the electrolyte composition used in this study were performed to calculate D_i . This quantity varies as a function of ionic concentration. A correct characterization of the parameters c_i and D_i goes beyond the scope of this study. Here, I suggest a method to analyse this problem on a first order approximation by assuming that the system can be described by considering two extreme situations. If the electrolyte conductivity is described by a "viscosity model" then D_i depends on the electrolyte viscosity, which increases with ionic concentration c_i , and all ions are assumed active. The measured conductivity of the electrolyte, G , can be then related to the diffusion coefficient D_i , by:

$$G = \frac{q^2 c_i D_i}{kT} , \quad \text{Eq. 4.6}$$

where in this case, c_i is the concentration of all ions in solution.

Alternatively, if using an "ion pairing" model, one can consider the ions diffusing with D_i equal to D_0 , which is the diffusion coefficient at infinite dilution conditions. To explain the drop in molar conductivity, the effective concentration of active ions must be less than the total ionic concentration. In this model, fitting molar conductivity (G_m) data (see Figure 4.7a) measured at low ionic concentrations with Kohlrausch's law (Eq. 4.7) enables the extraction of the molar conductivity at infinite dilution condition $G_{m,0}$.^[130]

$$G_m = G_{m,0} - \kappa c_i^{0.5} . \quad \text{Eq. 4.7}$$

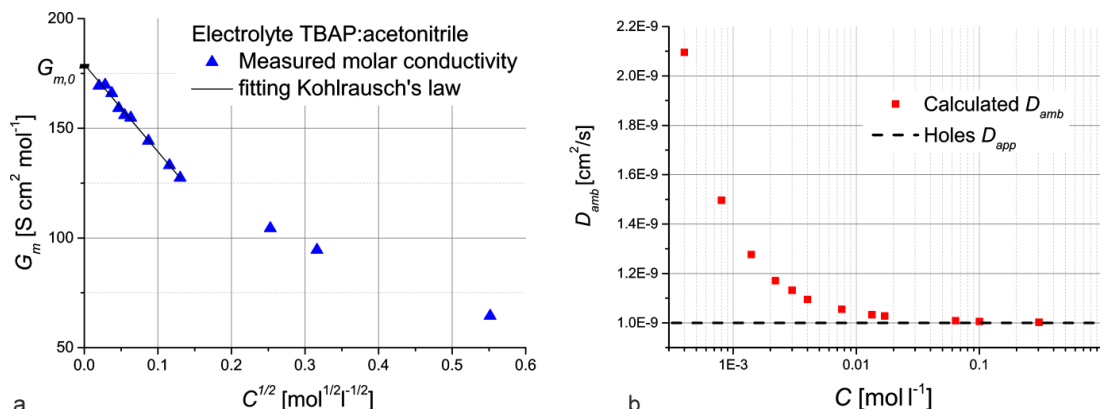


Figure 4.7. Molar conductivity of TBAP in acetonitrile (a) and estimated ambipolar diffusion coefficient (b) as a function of electrolyte concentration. When sufficiently high concentration values are used, D_{amb} shows a plateau at the value of D_{app} (in the right graph $D_{app} = 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $c_h = 10^{20} \text{ cm}^{-3}$).

From the value of $G_{m,0}$, which is indicated as the intercept of the linear fit in Figure 4.7a, the diffusion coefficient of the ions at infinite dilution condition can be calculated as $D_0 = G_{m,0} kT/q^2$. The effective concentration of active ions c_i at a certain concentration is then calculated by rearranging Eq. 4.6, given the measured conductivity of the electrolyte G and considering $D_i = D_0$.

Since acetonitrile gives rise to strong electrolyte solutions, the two models give very similar results. However, the "ion pairing" model gives an overestimate of the difference between D_{amb} and D_{app} . For this reason it is good to adopt it to keep a more conservative approach, especially in case of less polar solvent which may show significant difference between the two estimates. The use of 0.1 M as reference concentration results in accurate determination of D_{app} . In Figure 4.7b, the measurement of the molar conductivity of TBAP in acetonitrile at 22°C and a reference value of $10^{-9} \text{ cm}^2/\text{s}$ for D_{app} are considered as example. Given a maximum acceptable error for the determination of D_{app} from the measurement of D_{amb} , a constraint on the minimum molarity of the electrolyte is thus set through these considerations.

4.3.4 The effect of site blocking on diffusion

Only a single hole is assumed to reside at each molecular site on the surface lattice. The occupancy of the sites on the surface is given by $\theta = c_h/c_0$. Thus a region of the surface in which most of the dyes are oxidized (high lattice occupancy by

holes) could potentially reduce the rate of diffusion of subsequent holes in this region. This effect may be expected to result in a dependence of D_{app} on θ or c_h .

Below it is shown that site occupancy does *not* influence the measured value of D_{app} , so that the experimental values presented later in this chapter should be directly relatable to inter-molecular hole hopping frequency without worrying about the effects of site blocking. To demonstrate this, the discussion of diffusion in a Langmuir lattice described by Bisquert is followed.^[131] On a surface lattice the mean effective jump frequency of a hole, Γ , is reduced by increasing site occupancy, θ , because an attempted hopping event is only successful if the destination site is not blocked:

$$\Gamma(\theta) = (1 - \theta)\Gamma(0). \quad \text{Eq. 4.8}$$

This results in an occupancy dependent jump, or tracer, diffusion coefficient for the movement of an individual hole on the surface:

$$D_t(\theta) = (1 - \theta)D_t(0). \quad \text{Eq. 4.9}$$

However the jump diffusion coefficient, $D_t(\theta)$, does not represent the coefficient of the concentration gradient resulting in a flux of holes across the surface according to Fick's law: *hole flux* = $-D_{ch} dc_h/dx$. I will refer to this coefficient, D_{ch} , as the chemical diffusion coefficient. $D_t(\theta)$ and D_{ch} are related by a thermodynamic factor, χ_T :

$$D_{ch} = \chi_T D_t(\theta). \quad \text{Eq. 4.10}$$

The thermodynamic factor parameterizes the effects of a statistical average of many individual hole diffusion currents in the presence of other holes. This factor can be defined in terms of the chemical potential of the holes, E , by:^[132]

$$\chi_T = \frac{qc_h}{kT} \frac{\partial E}{\partial c_h} = \frac{q\theta}{kT} \frac{\partial E}{\partial \theta}. \quad \text{Eq. 4.11}$$

The chemical potential for the holes on the surface lattice is given by Fermi-Dirac statistics:

$$E = E_0 + \frac{kT}{q} \ln[\theta/(1 - \theta)]. \quad \text{Eq. 4.12}$$

so that:

$$\frac{\partial E}{\partial \theta} = \frac{kT}{q\theta(1-\theta)}. \quad \text{Eq. 4.13}$$

Substituting this expression into the expression for χ_T gives:

$$\chi_T = \frac{1}{1-\theta}. \quad \text{Eq. 4.14}$$

This results in the chemical diffusion coefficient being independent of the lattice occupancy:

$$D_{ch} = \frac{1}{1-\theta}(1-\theta)D_t(0) = D_t(0). \quad \text{Eq. 4.15}$$

Thus the chemical diffusion is equal to the low concentration limit of the jump diffusion coefficient, $D_t(0)$, and directly related to the jump frequency between molecules with no site blocking, $\Gamma(0)$. Experimentally, the apparent diffusion coefficient, D_{app} , is inferred from CV measurements using Fick's laws. This is because the observed current is assumed to be proportional to the hole concentration gradient. Thus D_{app} is directly connected to the chemical diffusion coefficient for holes on the surface as described previously.^[128]

4.3.5 The relation between D_{app} and the charge transfer rate

In the simple case of an isotropic arrangement of the dyes on the surface of the TiO_2 with constant intermolecular distance a , the relationship describing the 2D chemical diffusion D_{ch} and the charge transfer rate (at low site occupancy) can be expressed as:^[128]

$$D_{ch} = \frac{\Gamma(0)a^2}{4}. \quad \text{Eq. 4.16}$$

The measured apparent diffusion coefficient can be related to the 2D diffusion coefficient using the relationship:

$$D_{app} = \alpha_g D_{ch}. \quad \text{Eq. 4.17}$$

The factor α_g converts diffusion in two dimensions to diffusion in an interconnected network of three dimensional 2D surfaces, i.e. the layer of molecules coating the interconnected nanocrystals. α_g is equal to 2/3 when the arrangement of

the surfaces in the film corresponds to a dimensionality of 3. A lower value of this prefactor can be expected when considering the film geometry contribution in terms of the constrictivity, tortuosity of the surfaces, as well as incomplete connectivity between dyes on the surface.^[133]

The value of a calculated from dye loading measurements represents an average to the distribution of intermolecular distances of the disordered monolayer of dyes. The description of D_{app} at the nanoscale can be rephrased by considering the effective jump frequency of the holes that, in an isotropic and ordered lattice would result in an analogous observed apparent diffusion coefficient:

$$D_{app} = \alpha_g \frac{\Gamma_{eff} a^2}{4}, \quad \text{Eq. 4.18}$$

where Γ_{eff} is an effective charge transfer rate.

Considering the range of values of D_{app} ($10^{-8} - 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) and a ($0.7 - 1.5 \text{ nm}$) for the dyes investigated in this work (see next chapter), effective charge transfer rates in the order of $(1 \mu\text{s})^{-1}$ to $(10 \text{ ns})^{-1}$ are expected.

4.4 Measurement of reorganization energy

4.4.1 Results

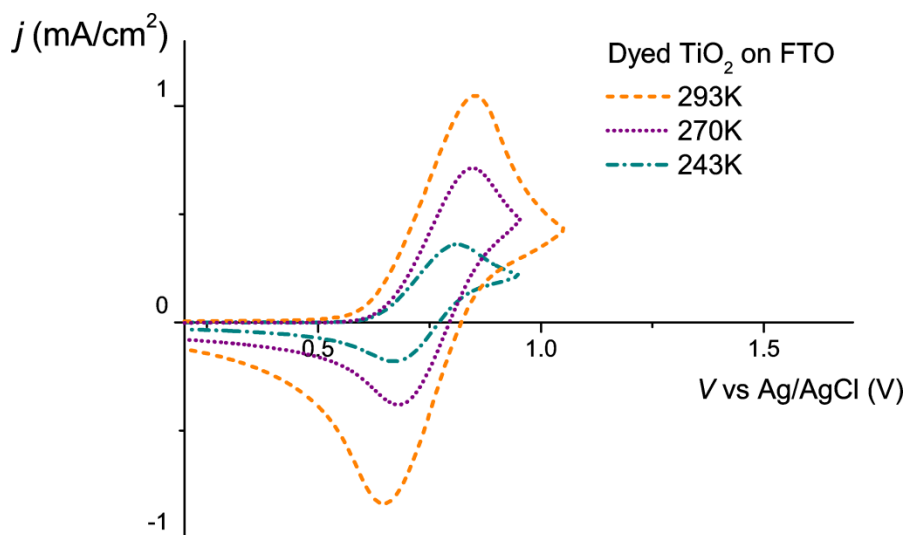


Figure 4.8. Cyclic voltammetry performed on A2 dye sensitized TiO₂ mesoporous films deposited on FTO coated glass in 0.1M TBAP in acetonitrile at different temperatures.

Figure 4.8 shows examples of cyclic voltammograms performed on dye sensitized TiO₂ films at different temperatures. The increase in the magnitude of the current density with increasing temperature suggests that the hole diffusion is thermally activated.

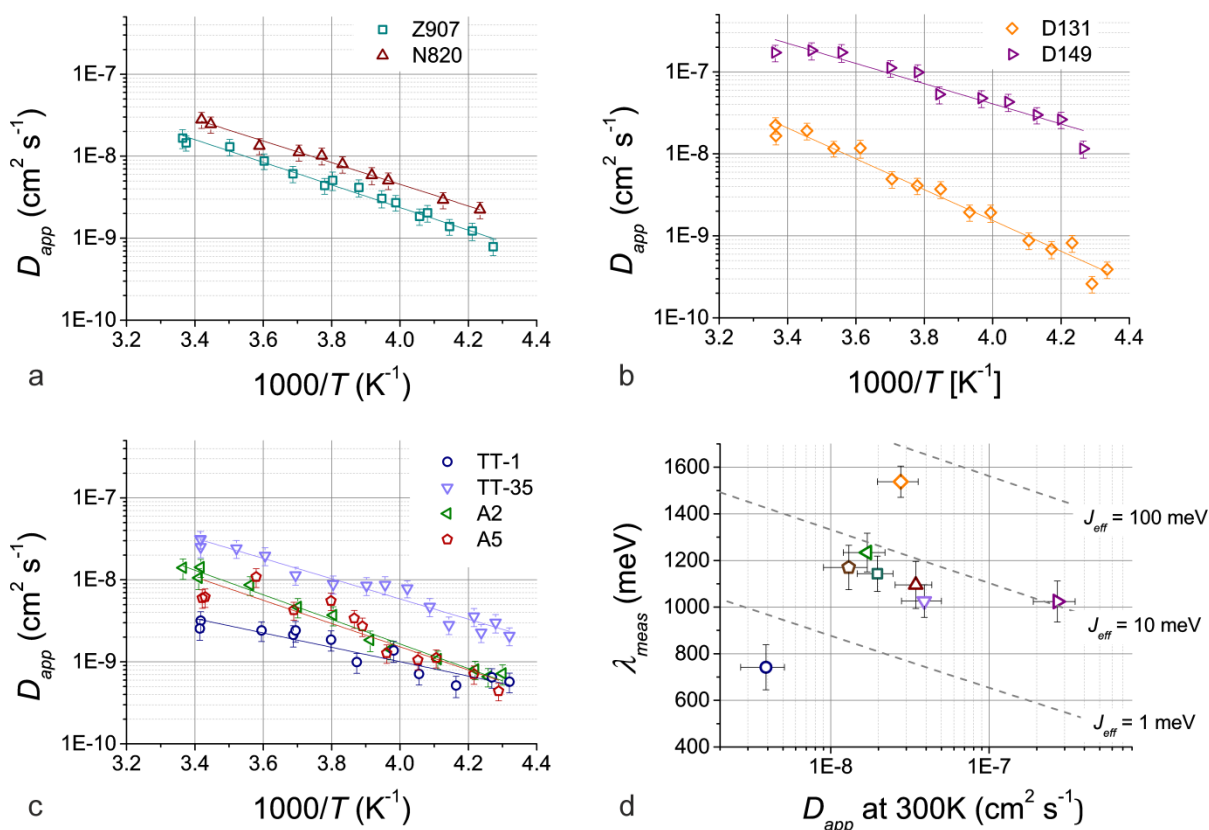


Figure 4.9. Temperature dependent values of the hole apparent diffusion coefficient (D_{app}) extracted from cyclic voltammetry performed on dye sensitized TiO₂ films on FTO in 0.1M TBAP in acetonitrile. For each dye, the fitting of the expression of a thermally activated process $D_{app} = D_0 \exp(-E_{act}/kT)$ to the data is shown. This enables the estimation of the activation energy E_{act} related to the charge transfer between dyes. Three classes of dyes were examined: ruthenium bipyridine complexes (a), indoline dyes (b) and phthalocyanines (c). In (d) the values of the reorganization energy λ_{meas} obtained by fitting the data using Eq. 4.1 and Eq. 4.18 are shown. The values are plotted against D_{app} at room temperature for all the dyes. Dashed lines represent the relation between λ_{meas} and D_{app} for different values of the effective electronic coupling J_{eff} and for a value of the mean intermolecular distance a of 1.35 nm (average over all the dyes considered).

The Arrhenius plots in Figure 4.9 a, b and c show the values of D_{app} for different dyes plotted as a function of temperature. They also show lines corresponding to the least square fits of the expression of a thermally activated process to the experimental data. The data quality is sufficient to discern differences in the values of the activation energy (E_{act}) between some of the systems (Table

4.2). Figure 4.9d shows the values of reorganization energy estimated from these data as described in the following paragraphs where they will be discussed further.

Data presented in Figure 4.9 are not compensated for the effect of the series resistance of the cell, and represent underestimates of D_{app} . The effect on the determination of the activation and reorganization energy of the process is expected to be within experimental error for all the dyes investigated except D149. For the case of dye TT-1, CV measurements showed two oxidation processes occurring at similar potential. Here, it is assumed that the current density peak for this material still represents an indication of the ability of holes to diffuse in the monolayer.

Assuming that the temperature dependence of D_{app} has the same functional form as the expression of the charge transfer rate shown in Eq. 4.1, it is possible to determine the reorganization energy describing the charge transfer reaction between the dye molecules anchored on the TiO_2 surface.

Furthermore, Eq. 4.18 enables to quantify an effective charge transfer rate (Γ_{eff}) based on the measured apparent diffusion coefficient (data in Figure 4.9), considering a simplified description of the problem. By fitting Marcus' formula (Eq. 4.1) to values of Γ_{eff} it is possible to extract values of an effective electronic coupling, J_{eff} , in the limit of weak coupling and negligible disorder. The values of J_{eff} obtained from this simple model parameterize the effects of dye chemical structure and of the distribution of dye separation on macroscopic hole diffusion. They do not directly correspond to the values of electronic coupling calculated for dyes on a surface as for example in ref ^[128].

The results of the fits of Eq. 4.1 for the values of the effective electronic coupling, J_{eff} , and of the reorganization energy, λ_{meas} , are shown in Table 4.2. The values of λ_{meas} are also displayed in Figure 4d, where they are plotted against the corresponding dye's apparent diffusion coefficient at room temperature. Lines representing the relation between the two quantities according to Eq. 4.1 and Eq. 4.18 are shown for different values of the effective electronic coupling using the average value of a over the dyes considered of 1.35 nm. Table 4.2 also shows the estimation of the activation energy, E_{act} (determined from the Arrhenius equation), the apparent diffusion coefficient at room temperature (D_{app}) and the measured dye loading (c_0) used for the estimation of J_{eff} . The measured values of reorganization energy (λ_{meas}) are compared to values calculated by Vaissier via quantum chemical

modelling (λ_{calc}) using the method described in Ref ^[128] for the case of 0.1 molar concentration of ions in acetonitrile as surrounding dielectric medium.

Table 4.2. Charge transfer parameters experimentally determined for different dye sensitized TiO₂ systems. For each dye, the dye loading of the sensitized film (c_0) was evaluated from absorbance measurements using a UV-vis spectrometer. The apparent diffusion coefficient at room temperature, the activation energy E_{act} , the effective electronic coupling J_{eff} and the reorganization energy λ_{meas} were determined from the temperature dependent cyclic voltammetry measurements shown in Figures 1 and 3. Here, J_{eff} is expressed for $\alpha_g = 2/3$. λ_{meas} is compared with the values obtained by Valérie Vaissier from quantum chemical modelling (λ_{calc}) using the method presented in Ref ^[128]. For the calculations, 0.1M singly charged ions in acetonitrile was used as surrounding solvent. Note that this simple model is independent on the radii of the ions.

Dye	c_0 (10 ¹⁹ cm ⁻³)	D_{app} at 300K (10 ⁻⁸ cm ² /s)	E_{act} (meV)	J_{eff}^* (meV)	λ_{meas} (meV)	λ_{calc} (meV)
Z907	9.1 ± 1.4	2.0 ± 0.5	274 ± 19	6.0 [*] / _{1.5}	1143 ± 76	976
N820	9.6 ± 1.5	3.5 ± 0.9	262 ± 25	6.4 [*] / _{1.7}	1095 ± 101	979
N719	6.6 ± 1.2	-	-	-	-	-
D131	8.8 ± 1.4	2.8 ± 0.8	373 ± 17	51 [*] / _{1.5}	1538 ± 67	1062
D149	6.6 ± 1.0	27 ± 8	244 ± 22	10 [*] / _{1.6}	1023 ± 88	914
ZnPP	4.2 ± 0.7	-	-	-	-	-
TT-1	13 ± 2	0.39 ± 0.12	174 ± 24	0.40 [*] / _{1.7}	742 ± 97	710
TT-35	4.4 ± 0.7	3.9 ± 1.1	245 ± 18	3.2 [*] / _{1.5}	1026 ± 70	680
A2	7.0 ± 1.1	1.7 ± 0.5	297 ± 21	7.6 [*] / _{1.6}	1234 ± 83	666
A5	2.7 ± 0.4	1.3 ± 0.4	281 ± 24	3.1 [*] / _{1.7}	1170 ± 95	669

* ^{*}/₁ expresses the geometric error.

In Figure 4.10 the comparison between theory and experiments is shown. Values of λ_{calc} are expressed as the sum of the inner sphere reorganization energy components (λ_i) and the outer sphere ones (λ_o). The dyes N719 and ZnPP showed highly irreversible behavior.

In the next sections I discuss the results in Table 4.2 and describe the behavior of the dyes in terms of hole diffusion in relation to their chemical structure. The HOMO delocalization, the rigidity and conjugation of the dyes, the presence of specific side groups or ligands, the anchoring mechanism and the configuration of the monolayer are considered to interpret the calculated and measured reorganization energies and effective electronic couplings are considered.

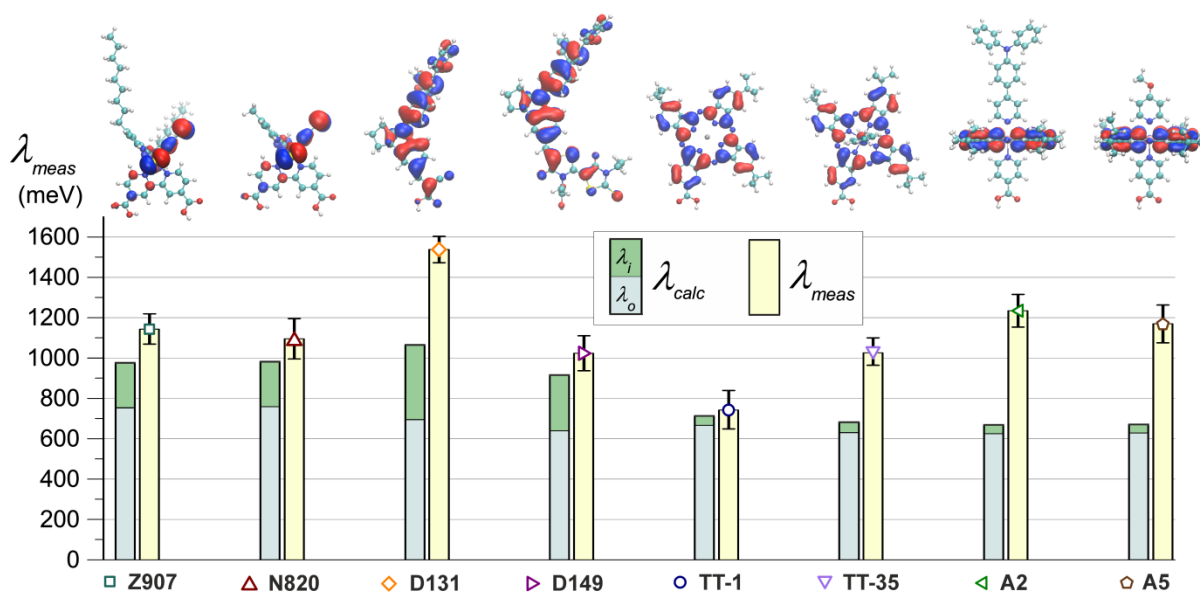


Figure 4.10. In the column chart, the measured reorganization energies (λ_{meas}) are compared to the calculated values (λ_{calc}) for the dyes investigated in this work. For the latter, the separate contributions of the inner sphere (λ_i) and the outer sphere (λ_o) reorganization energies components are shown. On top of the chart, the isosurfaces of the HOMOs for all the dyes in the unoxidized state are shown on their chemical structures. The isosurfaces correspond to the values of 0.02 and -0.02 electrons^{1/2} $a_0^{-3/2}$ for red and blue, where a_0 is the Bohr radius. The legend for the atoms is: Carbon green, Hydrogen light gray, Oxygen red, Nitrogen blue, Sulfur yellow.

