Characterisation of Organic Dyes for Solid State Dye-Sensitized Solar Cells

UTE CAPPEL
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Abstract

Energy from the sun can be converted to low cost electricity using dye-sensitized solar cells (DSCs). Dye molecules adsorbed to the surface of mesoporous TiO$_2$ absorb light and inject electrons into the semiconductor. They are then regenerated by the reduced redox species from an electrolyte, typically consisting of the iodide/tri-iodide redox couple in an organic solvent. In a solid state version of the DSC, the liquid electrolyte is replaced by an organic hole conductor. Solid state DSCs using 2,2’7,7’-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobifluorene (spiro-MeOTAD) have reached conversion efficiencies of up to 6%, which is about half of the efficiency of the best iodide/tri-iodide cells.

Measurement techniques, such as spectroelectrochemistry and photo-induced absorption spectroscopy (PIA), were developed and applied to study the working mechanism of organic dyes in solid state DSCs under solar cell operating conditions. The energy alignment of the different solar cell components was studied by spectroelectrochemistry and the results were compared to photoelectron spectroscopy. PIA was used to study the injection and regeneration processes. For the first time, it was shown here that the results of PIA are influenced by an electric field due to the electrons injected into the TiO$_2$. This electric field causes a shift in the absorption spectrum of dye molecules adsorbed to the TiO$_2$ surface due to the Stark effect.

Taking the Stark effect into consideration during the data analysis, mechanistic differences between solid state and conventional DSCs were found. A perylene dye, ID176, was only able to efficiently inject electrons into the TiO$_2$ in presence of lithium ions and in absence of a solvent. As a result, the sensitizer worked surprisingly well in solid state DSCs but not in liquid electrolyte ones. Regeneration of oxidised dye molecules by spiro-MeOTAD was found to be fast and efficient and spiro-MeOTAD could even reduce excited dye molecules.

Keywords: energy alignment, hole conductor, injection, interface, perylene, photo-induced absorption, regeneration, spectroelectrochemistry, spiro-MeOTAD, Stark effect, titanium dioxide

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Das Fräulein stand am Meere
Und seufzte lang und bang,
Es rührte sie so sehre
Der Sonnenuntergang.

„Mein Fräulein! Sein Sie munter,
Das ist ein altes Stück;
Hier vorne geht sie unter
Und kehrt von hinten zurück.”

Heinrich Heine

Für meine Eltern
List of Papers

This thesis is based on the following five papers, which are referred to in the text by their Roman numerals.

I Ute B. Cappel, Elizabeth A. Gibson, Anders Hagfeldt, Gerrit Boschloo
*Dye regeneration by spiro-MeOTAD in solid state dye-sensitized solar cells studied by photoinduced absorption spectroscopy and spectroelectrochemistry*

II Ute B. Cappel, Sandra M. Feldt, Jan Schöneboom, Anders Hagfeldt, Gerrit Boschloo
*The effect of local electric fields on photoinduced absorption in dye-sensitized solar cells*

III Ute B. Cappel, Martin H. Karlsson, Neil G. Pschirer, Felix Eickemeyer, Jan Schöneboom, Peter Erk, Gerrit Boschloo, Anders Hagfeldt
*A broadly absorbing perylene dye for solid-state dye-sensitized solar cells*

IV Ute B. Cappel, Amanda L. Smeigh, Stefan Plogmaker, Erik M. J. Johansson, Håkan Rensmo, Leif Hammarström, Anders Hagfeldt, Gerrit Boschloo
*Characterization of the interface properties and processes in solid state dye-sensitized solar cells employing a perylene sensitizer*

V Ute B. Cappel, Stefan Plogmaker, Erik M. J. Johansson, Anders Hagfeldt, Gerrit Boschloo, Håkan Rensmo
*Energy alignment and surface dipoles of rylene dyes adsorbed to TiO₂ nanoparticles*

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Comments on my own Contribution

I was the main responsible person for the project for all papers. I prepared samples, carried out most experiments and data analysis and wrote most parts of the manuscripts. I did not perform any quantum chemical calculations, organic synthesis or optimisation of solar cell efficiencies. I took part in photo-electron spectroscopy measurements and data analysis but was not the main responsible person. The SEM pictures presented in Paper I were taken by Dr. Elizabeth Gibson. Dr. Amanda Smeigh carried out the femtosecond transient absorption measurements presented in Paper IV, while I carried out most of the data analysis of them.

I am a co-author of the following papers which are not included in this thesis.