4.4.2 Chemical structure and calculated reorganization energy

From the calculated values, the outer sphere component of the reorganization energy represents the main contribution to the overall value of the reorganization energy for all the dyes investigated in this study. In the column chart in Figure 4.10, λ_o is between 65 and 95% of the total λ_{calc} depending on the dye. This is due to the highly polarizable surrounding medium used.^[128] The spatial location of the HOMOs is displayed in Figure 4.10 where the volume enclosed within the isosurface corresponding to the isovalues ± 0.02 electrons^{1/2} $a_0^{-3/2}$ is shown for the different structures. The value of the calculated outer sphere reorganization energy is inversely correlated to the 'size' of the HOMO. Greater delocalization of the HOMO results in lower values of λ_o . The ruthenium bipyridine complexes Z907 and N820 show the highest λ_o . For these two dyes the HOMO is localized on the two NCS ligands (see structures and column chart in Figure 4.10). λ_o is instead lower for the dye D131 and even lower for D149. For both these dyes, the HOMO is more evenly distributed on the whole molecular structure, which is slightly bigger in the case of D149. λ_o is also low for the phthalocyanine dyes, where the HOMO extends on the

phthalocyanine ring. Another observation is that λ_o is not directly affected by the size of the molecule. For example, the HOMO of Z907 does not expand into the non-conjugated alkyl chains, which significantly increase the overall size of the molecule when comparing it to N820. However, the values of λ_o for Z907 and N820 are almost identical. Similarly, only slight variations in λ_o are observed when comparing the phthalocyanine dyes. The HOMO localization in these complexes is essentially unaffected by the presence of the axial ligands or change in the core atom. Regarding the calculated inner sphere reorganization energy, almost identical values for the ruthenium dyes Z907 and N820 are reported. This suggests that the alkyl chains play a negligible role in the rearrangement of the molecular conformation of Z907 upon charge transfer. For the indoline dyes, D131 shows higher λ_i than D149, possibly due to the reduced size of the conjugated structure. Finally, the phthalocyanine dyes show very low values of λ_i . To be noted, the rigidity of the phthalocyanine ring (almost all atoms are braced by bonds to neighboring atoms, see Figure 3.1), where the HOMO is mainly located, constrains the unoxidized and the oxidized conformations to be similar. The planarity of the structure ensures high level of conjugation across the ring that provides easier accommodation for the hole.

4.4.3 Comparing measured and calculated reorganization energies

The experimental values of reorganization energy find good agreement with the calculations performed by Vaissier for the case of the ruthenium bipyridine complexes where λ_{meas} is very similar for Z907 and N820 and only slightly higher than the relative values of λ_{calc} . For the indoline dyes, higher value of reorganization energy for the D131 dye than for D149 is recorded, confirming the trend observed in the numerical simulation. However, the mismatch between calculation and experiment is significant for the case of D131 and the difference in reorganization energy between the two dyes is higher for the measured values than for the calculated ones. In the case of the phthalocyanine dyes, the measured value of the reorganization energy of TT-1 matches the calculated value within experimental error, whereas for the ruthenium phthalocyanines TT-35, A2 and A5, much higher reorganization energies than the ones predicted by the calculations were measured. The substitution of the zinc core atom with ruthenium and/or the presence of the axial ligands may underlie the observed increase in λ_{meas} . The exchange of the TPA group with the methoxy in the axial ligands of the dyes A2 and A5 seems not to

affect λ_{meas} . Finally, λ_{meas} is lower for TT-35, where the anchoring group is on the periphery of the phthalocyanine ring, than for A2 and A5, where the anchoring group is located on one of the axial ligands. This change in reorganization energy may be related to the differences in the molecular conformation and in the interaction with the TiO₂ surface deriving from the change in the anchoring group's position.

The analysis of the thermally activated charge transfer process with the non-adiabatic Marcus equation is based on reactions between redox sites of identical energy (see Eq. 4.1). In reality, it is expected that variations in the TiO₂ surface, in the configuration of the dyes on the surface and in the dielectric and electrostatic environment result in variations in site energy (energetic disorder). This introduces additional temperature dependence in the charge diffusion process and a distribution of values for the activation energy. If these effects are significant, they could lead to an overestimate of λ in the above experimental analysis. This could explain the mismatch between experiments and calculations.

4.4.4 Hole diffusion: effect of chemical structure, monolayer configuration and relevance to organic thin films

A slight decrease in apparent diffusion coefficient for Z907 is observed when compared to N820. In this case, the presence of the alkyl chains results in molecular configurations that still allow relatively effective hole transfer between neighboring dyes. This is consistent with the similar values of the dye loading measured for the two systems. Larger differences in the D_{app} resulting from the presence of alkyl chains were observed previously and may relate to a more significant impact of the chains on dye loading.^[24] The presence of non-conjugated side groups can affect the packing density as well as the relative arrangement of the dyes sensitizing the surface. This may limit the overlap of the HOMO of neighboring molecules and reduce the charge transfer rate.

The close packing of dyes on the TiO₂ surface is expected to increase the coupling between molecules and result in faster charge transport. The enhancement of hole diffusion for indoline dyes due to *J*-aggregation has already been discussed by Fattori *et al.*^[76] Moreover, it has been shown that the preferential adsorption mechanism of D149 on the TiO₂ surface occurs with lower packing and reduced interaction than for another indoline dye, D102, due to steric effects.^[134] In my experiments, D131 shows higher packing than D149 (see values of the dye loading

c_0 in Table 4.2), and probably adopts similar configurations to what has been presented for the indoline dye D102. The difference in packing results in different effective electronic coupling, which is higher in this case for D131 than D149 (see J_{eff} in Table 1). The faster diffusion measured for D149 at room temperature compared to D131 may be due to the difference in reorganization energy. Note that molecular fluctuations and their effect on configurational disorder have been shown to affect charge diffusion in these systems.^[122]

The phthalocyanine dye TT-1 adsorbs onto the TiO_2 with very high packing density. Its slow hole diffusion at room temperature can be ascribed to the presence of the tert-butyl groups or to unfavorable relative orientations of neighboring dyes. The ruthenium phthalocyanines show significantly lower dye loading than TT-1 due to the presence of axial ligands, in the case of TT-35, and to the different anchoring scheme, for A2 and A5, (c_0 is particularly low for A5, which I am not able to explain on the basis of the dye's chemical structure). For these dyes, apparent diffusion coefficients at room temperature above $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ have been recorded. All the phthalocyanine dyes investigated here are particularly interesting given the high degree of reversibility observed when performing multiple CV measurements on the same sample.

The corresponding value of mobility that can be calculated from the measurement of D_{app} at room temperature for the dyes investigated here ranges between 10^{-7} and $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These values are lower than the mobilities recorded for solution processable amorphous organic semiconductors (up to $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This may be because of the different dimensionality of a dye monolayer on a mesoporous structure compared to the bulk of a thin film. Mobility greater than $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was reported using solution processable oligothiophenes in self assembled monolayer field effect transistors (SAMFETs), suggesting a potential improvement for the case of dyes that are able to order when sensitizing a surface.^{[30],[31]} Organic semiconductor monolayers can occupy only about 10% volume fraction of a mesoporous film, and can revolutionize the provision/extraction of charge carriers in the bulk of a film. 2D transport across a semiconductor (Perovskite) sensitized nanocrystal was observed by Lee *et al.* and enabled the fabrication of high efficiency solid state solar cells.^{[135],[136]}

The method presented here has potential application beyond the field of DSSCs for the characterization of charge transport between semiconducting

molecules. Traditionally, it has been difficult to resolve the contributions from energetic disorder and reorganization energy from observed temperature dependence of transport in these materials.^[137] Indeed, there is, as yet, no straightforward technique to determine λ experimentally. The experimental and theoretical methods used here could be applied to organic semiconducting moieties when attached to the surface of a supporting scaffold and used to study the reorganization energy in different dielectric environments. In the surface attached configuration a lower degree of disorder than in a three-dimensional solid film may be expected. However, as mentioned previously in this discussion, variations in the surface and in the configuration of the molecules could still make a significant contribution to the temperature dependence of hole diffusion.

4.5 Summary

I presented a method to determine the diffusion coefficient and the reorganization energy for the transport of holes across monolayers of dyes anchored to nanocrystalline surfaces via temperature dependent cyclic voltammetry.

I analysed materials that belong to different classes of dyes and discussed the influence of their chemical structure on their conduction properties. The results suggested that low values for the reorganization energy are achieved when dyes present a rigid structure, extended conjugation and when the HOMO is delocalized over a large volume. The presence of non-conjugated side groups potentially have a detrimental effect on the rate of charge transfer between molecules, as high packing densities are desirable to enhance the hole diffusion.

The technique can be extended to any redox active molecules able to attach to surfaces. The measurements of reorganization energy show agreement with quantum chemical calculations of the reorganization energy performed by Valérie Vaissier. This indicates that the method can be used to design chemical structures for the optimization of the charge transfer properties of dyes. Beside the analysis of the hole hopping for molecules anchored to a surface, measuring the reorganization energy and estimating the effective electronic coupling is of high importance in the general study of charge transport in organic semiconductors.

Chapter 5 Hole transport in dye sensitized nanocrystals and its role on charge recombination

In this chapter² I discuss hole transport between dyes anchored to the surface of nanoparticulate TiO₂ immersed in an inert electrolyte as a function of dye surface coverage. I show results from electrochemical and transient absorption anisotropy measurements to study the hole diffusion at different length and time scales and discuss the presence of a percolation threshold. I investigate the influence of photo-generated holes hopping in the dye monolayer on their recombination with electrons in the TiO₂ in terms of rate and dynamics. I finally present simulations that aim to reproduce the dynamics observed in transient absorption anisotropy experiments.

5.1 Introduction

Electrochemical studies of charge transport in dye monolayers anchored to oxide nanocrystals have shown the presence of a percolation threshold around 50% dye surface coverage (see section 2.3.1). This is consistent with percolation theory of diffusion in a randomly populated 2D lattice. Electrochemistry measurements of dye sensitized nanocrystalline films probe the macroscopic response of the system and cannot give a microscopic characterization of the charge transfer processes. Here, I use transient absorption anisotropy measurements performed on dye sensitized mesoporous TiO₂, following the method presented by Ardo and Meyer,^[28] to investigate hole behavior on a microscopic scale. I discuss the possible models to interpret the measurements, showing that hole diffusion across the dye monolayer is likely to underlie the observed dynamics. Electrochemical measurements of hole diffusion in D131 sensitized TiO₂ mesoporous films in 0.1M TBAP in acetonitrile are compared to the transient anisotropy response of the same system in the same electrolyte. The observation of a percolation behavior for both measurements is discussed.

² The results and discussion reported in this chapter are currently under consideration for publication in the *Journal of Physical Chemistry C*

The kinetics of electron-hole recombination in dye sensitized TiO₂ has been extensively investigated in the literature. As discussed in section 2.4.1, transient absorption measurements of this reaction can be interpreted in terms of electron transport and effect of dye chemical structure on reaction limitation. In this chapter I present evidence showing that hole diffusion within the dye monolayer plays a role in determining the electron-hole recombination rate.

5.2 Method

Sample preparation: TiO₂ mesoporous films have been fabricated following the procedure described in section 3.2.1. The commercial paste DS 18NR-T was used unless stated otherwise. Films fabricated with paste DS 30NRD and DS 18NR-AO were fabricated following the same procedure. Full coverage films were dyed using 0.1 mM D131 solution in 1:1 acetonitrile:tert-butyl alcohol. Control on the dye loading was attained by introducing cheno-deoxycholic acid (DCA) in the D131 solution at different D131:DCA ratios (between 1:0 and 1:200). Dyeing time of 3.5 hours was used except for films dyed overnight in D131 only solution. Dye desorption was also investigated following the recipe shown in reference ^[138]. D131 sensitized samples were left in solutions of between 0.05 and 0.2 mM tetra methyl ammonium hydroxide in acetonitrile for 30 minutes and subsequently rinsed in acetonitrile for 15 minutes. The procedure was repeated several times to achieve the desired dye coverage. For bias dependent spectroscopy measurements, a compact layer of TiO₂ was deposited before doctor blading the nanoparticulate film (see section 3.2.1). This was done in order to reduce the contribution of surface recombination at the FTO electrode to the observed dye cation signal relaxation.^[139]

In order to qualitatively assess the uniformity of the dyeing process, the technique introduced in reference ^[138] was followed. 7 μm thick TiO₂ nanocrystalline films were fabricated by doctor blading a 20 nm TiO₂ nanoparticle paste containing a small fraction of larger particles, up to about 450 nm (DS 18NR-AO). The resulting films were opaque at the dye absorption wavelength and enabled the extent of dye loading at the front and back (glass) side of the sample to be visually assessed.

Electrochemistry: cyclic voltammetry was performed on D131 sensitized TiO₂ films on FTO as described in section 3.3.2.

Spectroscopy: Transient absorption spectroscopy and bias dependent spectroscopy were carried out following the method described in section 3.3.4 and 3.3.6. Fluence of the pump was kept below 5 $\mu\text{J cm}^{-2}$ per pulse in all experiments.

Stretched exponentials were fitted to the transient absorption data according to:

$$\Delta OD(t) = A \exp\left(-\frac{t}{\tau}\right)^\alpha + \Delta OD_\infty \quad \text{Eq. 5.1}$$

Where A represents the amplitude of the perturbation, τ and α are the time constant and the stretching factor of the stretched exponential function. ΔOD_∞ was introduced to account for baseline offset for measurements that showed incomplete relaxation. The mean relaxation time $\langle \tau \rangle$ was calculated as:

$$\langle \tau \rangle = \frac{\tau}{\alpha} \Gamma\left(\frac{1}{\alpha}\right), \quad \text{Eq. 5.2}$$

where Γ is the Gamma function.

Electrical bias dependent TAS measurements were performed following the method described in section 3.3.6.

Random walk and transient anisotropy simulations: calculations were carried out following the method described in section 3.4. An average electronic coupling of $2.13 \cdot 10^{-4}$ eV and a reorganization energy of 1.014 eV were used in the simulations.

5.3 Results and discussion

5.3.1 Dye loading uniformity

The analysis of 7 μm opaque TiO_2 films enabled the uniformity of the dyeing process to be assessed as a function of time for D131 sensitized films and when the coadsorbent chenodeoxycholic acid (DCA) was included in the dye solution.

In Figure 5.1, photographs taken for the film and the glass side of the samples at different times after the start of the dyeing step are shown. For the case of films dyed with D131 only, a sufficiently long dyeing time is needed to guarantee full coverage throughout the depth of the film, as also discussed in reference ^[138]. Common dyeing procedures used to fabricate DSSCs using organic dyes involve relatively short dyeing times (in the order of 1 hour). This result suggests that,

depending on the thickness of the TiO_2 film, a gradient in dye loading may arise from this approach.

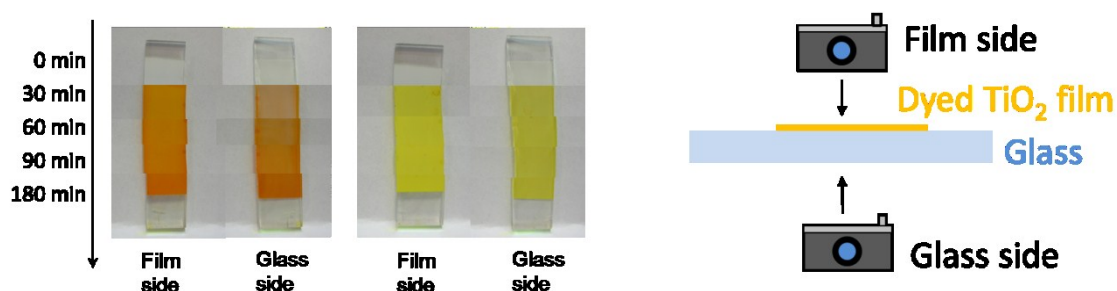


Figure 5.1. Sets of photographs of 7 μm thick D131 (left) and D131:DCA 1:200 (right) sensitized TiO_2 opaque films taken for the film side and the glass side of the samples at different times after the start of the dyeing process.

When the inert coadsorbent (DCA) is added to the dye solution, a different color from the D131 only case is observed (light yellow versus orange). Variation in optical density profile is noticeable for dyed transparent films. The addition of DCA to the dye solution results in a red shift in the absorption peak (see Figure 5.2). This can be related to different intermolecular interaction between D131 molecules with each other or with DCA molecules. Also, differences in the magnitude of the optical density would influence the reflectivity spectra of the films, resulting in color changes.

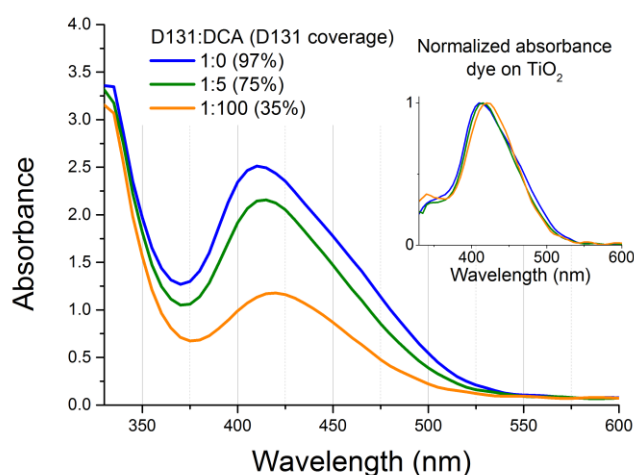


Figure 5.2. Absorbance spectra for TiO_2 mesoporous films dyed from solutions containing different ratios of D131 dye to DCA coadsorbent. The inset shows the normalized absorbance of the dye.

When the coadsorbent DCA was included in the dye solution to obtain lower dye loading, slow uptake of D131 on the surface due to the presence of the DCA was observed. Furthermore, dyeing of the bottom of the film occurred more quickly so that uniformity could be achieved with shorter dyeing times than without DCA. This result suggests that the “slow” diffusion of D131 molecules through the pores of the TiO_2 observed during the dyeing of the samples without DCA is actually due to the rapid uptake of the dyes on the surface of the nanocrystal which depletes the dye solution as it infiltrates the pores.

The dyeing process can therefore be seen as a “dyefront”, the speed of which is in kinetic competition with the dye uptake. Similar behavior for the transparent mesoporous TiO_2 films used in the rest of this study is likely. Note that the absence of large scattering particles might change the infiltration rate and possibly show different surface properties.

5.3.2 Study of hole percolation at different scales

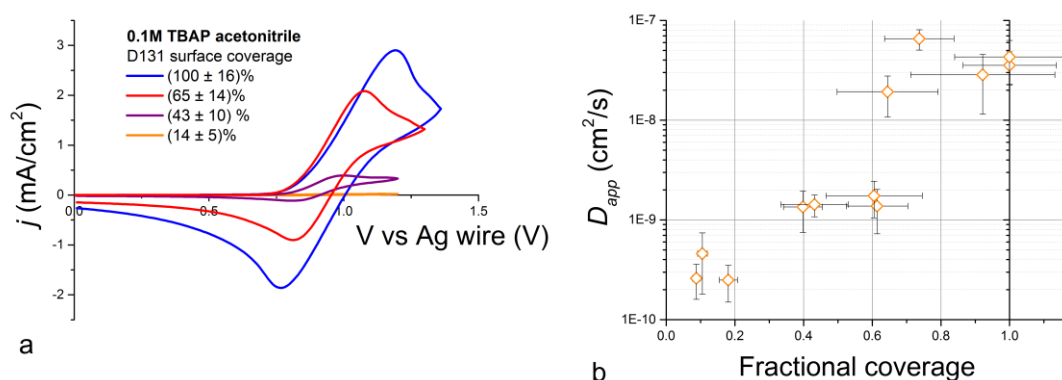


Figure 5.3. Analysis of hole transport in D131 monolayers anchored to mesoporous TiO_2 using cyclic voltammetry. Different values of dye surface coverage are considered. (a) Cyclic voltammograms of D131:DCA sensitized mesoporous TiO_2 films on FTO glass measured at 0.2 V s^{-1} scan rate in 0.1M TBAP:acetonitrile, where j is the current density. (b) Apparent diffusion coefficient (D_{app}) plotted against surface coverage, calculated as the dye loading of the sample divided by the maximum dye loading recorded for the experiment.

In this section the observation of a hole percolation threshold is discussed, both at the film thickness (μm) scale, and at the particle (10 nm) scale when the concentration of dyes on the TiO_2 surface is decreased.

Cyclic voltammetry of dye sensitized TiO_2 films showed a strong dependence on the dye loading. When decreasing the dye surface coverage of the TiO_2 film, the

measured cyclic voltammogram showed a significant drop in the magnitude of the current density peak for similar scan rate conditions (Figure 5.3a). The holes' apparent diffusion coefficient relative to each measurement is corrected for the effect of series resistance as described in section 4.3.2 and shown in Figure 5.3b as a function of surface coverage.

For samples with fractional coverage below ~30%, the integrated current of the first cyclic voltammogram peak becomes comparable to the value expected from an oxidation experiment for a monolayer of dyes in direct contact with the FTO substrate. This implies that the use of the term diffusion coefficient is no longer meaningful at low dye loading (below percolation). A percolation threshold is observed at dye loadings corresponding to about 40 to 60% of the maximum value of surface coverage measured in the experiment. The observed trend is consistent with previous reports on hole or electron diffusion on the surface of nanocrystals measured with electrochemistry.^{[66],[24],[74]}

Monitoring the changes in polarization of holes photogenerated via polarized laser pulses can also give insights into the diffusion of the charges within a dye monolayer. This information can be expressed by measuring the dye cation absorption anisotropy as described in section 2.2.4. Figure 5.4a and b show transient absorption anisotropy and transient absorption measurements for D131:DCA sensitized TiO₂ films immersed in 0.1M TBAP in acetonitrile. Loss in anisotropy occurred within tens of μ s for samples with complete coverage. On the other hand, samples where the coverage was below 30% showed a constant value of anisotropy up to about 100 μ s and a decay at longer timescale.

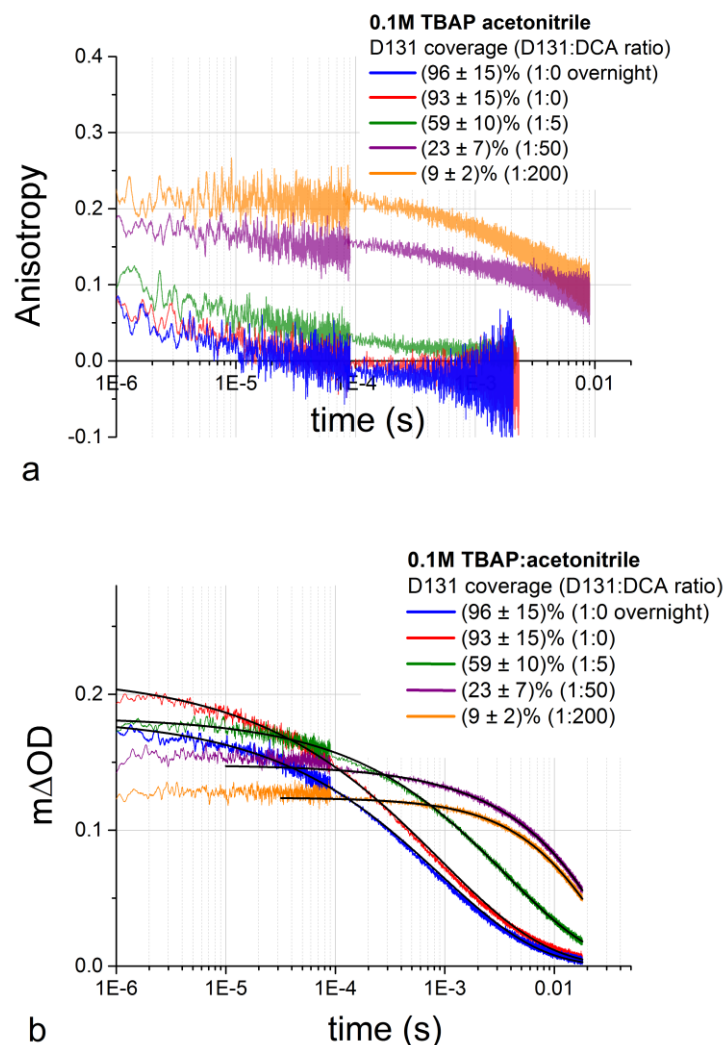


Figure 5.4. (a) Transient anisotropy, $r(t)$, measurements of D131:DCA sensitized TiO_2 films immersed in 0.1M TBAP:acetonitrile. The samples were excited with polarized laser pulses at 450 nm (repetition rate 20 Hz). (b) Transient absorption decay measured at the magic angle.

A number of different factors could cause the loss in anisotropy for the cation's absorption signal shown in Figure 5.4a. Based on arguments listed below, I conclude that hole transfer between dyes on the surface of the TiO_2 (i) is likely to be the dominant mechanism for anisotropy decay in this experiment.

(i) *Hole transfer to other dyes with different dipole moment orientation.*

Hole diffusion in the monolayer of dyes on a facet of the TiO_2 could result in loss of anisotropy. The extent to which this happens depends on the degree of disorder of the collection of dyes. In particular, it depends on the orientation of the probed transition dipole moment of the cation and its relation to the geometric configuration of the dyes on

the surface. The electrochemical measurements shown in Figure 5.3 indicate that holes can hop across the edges of the crystals' surface and junctions between particles. This is because the total charge injected in the dyed film during the CV corresponds to the oxidation of more dyes than are expected on the TiO_2 particles in contact with the FTO. When the individual hole hops across facets, an abrupt variation in its dipole alignment is expected which contributes to the anisotropy decay. Therefore, even if each facet of the nanocrystal were covered by dyes arranged such that the orientation of the relevant dipole moment is conserved, loss in anisotropy would be expected due to hole transfer between different facets of the nanocrystal.

- (ii) *Fluctuation in the dyes' conformation.* It has been proposed that the movement of dye molecules on the surface of the TiO_2 could explain the high apparent diffusion coefficient observed for the indolene dyes D102 and D149 from electrochemical measurements.^[122] The percolation behavior observed could be justified by this phenomenon if the movement of D131 could be inhibited by the presence of the coadsorbent DCA. However, the value of the transient anisotropy would be very unlikely to reach 0 (as shown in Figure 5.4) solely due to fluctuation of dyes' conformation, as the chemical bond to the TiO_2 surface and the presence of the surrounding dyes constrain the set of possible geometrical conformations of the dye on which a hole resides.
- (iii) *Desorption of the dyes upon photo-oxidation.* This is unlikely to be a dominant process unless the desorption were inhibited by the presence of the DCA coadsorbents.
- (iv) *Other chemical reactions involving the photo-oxidized dyes* could also result in transient anisotropy decay. This explanation is not consistent with the measurement of long lived signals for the transient absorption of the samples.

I therefore interpret the features of the transient anisotropy decays of Figure 5.4a predominantly as a measure of hole transfer between dyes that operates only above the dye loading percolation threshold. Below the percolation threshold, holes are unlikely to reach a different facet from the one where they were generated within

the time scale of the measurement since no complete decay in anisotropy is observed.

Table 5.1: Fitting parameters of the model described by Eq. 5.1 applied to the data shown in Figure 5.4. The averaged time constant $\langle \tau \rangle$ was calculated using

D131 coverage %	τ (ms)	α	$\langle \tau \rangle$ (ms)
96 ± 15	0.912 ± 0.002	0.477	1.99
93 ± 15	0.897 ± 0.002	0.442	2.31
59 ± 10	3.61 ± 0.005	0.522	6.69
23 ± 15	177 ± 22	0.636 ± 0.005	248
9 ± 2	29.9 ± 0.8	0.809 ± 0.013	43.1

In Figure 5.4b, a slowdown in the transient absorption decay referred to the dye cation occurred when dye loading was decreased. Table 5.1 displays the value of the fitting parameters obtained by fitting Eq. 5.1 to the data. More than one order of magnitude slowdown in the mean relaxation time is observed when the dye loading is decreased from 100% to about 9%. This finding is consistent with the study reported by Ogawa *et al.* where the addition of DCA resulted in longer lived photogenerated holes.^[91] Also, different dye configuration on the surface in the presence of DCA has previously been reported as possible explanation for a similar observation.^[92] In the next section, contribution from hole diffusion in the D131 monolayer to the recombination rate will be discussed.

The final observation is that decrease in dye loading corresponds to a decrease in the degree of dispersion in the decay dynamics: the stretching parameter value varies from about 0.45 for the fully covered samples to about 0.8 for the case of 9% coverage. This suggests that different mechanisms of recombination occur depending on the dye loading and/or upon addition of the coadsorbent DCA on the surface of the TiO_2 .

5.3.3 Hole diffusion and electron-hole recombination rate

The results displayed in Figure 5.4a, b show correlation between transient absorption and transient absorption anisotropy decays referred to the dye cation signal in dye sensitized TiO_2 samples. This suggests that there may be a correlation between hole diffusion in the dye monolayer and the hole recombination rate with electrons in the TiO_2 . Note that, since the samples in Figure 5.4 had different levels

of dye loading, the measurements were not performed on equal electron density conditions. The observed trend could therefore be explained considering the different charge density in the different films during the TAS experiments. Figure 5.5 shows the electrical bias dependent transient absorption decays corresponding to the D131 cation population upon laser excitation for different dye sensitized TiO₂ samples. Stretched exponentials were fitted to the decays. The graphs also show (right axis) measurements of transient absorption anisotropy at the same probe wavelength. For the 100% sample the anisotropy is shown for two different values of charge density (which show an identical trend). For the other samples the anisotropy measured at open circuit is displayed.

In agreement with the data shown in Figure 5.4a, for the 100% dye loading case the anisotropy signal decays in few hundreds of microseconds. No significant effect of the electron density on the anisotropy decay is observed. Anisotropy is preserved within the timescale of the measurement in all the other samples. Note that the 67% coverage sample was dyed in D131 only solution and for a short time (2.5 hours), implying non uniform coverage throughout the depth of the film. Given that excitation was directed through the glass side of the sample, a portion of the film with lower than 67% coverage is expected to be probed. Measurements of two samples dyed with D131:DCA showing D131 loading below 10% are also presented.

In all cases the decay of the TAS signal becomes more rapid with more negative applied potentials, consistent with faster recombination dynamics as the background electron concentration in the TiO₂ increases.^[82] Stretched exponential fits to the TAS decays yielded the recombination time constants shown in Figure 5.6. The half lifetime $t_{50\%}$ and the mean relaxation time $\langle \tau \rangle$ are plotted as a function of electron concentration in the film inferred from the charge extraction measurements (e.g. Figure 5.5f).

At sufficiently negative potentials, the electrochemically induced electron density is significantly higher than the photo-induced counter-part. Under these conditions similar dynamics of photo-induced electron-hole relaxation is expected throughout the thickness of the film. At the fluence level used in the experiment ($\sim 3 \mu\text{J cm}^{-2}$), the electrochemical charge density is expected to equal the peak photo-induced component in the film at about $n = 10^{16} \text{ cm}^{-3}$ for low dye loading samples up to about 10^{17} cm^{-3} for the high loading considered here.

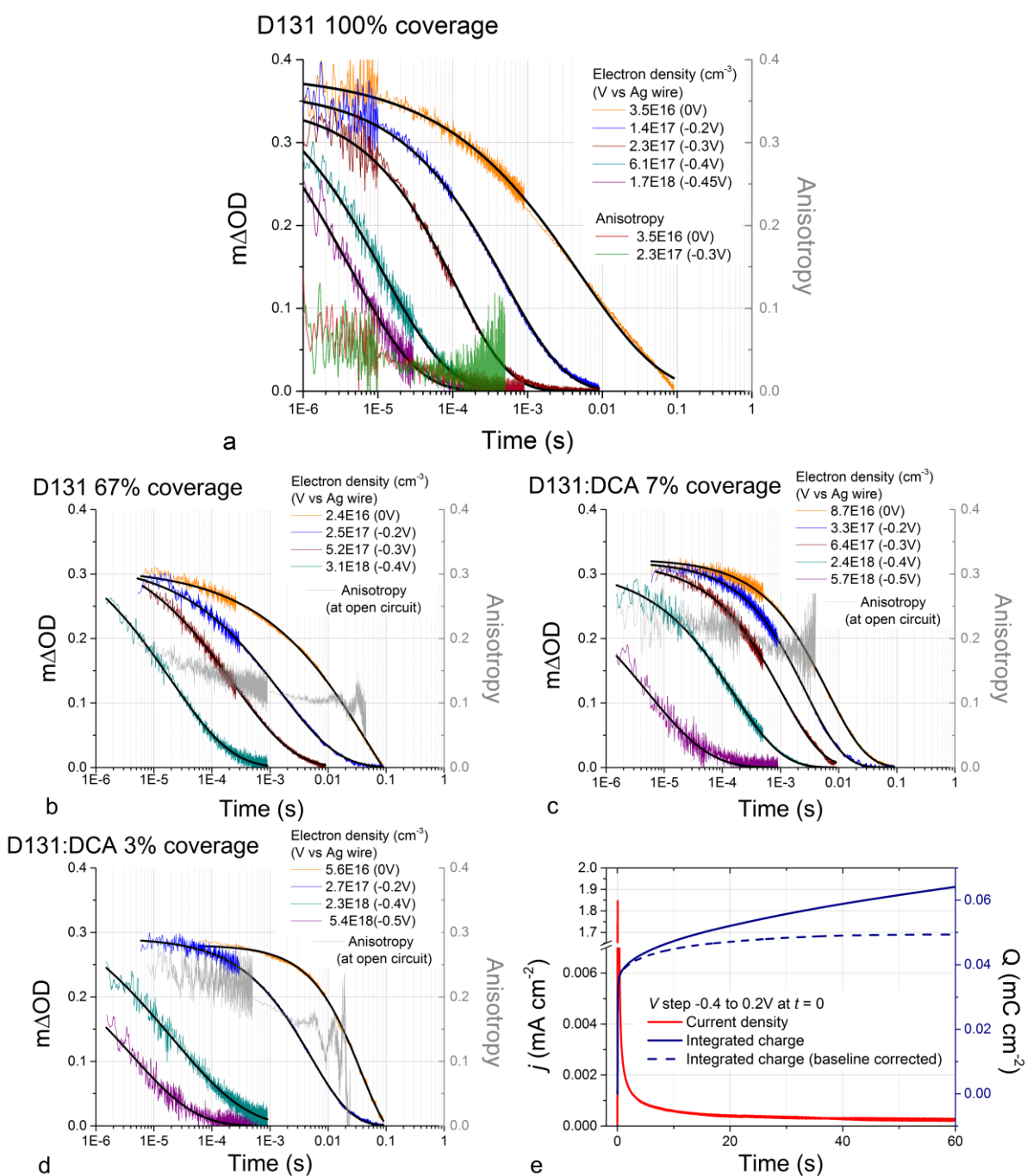


Figure 5.5. (a-d) Bias dependent transient absorption measurements. The left axes show the photo-induced hole recombination with electrons in the TiO₂ measured with TAS. The right axes show the transient absorption anisotropy decays. For both signals, 450 nm was used as pump and 1000 nm as probe wavelengths. The latter is ascribed to the dye (D131) cation signal. Different dyeing conditions were used for the samples: (a) dyeing in D131 solution for 20 hours; (b) dyeing in D131 solution for 2.5 hours; (c) dyeing in D131:DCA 1:100 solution for 1 hour; (d) dyeing in D131:DCA 1:200 solution for 30 minutes; (e) Example of charge extraction performed on sample (a) after carrying out the TAS measurement at V = -0.4V vs silver wire. The graph also displays the charge obtained by integrating the current density during the measurement and the approximated charge density in the film obtained from the baseline corrected current density.

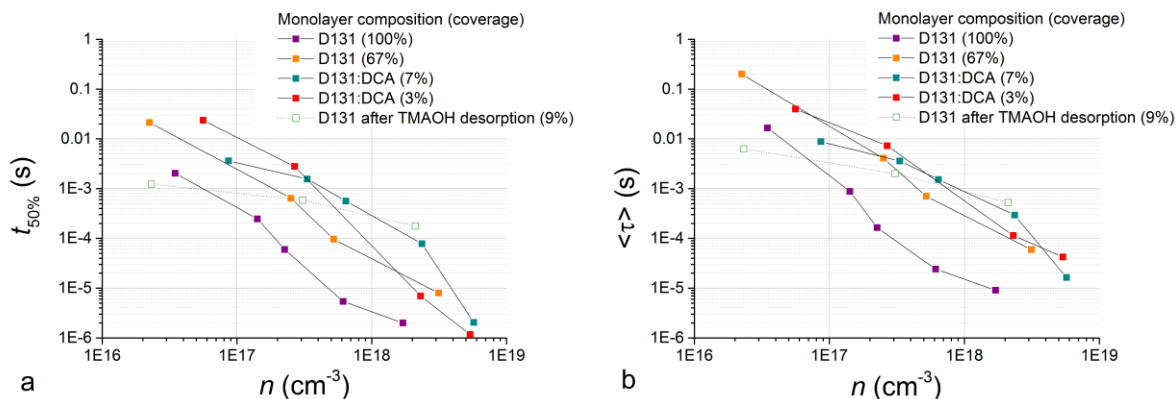


Figure 5.6. Half lifetimes and mean relaxation times obtained from the fits shown in Figure 5.4 as a function of electron density n . n was estimated from charge extraction (chronoamperometry) measurements.

The results displayed in Figure 5.6 show that, even for $n > 10^{18} \text{ cm}^{-3}$, ‘fast hole hopping’ corresponds to consistently faster dye cation decay. For the samples where short dyeing time was used or DCA was included in the dye solution, slower decay of anisotropy *and* slower electron hole recombination are observed. Figure 5.6 also shows data for a sample where D131 dyes were desorbed to a controlled extent prior to the measurement. Also for this sample slower excited state decay at high charge density compared to the fully dye loaded film is observed. Note that modification of the TiO_2 surface properties may be expected from the application of the alkaline treatment.

The timescale of anisotropy decay for the case of full surface coverage is $\sim 100 \text{ } \mu\text{s}$. This suggests that under these conditions a large fraction of the photo-generated holes recombine after ‘visiting’ a different facet from the one on which they were generated. On the other hand, for samples that show reduced/no hole transport between dyes, a large fraction of holes are expected to undergo recombination to electrons before reaching the particle facet’s edges even though the recombination takes around an order of magnitude longer to occur.

These observations imply that under some circumstances in liquid junction DSSCs hole transport in the monolayer of dyes can be detrimental to the performance of devices since electron-dye recombination is accelerated by this process. They also suggest that there may be localized electronic surface states through which recombination occurs most rapidly. These states can be accessed with higher probability when surface transport of holes is possible. However it is

important to stress that, in an optimized DSSC, electron-dye cation recombination is seldom a dominant factor limiting device performance. This process can become important in devices where the dye electrolyte combination result in slow regeneration.

5.3.4 Dynamics of transient absorption anisotropy decay

My analysis of transient absorption anisotropy in the previous sections focused solely on the evaluation of the time scale at which the observed decay occurred. It is conceivable that more information about the hole transport dynamics and the monolayer configuration can be extracted from this measurement. In this section I show experimental and computational results which aim to give a better understanding of transient absorption anisotropy measurement performed on the systems described in this thesis.

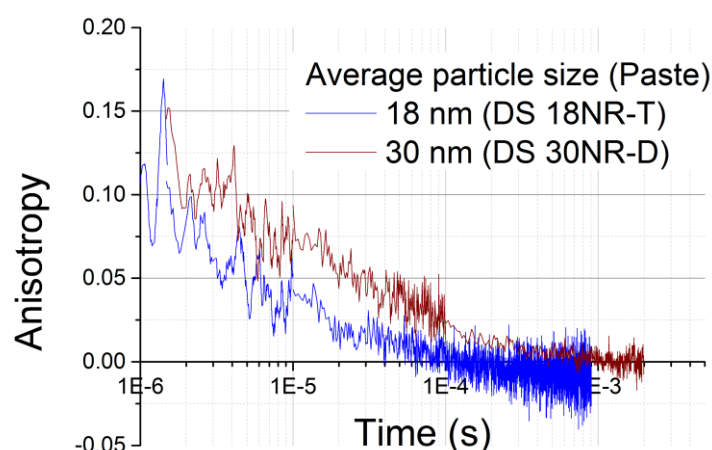


Figure 5.7. Transient absorption anisotropy measurements performed on D131 sensitized TiO_2 mesoporous films immersed in 0.1M TBAP:acetonitrile. The films were fabricated from two different pastes with different average particle size.

Figure 5.7 shows the transient absorption anisotropy decay of D131 sensitized TiO_2 films dyed overnight. The two films are made of particles with different average particle size. For both traces the decay occurs with similar dispersion, over several orders of magnitude in time scale. The difference between the two profiles could be explained in terms of difference in the mean relaxation time, which is consistent with the longer distance that a hole needs to cover in order to reach the edge of larger facets. This result suggests that the observed decay in

anisotropy is at least in part related to the diffusion of the charges across different facets.

The presence of pronounced stretching character for both decays could be partially explained by considering a spread in the particle size. Disorder in the connection between particles is also likely to increase stretching. However, these factors would account only for a relatively narrow distribution of time constants related to the different time taken by the holes to reach the edge of facets or to jump between different particles. The dispersive behavior observed at the long time scales is likely to be related to disorder in the monolayer which introduces a broad distribution of values of charge transfer between dyes.

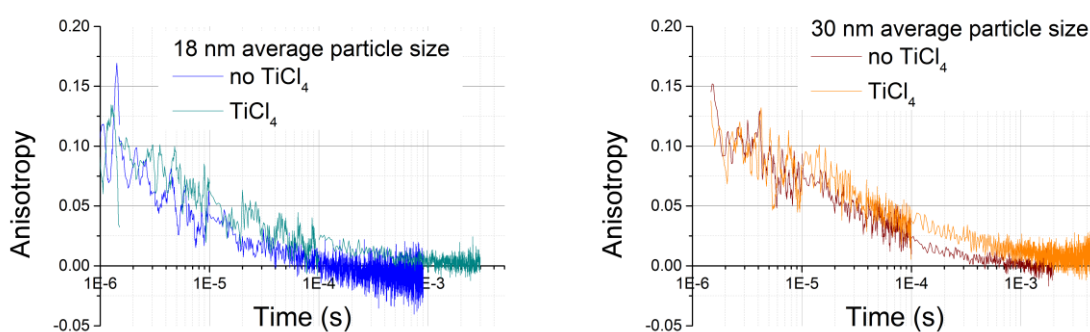


Figure 5.8. Transient absorption anisotropy measurements performed on D131 sensitized TiO₂ mesoporous films immersed in 0.1M TBAP:acetonitrile. The two graphs show measurements on films made of particles with different average size. Each graph compares the cases of films that did or did not undergo TiCl₄ treatment before sensitization.

As additional test, Figure 5.8 compares the anisotropy decay for the two films with different particle size discussed above with analogous samples which underwent TiCl₄ treatment before dye sensitization. The results show that such treatment induces a slowdown of the decay but does not have significant influence on the stretching of the profile. The disorder in the monolayer is therefore not significantly affected by TiCl₄ treatment. This would be consistent with the hypothesis of epitaxial growth of TiO₂ during the treatment only marginally affects the particle in terms of size, but not in terms of surface properties.^[140] It is however possible that the degree of disorder in the D131 monolayer is not sensitive to disorder on the surface of the TiO₂.

Figure 5.9 shows random walk simulations of transient absorption anisotropy decays that were run on the surface of a cubic space. In the simulations, I consider the simplified case where the value of the anisotropy is conserved within each facet and the transition dipole moments of the dyes in the neutral and charged states are collinear. The graphs present the effect of different sources of disorder in the monolayer. I analyse the influence of surface coverage, configurational disorder and energetic disorder on the dynamics of the decay.

Figure 5.9a shows that a percolation threshold between 50% and 30% occurs in the model system under consideration, consistent with the experimental results shown in Figure 5.4a. Incomplete coverage represents a form of disorder in the monolayer. Despite a significant slowdown in the decay, only a limited contribution to the stretching of the anisotropy decay traces is observed for surface coverage fractions between 0.6 and 1. This suggests that incomplete surface coverage is only marginally contributing to the dispersion of transport.

Figure 5.9 b and c show the effect of configurational and energetic disorder in the monolayer. The resulting trends for the two graphs are very similar. This implies that discriminating between the two factors on the basis of the transient anisotropy profile is not straightforward. However, while the values of standard deviation used for the energetic disorder study are reasonable, the examples shown in Figure 5.9b largely underestimate the expected configurational disorder in a dye monolayer. Distributions of electronic coupling, J , spanning several orders of magnitudes have been calculated on the basis of molecular dynamics for the indolene dyes D102 and D149. The evaluation of such conditions is expected to result in even more pronounced stretching of the anisotropy decay. On the other hand, the time scale of the experimental decay would not be reproduced by such model, as already evident in Figure 5.9b. Molecular fluctuations varying the coupling between dyes in time and assisting the charge diffusion in these systems was proposed by Vaissier to explain the high experimental diffusion coefficient observed.^[122]

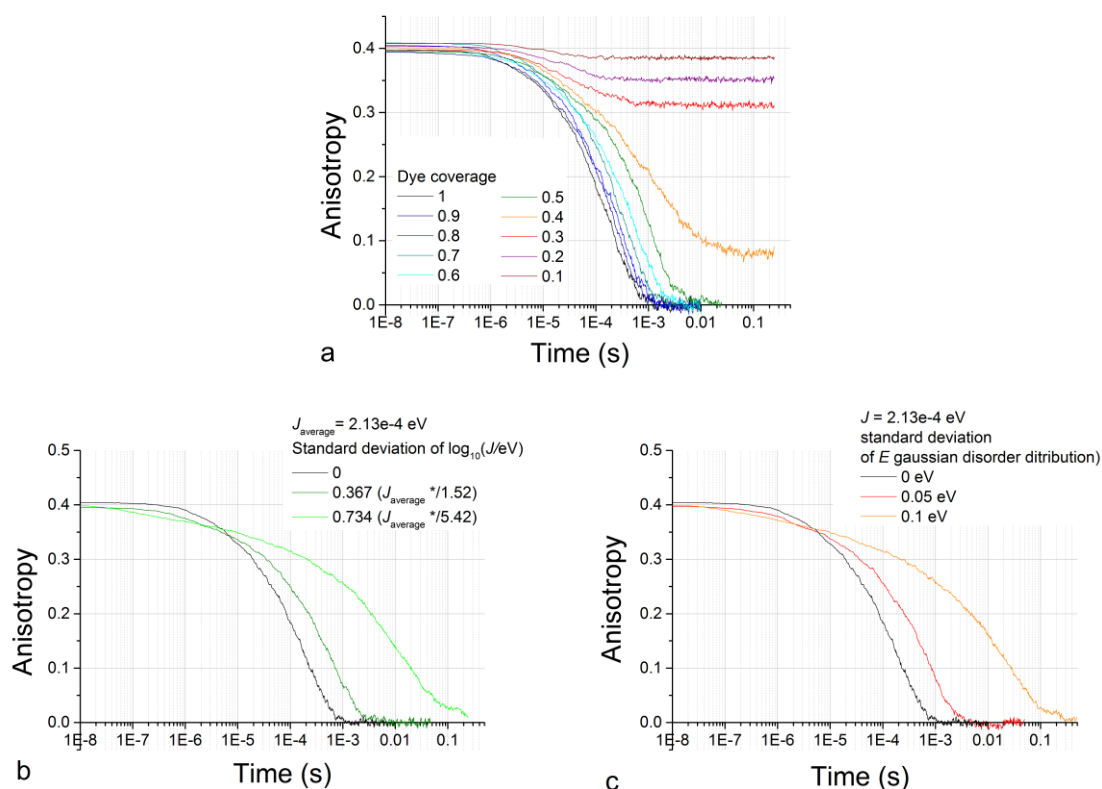


Figure 5.9. Simulated transient anisotropy results showing the effect of (a) dye coverage, (b) configurational disorder and (c) energetic disorder on the simulated profile of transient absorption anisotropy of dye sensitized TiO_2 nanocrystalline films. Each trace was obtained by averaging the calculated anisotropy from 10^4 random walk experiments on the surface of a cube with $20 \times 20 \times 6$ sites.

5.4 Summary

In this chapter I presented the experimental characterization of hole transport in monolayers of D131 sensitized TiO_2 mesoporous films immersed in an inert acetonitrile based electrolyte as a function of TiO_2 surface fraction covered by the dyes. From a qualitative analysis of the uniformity of the dye loading I showed that incomplete but uniform dye surface coverage can be attained by using the inert coadsorbent chenodeoxycholic acid. I investigated the hole diffusion in the dye monolayer for different dye loading conditions. Cyclic voltammetry measurements show a percolation threshold at about 50% coverage consistent with previously reported results. In addition, I presented transient absorption anisotropy measurements for samples prepared with similar procedure. The results show decay in time of the dye cation absorption anisotropy for samples with complete dye surface coverage. The decay was interpreted as a measure of hole transfer between

dyes at the nanoscale. The spectroscopic data show slowdown in the anisotropy decay at low dye loading below about 50%. The result is consistent with the presence of a hole percolation threshold at the nanoparticle scale.