- Rebecca S. Sage, Ute B. Cappel, Michael N. R. Ashfold, Nicholas R. Walker
  Quadrupole mass spectrometry and time-of-flight analysis of ions resulting from 532 nm pulsed laser ablation of Ni, Al, and ZnO targets

- Ute B. Cappel, Ian M. Bell, Laura K. Pickard
  Removing cosmic ray features from Raman map data by a refined nearest neighbour comparison method as a precursor for chemometric analysis

- Sandra M. Feldt, Ute B. Cappel, Erik Johansson, Gerrit Boschloo, Anders Hagfeldt
  Characterization of surface passivation by poly(methysiloxane) for dye-sensitized solar cells employing the ferrocene redox couple
Abbreviations and symbols

A  electron acceptor in organic dye molecules
A  absorbance
ΔA  change or difference in absorbance
APCE  absorbed photon to current conversion efficiency
c  the speed of light
C  concentration
CB  conduction band
CE  counter electrode
CE(λ)  colouration efficiency
CV  cyclic voltammetry
D  electron donor in organic dye molecules
DCM  dichloromethane
DPV  differential pulse voltammetry
DSC  dye-sensitized solar cell
e  elementary charge
E  energy
E_{0-0}  transition energy between the relaxed ground-state and excited state
E_{F,\text{redox}}  redox Fermi level (energy)
E_{F,\text{TiO}_2}  Fermi level (energy) of the TiO\textsubscript{2}
EA  electroabsorption spectroscopy
f  frequency
F  Faraday’s constant
\overrightarrow{F}  electric field
Fc  ferrocene
ff  fill factor
FTO  fluorine doped tin oxide
h  Planck’s constant
HOMO  highest occupied molecular orbital
I  current
I_0  photon flux
ICT  internal charge transfer
IPCE  incident photon to current conversion efficiency
J  current density (current per area)
J_{Ph}  photocurrent (density)
J_{SC}  short-circuit current (density)
$k$ rate constant
$l$ path length or thickness
LHE light harvesting efficiency
LiTFSI $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$
LUMO lowest unoccupied molecular orbital
MeCN acetonitrile
MPN 3-methoxypropionitrile
$N_A$ Avogadro’s constant
$n_{CB}$ density of conduction band electrons
$N_{CB}$ density of states in the conduction band
NHE normal hydrogen electrode
$P$ power, usually given as a power density
$P_{\text{in}}$ power density of a light source
PES photoelectron spectroscopy
PIA photo-induced absorption (spectroscopy)
PMMA poly(methyl methacrylate)
$Q$ charge (per unit area)
RE reference electrode
$[s]$ the number of moles of species $s$ per unit area
sDSC solid state dye-sensitized solar cell
spiro-MeOTAD $2,2’7,7’$-tetrakis-($N,N’$-di-$p$-methoxyphenyl-amine)-9,9’-spirobifluorene
$T$ transmission
TAS transient absorption spectroscopy
TBA tetrabutylammonium
$t\text{BP}$ 4-tertbutylpyridine
$U$ potential
$U_{\text{F,redox}}'$ formal redox potential
$V$ voltage
$V_{\text{OC}}$ open-circuit voltage
VB valence band
WE working electrode
$\alpha$ a constant between 0 and 1
$\beta$ a constant describing the recombination order
$\epsilon$ extinction coefficient
$\eta$ efficiency of a solar cell
$\eta_{\text{cc}}$ charge collection efficiency
$\lambda$ wavelength or reorganisation energy
$\mu$ dipole moment
$\pi$ conjugated linker in organic dye molecules
$\tau$ time constant
$\Phi_{\text{inj}}$ quantum efficiency of photo-induced electron injection
$\Phi_{\text{reg}}$ quantum efficiency of oxidised dye regeneration
$\omega$ angular frequency
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1. Introduction

1.1 Energy from the sun

The effects of CO₂ emissions on the climate and the limited amount of fossil fuel resources are the two main driving forces for the research into renewable energies. Renewable energy sources include sunlight, wind, rain, tides, and geothermal heat. Energy from the sun is the largest one of these sources.¹

1.7 ·10⁵ TW of solar power strike the earth’s atmosphere and the practical terrestrial global solar potential is estimated to be about 600 TW. The current global power consumption is approximately 15 TW and is expected to rise in the coming decades.