I used bias dependent transient absorption measurements and charge extraction to analyse the recombination dynamics of photo-generated holes on the dyes with electrons in the TiO_2 . The results show correlation between the holes lifetime and the extent of hole diffusion in the dye monolayer. By decreasing the dye loading using different techniques, slower anisotropy decay *and* slower recombination are observed in comparison to the case of a fully loaded D131 TiO_2 sample. This suggests that hole transport between dyes may be contributing to faster recombination in dye sensitized systems in inert electrolytes. The result is relevant to photocatalytic devices where long-lived charges that are photo-generated on surface adsorbates are desirable. This phenomenon may also occur in liquid junction DSSCs showing slow dye regeneration. Finally I show that configurational disorder and energetic disorder in the dye monolayer could explain the observed stretching in the experimentally observed transient anisotropy decay of the dye cation absorption.

Chapter 6 Hole transport between dyes in solid state dye sensitized solar cells

In this chapter³ I discuss the dependence of the dye regeneration efficiency of solid state DSSCs on the dye surface coverage. I quantify the fraction of the hole transfer yield from the photo-oxidized dyes to the hole transporting material that is assisted by hole transport in the dye monolayer. I present results for different values of the pore filling fraction of the dyed mesoporous TiO_2 by the HTM.

6.1 Introduction

The role of hole transport in the dye monolayer of solid state DSSCs has been qualitatively discussed in previous studies (see section 2.4.2). Its contribution at assisting dye regeneration in this class of devices has been proposed to justify high values of the regeneration yield even for low levels of pore filling by the HTM. Nevertheless, no evidence of hole transport occurring in these devices (i.e. in the absence of a supporting electrolyte) has been reported to date.

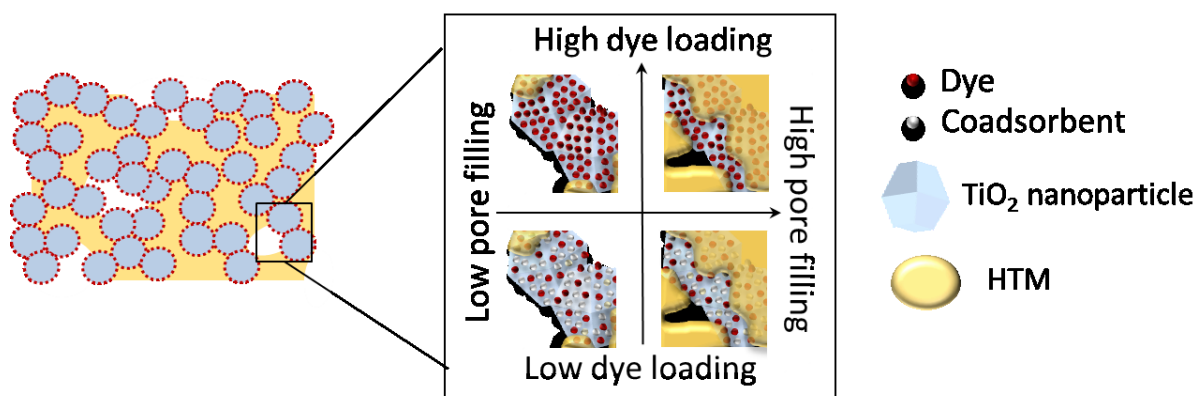


Figure 6.1. Solar cell devices investigated in this study: mesoporous films of TiO_2 have been sensitized with solutions containing the dye and an inert, colorless, coadsorbent in order to obtain different dye loading conditions. The dyed film was then infiltrated with a hole transporting material (HTM). This was done via spin coating of solutions containing different concentrations of the HTM in order to control the pore filling.

In this chapter, the following questions will be addressed: does hole hopping between dye molecules anchored to the nanocrystalline surface of TiO_2 occur in

³ The results and discussion reported in this chapter are currently under consideration for publication in the *Journal of Physical Chemistry C*

solid state DSSCs? If so, does this phenomenon lead to an improvement in power conversion efficiency of the device? Furthermore, is collection efficiency of current solid state devices still limited by poor surface coverage by the HTM, hence, would the design of dye molecules showing faster hole hopping further improve the performance of this class of solar cells? By using transient absorption and transient anisotropy spectroscopy I investigated solar cell structures where both dye coverage and pore filling by the hole transporting material (HTM) are varied (see Figure 6.1). The mechanism of dye regeneration in this class of devices is discussed.

6.2 Method

Sample and device fabrication: samples used for transient absorption measurements to evaluate regeneration of the dyes by the spiro OMeTAD were fabricated according to the procedure described in section 3.2.1. This resulted in 2.3 μm thick films. Devices were fabricated following the procedure described in section 3.2.2. 0.1 mM D131 and 0.06 mM of D149 dyes were dissolved in a 1:1 mixture of acetonitrile and tert-butyl alcohol and used to dye the TiO_2 . Control of hole transport across the D131 or D149 dye monolayer was obtained by using the coadsorbent chenodeoxycholic acid (DCA) as already shown in Chapter 5. The coadsorbent was dissolved in the dye solution at different molar ratios ranging between 1:0 and 1:100 dye to DCA. The samples were dyed for 2 hours, rinsed in acetonitrile and left to dry in air. The solution for the HTM deposition was prepared and processed on the dyed TiO_2 films following the procedure described in section 3.2.2.

Electrochemistry: for measuring the extinction coefficient of the dye cation, cyclic voltammetry was performed at 10 mV s^{-1} and spectra were recorded at a frequency of 1 Hz. The extinction coefficient $\epsilon(\lambda)$ of dyes in the oxidized state at a certain wavelength (λ) was extracted from the slope of a line fitted to the measured absorbance (A) plotted versus the total charge per unit area Q' injected in the sample using the relation $\epsilon(\lambda) = qN_A dA(\lambda)/dQ'$ (q is the elementary charge of the electron and N_A is Avogadro's number), assuming that the measured current was entirely related to the oxidation of the dyes.

Transient absorption measurements: transient absorption spectroscopy measurements were performed using the setup described in section 3.3.4. Pump wavelength of 450 nm was used. For measurements of dye regeneration yield, samples were placed perpendicularly to the pump beam, which was directed from

the laser output through a beam-guide, and slightly offset (about 30°) with respect to the main optical axis defined by the probe beam.

Table 6.1 shows the values of the extinction coefficients used in this study. 1000 and 1500 nm were used as probe wavelengths. The absorption of electrons in the conduction band of the TiO₂ was neglected in all cases.^[141]

Table 6.1. List of the values of extinction coefficient in M⁻¹ cm⁻¹ used in this study for D131 and spiro OMeTAD cations. The letter in square brackets refers to the method used to extract the value according to the following legend: [a] taken from spectroelectrochemistry measurements in 0.1 TBAP acetonitrile (see above Electrochemistry paragraph); [b] these values have been calculated by comparing the ΔOD measured at the relevant wavelength and at 1000 nm for dye sensitized films in air, given the value of the extinction coefficient measured at 1000 nm in 0.1 TBAP acetonitrile using method [a]; [c] taken from reference ^[93].

Probe wavelength	D131 cation	Spiro OMeTAD cation
1000 nm	20573 [a]	3000 [c]
1500 nm	0 (<1500 [b])	30000 [c]

Transient absorption data have been processed by assigning the observed signals to the contribution from holes on the dyes or in the spiro OMeTAD phase. The hole density per unit geometric area in species *i* is defined here as

$$p_i(t) = \int_0^d p_i(z,t) dz \text{ (cm}^{-2}\text{)}. \text{ } z \text{ corresponds to the axis perpendicular to the plane (} z = 0 \text{)}$$

defined by the sample's substrate, *d* is the thickness of the film in cm and *p_i(z,t)* is the hole density per unit volume along the thickness of the film (cm⁻³). For D131 sensitized samples, ΔOD measured at 1000 and 1500 nm can be expressed as a function of *p_{D131}(t)* and *p_{spiro}(t)* by using the following model:

$$\begin{bmatrix} \Delta OD_{1000nm}(t) \\ \Delta OD_{1500nm}(t) \end{bmatrix} = \begin{bmatrix} \epsilon_{D131+,1000nm} & \epsilon_{spiro+,1000nm} \\ \epsilon_{D131+,1500nm} & \epsilon_{spiro+,1500nm} \end{bmatrix} \begin{bmatrix} p_{D131}(t) \\ p_{spiro}(t) \end{bmatrix}. \quad \text{Eq. 6.1}$$

In Eq. 1.1, $\epsilon_{i,\lambda}$ is the extinction coefficient of species *i* at wavelength λ in M⁻¹ cm⁻¹. From the time evolution of *p_{D131}(t)* and *p_{spiro}(t)* a time dependent dye regeneration yield is defined as:

$$\eta_{reg}(t) = \frac{p_{spiro}(t)}{p_{spiro}(t) + p_{D131}(t)}. \quad \text{Eq. 6.2}$$

For all samples, the decay of the signals due to recombination of holes on the dyes or in the spiro OMeTAD were negligible up to few tens of microseconds. This model neglects any recombination happening at this or earlier timescales.

Dye regeneration yields were calculated by taking the average of $\Delta OD_{1000\text{nm}}(t)$ and of $\Delta OD_{1500\text{nm}}(t)$ between 2 and 40 μs . These values were used in Eq. 6.1 to find the averaged hole densities $\langle p_{D131} \rangle_{2-40\mu\text{s}}$ and $\langle p_{\text{spiro}} \rangle_{2-40\mu\text{s}}$. The regeneration yield was then calculated as:

$$\eta_{\text{reg}} = \frac{\langle p_{\text{spiro}} \rangle_{2-40\mu\text{s}}}{\langle p_{\text{spiro}} \rangle_{2-40\mu\text{s}} + \langle p_{D131} \rangle_{2-40\mu\text{s}}} . \quad \text{Eq. 6.3}$$

Measurements of regeneration in solid state DSSCs were carried out within 8 hours after spin coating of the spiro OMeTAD.

Transient anisotropy spectroscopy was carried out as explained in section 3.3.6. The dye loading dependence of the dye cation's absorption anisotropy decay was performed on samples that did not undergo TiCl_4 treatment. The samples were measured after being taken out of an acetonitrile solution where they had been stored in the dark for less than 5 hours after dyeing.

Electrical and photovoltaic characterization of solar cells: current voltage measurements under solar-simulated AM 1.5 sunlight were performed following the procedure described in section 3.3.7.

Pore filling calculation: the pore filling fraction was evaluated by using the method presented in reference ^[109]. The volume fraction of the pores in the dyed TiO_2 occupied by the HTM is estimated from comparing the thickness of the HTM spin coated on a flat dyed TiO_2 layer and the thickness of the capping layer resulting from spin coating the HTM solution on the dyed mesostructure. The total volume of hole conductor filling the pores is calculated as sum of two contributions: the material present in the pores after the solution has been dispensed, assuming that the solution fills all the pores and that the concentration of the solute is uniform along the depth of the film at the start of the spin coating process; the difference between the volume of hole conductor film coated on the flat surface and the volume of hole conductor forming the capping layer on top of the nanocrystalline film. This method requires knowledge of a number of parameters. First, the porosity of the dyed TiO_2 film, p_{film} , is required. p_{film} was calculated as $p_{\text{film}} = p_{\text{TiO}_2} - v_{\text{dye}}$ where p_{TiO_2} is the porosity of the TiO_2 film before dyeing and v_{dye} is the volume fraction occupied by the dye monolayer. p_{TiO_2} was quantified from the interference fringes observed in a specular transmission measurement of the film.^[113] v_{dye} was determined by desorbing the dye from films sensitized without coadsorbent. In this way the molar

concentration of dyes in the film c_0 (mol cm⁻³) can be estimated. Assuming density ρ of 1 g cm⁻³ for the collection of dyes anchored to the TiO₂, $v_{dye} = c_0 * M_w / \rho$ where M_w is the molecular weight of the dye. This value of v_{dye} was calculated for the full dye loading case and used for samples with different relative concentration of dye and DCA. Another parameter needed to evaluate the pore filling fraction is d_{sol} , which is the estimated thickness of the spin coated solution on top of the mesostructure. This was evaluated by spin coating the solution of spiro OMeTAD on compact layers of TiO₂ sensitized in different conditions. From the thickness of the resulting layer, a thickness of the original wet film of 5.42 ± 0.27 μ m was calculated. This value was the same within experimental error for 136 mg/ml spiro OMeTAD in chlorobenzene solutions with and without additives spin coated on D131:DCA sensitized TiO₂ compact layer at a ratio of 1:0 and 1:100. This value was used for all pore filling calculations in this study. Finally the thickness of the dyed TiO₂ film (d) and the thickness of the capping layer of spiro OMeTAD left on top of the dyed nanocrystalline film upon spin coating of the hole conductor (d_{cap}) are needed. Multiple measurements of the film thickness were taken after scratching the sample. Thickness in the same areas was then remeasured after removing the spiro OMeTAD with acetone. d_{cap} was evaluated as the difference between the average of measurements taken before and after the spiro OMeTAD removal.

The pore filling fraction can therefore be calculated as:

$$PF = c + \frac{d_{sol}c - d_{cap}}{dp_{film}} . \quad \text{Eq. 6.4}$$

In equation 5, c is the volume fraction of spiro OMeTAD in the spin coating solution, which is calculated assuming the density of the hole conductor to be 1 g/ml.^[142]

6.3 Results and discussion

6.3.1 Inter-dye hole transport in ambient conditions

Figure 6.2 shows the transient absorption anisotropy measurements performed on D131:DCA sensitized films at different levels of dye surface coverage. Compared to the case of hole diffusion in acetonitrile based electrolyte (see Chapter 5), samples in ambient conditions showed much slower anisotropy decays. For full dye coverage samples, finite values of anisotropy were recorded up to milliseconds after the laser excitation. Decay in anisotropy was significantly slower in samples with low dye coverage.

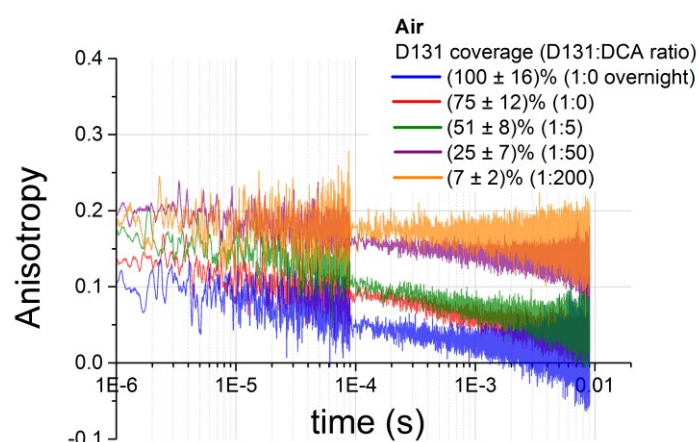


Figure 6.2. Transient absorption anisotropy measurements for D131:DCA sensitized TiO₂ nanocrystalline films in ambient conditions.

These results suggest that hole transport occurs in dye monolayers anchored to mesoporous TiO₂ films even in absence of supporting electrolyte and therefore in principle also in solid state devices. They also show that percolation can be stopped by decreasing the dye loading of the films.

The observation that diffusion of holes appears around 100× slower in air than in the presence of electrolyte could be explained considering the absence of a polar environment able to screen the dyes from each other. This may result in more distorted configurations of and poorer coupling to neighboring dyes when a hole is present in the monolayer.

6.3.2 Dye regeneration dependence on pore filling and dye loading

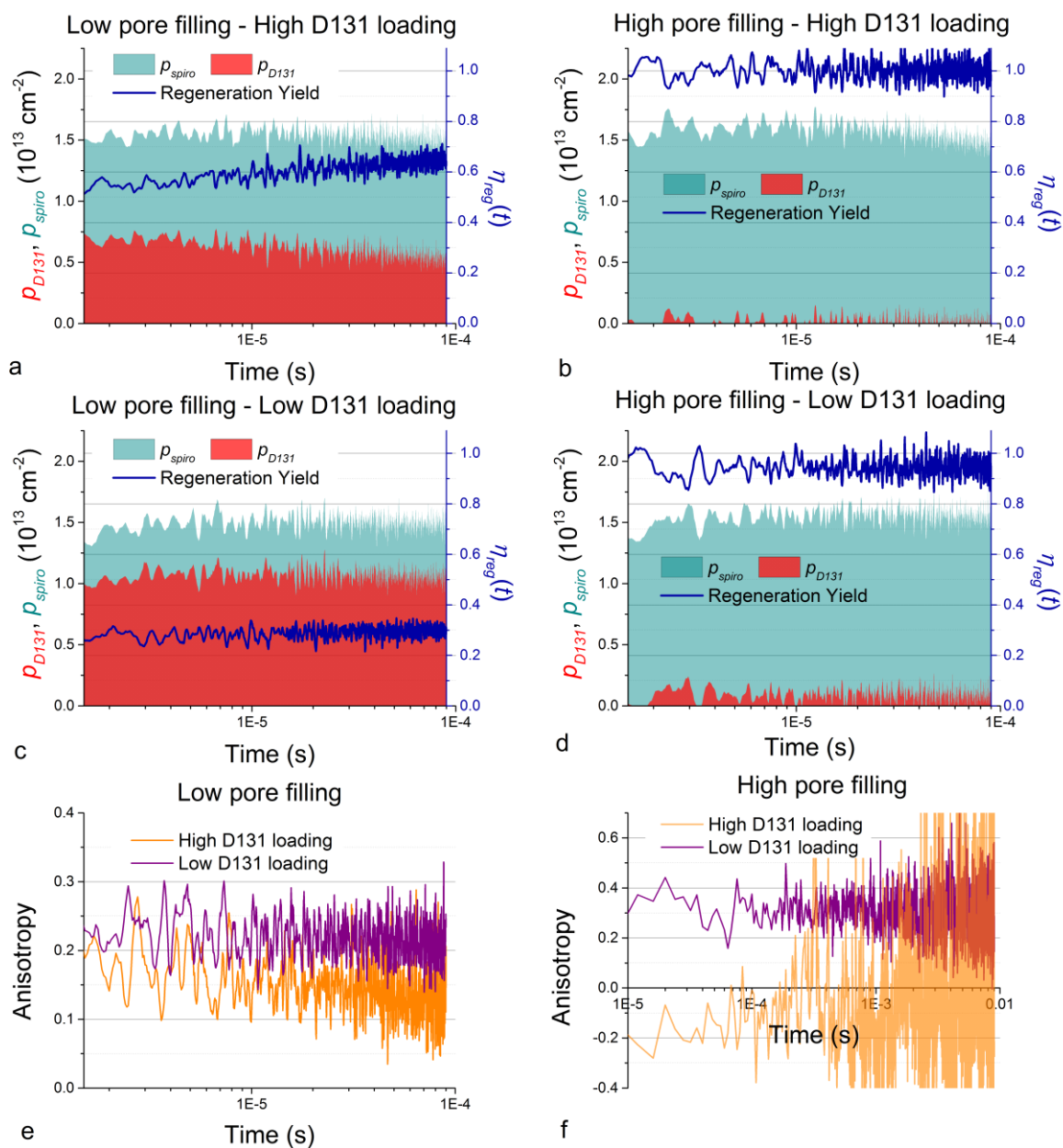


Figure 6.3. (a-d) Analysis of the kinetics for holes on D131 dyes and on spiro OMeTAD obtained by inverting the linear problem expressed in Eq. 6.1 for transient absorption measurements at 1000 and 1500 nm. The left axis displays the hole density dynamics in the dye layer (p_{D131}) and the HTM (p_{spiro}) in the different devices upon laser excitation, whereas the right axis gives an estimate of the time dependent regeneration efficiency (η_{reg}) of the devices as a function of time. The calculated pore filling fraction and dye loading for the devices were respectively: (a) 3.4%, 88%; (b) 81%, 87%; (c) 3.4%, 35%, (d) 81%, 39%. (e, f) Transient anisotropy, $r(t)$, of the oxidized dye signal, p_{D131} , for the 4 devices analysed in the top 4 figures. Note that the timescale in figure 3f is different from the one used in the other graphs.

TiO₂ nanocrystalline films sensitized with D131:DCA infiltrated with spiro OMeTAD and the additives LiTFSI and tBP were measured via transient absorption

spectroscopy. Figure 6.3a-d show the concentration of holes on D131 dyes and in spiro OMeTAD (left axes) as a function of time within the μs to $100\ \mu\text{s}$ time scale for a set of devices. These quantities were obtained from the analysis of TAS data measured at 1000 and 1500 nm using Eq. 6.1. High and low pore filling cases are considered for both full and below 50% D131 coverage. In Figure 6.3a-d (right axes) the time dependent regeneration yield, calculated using Eq. 6.2, is also shown.

From these graphs the following observations can be drawn. Low pore filling results in a significant fraction of holes being left on the dyes at the earliest timescale resolved ($\sim 1.5\ \mu\text{s}$). For the case of full D131 coverage, the regeneration yield at $1.5\ \mu\text{s}$ is higher than for the case of low D131 coverage (0.5 against 0.3). Moreover, for the first case, an increase in the hole density in the spiro OMeTAD is observed, corresponding to about 20% increase in regeneration yield during the 1 to $100\ \mu\text{s}$ timespan. The final value is higher than the low dye loading sample by a factor of more than 2. The low D131 coverage case did not show any increase in the regeneration yield within the measured time window. Samples fabricated with high pore filling, showed very high regeneration yield. For the high dye loading case $\eta_{\text{reg}} = 1$ (within the error) throughout the timescale of the measurement. However, the low dye loading, high pore filling film showed a constant value of $\eta_{\text{reg}} = 0.95$. This suggests that for the low dye loading case, even under optimized pore filling conditions, a fraction of holes are left on dye molecules and are not able to reach the HTM. This was not the case when holes were able to move on the surface of the TiO_2 in the high dye loading, high pore filling sample. Indeed, these observations suggest that for the latter case either direct or hole percolation assisted regeneration occurs for all the photo-excited dyes that injected an electron in the TiO_2 . Once again, any recombination process that occur at timescales faster than the system resolution ($\sim 1\ \mu\text{s}$) is neglected in this analysis. This would decrease the absolute value of the regeneration yield but would not change the observed trends.

To further confirm these findings, transient anisotropy spectroscopy was applied to the same samples. The anisotropy signal related to the holes on the dyes (p_{D131}) was extracted from anisotropy measurements at 1000 nm and by subtracting the spiro OMeTAD contribution at 1000 nm calculated from the signals at 1500 nm. This operation was carried out under the assumption that the absorption tail of the spiro OMeTAD cation at 1000 nm refers to the same dipole moment as the

absorption at 1500 nm. In Figure 6.3e and Figure 6.3f the transient anisotropy signal assigned to p_{D131} for the same 4 devices corresponding to Figure 6.3a-d are shown.

From Figure 6.3e, a drop in anisotropy for the high coverage device is detected, whereas no significant variation can be noted for the low coverage case. Thus for samples with dye loading greater than 50% a simultaneous increase in regeneration yield and drop in anisotropy for the signal related to holes on D131 dyes is observed. This corroborates the hypothesis that hole hopping between dyes provides a route for the regeneration of dyes that are not in direct contact with the HTM. The hypothesis is also consistent with the observation that, when low dye loading is considered, both the regeneration yield and the anisotropy profile related to the dye cations population remain constant between 1 and 100 μ s. Figure 6.3f on the other hand gives an interesting insight into the regeneration performance when pore filling is optimized. When the dye loading of the device is low so that percolation of holes through the dyes is prevented, a finite and constant anisotropy signal is detected for p_{D131} up to the 10 ms timescale. This is consistent with a finite fraction of photo-generated holes not being transferred to the HTM from the dye monolayer. On the other hand, no clear anisotropy signal for p_{D131} could be resolved for the device fabricated with high dye loading. This is consistent with the negligible density of holes remaining on the D131 dyes after 1 μ s.

Transient absorption spectroscopy was carried out for devices fabricated with gradually increasing pore filling fraction and for three different dye solution compositions. The D131:DCA ratios of 1:0, 1:5 and 1:100 were chosen in order to obtain two sets of devices with dye loading above 50% D131 coverage, one with and one without inert coadsorbent, and one with less than 50% D131 coverage. Figure 6.4 shows the resulting trends of regeneration efficiency (calculated as shown in Eq. 6.3) as a function of pore filling for the different dye loading conditions. The graph shows very clearly that regeneration of the dyes in the architecture investigated here depends significantly on the pore filling of the HTM in the pores of the TiO_2 but also on the dye monolayer composition.

The resolution of the kinetics shown in Figure 6.3 and the quantification of the regeneration yield displayed in Figure 6.4 rely on the knowledge of the extinction coefficient of the oxidized dye and HTM at the probed wavelengths. The values of extinction coefficient used in this work were extracted from electrochemical measurements, in the presence of an electrolyte. Such values can vary when

considering different environments. The relative trend which is discussed here between different samples should however remain valid.

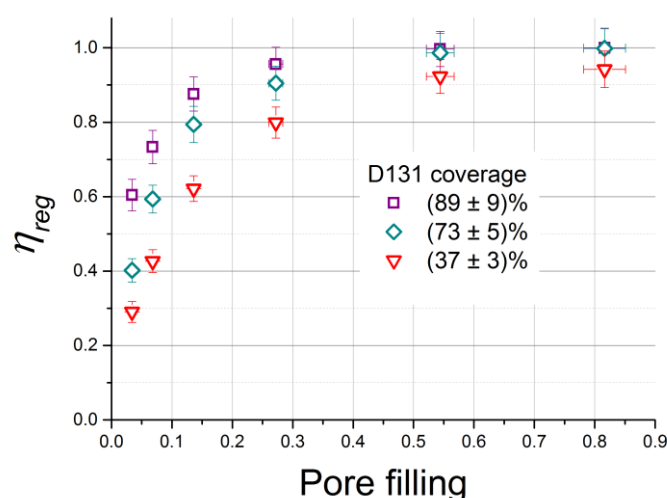


Figure 6.4. Regeneration efficiency calculated from transient absorption measurements using Eq. 6.3 on D131:DCA sensitized TiO_2 films infiltrated with spiro OMeTAD as HTM as a function of pore filling. The experiment was carried out for three different dye solution compositions to vary the dye coverage.

6.3.3 The role of the additives LiTFSI and tBP on regeneration

The use of the additives LiTFSI and tBP substantially improves the performance of solid state DSSCs employing spiro OMeTAD as hole transporting material. The presence of these additives was shown or argued to produce variations on several parameters. Improvements related to more favorable surface energetics, higher electron injection efficiency in the TiO_2 , slower recombination kinetics, surface traps passivation, doping of the HTM, pore filling ability by the HTM are among the most commonly cited. Some of these aspects are however still under debate. From a practical point of view, the fabrication of optimized devices (solid state DSSCs but also Perovskite based) including the hole conductor spiro OMeTAD typically envisages the inclusion of both LiTFSI and tBP. Data reported so far refer to solid state dye sensitized structures where additives were included in the HTM solution at constant concentration. The value was chosen on the basis of the typical range of concentrations resulting in optimal performance in solid state DSSCs where the HTM is infiltrated in the mesostructure to achieve high values of pore filling. However, when varying the concentration of spiro OMeTAD in solution, this results in different molar ratio between the additives and the hole conductor.

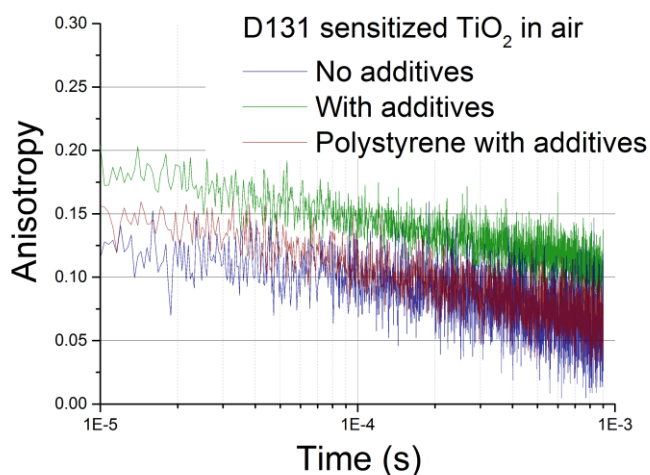


Figure 6.5. Transient anisotropy decays for D131 sensitized TiO_2 mesoporous films obtained by exciting the samples with laser pulses at 450 nm (10Hz repetition rate) and by probing the D131 cation absorption at 1000 nm. The graph shows how the presence of LiTFSI and tBP and of the same additives dispersed in polystyrene influence the anisotropy dynamics.

Transient absorption anisotropy was measured for dye sensitized samples on top of which a solution of the additives in chlorobenzene was spun before the measurement. In Figure 6.5, this measurement is compared to a reference D131 dyed TiO_2 sample without additives. The case of a D131 sensitized TiO_2 film infiltrated with additives and polystyrene (at a concentration of 45 mg ml^{-1}), deposited from the same solution in chlorobenzene is also considered. This last case was investigated as attempt to reproduce the dielectric environment of an actual solid state DSSC infiltrating the pores with an organic phase which is however electrically inert. When comparing the samples with and without additives, a slowdown by about one order of magnitude in the anisotropy decay upon inclusion of LiTFSI and tBP on the surface of the dyed TiO_2 is observed. This could be related to a slower hole diffusion in the monolayer, or a significant variation in the monolayer configuration. The addition of LiTFSI and tBP on the dyed surface of the TiO_2 is unlikely to decrease the level of disorder in the monolayer. It can therefore be concluded that the presence of the additives on the surface of the dyed TiO_2 hinders the diffusion of holes. The sample infiltrated with additives and polystyrene showed on the other hand only slightly slower anisotropy decay than the sample with no additives. Note that this decay occurs on a similar timescale as the one reported in Figure 6.3e for the high dye loading case.

Solid state DSSCs with and without additives and for two levels of pore filling were considered. The evaluated regeneration yields of these structures is shown in Figure 6.6.

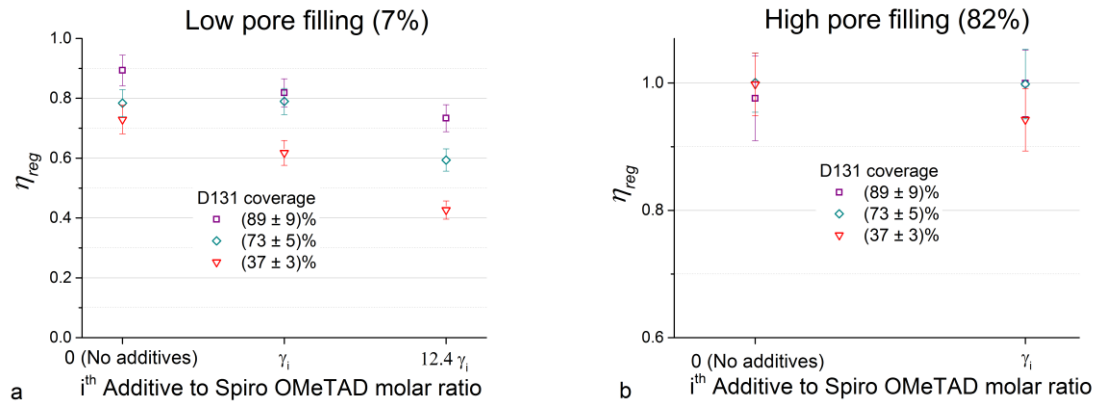


Figure 6.6. Regeneration yield in solid state DSSCs devices where the HTM solution processed on top of the dyed TiO_2 mesostructure included different concentrations of the additives LiTFSI and tBP. γ_i is molar the ratio of i^{th} additive ($i = \text{LiTFSI}$ or tBP) to spiro OMeTAD used for the optimized performance devices in this work. The analysis is shown for the cases of (a) low and (b) high pore filling.

The molar ratio between the two additives was kept constant in all cases ($M_{tBP}/M_{\text{LiTFSI}} = 2.8$). On the other hand, using different concentration of HTM and keeping the concentration of the additives constant, results in different additive to spiro OMeTAD molar ratios. I define the molar ratio $\gamma_i = M_i/M_{\text{spiro, high PF}}$, where M_i is the molar concentration of additive i (i is either tBP or LiTFSI) and $M_{\text{spiro, high PF}}$ is the spiro OMeTAD molar concentration for the highest pore filling structures considered in the previous sections ($\gamma_{tBP} = 0.59$, $\gamma_{\text{LiTFSI}} = 0.21$). Figure 6.6a refers to a 7% pore filling sample. It illustrates the cases of HTM processing with no additives and with additives added as in the study shown in Figure 6.4 (for this particular level of pore filling, an additives to spiro OMeTAD molar ratio of $12.4 \gamma_i$ is used). The case of additives at a molar ratio corresponding to γ_i versus spiro OMeTAD is also considered. The trend shows that regeneration is hindered by the presence of LiTFSI and/or tBP. In particular, considering the results shown in Figure 6.5, this observation suggests that a slower diffusion of holes in the dye monolayer results from the inclusion of these additives. Strikingly, such dependence is observed also for the regeneration yield of the low dye loading samples. This implies that, even below the macroscopic percolation threshold, the fraction of photo-generated holes that are able to travel far enough at the nanoscale to reach an HTM island is

significant. This is also consistent with what observed in Figure 5.4 where, even for D131 sensitized TiO_2 samples with 25% dye loading in the absence of additives, a mild decay in anisotropy is detected already in the 1-100 μs time scale.

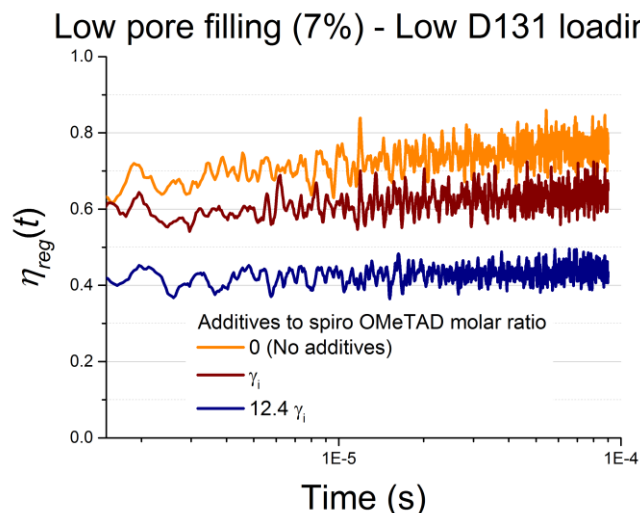


Figure 6.7. Influence of the additives LiTFSI and tBP on the time dependent regeneration yield for low (40%) D131 surface fractional coverage and low pore filling conditions.

Figure 6.7 shows the time dependent regeneration for the low dye loading samples shown in Figure 6.6a. The blue line refers to the sample fabricated using the high concentration of additives. For this case, a flat profile at a value of about 0.45 is observed, consistent with data reported in Figure 6.4 for the low pore filling, low dye loading case. When a lower concentration of additives is considered, the regeneration yield observed at 1.5 μs starts from a higher value and it shows a mild increase over a few tens of μs . For the “no additives” case this behavior is even more pronounced and a regeneration yield as high as 0.75 is reached. These observations strongly suggest that hole transfer between dyes occurs at the nanoscale to a detectable extent even below the macroscopically observed percolation threshold.

To summarize, the presence of additives reduces the diffusion of holes in the dye monolayer and results in remarkably lower regeneration yield under low pore filling conditions. Notably, the latter effect is observed for all dye loadings investigated here, including samples with dye surface coverage below 40%.

6.3.4 Inter-dye hopping and device performance

The photovoltaic performance of solid state DSSCs using the dye D149 have been tested. The aim of the study was to assess the effect of pore filling and dye loading on the charge collection efficiency of devices where these two parameters were varied similarly to the analysis presented in section 6.3.2. Current voltage measurements were carried out in the dark and under simulated AM1.5 solar spectrum. A fraction of the devices with low pore filling showed low shunting resistance, possibly due to the contact of the silver anode and the dyed TiO_2 . In Figure 6.8 the statistics of the short circuit current density is shown, average of at least 4 devices as a function of pore filling for three different dye loading conditions. To be noted, low shunt resistance values do not affect the measurement of j_{sc} .

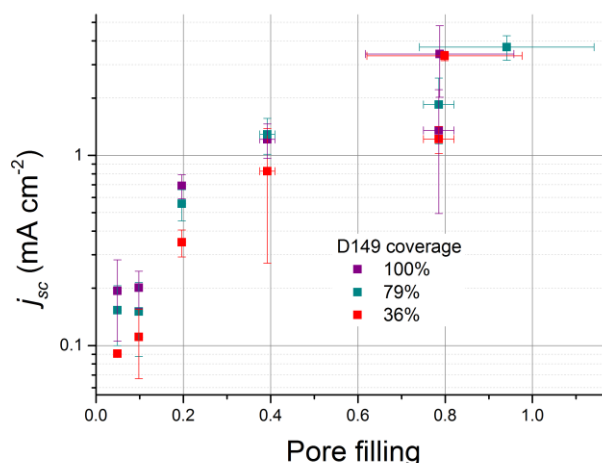


Figure 6.8. Statistics on the measured short circuit current density for solid state DSSCs as a function of the pore filling of the dyed TiO_2 film by the HTM. The study was carried out for three different dye coverage values.

The first observation is that, regardless of the dye loading conditions, the photocurrent of the devices strongly depends on the pore filling by the HTM. j_{sc} was found to increase throughout the range of pore filling values tested (about 5 to 80%). Photocurrent is therefore sensitive to pore filling even under pore filling conditions close to the optimum, as already previously reported.^{[113],[114]}

Dyeing of the films with different D149:DCA ratios is expected to have several effects on the performance of the device. Most importantly it has an effect on:

- Light harvesting efficiency (LHE): lower dye loading results in lower LHE of the solar cell. A factor of about 1.9 can be calculated between

the LHEs of the 100% and the 36% loading cases considering a perfectly reflecting back contact. This value is expected to be higher if one also includes the losses due to the absorption of the doped spiro OMeTAD which have higher influence the lower the dye loading.

- b) Electron injection efficiency: the inclusion of DCA in the dye solution has been previously reported to decrease the aggregation of the dyes on the surface and tune the energetics at the interface.^{[143],[144],[145],[146]} Variation in electron injection efficiency may therefore be expected.^[147]
- c) Recombination kinetics: the presence of DCA has been argued to vary the blocking ability of the sensitized surface which influences the recombination rate between electrons in the TiO₂ and holes in the HTM phase.^{[144],[143]}
- d) Hole transport between dyes on the surface: as shown in Figure 6.4, there is a dependence of the regeneration yield in the μ s timescale on the ability of holes to diffuse in the monolayer of dyes on the surface of TiO₂.

Figure 6.8 shows that the j_{sc} for the low dye loading devices is consistently lower than for the above percolation DSSCs. A factor slightly greater than 2 between the mean photocurrent values of devices with 100% and 36% dye loading is observed when the pore filling is below 20%. As discussed in (a), this difference could be explained on the basis of the different light harvesting efficiency of solar cells with high or low dye loading. However, at high levels of pore filling, devices with different dye loadings show very similar values of photocurrent. This suggests that including DCA in the dyeing process is beneficial to another process involved in the photo-conversion of simulated sunlight and that the evident gap at low pore filling levels is likely to be due to the presence/absence of hole diffusion in the dye monolayer assisting regeneration.

6.3.5 Hole diffusion as a probe of the surrounding environment: hole transporting material film formation

From the above discussion, it can be concluded that in a solid state DSSC device a decrease in dye loading results in decreased regeneration yield. The results also suggest that this trend is related to the ability of holes to diffuse within the dye monolayer. If one assumes that when the dye loading is below the percolation

threshold, hole transfer between dyes at the nanoscale is negligible, then the only dyes that can be regenerated are those that are in contact with the HTM. This implies that the regeneration yield in this type of architecture would be a close estimate of the fraction of the dyed TiO_2 surface covered by the HTM in the device. Above the percolation threshold, this concept should not be valid, given the contribution of hole transfer between dyes to the regeneration yield discussed in the sections above.

The morphology of the HTM is expected to be sensitive to different conditions on the surface of the mesoporous film. For example, the coadsorbent DCA is known to have different wetting properties than the dyes used in this work.^[148] This could indeed significantly vary the contact angle of the HTM solution when wetting the pores during the spin coating step as well as offer different surface properties for the HTM film formation. Surface wetting analysis was carried out for TiO_2 compact layers in the case of bare surface and of surface sensitized with the dye D149 or sensitized with DCA. Both chlorobenzene and a solution of 136 mg ml^{-1} spiro OMeTAD in chlorobenzene with the additives LiTFSI and tBP were found to wet all these different surfaces with a contact angle lower than 15° . The very good wetting properties of the sensitized surfaces suggests that pore infiltration by the HTM solution may occur in a similar way for the different dye compositions used in this work. The hypothesis that the HTM film formation dynamics are similar for the different dye loadings considered in this study is however more difficult to verify but not unreasonable. Based on these observations, if no influence on the morphology of the HTM by the dye loading is assumed, then it is possible to use the results in Figure 6.4 to infer information about the dyed TiO_2 surface coverage by the HTM.

Figure 6.9a shows the regeneration yield data from Figure 6.4 plotted versus the dyed TiO_2 surface fraction covered by the HTM assuming that the latter is equal to the regeneration yield for the case of low dye loading, $\eta_{\text{reg, low loading}}$. It is apparent that the relationship between the fraction of the dyed TiO_2 surface covered by HTM and regeneration yield for the systems where the dye loading is above the percolation threshold is not linear.

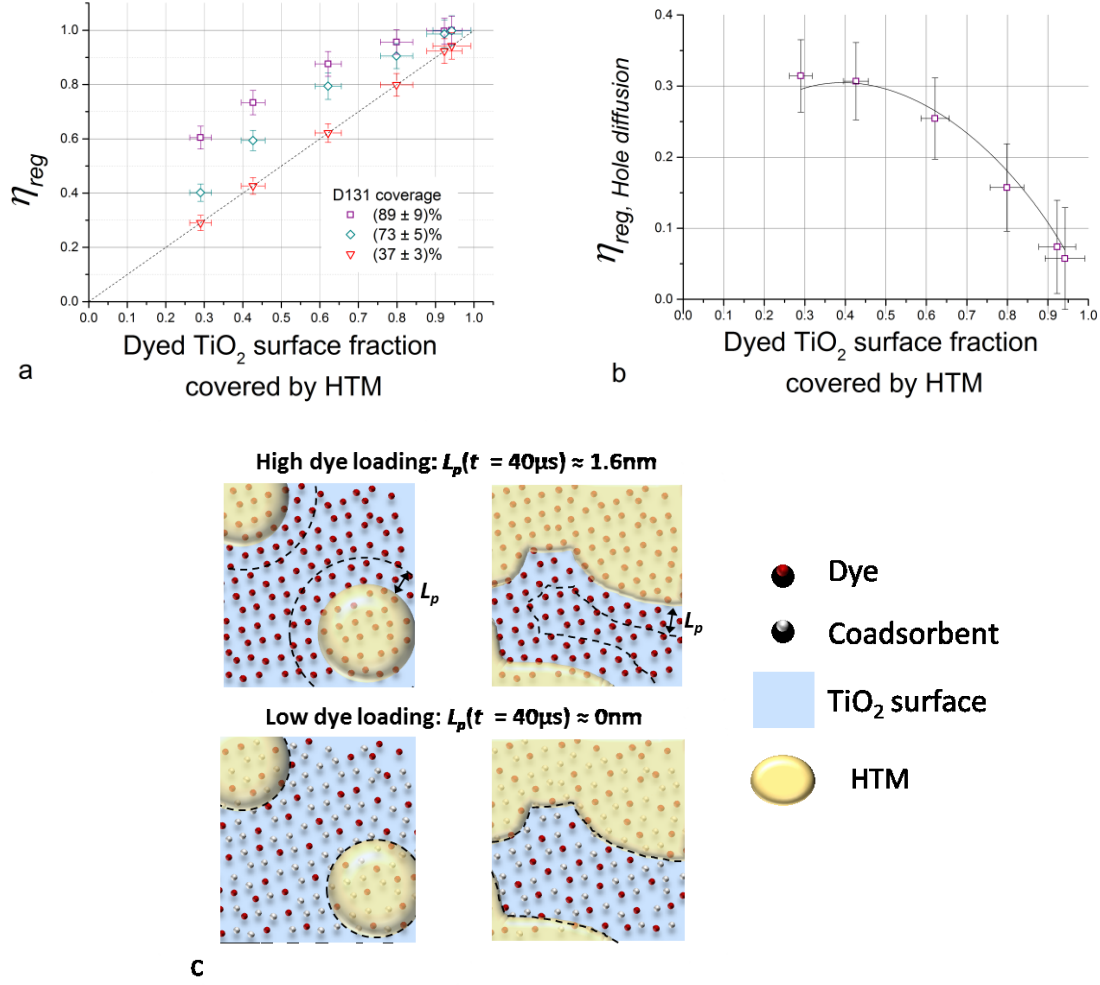


Figure 6.9. (a) Regeneration efficiency (from Figure 6.4) plotted as function of dyed TiO_2 surface fraction covered by the HTM spiro OMeTAD. The latter is considered to be equal to the regeneration yield at low dye loading conditions (dashed line in Figure 6.9a). (b) Component of regeneration yield that can be ascribed to hole diffusion in the dye monolayer for the above percolation dye loading case. (c) This quantity can be approximated as the fraction of the surface area conformal to the perimeter of the HTM islands with thickness L_p shown in the schematic. L_p is an estimate of the distance covered by the holes in the dye monolayer within 40 μs from photogeneration. The solid line in Figure 6.9b is the fit of the expression for this fraction of the surface (HTM perimeter $\times L_p$) as a function of HTM coverage to the data.

Given the above model, the regeneration yield due to hole diffusion between dyes ($\eta_{reg, \text{holediff}}$) can be calculated. This is the fraction of holes that reached the spiro OMeTAD phase through transport in the dye monolayer, always assuming that such phenomenon does not occur to a significant extent in the case of low dye coverage. Therefore:

$$\eta_{reg,holediff} = \eta_{reg} - \eta_{reg,lowloading} \quad \text{Eq. 6.5}$$

where η_{reg} is the total regeneration yield and $\eta_{reg,lowloading}$ is the total regeneration yield for the low dye loading case. The observed trend in regeneration due to hole diffusion in the dye monolayer refers to the specific morphology of the “islands” of HTM in contact with the sensitized surface. Therefore, assuming a known hole transport regime in the dye monolayer one could extract information about the HTM film morphology or *vice versa*. Here, I interpret $\eta_{reg,holediff}$ as the fraction of the dyed surface which is uncovered by HTM and from which hole diffusion in the dye monolayer assisting regeneration is possible. This area can be approximated as the product of the HTM islands’ perimeter P and the distance travelled by the holes in the uncovered monolayer of dyes L_p as shown in Figure 6.9c.

P is a function of the pore surface coverage. In particular, for a constant density of, randomly distributed, simultaneous surface nucleation centers, an analytical solution to the problem has been demonstrated.^[149] The perimeter per unit surface area P' can be expressed as:

$$P'(C) = (1 - C) \sqrt{4\pi N \ln\left(\frac{1}{1 - C}\right)} \quad \text{Eq. 6.6}$$

where C is the fractional dyed TiO_2 surface coverage by the HTM and N is the density of nucleation centers (cm^{-2}).

Figure 5b displays the plot of $\eta_{reg,holediff}$ against dyed TiO_2 surface coverage by the HTM for the set of samples with complete dye loading. The fit to the data corresponds to the expected trend of the product $L_p \times P'$ assuming a constant density of randomly distributed nucleation centers on the surface for all the different spiro OMeTAD concentrations considered. The only fitting parameter used is the product $L_p \times N^{1/2}$ and is equal to 0.20.

L_p can be calculated as $(D_{2D} t_d)^{0.5}$ (where D_{2D} is the holes diffusion coefficient on the surface of the TiO_2 and t_d is diffusion time of the holes). From electrochemical measurements of the apparent diffusion coefficient $D_{app} \approx 4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ is obtained for the case of fully covered D131 TiO_2 nanocrystalline films immersed in 0.1M TBAP in acetonitrile. This value can be translated into a 2D diffusion coefficient by considering that $D_{2D,electrolyte} = \alpha_g D_{app}$ where α_g accounts for the dimensionality of the

mesoporous film's surface. A value of $\alpha_g > 3/2$ is expected,^[128] which implies that the holes diffusion coefficient on the surface of the TiO₂ in this particular inert electrolyte is $D_{2D,electrolyte} > 6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. From the transient anisotropy measurements of films fully covered in D131 dyes, the anisotropy decay occurs at a timescale which is about two orders of magnitude slower for the case of the D131 sensitized TiO₂ film in air than the case in the electrolyte used for electrochemical measurements. Here I assume that the influence of the electrolyte on the dye monolayer conformation does not significantly vary the orientation of the dyes as well as the relative orientation of the cation's dipole moment probed spectroscopically. Then, the hole diffusion can be described by a diffusion coefficient which is about two orders of magnitude lower than the one calculated in presence of the electrolyte, i.e. $D_{2D,air} = 6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ if for example one considers $\alpha_g = 3/2$. $t_d = 40 \text{ } \mu\text{s}$ can be assumed. Note that the calculated regeneration yield (see Eq. 6.3) represents a slight underestimate of the time dependent regeneration yield at 40 μs . A value in the order of 1.55 nm for L_p is obtained. This would result in a nucleation center density value of $N = 1.66 \times 10^{12} \text{ cm}^{-2}$, which corresponds to 1 nucleation center every about 8^2 nm^2 . This value of surface area is in the same order of magnitude as the surface area of a TiO₂ particle facet. The implication is that growth of the spiro OMeTAD film occurs starting from a density of nuclei that is comparable to the density of TiO₂ particles' facets. This would therefore imply that the morphology of the HTM in the pores is similarly coarse as the nano-morphology of the TiO₂ scaffold, resulting in few but relatively large areas of dyed TiO₂ being uncovered. Despite the good quality of the fit shown in Figure 6.9b, different nucleation growth behaviors may be expected for different concentrations of the spiro OMeTAD solution. Also, this analysis assumes homogeneous hole transport properties in the dye monolayer. Notably, the anisotropy decays in Figure 5.3 show highly dispersive character which suggests that describing holes migration across the particle's surface with a basic diffusion model is an oversimplification. According to Figure 6.9a, for the high dye loading case, hole transport between dyes results in collection of all the photo-generated holes on uncovered dyes at minimum dyed TiO₂ surface coverage by the HTM of about 80 to 90%. This is therefore consistent with two possible scenarios: a coarse distribution of HTM (on a pore to pore scale as described by the model above) and/or a dye monolayer showing high degree of disorder. Inhomogeneous coverage by the HTM (specifically, non-uniform filling of the pores) would be expected if the

ability of the HTM to infiltrate in the dyed mesostructure were a function of the pore size. Also, the presence of air bubbles in the pores during the HTM spin coating process could lead to specific regions of the film not being filled by the HTM. SEM analysis of pore filling and HTM film morphology has previously been reported.^{[109],[107]} However, SEM is a surface analysis technique and has some limitations for studies of bulk properties (even in the cross sectional case, samples need to be cut or cleaved in order to expose an “internal” surface to the measurement). Given the relationship between hole percolation assisted regeneration and HTM morphology, this analysis represents a useful non-invasive, contact-less, technique to investigate the interfacial properties in the bulk of solid state dye sensitized devices. Also, hole transport between dyes on surfaces could be used as “probe” to study the surrounding local environment in other systems.

In the model discussed so far, regeneration of dyes has been evaluated for the timescale at which negligible recombination occurs. Regeneration can however occur at later timescales. Thus, the values reported in Figure 6.4 represent underestimates of the total regeneration yield for this experiment. In particular, the hole diffusion length can be calculated as $L = (D_{2D,air} \langle \tau \rangle)^{1/2}$, where $\langle \tau \rangle$ is the mean relaxation time related to the hole recombination to electrons in the TiO₂. $\langle \tau \rangle$ can be calculated by fitting a stretched exponential to the cation decay measured for a solar cell structure in the absence of the HTM. Similarly to the cases already described in Figure 6.5 the following situations can be considered: D131 sensitized TiO₂ without additives, with additives spun from chlorobenzene and with additives spun from a chlorobenzene solution of Polystyrene. The different decays are shown in Figure 6.10.

Values of L ranging between 10 and 35 nm imply that close to unity regeneration would be expected for the high dye coverage even at low HTM pore filling. This however relies on the assumption of normal and homogeneous diffusion. Importantly, L is a function of light intensity and would have significantly shorter value at, for example, 1 sun equivalent illumination. L is also likely to vary due to different pore filling conditions and with different amount of additives present on the surface.

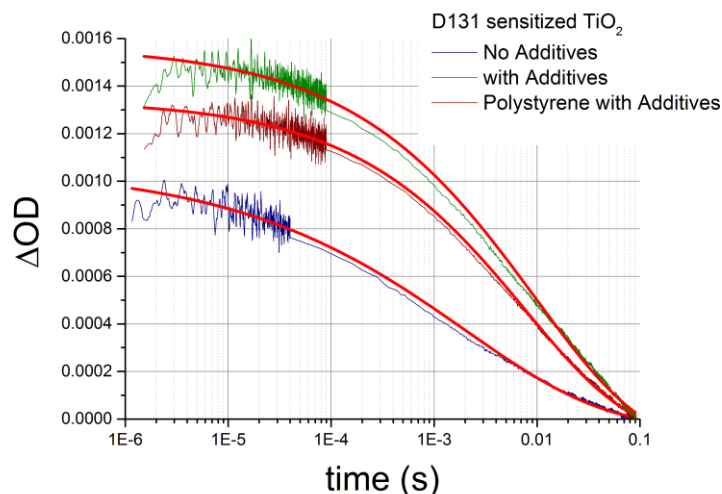


Figure 6.10. D131 cation signal decay measured at 1000 nm upon laser excitation at 450 nm for a D131 sensitized TiO_2 film (after TiCl_4 treatment) under different conditions. The red lines correspond to fits of offset stretched exponentials to the data. Results of the fits are reported in Table 6.2.

Table 6.2. Fitting parameters of stretched exponentials fitted to the data shown in Figure 6.10. $\langle \tau \rangle$ is the mean relaxation time. An approximation of the value of $D_{2D,air}$ is also reported based on the transient anisotropy data shown in Figure 5.3 and in Figure 6.5. From $\langle \tau \rangle$ and $D_{2D,air}$ the value of the holes diffusion length L is estimated.

Conditions	τ (ms)	α	$\langle \tau \rangle$ (ms)	$D_{2D,air}$ ($\text{cm}^2 \text{s}^{-1}$)	L (nm)
No additives	2.03 ± 0.04	0.33	13.1	$6\text{e-}10$	28
+ Additives	9.56 ± 0.13	0.42	28.5	$6\text{e-}11$	13
Polystyrene + Additives	7.75 ± 0.09	0.44	20.0	$6\text{e-}10$	35

6.4 Summary

In this chapter I discussed the influence of hole transport in dye monolayers on the mechanism of dye regeneration in solid state DSSCs. I showed that the regeneration yield of devices using the dye D131 and the hole transporting material spiro OMeTAD increases with the pore filling of the dyed mesostructure by the HTM, consistently with previous reports for different dyes, but also increases with the dye surface coverage. I have coupled this finding with transient absorption anisotropy characterization of solar cell devices to monitor the diffusion of holes on the sensitized surface. This resulted in the deconvolution of the contribution of dyes which are left uncovered from the contribution of dyes in contact with the HTM phase to the measured regeneration yield of the solar cell. I therefore showed strong evidence for inter-dye hole transport to be an important part of the working principle

of this class of devices. Developing new strategies to characterize charge diffusion in molecular monolayers can lead to a deeper understanding of devices including sensitized oxide nanostructures. In this study, I showed the example of using holes on dyes to explore the nanomorphology of the environment resulting from the solution processing of the HTM in the dyed TiO₂ mesostructure. My analysis suggests that the spiro OMeTAD phase presents a coarse morphology in these devices, comparable to the nanomorphology of the mesoporous TiO₂.

Chapter 7 Dye monolayers used as hole transport medium in DSSCs: the ‘dry cell’

In this chapter⁴ I demonstrate that intermolecular hole hopping through dye monolayers is sufficient to make working photovoltaic devices based on the DSSC architecture *without* the infiltration of a redox electrolyte or hole transporting material to regenerate the oxidized dyes.

7.1 Introduction

Common descriptions of the working principle of DSSCs do not consider the possibility of hole transfer between dyes anchored on the surface of TiO₂. The infiltration of a hole transporting material in the mesostructure aims to provide a medium that allows the regeneration of photo-oxidized dyes as well as the transport of photo-generated holes to the counter electrode of the cell. This approach results in the fabrication of efficient solar cells. However, some drawbacks are also involved. For example, compatibility between the processing steps to fabricate the active layer of the DSSCs can be an issue. Also, hole transfer to the HTM requires a sufficient driving force in order for it to occur efficiently, resulting in systematic energetic losses. Results presented in Chapter 6 suggest that transport of holes across the surface of TiO₂ nanoparticles occurs in solid state DSSCs, contributing to the device photo-conversion efficiency. In this chapter I address the question of whether conduction in dye monolayers occurs to a sufficient extent to implement the hole collection process in solar cells. Thereby, I propose a third architecture of DSSC, which I refer to as ‘dry’ dye sensitized solar cell, that does not include a dye regeneration phase in the device’s active layer.

7.2 Method

Figure 7.1 shows the architectures examined: an FTO glass substrate was coated with a compact TiO₂ layer, this was covered by a 1.2 to 1.5 μm thick photoactive layer formed from mesoporous film of TiO₂ nanocrystals sensitized with the indoline dyes D131 or D149. A metal contact (silver or gold) was evaporated as

⁴ The results and discussion reported in this chapter are currently under consideration for publication in *Advanced Materials*

the counter electrode. In some cases, a semitransparent contact was used (40 nm thick), enabling illumination from both sides of the device. The cleaning of the substrates and processing of the individual layers (TiO₂ hole blocking layer, TiO₂ mesoporous layer and TiCl₄ treatment, metal evaporation) of the ‘dry’ solar cell structures have been carried out following the procedure described in section 3.2.2.

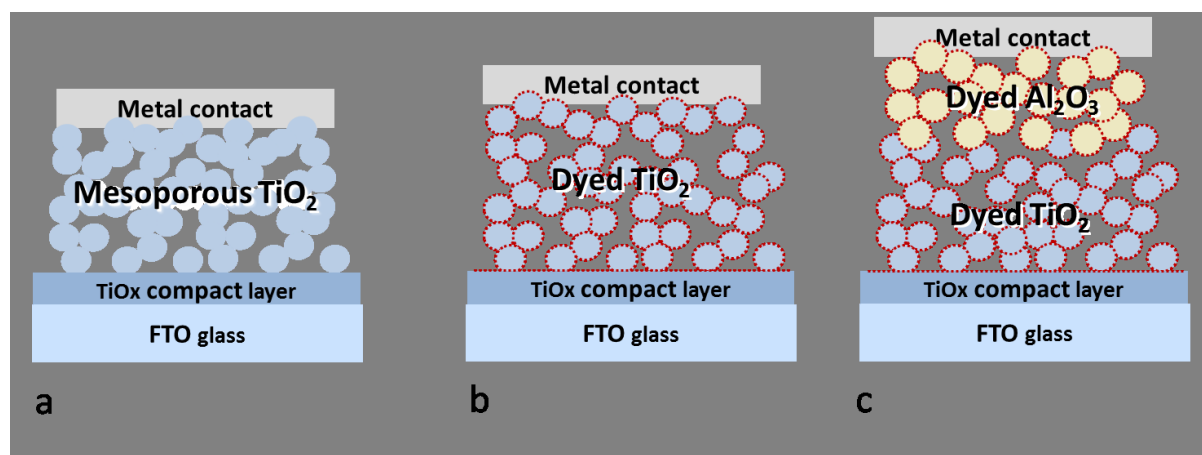


Figure 7.1. Solar cell devices investigated in this study: (a) mesoporous TiO₂ ‘dry cell’ where no dye or other hole transporting material (HTM) is included in the device; (b) dye sensitized TiO₂ ‘dry cell’ where the dye monolayer acts as HTM; (c) dye sensitized TiO₂ ‘dry cell’ including a dye sensitized Al₂O₃ mesoporous film.

Although this device concept is referred to as a ‘dry cell’, all measurements were performed in air, so the term ‘dry’ should not be taken literally, as water is expected to be present on the surface of the TiO₂ in ambient conditions. To further verify the role of hole transport between dyes in photocurrent generation, architectures where an additional insulating nanocrystalline Al₂O₃ layer (0.15 μm) was deposited on top of 0.9 μm thick TiO₂ film before sensitization were considered. This layer blocks transfer of electrons to the counter electrode and also prevents direct regeneration of oxidized dye molecules on the TiO₂ by the metal. For devices including an Al₂O₃ buffer layer, this was obtained by spin coating a homemade paste of alumina nanoparticles (see Appendix A for paste preparation recipe). Sintering at 450°C for 45 minutes of the film resulted in a 150 nm thick layer of mesoporous Al₂O₃. The substrates were then cooled down to 70°C before immersion in dye solutions for 3 hours. 0.1 mM D131 and 0.06 mM of D149 dyes were dissolved in a 1:1 mixture of acetonitrile and tert-butyl alcohol and used to dye the TiO₂ and the

TiO₂/Al₂O₃ structures. The electrical and photovoltaic characterization of solar cells was carried out following the procedure described in the section 3.3.7.

7.3 Results and discussion

Figure 7.2a and Figure 7.2b show the control measurements made on an unsensitized mesoporous TiO₂ film. The dark *j*-*V* curve indicated rectifying behavior from the device. Upon illumination with a simulated AM1.5 spectrum, a photocurrent and photovoltage were observed. The presence of a space charge region in the TiO₂ in proximity of either contact would explain this observation. This would assist the separation of photogenerated holes and electrons formed from optical excitations across the anatase band gap. The shape of the *j*-*V* curve close to *V*_{oc} suggests that a barrier is formed at both the TiO₂/Ag and the TiO₂/FTO interfaces. The action of UV light on the device is confirmed by the IPCE spectrum which is greatest (about 25%) at 350 nm when the device is illuminated from the FTO side and tracks the absorptance profile of anatase above its band gap. The lower value of IPCE for the Ag side illumination observed for this particular device suggests that efficient charge separation in the TiO₂ semiconductor occurs mainly close to the interface with FTO. For other devices showing similar *j*-*V* curves, the IPCE recorded was very low (<1%), possibly due to a super linear relation between light intensity and *j*_{sc}.

Figure 7.2c-h show the photovoltaic characterization for the dye sensitized TiO₂ devices. Rectifying behavior was again observed in the dark in most cases. The 'dry cells' showed remarkable photocurrent with *j*_{sc} exceeding 1 mA cm⁻² for the best performing device (Figure 7.3a). A clear contribution to the IPCE corresponding to the dye absorption (also shown), with values up to 13% (see Figure 7.3b), was observed. Note that some hysteresis is evident in the *j*-*V* curves (which were scanned at 0.15 V s⁻¹). This implies that the measurement is far from being a steady state assessment of the device performance in terms of power conversion efficiency.

Working cells were sufficiently stable for photo-electrical characterization. For example, Figure 7.3c shows multiple scans performed on the same device in the dark or under 1 sun illumination. Decrease in *V*_{oc} and FF is observed, while the short circuit current held to a consistent value over the 5 scans in the light.

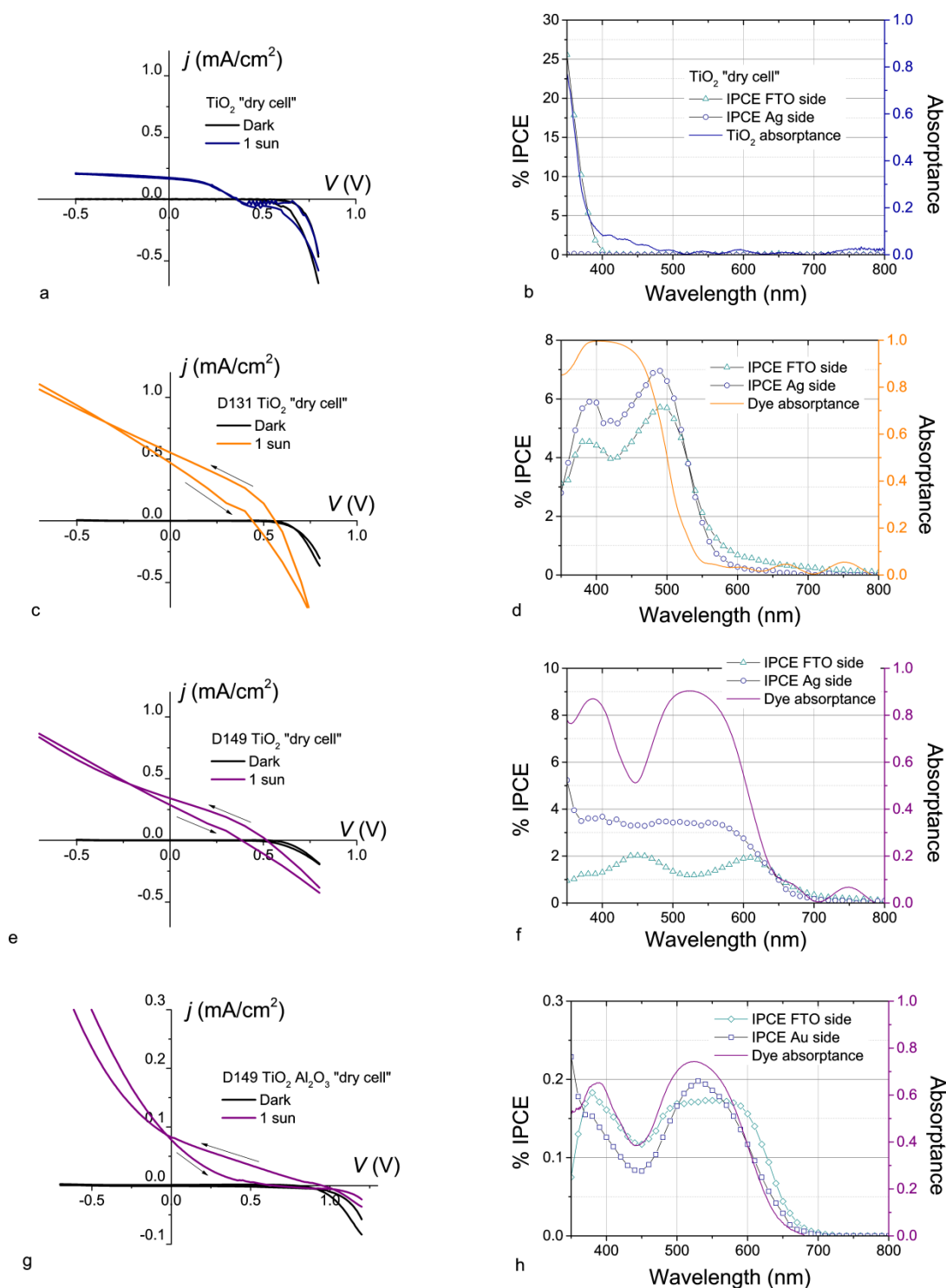


Figure 7.2. Current density-voltage and IPCE measurements performed on (a, b) unsensitized TiO_2 , (c, d) D131, (e, f) D149 sensitized TiO_2 “dry cells” and (g, h) D149 sensitized “dry cells” including a dyed mesoporous alumina layer. The IPCE measurements were performed with a LED bias light at 0.1 sun equivalent intensity and the illumination of the device was directed to the FTO glass side or to the silver or gold side. An estimate of the absorptance spectrum of the absorber (TiO_2 in b, dyes in d, f and h) is also shown to be compared with the IPCE profiles.

The photocurrent in these devices showed a strong dependence on electrical bias: it increased almost linearly with reverse bias, in contrast to the unsensitized control device. A large spread in the distribution of photocurrent values was observed. Also, low shunt resistance affected some of the devices, for cells having either gold or silver as metal contact. In a few cases, shunting occurred during the j - V measurement, either in the dark or under illumination.

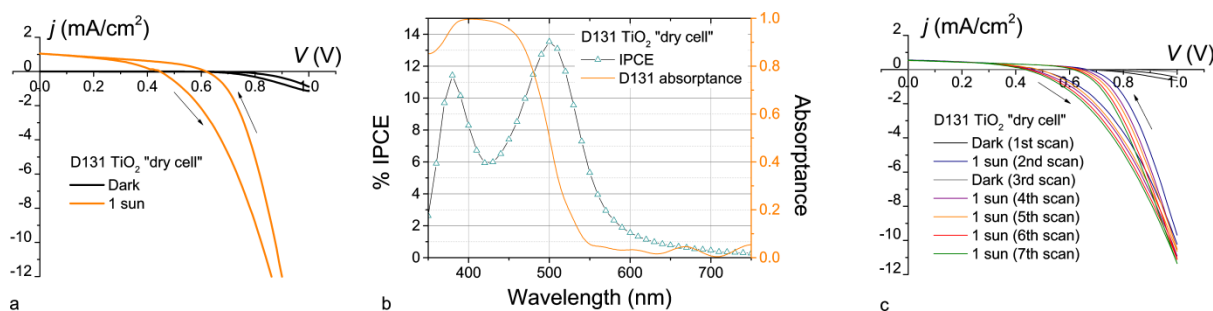


Figure 7.3. (a, b) j - V and IPCE measurements on the best performing 'dry cell'. (c) Multiple j - V measurement on a D131 sensitized TiO₂ 'dry cell'.

The observed photocurrent could be explained in terms of regeneration of dyes in direct contact with the metal electrode. DSSCs made of a monolayer of dyes on a flat TiO₂ layer have been demonstrated in the past suggesting that this can be an efficient process.^[150] In the case considered here, the evaporated metal layer would have to be in contact with a sensitized area corresponding to more than 200 nm of the top layer of particles in order to account for the IPCE spectrum shown in Figure 7.3b by direct regeneration. For this conservative estimate, specular back reflection of the capping section of the metal contact and 100% electron injection efficiency were also assumed. Thus it seems very unlikely that direct regeneration by the metal gives a dominant contribution to the photocurrent.

Devices with the additional dyed Al₂O₃ electron blocking layer on top of the titania mesoporous film were characterized following a similar approach to confirm that direct regeneration by the metal contact is not required. For the case of D149, the photocurrent was high enough (Figure 7.2g) to enable the measurement of the device's spectral response which can be seen to correspond to the absorption spectrum of the dye (Figure 7.2h). The observed response of this architecture indicates that the photocurrent could not be solely attributed to direct regeneration of dye molecules by the evaporated contact since charge injection does not occur on Al₂O₃. Furthermore, the addition of the electron blocking layer resulted in values of

V_{oc} up to 0.86 V for forward scan j - V (scanning from negative to positive voltage values) and 0.97 V for the reverse scan case. Devices with this architecture also showed a strong increase in photocurrent under reverse bias.

This bias dependence is unlikely to be related to variation in the rate of electron injection from the dye since transient absorption and photoluminescence studies have repeatedly demonstrated highly efficient injection from sensitized TiO_2 films in air.^{[98],[151],[152]} Given the clear rectification observed in the dark current, the increase in photocurrent with reverse bias is instead likely to be related to E-field assisted charge collection within the devices. In this case there is significant competition between electron in the TiO_2 to oxidized dye recombination and the transport of the charge carriers by diffusion and drift in the device. This is in stark contrast to standard liquid or solid state DSSCs where the infiltrated hole transporting medium can be considered as highly p-type. The high density of background holes in the pores screens charges within the TiO_2 such that electron transport is dominated by diffusion.^{[153],[154],[62]} Consequently field-dependent charge collection is not normally seen in devices with electrolytes or doped solid state hole transporting media.

Some of the IPCE spectra in Figure 7.2 show antibatic character in particular for FTO side illumination. Specifically, the shape of these IPCE spectra indicate that charges generated by light at wavelengths absorbed most strongly close to the contact from which photons enter the device are collected less efficiently than those generated close to the opposite electrode. For Figure 7.2d, this would also imply that collection of holes from dyes that are directly in contact with the metal film is not the dominant component for the generated photocurrent under back (semi-transparent Ag side) illumination.

7.4 Summary

The direct collection of photo-generated holes by monolayers of dye molecules has been demonstrated. Hole collection can occur without the requirement of an additional phase to regenerate the dyes. At present the performance of the devices appear limited by the competition between field assisted charge transport and electron-dye cation recombination. This demonstration illustrates the potential of molecular conductive coatings using multi-functional

molecules, and suggests interesting new possibilities for the construction of organic electronic devices and sensors.

Chapter 8 Future work

In this chapter I present some of the directions for future research on the subject of intermolecular charge transport in dye monolayers.

8.1 Stability

Electrochemical and photochemical degradation of organic semiconductors represents the main issue limiting the commercialization of organic and plastic based optoelectronic devices to date. Dye monolayers are a convenient model system to investigate this issue. The well understood spectroelectrochemical characterization of dye sensitized films can be used to analyse the formation and spectral signature of degradation by-products. Screening of molecular structures that show promising performance in terms of electrochemical cyclability is a potentially constructive direction to design organic semiconductors showing better lifetime performance.

8.2 Modelling charge transport and electron-hole recombination in dye sensitized nanocrystals

The investigation that I presented in Chapter 5 on transient anisotropy spectroscopy represents a starting point at using this technique to deconvolve the properties of a dye monolayer from the study of its conduction performance at the nanoscale. By coupling this information to the electron hole recombination measurements, it is in principle possible to formulate a complete model for charge dynamics and recombination in dye sensitized systems. This would result in further understanding of the factors triggering recombination in nanostructured films for solar cells and photocatalysis.

8.3 Solvent dependence of charge diffusion in dye monolayers

The dielectric environment that surrounds dye molecules anchored to an oxide nanocrystal is expected to have significant influence on their charge transfer properties.^{[128],[155]} In particular, the value of the outer sphere reorganization energy of charge transfer is related to the relative permittivity of the medium. As a consequence, lower reorganization energies and therefore faster diffusion would be expected for less polar solvents. However, early work on this subject has proved controversial (see Figure 8.1a). The general trend observed for example by Bonhôte

et al.^[66] and Wang *et al.*^[24] is that the lower the dielectric permittivity of the solvent used in the electrolyte for the electrochemical evaluation of hole diffusion, the lower the observed value of D_{app} (see Table 8.1).

Table 8.1. Values of D_{app} evaluated for a phosphonated tri-aryl amine dye (see structure 1 in Figure 2.13) in different electrolytes. The solvent was mixed at 1:1 ratio with EtMeIm⁺Tf₂N⁻. Reprinted with permission from “Efficient Lateral Electron Transport inside a Monolayer of Aromatic Amines Anchored on Nanocrystalline Metal Oxide Films” P. Bonhôte, E. Gogniat, S. Tingry, C. Barbe, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, J. Phys. Chem. B 1998, 5647, 1498. Copyright 1998 American Chemical Society.

nanocrystalline material	solvent	ϵ^b	$D_{app}^c/10^{-12} \text{ m}^2 \text{ s}^{-1}$
TiO ₂	diglyme ^a	7	2.6
TiO ₂	EtMeIm ⁺ Tf ₂ N ⁻	≤10	2.8
TiO ₂	4-methyl-2-pentanone	13	5.0
TiO ₂	3-methoxypropionitrile	20	9.1
TiO ₂	acetonitrile	37	11
Al ₂ O ₃	EtMeIm ⁺ Tf ₂ N ⁻	≤10	0.035
ZrO ₂	acetonitrile	37	4.6

Measurements of reorganization energy for hole transfer between Z907 dyes sensitizing TiO₂ using the method described in Chapter 4 are shown in Figure 8.1b. The two solvents acetonitrile and tetrahydrofuran (THF) are considered. The Pekar factor, defined on the basis of the optical and the static dielectric constants of the medium as $(\epsilon_{opt}^{-1} - \epsilon_s^{-1})$ is equal to 0.56 acetonitrile and 0.49 for THF. This factor is related to the outer sphere component of the reorganization energy.

The results of the fit of non-adiabatic Marcus rate to the sets of data relative to acetonitrile and THF based electrolytes are shown in Table 8.1.

The data suggest that:

- Only a minor variation in reorganization energy is observed when using solvents having very different relative dielectric permittivity values (about 7.5 for THF, versus over 36 for acetonitrile).
- A more than one order of magnitude drop in the measured diffusion coefficient is observed when using 0.1M TBAP in THF compared to the reference measurement in acetonitrile based electrolyte.

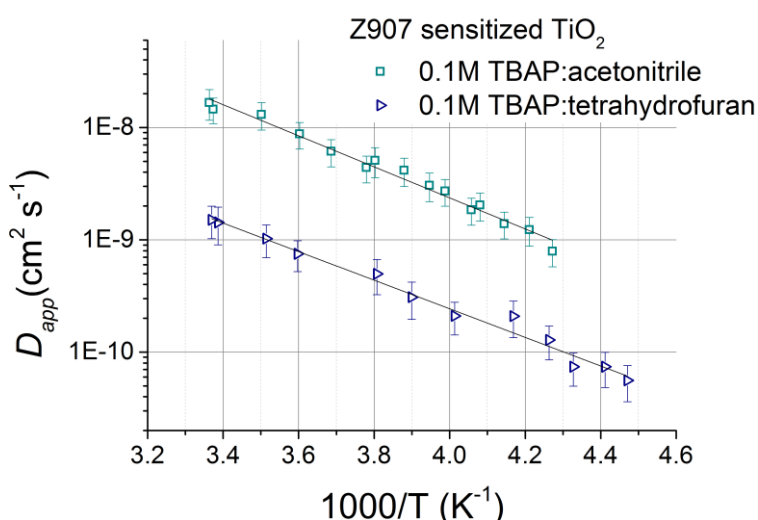


Figure 8.1. (a) The elephant in the laboratory, taken from ^[156]. (b) Temperature dependence of the apparent hole diffusion coefficient measured for Z907 sensitized TiO₂ mesoporous films on FTO glass. The measurement is performed in 0.1M TBAP dissolved in either acetonitrile or tetrahydrofuran. The corresponding value of λ_{meas} for the two measurements is 1143 (acetonitrile) and 1056 meV (THF).

Observation a) can be partially explained by considering that the presence of the ions can change significantly the dielectric properties of the solvent. Consistently, the calculated reorganization energy for the case of THF is only marginally lower than the calculated value for acetonitrile.

Observation b) is on the other hand harder to explain. The effective electronic coupling extracted from the diffusion model suggests a significantly lower electronic interaction between the dyes when the low polarity solvent is used. This is also consistent with the results shown in Chapter 5 and Chapter 6 for the absorption anisotropy decays related to D131 cation on TiO₂ in either 0.1M TBAP:acetonitrile or ambient conditions.

Table 8.2. Charge transfer parameters experimentally determined for Z907 sensitized TiO₂ in different electrolytes. The apparent diffusion coefficient at room temperature, the activation energy E_{act} , the effective electronic coupling J_{eff} and the reorganization energy λ_{meas} were determined from the temperature dependent cyclic voltammetry measurements shown in Figure 8.1. Values of λ_{calc} were calculated by Valérie Vaissier.

Electrolyte	D_{app} at 300K (10 ⁻⁸ cm ² /s)	E_{act} (meV)	J_{eff}^* (meV)	λ_{meas} (meV)	λ_{calc} (meV)
0.1M TBAP:acetonitrile	2.0 ± 0.5	274 ± 19	6.0 ^x , 1.5	1143 ± 76	976
0.1M TBAP:tetrahydrofuran	0.17 ± 0.06	253 ± 20	1.1 ^x , 1.6	1056 ± 81	880

Further investigation is needed to discriminate the role of solvent polarity on conduction of dye monolayers. Molecular dynamics calculations may illustrate the role of molecular fluctuations on the charge transfer step for different value of relative permittivity and viscosity of the environment.

As discussed in the previous section, transient anisotropy spectroscopy would be a suitable tool to investigate this question experimentally as the measurement can be performed on samples immersed in pure solvents.

8.4 Quasi 2D SAMFETs and electrochemical transistors

The results that I presented in Chapter 7 on the ‘dry cell’ concept open the possibility to build porous electronic devices and sensors. Beside solar cells, transistors could also be fabricated following a similar approach. Figure 8.2 shows the current voltage measurement performed on a transistor where a dye (MP13) sensitized mesoporous film of Al₂O₃ is used as semiconducting channel of the device.⁵

The I - V measurement is compared to the control signal given by the unsensitized film. This result suggests that porous electronic devices involving conduction in molecular monolayers can be fabricated on horizontal structures. Addition of an electrolyte and the use of a reference electrode as gate contact is a promising direction to obtain quasi 2D electrochemical transistors showing high surface area involved in the gating.

⁵ The dye MP13 was provided by Prof. Neil Robertson from University of Edinburgh; The Al₂O₃ water based paste was prepared by Dr. Xiaoe Li; I - V measurement was performed by Dr. Nikolay Vaklev.

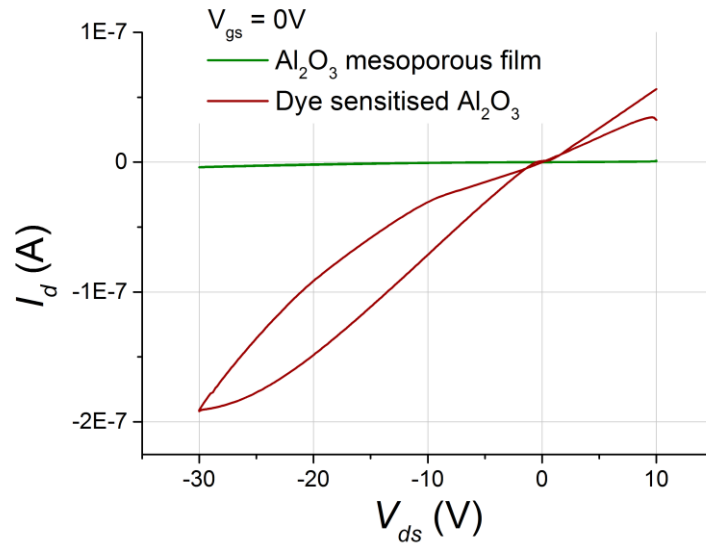


Figure 8.2. Output characteristics measured for a transistor using a MP13 sensitized aluminum oxide mesoporous film as channel of the device. The case of an unsensitized film is also shown. Channel length and width of the transistor were respectively 2.5 μm and 10 mm.

Conclusions

Main outcomes of this thesis

Intermolecular charge transport in dye monolayers sensitizing the surface of nanocrystalline oxide films has been investigated in several studies since the late 1990s. The process has been analysed electrochemically^{[67],[66]} and spectroscopically^[28] and its successful application to lithium ions batteries,^[27] solar fuel catalysis,^{[25],[29]} electrochromic devices^[157] and self-assembled monolayer field effect transistors^[30] has been demonstrated.

Before this thesis, limited knowledge on the regime of charge transport between the dyes was available. I presented experimental results showing that charge transport in the dye monolayer on TiO₂ immersed in an inert electrolyte is thermally activated. Moreover, the interpretation of the data in terms of non-adiabatic Marcus theory resulted in estimates of the reorganization energy of charge transfer between the dyes that are in agreement with calculations performed by former PhD student Valérie Vaissier.^{[128],[20]} Also, estimates of the effective electronic coupling between the dyes are consistent with the weak coupling regime of charge transfer assumed in the analysis (Chapter 4).

One of the critical outcomes of this thesis is the dependence of charge diffusion in the dye monolayer on the fraction of the oxide surface covered in dyes (dye loading). Previous reports considered the evaluation of the charge percolation threshold in the dye monolayer based on the macroscopic electrochemical response of dyed nanocrystals as a function of dye loading.^{[66],[24],[74]} In this thesis, I presented a combined electrochemical and spectroscopic study where I analysed charge diffusion in monolayers of D131 dyes on TiO₂ for samples showing different values of surface coverage. This resulted in the observation of a percolation threshold for hole diffusion both at the film and at the nanoparticle scale (section 5.3.2).

On the basis of this finding, I considered samples where hole transport in dye monolayers is allowed or stopped to investigate the role of such process within dye sensitized photo-electrochemical systems. Prior to this thesis, the study of charge transfer processes at dye sensitized nanocrystalline oxides has commonly followed a 1D analysis of the interface between dyes, oxide and surrounding environment. I presented evidence showing that including lateral effects due to charge transport in

the dye monolayer is a critical point to the understanding and optimization of these systems. Two key examples are summarized below.

I showed that when a high fraction of the TiO₂ surface is covered by dyes, the dyes catalyse recombination of photo-generated holes (which are mobile within the dye monolayer) with electrons in the TiO₂. This effect is observed at different levels of electron density in the TiO₂ film, up to over 10¹⁸ cm⁻³ (section 5.3.3). This result is consistent with the study reported by Ogawa *et al.*^[91] This observation is significant to photo-electrochemical systems where long lifetime of photo-generated charges on surface adsorbates is desirable such as electrodes for solar fuel generation. The effect is less relevant to current architectures of liquid junction DSSCs where regeneration of the photo-oxidized dyes occurs at sufficiently fast time scales. Future optimization of this class of devices may however involve the adoption of dyes and redox couples showing lower driving forces for regeneration to reduce the energy loss involved in such process. This would potentially imply slower hole transfer from the dye to the redox couple, resulting in the dye cation recombination to the electrons in the TiO₂ becoming a significant process competing with regeneration. Under these circumstances controlling lateral hole transport would become critical.

Lateral transport in dye monolayers has not been addressed in most studies of solid state DSSCs. In some cases, the possibility that contribution to the photo-conversion efficiency of the device could come from this process has been proposed.^{[19],[21],[114]} Nevertheless, no quantitative analysis of its role in the charge transfer dynamics of the device was available prior to this thesis. I verified that holes are transported within monolayers of D131 on TiO₂ when the film is infiltrated with a solid state material or in air. A percolation threshold was observed also in this case. For DSSC devices using the dye D131 and the HTM spiro OMeTAD, I demonstrated that a significant fraction of the photo-generated holes that are transferred to the HTM are, first, transported within the dye monolayer. The estimate for this fraction ranges between 50% and 5% of the dye regeneration yield (depending on the level of the pore filling by the HTM). In light of this result, I clarified the role of hole transport between dyes in solid state DSSCs and proposed a more complete description of the working principle of these devices.

These results imply that the, previously overlooked, process of charge transport in dye monolayers plays a central role in the charge transfer dynamics of devices based on dye sensitized nanocrystalline oxides. For this reason, they

represent an advance in the state of the art of the field of DSSCs. Moreover, I demonstrated that control of this process results in reduced charge recombination and improved charge collection in solar cells. Therefore, the significance of my work lies on the improved fundamental understanding of these systems which impacts future directions towards solar energy conversion devices with higher efficiency.

Below I give a summary of other observations and conclusions that resulted from my research and that represent further advances to the field of DSSCs. I divide them into subsections depending on the aspect of the field to which they contribute. Finally I give my outlook on the subject.

Characterization techniques for dye based systems

I have shown the use of cyclic voltammetry (CV) for estimating the apparent diffusion coefficient of holes in dye monolayers sensitizing nanocrystalline films and its temperature dependence. From the analysis of the validity of the technique I concluded that:

- a) Compensation for series resistance effects should be accounted for in this measurement, especially for dyes showing high diffusion coefficients. Previous attempts to study fast diffusion using cyclic voltammetry resulted in the overestimate of the diffusion coefficient, due to this factor.^[158]
- b) Scan rate and thickness of the film have to comply with the semi-infinite slab approximation underlying the use of the Randles-Sevcik equation.
- c) I gave evidence that no limitation is expected from the diffusion of ions in solution for the acetonitrile based electrolyte used in my work. This factor has been raised as the possible explanation for the observed dependence of D_{app} on solvent polarity. My investigation is limited to diffusion of ions in the bulk of the solvent. Other effects due to ion binding to the molecules might influence the measured ambipolar coefficient.
- d) I discussed the hole concentration in the monolayer as a potential factor influencing the measured D_{app} . I have shown that the measured D_{app} relates directly to the chemical diffusion coefficient which is used in the Fick's equation. Furthermore, the 2D diffusion coefficient which can be

estimated from D_{app} correspond to the tracer diffusion coefficient of holes transported in a monolayer of dyes on a nanocrystal's facet.

- e) I developed temperature dependent cyclic voltammetry measurements on dye sensitized films: this tool can be used to correlate interfacial charge transfer processes involving dye monolayers and thermal activation energies.
- f) The numerical model to analyse CV measurements used in this thesis used a linearized series resistance factor, which enabled the peak shift of the CV observed experimentally to be reproduced. However the model gave a poor reproduction of the shape of cyclic voltammograms in most cases. Further investigation is needed to address a better description of other kinetic limitations to charge diffusion in the film.

Secondly, I have demonstrated the use of transient absorption and transient absorption anisotropy spectroscopy to monitor the charge percolation process occurring in the dye monolayer in solid state DSSCs. This technique enables:

- a) The interpretation of the time dependent dye regeneration measured via TAS in the device and directly shows the cause of inefficient dye regeneration (e.g. incomplete HTM coverage of the dyed nanostructure, hindered hole transport in the dye monolayer).
- b) The use of holes on dyes to probe the surrounding morphological environment resulting from the infiltration of a third (regenerating) phase in mesoporous structures. The length scale of the voids between regions of the infiltrated phase can be estimated using this technique.

I carried out the analysis of dyeing procedures to obtain uniform coverage. Based on the approach reported by O'Regan *et al.*^[138] I discussed the uniformity of films sensitized using the organic dye D131. I showed that for the case of cosensitization of the same dye with the inert coadsorbent chenodeoxycholic acid (DCA) slower uptake of the dye is observed. This observation is accompanied by evidence for more uniform dyeing through the thickness of the film at early dyeing times. This study is relevant to the subject of hole transport in dye monolayers as well as to the industrial fabrication of dye cells using coadsorbents (e.g. inert coadsorbents, multiple dyes for panchromatic light harvesting).

Contributions to the understanding of hole conduction in dye monolayers

Temperature dependent CV measurements were carried out for different dyes used in DSSCs. Interpretation of the data in terms of non-adiabatic Marcus theory of charge transfer led to the following observations:

- a) The trend observed for the measured reorganization energy of charge transfer between dyes, λ_{meas} , suggests that low outer sphere reorganization energy can be achieved by increasing the volume of the HOMO of the dye rather than the volume occupied by the whole molecule.
- b) Furthermore, when the HOMO is localized on a large and rigid chemical structure both in the neutral and in the cationic state, limited distortion is expected upon charge transfer which correlates with low values of calculated inner sphere reorganization energy.
- c) Experimentally, higher values of λ_{meas} were systematically extracted from temperature dependent CV when compared to calculated values. The role of disorder in the monolayer is expected to increase the effective activation energy observed and might explain the observed trend.
- d) Estimates of an effective electronic coupling (J_{eff}) for these systems were drawn. Values in the order of 0.5 to 50 meV were obtained from the analysis, consistent with the assumption of transport occurring in the weak coupling regime. High values of J_{eff} were obtained for organic dyes that do not include saturated side groups. This is consistent with the high coupling expected for closely packed and aggregated molecules.

From the study of transient absorption anisotropy applied to D131 sensitized TiO_2 films, I discussed the following points:

- a) Consistently with previous work by Ardo and Meyer, I concluded that hole diffusion in the dye monolayer is the dominant component in the observed decay of the dye cation absorption anisotropy signal, following laser pulse excitation.
- b) Transient anisotropy measurements showed that hole transport between D131 dyes on TiO_2 is about 2 orders of magnitude slower when the dye sensitized film is in ambient conditions than in the presence of an inert electrolyte. This is in agreement with previous observations showing an

inverse correlation between polarity of the medium and charge diffusion. Explanation for such correlation is still not clear.

- c) The observed dispersion of the transient anisotropy decay could be reproduced with simulations including configurational and energetic disorder in the dye monolayer.

Relevance of hole transport in dye monolayers for dye-based devices

From the analysis of the regeneration dynamics in solid state DSSCs, I presented the following observations:

- a) Minimum values of about 0.2 pore filling are enough to guarantee efficient (>0.9) regeneration yield in DSSCs with complete dye coverage, consistently with previous reports. Pore filling fraction greater than 0.6 are instead needed to ensure similar level of regeneration in devices with dye coverage below 50%.
- b) The presence of the additives tert-butylpyridine and lithium TFSI correlated with lower regeneration efficiency in solid state DSSCs. This effect is not significant for devices with optimized pore filling. Observation of slower transient anisotropy decay for the dye cation signal in dye sensitized systems including these additives has been presented. This suggests that the additives inhibit hole diffusion which results in decreased dye regeneration yield. Changes in the HTM distribution in the pores upon addition of these additives would also partially explain this trend.
- c) The performance of solid state DSSCs can be optimized by ensuring that hole transport in the dye monolayer is allowed in order to assist photo-oxidized dye regeneration. This implies that surface coverage beyond 50% is desirable. On the other hand, using complete (100%) dye surface coverage may not ultimately result in optimized performance due to other factors.

Innovative device concepts

In this thesis I have presented the fabrication of 'dry solar cells'. This device is based on the classic DSSC architecture although its active layer does not include

any phase performing dye regeneration. The characterization of this new device concept resulted in the following observations:

- a) Dye monolayers can be used as both the light absorbing and HTM phase of solar cells. The 'dry cell' is an example of DSSC architecture using self-regenerative dye monolayers.
- b) 'Dry cell' devices including an electron blocking layer have been presented to demonstrate the role of hole diffusion in the dye monolayer during the hole collection process. These devices showed V_{oc} values in the order of 0.9V. This result suggests that by removing regeneration by a separate HTM phase, significant energetic loss can be avoided.
- c) Molecular conductive coatings in dry environments or immersed in inert electrolytes present an interesting direction for fabricating new concepts of optoelectronic devices and sensors.

Outlook

In this thesis I clarified the relevance of intermolecular charge transport in molecular monolayers for the functioning of some dye based photo-electrochemical devices. Further questions still need to be addressed to improve the current understanding of the process, on the basis of results reported in the literature and in this thesis (see Chapter 8 on future work).

The design of device concepts utilizing the process of charge hopping in dye monolayers shows the attractive possibility to achieve percolating conduction in the bulk of a system while 'paying' a negligible cost in terms of volume occupied by the conducting phase. Molecular sensitization offers simplicity of fabrication (self-assembly) and high potential in terms of tailoring optoelectronic and catalytic properties of the sensitizers. These aspects are the clear advantages of the technology when comparing it to sensitization through chemical grown inorganic semiconductors. Nevertheless, in my opinion, the stability of molecular semiconductors still represents the real challenge that needs to be addressed in order to release such potential. Focus on stability, lifetime, cyclability as main figures of merit would define the design rules for the synthesis of new chemical structures that can be applied to commercial devices. This approach can reveal the long term

practical potential of molecular semiconductors for solar energy conversion and electronic applications.

Bibliography

- [1] J. Nelson, *The Physics of Solar Cells*; Imperial College Press, 2003.
- [2] P. Würfel, *Physics of Solar Cells*; 2005.
- [3] G. Lanzani, *The Photophysics behind Photovoltaics and Photonics*; Gmbh, C. W. V., Ed.; 2012.
- [4] B. C. O'Regan, J. R. Durrant, *Acc. Chem. Res.* **2009**, *42*, 1799.
- [5] P. E. Laibinis, J. J. Hickman, M. S. Wrighton, G. M. Whitesides, *Science*. **1989**, *245*, 4.
- [6] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595.
- [7] F. C. Krebs, *Org. Electron. physics, Mater. Appl.* **2009**, *10*, 761.
- [8] C. Girotto, D. Moia, B. P. Rand, T. Aernouts, P. Heremans, *Conf. Rec. IEEE Photovolt. Spec. Conf.* **2010**, 1068.
- [9] G. A. Chamberlain, *Sol. Cells* **1983**, *8*, 47.
- [10] C. W. Tang, *Appl. Phys. Lett.* **1986**, *48*, 183.
- [11] B. C. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737.
- [12] J. Nelson, C. J. M. Emmott, P. T. R. S. A, *Philos. Trans. R. Soc. A* **2013**.
- [13] *IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation Summary for Policymakers*; 2011.
- [14] C. J. M. Emmott, N. J. Ekins-Daukes, J. Nelson, *Energy Environ. Sci.* **2014**, *7*, 1810.
- [15] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, E. D. Dunlop, *Prog. Photovoltaics Res. Appl.* **2015**, *23*, 1.
- [16] N. Espinosa, M. Hösel, D. Angmo, F. C. Krebs, *Energy Environ. Sci.* **2012**, *5*, 5117.
- [17] U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissoertel, J. Salbeck, H. Spreizer, M. Grätzel, *Nature* **1998**, *395*, 583.
- [18] A. Hagfeldt, M. Gratzel, *Chem. Rev.* **1995**, *95*, 49.

- [19] G. Boschloo, T. Marinado, K. Nonomura, T. Edvinsson, A. G. Agrios, D. P. Hagberg, L. Sun, M. Quintana, C. S. Karthikeyan, M. Thelakkat, A. Hagfeldt, *Thin Solid Films* **2008**, 516, 7214.
- [20] D. Moia, V. Vaissier, I. López-Duarte, T. Torres, M. K. Nazeeruddin, B. C. O'Regan, J. Nelson, P. R. F. Barnes, *Chem. Sci.* **2014**, 5, 281.
- [21] L. Yang, U. B. Cappel, E. L. Unger, M. Karlsson, K. M. Karlsson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, E. M. J. Johansson, *Phys. Chem. Chem. Phys.* **2012**, 14, 779.
- [22] C. T. Weisspfennig, D. J. Hollman, C. Menelaou, S. D. Stranks, H. J. Joyce, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Funct. Mater.* **2013**, 24, 668.
- [23] A. J. Bard, L. Faulkner, *Electrochemical Methods: Fundamentals and Applications*; 2nd ed.; John Wiley & Sons, 2001.
- [24] Q. Wang, S. M. Zakeeruddin, M. K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2006**, 128, 4446.
- [25] S. Ardo, G. J. Meyer, *J. Am. Chem. Soc.* **2011**, 133, 15384.
- [26] Q. Wang, N. Evans, S. M. Zakeeruddin, P. Péchy, I. Exnar, M. Grätzel, *J. Power Sources* **2007**, 174, 408.
- [27] Q. Wang, N. Evans, S. M. Zakeeruddin, I. Exnar, M. Grätzel, *J. Am. Chem. Soc.* **2007**, 129, 3163.
- [28] S. Ardo, G. J. Meyer, *J. Am. Chem. Soc.* **2010**, 132, 9283.
- [29] B. J. Brennan, A. C. Durrell, M. Koepf, R. H. Crabtree, G. W. Brudvig, *Phys. Chem. Chem. Phys.* **2015**.
- [30] S. G. J. Mathijssen, E. C. P. Smits, P. a van Hal, H. J. Wondergem, S. a Ponomarenko, A. Moser, R. Resel, P. a Bobbert, M. Kemerink, R. a J. Janssen, D. M. de Leeuw, *Nat. Nanotechnol.* **2009**, 4, 674.
- [31] M. Defaux, F. Gholamrezaie, J. Wang, A. Kreyes, U. Ziener, D. V Anokhin, D. a Ivanov, A. Moser, A. Neuhold, I. Salzmann, R. Resel, D. M. de Leeuw, S. C. J. Meskers, M. Moeller, A. Mourran, *Adv. Mater.* **2012**, 24, 973.
- [32] C. Kittel, *Introduction To Solid State Physics 8Th Edition*; 2005.
- [33] N. W. Ashcroft, N. D. Mermin, *Solid State Physics*; Saunders, 1976.
- [34] L. Landau, *Phys. Z. Sowjetunion* **1933**, 3, 644.
- [35] T. Holstein, *Ann. Phys. (N. Y.)* **1959**, 8, 325.

- [36] J. J. Kwiatkowski, From molecules to mobilities: modelling charge transport in organic semiconductors, PhD thesis, Imperial College London, 2008.
- [37] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, J.-L. Bredas, *Chem. Rev.* **2007**, 926.
- [38] R. A. Marcus, *J. Chem. Phys.* **1984**, 91125, 4494.
- [39] K. A. Hansen, *Curr. Popul. Reports* **1998**.
- [40] H. Scher, E. N. Montroll, *Phys. Rev. B* **1975**, 12.
- [41] M. Grünewald, M. Grünewald, P. Thomas, P. Thomas, *Phys. Status Solidi* **1979**, 94, 125.
- [42] F. R. Shapiro, D. Adler, *J. Non. Cryst. Solids* **1985**, 74, 189.
- [43] H. Bässler, *Phys. Status Solidi* **1993**, 175.
- [44] A. Miller, E. Abrahams, *Phys. Rev.* **1960**, 120, 745.
- [45] H. Park, E. Bae, J. J. Lee, J. Park, W. Choi, *J. Phys. Chem. B* **2006**, 110, 8740.
- [46] F. Ambrosio, N. Martsinovich, A. Troisi, *J. Phys. Chem. C* **2012**, 116, 2622.
- [47] M.-A. Neouze, U. Schubert, *Monatshefte für Chemie - Chem. Mon.* **2008**, 139, 183.
- [48] A. Fujishima, K. Honda, *Nature* **1972**.
- [49] J. Tang, J. R. Durrant, D. R. Klug, *J. Am. Chem. Soc.* **2008**, 130, 13885.
- [50] M. Ni, M. K. H. Leung, D. Y. C. Leung, K. Sumathy, *Renew. Sustain. Energy Rev.* **2007**, 11, 401.
- [51] B. O'Regan, M. Gratzel, *Nature* **1991**, 353, 737.
- [52] N.-G. Park, J. van de Lagemaat, a J. Frank, *J. Phys. Chem. B* **2000**, 104, 8989.
- [53] H. Tang, K. Prasad, R. Sanjines, P. E. Schmid, F. Levy, *J. Appl. Phys.* **1994**, 75, 2042.
- [54] G. Boschloo, D. Fitzmaurice, *J. Phys. Chem. B* **1999**, 103, 2228.
- [55] H. Wang, J. He, G. Boschloo, H. Lindstro, *J. Phys. Chem. B* **2001**, 105, 2529.
- [56] B. J. Morgan, G. W. Watson, *J. Phys. Chem. C* **2010**, 114, 2321.

- [57] W. H. Leng, P. R. F. Barnes, M. Juozapavicius, B. C. O'Regan, J. R. Durrant, *J. Phys. Chem. Lett.* **2010**, *1*, 967.
- [58] J. Bisquert, V. S. Vikhrenko, *J. Phys. Chem. B* **2004**, *108*, 2313.
- [59] K. Schwanitz, U. Weiler, R. Hunger, T. Mayer, W. Jaegermann, *J. Phys. Chem. C* **2007**, *111*, 849.
- [60] N. Serpone, D. Lawless, R. Khairutdinov, *J. Phys. Chem.* **1995**, *99*, 16646.
- [61] H. J. Zhai, L. S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 3022.
- [62] P. R. F. Barnes, K. Miettunen, X. Li, A. Y. Anderson, T. Bessho, M. Grätzel, B. C. O'Regan, *Adv. Mater.* **2013**, *25*, 1881.
- [63] U. Diebold, *Surf. Sci. Rep.* **2003**, *48*, 53.
- [64] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*; 3rd ed.; Springer Science + Business Media: New York, 2006.
- [65] J. a Levitt, M. K. Kuimova, G. Yahiolu, P. Chung, K. Suhling, D. Phillips, *J. Phys. Chem. C* **2009**, *113*, 11634.
- [66] P. Bonhôte, E. Gogniat, S. Tingry, C. Barbe, N. Vlachopoulos, F. Lenzmann, P. Comte, M. Grätzel, *J. Phys. Chem. B* **1998**, *5647*, 1498.
- [67] T. A. Heimer, S. T. D. Arcangelis, F. Farzad, J. M. Stipkala, G. J. Meyer, *Inorg. Chem.* **1996**, *1669*, 5319.
- [68] V. Aranyos, H. Grennberg, S. Tingry, S. Lindquist, A. Hagfeldt, *Sol. Energy Mater. Sol. Cells* **2000**, *64*, 97.
- [69] V. Aranyos, J. Hjelm, H. Grennberg, *Dalt. Trans.* **2003**, 1280.
- [70] S. A. Trammell, T. J. Meyer, *J. Phys. Chem. B* **1999**, *103*, 104.
- [71] P. Qu, G. J. Meyer, *Langmuir* **2001**, *17*, 6720.
- [72] N. Papageorgiou, M. Grätzel, O. Enger, D. Bonifazi, F. Diederich, *J. Phys. Chem. B* **2002**, *106*, 3813.
- [73] Q. Wang, S. M. Zakeeruddin, J. Cremer, P. Bäuerle, R. Humphry-Baker, M. Grätzel, *J. Am. Chem. Soc.* **2005**, *127*, 5706.
- [74] X. Li, M. K. Nazeeruddin, M. Thelakkat, P. R. F. Barnes, R. Vilar, J. R. Durrant, *Phys. Chem. Chem. Phys.* **2011**, *13*, 1575.
- [75] A. Fattori, L. M. Peter, S. R. Belding, R. G. Compton, F. Marken, *J. Electroanal. Chem.* **2010**, *640*, 61.

- [76] A. Fattori, L. M. Peter, H. Wang, H. Miura, F. Marken, *J. Phys. Chem. C* **2010**, 205, 11822.
- [77] E. Galoppini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu, G. J. Meyer, *J. Am. Chem. Soc.* **2002**, 124, 7801.
- [78] K. Westermark, S. Tingry, P. Persson, H. Rensmo, S. Lunell, A. Hagfeldt, H. Siegbahn, *J. Phys. Chem. B* **2001**, 7182.
- [79] B. O'Regan, J. Moser, M. Anderson, M. Grätzel, *J. Phys. Chem.* **1990**, 94, 8720.
- [80] P. V Kamat, I. Bedja, S. Hotchandani, L. K. Patterson, *J. Phys. Chem.* **1996**, 100, 4900.
- [81] S. G. Yan, J. T. Hupp, *J. Phys. Chem.* **1996**, 100, 6867.
- [82] S. A. Haque, Y. Tachibana, D. R. Klug, J. R. Durrant, *J. Phys. Chem. B* **1998**, 11, 1745.
- [83] C. A. Kelly, F. Farzad, D. W. Thompson, J. M. Stipkala, G. J. Meyer, *Langmuir* **1999**, 7047.
- [84] J. Nelson, *Phys. Rev. B* **1999**, 59, 374.
- [85] J. Nelson, S. Haque, D. Klug, J. Durrant, *Phys. Rev. B* **2001**, 63, 1.
- [86] J. N. Clifford, G. Yahioğlu, L. R. Milgrom, J. R. Durrant, *Chem. Commun.* **2002**, 1260.
- [87] J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Grätzel, J. Nelson, X. Li, N. J. Long, J. R. Durrant, *J. Am. Chem. Soc.* **2004**, 126, 5225.
- [88] J. Nelson, R. E. Chandler, *Coord. Chem. Rev.* **2004**, 248, 1181.
- [89] a. V. Barzykin, M. Tachiya, *J. Phys. Chem. B* **2002**, 106, 4356.
- [90] J. Bisquert, *J. Phys. Chem. C* **2007**, 111, 17163.
- [91] J. Ogawa, N. Koumura, K. Hara, S. Mori, *Jpn. J. Appl. Phys.* **2014**, 1.
- [92] G. De Miguel, M. Marchena, M. Ziólek, S. S. Pandey, S. Hayase, a. Douhal, *J. Phys. Chem. C* **2012**, 116, 12137.
- [93] U. B. Cappel, T. Daeneke, U. Bach, *Nano Lett.* **2012**, 12, 4925.
- [94] A. Abate, T. Leijtens, S. Pathak, J. Teuscher, R. Avolio, M. E. Errico, J. Kirkpatrick, J. M. Ball, P. Docampo, I. McPherson, H. J. Snaith, *Phys. Chem. Chem. Phys.* **2013**, 15, 2572.

- [95] S. E. Koops, B. C. O'Regan, P. R. F. Barnes, J. R. Durrant, *J. Am. Chem. Soc.* **2009**, *131*, 4808.
- [96] S. Y. Huang, G. Schlichthorl, a J. Nozik, M. Gratzel, a J. Frank, *J. Phys. Chem. B* **1997**, *101*, 2576.
- [97] K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *Langmuir* **2004**, *20*, 4205.
- [98] J. E. Kroeze, N. Hirata, L. Schmidt-Mende, C. Orizu, S. D. Ogier, K. Carr, M. Grätzel, J. R. Durrant, *Adv. Funct. Mater.* **2006**, *16*, 1832.
- [99] K. Tennakone, G. R. R. A. Kumara, A. R. Kumarasinghe, K. G. U. Wijayantha, P. M. Sirimanne, *Semicond. Sci. Technol.* *10*, 1689.
- [100] B. O'Regan, F. Lenzmann, R. Muis, J. Wienke, *Chem. Mater.* **2002**, 5023.
- [101] A. Abrusci, R. S. Santosh Kumar, M. Al-Hashimi, M. Heeney, A. Petrozza, H. J. Snaith, *Adv. Funct. Mater.* **2011**, *21*, 2571.
- [102] L. Yang, U. B. Cappel, E. L. Unger, M. Karlsson, K. M. Karlsson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, E. M. J. Johansson, *Phys. Chem. Chem. Phys.* **2012**, *14*, 779.
- [103] S. a Haque, T. Park, A. B. Holmes, J. R. Durrant, *Chemphyschem* **2003**, *4*, 89.
- [104] C. T. Weisspfennig, M. M. Lee, J. Teuscher, P. Docampo, S. D. Stranks, H. J. Joyce, H. Bergmann, I. Bruder, D. V Kondratuk, M. B. Johnston, H. J. Snaith, L. M. Herz, *J. Phys. Chem. C* **2013**.
- [105] U. Bach, Y. Tachibana, J. Moser, S. A. Haque, J. R. Durrant, M. Grätzel, *J. Am. Chem. Soc.* **1999**, *2*, 7445.
- [106] L. Schmidt-Mende, M. Grätzel, *Thin Solid Films* **2006**, *500*, 296.
- [107] U. B. Cappel, E. a. Gibson, A. Hagfeldt, G. Boschloo, *J. Phys. Chem. C* **2009**, *113*, 6275.
- [108] H. J. Snaith, R. Humphry-Baker, P. Chen, I. Cesar, S. M. Zakeeruddin, M. Grätzel, *Nanotechnology* **2008**, *19*, 424003.
- [109] H. J. Snaith, R. Humphry-Baker, P. Chen, I. Cesar, S. M. Zakeeruddin, M. Grätzel, *Nanotechnology* **2008**, *19*, 424003.
- [110] C. Olson, D. Veldman, K. Bakker, F. Lenzmann, *Int. J. Photoenergy* **2011**, *2011*, 1.
- [111] I.-K. Ding, N. Tétreault, J. Brillet, B. E. Hardin, E. H. Smith, S. J. Rosenthal, F. Sauvage, M. Grätzel, M. D. McGehee, *Adv. Funct. Mater.* **2009**, *19*, 2431.

- [112] J. Melas-Kyriazi, I.-K. Ding, A. Marchioro, A. Punzi, B. E. Hardin, G. F. Burkhard, N. Tétreault, M. Grätzel, J.-E. Moser, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 407.
- [113] P. Docampo, A. Hey, S. Guldin, R. Gunning, U. Steiner, H. J. Snaith, *Adv. Funct. Mater.* **2012**, *22*, 5010.
- [114] C. T. Weisspfennig, D. J. Hollman, C. Menelaou, S. D. Stranks, H. J. Joyce, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Funct. Mater.* **2013**, *24*, 668.
- [115] M. G. Walter, A. B. Rudine, C. C. Wamser, *J. Porphyr. Phthalocyanines* **2010**, *14*, 759.
- [116] J.-J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 8358.
- [117] I. Lopez-Duarte, Phthalocyanines: Robust Red-Absorbing Dyes for Molecular Photovoltaics, PhD thesis, University Autonoma of Madrid, 2010.
- [118] A. Morandeira, I. Lopez-Duarte, B. C. O'Regan, M. V. Martínez-Díaz, A. Forneli, E. Palomares, T. Torres, J. R. Durrant, *J. Mater. Chem.* **2009**, *19*, 5016.
- [119] A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diao, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629.
- [120] A. Fattori, L. M. Peter, K. L. McCall, N. Robertson, F. Marken, *J. Solid State Electrochem.* **2010**, *14*, 1929.
- [121] A. Y. Anderson, P. R. F. Barnes, J. R. Durrant, B. C. O'Regan, *J. Phys. Chem. C* **2011**, 2439.
- [122] V. Vaissier, E. Mosconi, D. Moia, M. Pastore, J. M. Frost, F. De Angelis, P. R. F. Barnes, J. Nelson, *Chem. Mater.* **2014**, 4731.
- [123] Y. Tachibana, S. A. Haque, I. P. Mercer, J. E. Moser, D. R. Klug, J. R. Durrant, *J. Phys. Chem. B* **2001**, *105*, 7424.
- [124] J. F. Smalley, H. O. Finklea, C. E. D. Chidsey, M. R. Linford, S. E. Creager, J. P. Ferraris, K. Chalfant, T. Zawodzinsk, S. W. Feldberg, M. D. Newton, *J. Am. Chem. Soc.* **2003**, *125*, 2004.
- [125] A. D. Abhayawardhana, T. C. Sutherland, *J. Phys. Chem. C* **2009**, *113*, 4915.
- [126] H. O. Finklea, N. Madhiri, *J. Electroanal. Chem.* **2008**, *621*, 129.
- [127] A. B. Myers, *Chem. Rev.* **1996**, *96*, 911.

- [128] V. Vaissier, P. R. F. Barnes, J. Kirkpatrick, J. Nelson, *Phys. Chem. Chem. Phys.* **2013**, *15*, 4804.
- [129] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*; 2001.
- [130] P. Atkins, J. de Paula, *Physical Chemistry*; 2006.
- [131] J. Bisquert, *J. Phys. Chem. B* **2004**, *108*, 2323.
- [132] R. Gomer, *Reports Prog. Phys.* **1990**, *53*, 917.
- [133] D. W. Oscarson, *Clays Clay Miner.* **1994**, *42*, 534.
- [134] M. Pastore, F. De Angelis, *ACSNANO* **2010**, *4*, 556.
- [135] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, *Science*. **2012**, *338*, 643.
- [136] J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Grätzel, *Nature* **2013**.
- [137] H. Baessler, A. Koehler, In *Unimolecular and Supramolecular Electronics I*; Metzger, R. M., Ed.; Springer Berlin Heidelberg, 2012; Vol. 312, pp. 1–65.
- [138] B. O'Regan, X. Li, T. Ghaddar, *Energy Environ. Sci.* **2012**, *5*, 7203.
- [139] P. Bonhote, J. Moser, R. Humphry-baker, N. Vlachopoulos, S. M. Zakeeruddin, L. Walder, M. Gra, **1999**, 1324.
- [140] P. M. Sommeling, B. C. O'Regan, R. R. Haswell, H. J. P. Smits, N. J. Bakker, J. J. P. Smits, J. M. Kroon, J. A. M. V. R. Roosmalen, *J. Phys. Chem. B* **2006**, *110*, 19191.
- [141] T. Berger, J. A. Anta, V. Morales-Flórez, *J. Phys. Chem. C* **2012**.
- [142] P. Docampo, A. Hey, S. Guldin, R. Gunning, U. Steiner, H. J. Snaith, *Adv. Funct. Mater.* **2012**, *22*, 5010.
- [143] Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, a. Shinpo, K. Hara, *J. Phys. Chem. C* **2007**, *111*, 7224.
- [144] N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel, A. J. Frank, *J. Phys. Chem. B* **2005**, *109*, 23183.
- [145] S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun. (Camb)*. **2008**, 5194.
- [146] E. L. Unger, A. Morandeira, M. Persson, B. Zietz, E. Ripaud, P. Leriche, J. Roncali, A. Hagfeldt, G. Boschloo, *Phys. Chem. Chem. Phys.* **2011**, *13*, 20172.

- [147] A. El-Zohry, A. Orthaber, B. Zietz, *J. Phys. Chem. C. Nanomater. Interfaces* **2012**, 116, 26144.
- [148] C. Law, O. Moudam, S. Villarroya-Lidon, B. O'Regan, *J. Mater. Chem.* **2012**, 22, 23387.
- [149] M. Tomellini, M. Fanfoni, *Surf. Sci.* **1996**, 349, L191.
- [150] F. O. Lenzmann, B. C. O'Regan, J. J. T. Smits, H. P. C. E. Kuipers, P. M. Sommeling, L. H. Slooff, J. a. M. van Roosmalen, *Prog. Photovoltaics Res. Appl.* **2005**, 13, 333.
- [151] R. J. Ellingson, J. B. Asbury, S. Ferrere, H. N. Ghosh, J. R. Sprague, T. Lian, A. J. Nozik, *J. Phys. Chem. B* **1998**, 2, 6455.
- [152] S. K. Pathak, A. Abate, T. Leijtens, D. J. Hollman, J. Teuscher, L. Pazos, P. Docampo, U. Steiner, H. J. Snaith, *Adv. Energy Mater.* **2014**, n/a.
- [153] F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2009**, 131, 558.
- [154] P. R. F. Barnes, A. Y. Anderson, S. E. Koops, J. R. Durrant, B. C. O'Regan, *J. Phys. Chem. C* **2009**, 113, 1126.
- [155] F. Manke, J. M. Frost, V. Vaissier, J. Nelson, P. R. F. Barnes, *Phys. Chem. Chem. Phys.* **2015**, 17, 7345.
- [156] The elephant in the laboratory.
<http://www.integratedcatholiclife.org/2014/09/trasancos-elephant-in-laboratory/>.
- [157] P. Bonhôte, E. Gogniat, M. Grätzel, P. V. Ashrit, **1999**, 350, 269.
- [158] A. Fattori, L. M. Peter, H. Wang, H. Miura, F. Marken, *J. Phys. Chem. C* **2010**, 205, 11822.

Appendix A

The alumina paste used in Chapter 7 was prepared by Andrew Hey at Oxford University according to the following procedure. A commercial (from Sigma Aldrich) aluminum oxide (< 50 nm) dispersion 10 wt% in water was washed by centrifuging at 7500 RPM for 6 hours and redispersing in absolute ethanol with an ultrasonic probe at a duty cycle of 50 % for a duration of 5 minutes. This was repeated three times. A paste was then made with the following composition 1 g Al_2O_3 to 3.33 g of α -terpineol to 5 g of a 50:50 mix of ethyl-cellulose 10 cP and 46 cP in ethanol 10 wt %. After each addition, the mix was stirred for 2 minutes and sonicated for one minute. Finally, the resulting mixture was introduced into a rotary evaporator to remove excess ethanol in order achieve the required paste consistency suitable for doctor blading, spin-coating or screen-printing.

Appendix B



Royal Society of Chemistry
Thomas Graham House
Science Park
Milton Road
Cambridge
CB4 0WF

Tel: +44 (0)1223 420 066
Fax: +44 (0)1223 423 623
Email: contracts-copyright@rsc.org

www.rsc.org

Acknowledgements to be used by RSC authors

Authors of RSC books and journal articles can reproduce material (for example a figure) from the RSC publication in a non-RSC publication, including theses, without formally requesting permission providing that the correct acknowledgement is given to the RSC publication. This permission extends to reproduction of large portions of text or the whole article or book chapter when being reproduced in a thesis.

The acknowledgement to be used depends on the RSC publication in which the material was published and the form of the acknowledgements is as follows:

- For material being reproduced from an article in *New Journal of Chemistry* the acknowledgement should be in the form:
 - [Original citation] - Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC
- For material being reproduced from an article *Photochemical & Photobiological Sciences* the acknowledgement should be in the form:
 - [Original citation] - Reproduced by permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association, and RSC
- For material being reproduced from an article in *Physical Chemistry Chemical Physics* the acknowledgement should be in the form:
 - [Original citation] - Reproduced by permission of the PCCP Owner Societies
- For material reproduced from books and any other journal the acknowledgement should be in the form:
 - [Original citation] - Reproduced by permission of The Royal Society of Chemistry

The acknowledgement should also include a hyperlink to the article on the RSC website.

The form of the acknowledgement is also specified in the RSC agreement/licence signed by the corresponding author.

Except in cases of republication in a thesis, this express permission does not cover the reproduction of large portions of text from the RSC publication or reproduction of the whole article or book chapter.

A publisher of a non-RSC publication can use this document as proof that permission is granted to use the material in the non-RSC publication.



Title: Efficient Lateral Electron Transport inside a Monolayer of Aromatic Amines Anchored on Nanocrystalline Metal Oxide Films

Author: Pierre Bonhôte, Eric Gogniat, Sophie Tingry, et al

Publication: The Journal of Physical Chemistry B

Publisher: American Chemical Society

Date: Feb 1, 1998

Copyright © 1998, American Chemical Society

[LOGIN](#)

If you're a [copyright.com user](#), you can login to RightsLink using your copyright.com credentials. Already a [RightsLink user](#) or want to [learn more?](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.