The spectrum of the sun’s radiation is close to that of a black body at a temperature of 5800 K. The spectrum reaching the earth’s surface is influenced by absorption in the earth’s atmosphere and therefore also by the path length of photons through the atmosphere. Figure 1.1 shows the solar irradiance at an airmass of 1.5 (AM 1.5 G) from 300 to 1400 nm. This spectrum is normalised so that the irradiance integrates to 1000 W m⁻² and is used as the standard solar spectrum on earth in calibrations. Figure 1.2 shows the AM 1.5 G spectrum expressed as a photon flux instead of irradiance. It can be seen that while the power from the sun is highest at about 460 nm, the number of photons is largest at 680 nm.

Solar energy can be converted to electricity using solar thermal systems or solar cells (photovoltaics). The industries of both technologies have been experiencing large growth rates in the last decade and the global installed capacity of solar cells reached 24 GW in 2009.² However, in order to provide a significant fraction of the total global energy production, both industries will have to grow enormously in the future.³ For such a growth, it is important that solar cells become cheaper or more efficient and that a variety of solar cell technologies, which use accessible and affordable materials, are available.

1.2 The dye-sensitized solar cell

Dye-sensitized solar cells (DSCs)⁴–⁶ have attracted much attention since Brian O’Regan and Michael Grätzel demonstrated in 1991⁷ that they can be used to convert sunlight to electricity at a low cost. Record efficiencies of up to 12 % have now been achieved with small devices⁸,⁹ and sub-module efficiencies have reached almost 10 %.¹⁰
Figure 1.1: Solar irradiance at the surface of the earth with the visible part of the solar spectrum indicated by its colours.

Figure 1.2: Photon flux at the surface of the earth with the visible part of the solar spectrum indicated by its colours.
Dye-sensitized solar cells are a type of photoelectrochemical cell. One of the main differences between dye-sensitized solar cells and other types of solar cells is the way charges are separated. In DSCs, dye molecules attached to a semiconductor surface (usually TiO$_2$) absorb visible light leading to an electronic transition in the molecules. The excited dye then injects an electron into the conduction band of titanium dioxide. This means that charge separation takes place before charge transport, and therefore no transport of excitons or minority charge carriers is required in the cell. In order to have good light harvesting, a large surface area of the semiconductor is required at which the dye can absorb and at which charge separation can occur. This is obtained by employing a mesoporous TiO$_2$ electrode consisting of nanoparticles of approximately 20 nm diameter in the cells (Figure 1.3). The pores of this semiconductor are usually filled with a redox electrolyte, containing the redox couple, iodide/tri-iodide, in an organic solvent such as acetonitrile. The redox electrolyte serves to regenerate dye molecules, which are in their oxidised form after having injected an electron into the TiO$_2$, and to transport the holes to the counter electrode, which consists of a layer of platinised fluorine doped tin oxide (FTO) on a glass substrate. Electrons travel through the mesoporous TiO$_2$ network by diffusion to the FTO substrate of the working electrode, completing the circuit. The voltage which can be generated in such a device depends on the difference of the redox potential of the electrolyte and the Fermi level of the TiO$_2$ under illumination. How much current can be generated depends on the absorption spectrum of the dye and how well it is matched to the solar spectrum (Figure 1.2).

The large TiO$_2$ surface area leads to a large contact area between the semiconductor, the dye molecules and the redox mediator. The charge transport of carriers in the TiO$_2$ therefore has to be faster than the recombination of...
charge carriers across this interface in order to avoid recombination losses. The recombination of electrons in TiO$_2$ with tri-iodide is very slow under solar cell working conditions (tens to hundreds of milliseconds) allowing the DSC to function.$^{6,11}$

The two main areas for academic research on dye-sensitized solar cells have been the development and testing of new or different components and the study of the complicated working mechanism underlying the operation of the cell. In this thesis, a solid state version of the conventional DSC was studied. In this solid state DSC, the liquid electrolyte has been replaced by the organic hole conductor 2,2$'$/7,7$'$-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9$'$-spirobifluorene (spiro-MeOTAD).$^{12,13}$ This potentially offers advantages over standard DSCs in terms of stability and large-scale processing, and efficiencies of up to 6% have been achieved in solid state DSCs.$^{14,15}$

1.3 The aim and content of this thesis

The aim of this thesis work was to study the working mechanism of organic dyes in solid state DSCs. Of particular interest was a perylene dye, termed ID176, which showed much better performances in solid state than liquid electrolyte DSCs. However, before I was able to study and understand this problem, I spent time adapting characterisation techniques for use in solid state DSCs (Paper I). This work lead to the observation of a Stark effect in photo-induced absorption spectroscopy of sensitised TiO$_2$ films (Paper II). Paper III and IV contain the studies of the sensitizer ID176: Paper III summarises its solar cell performance while in Paper IV, the energy alignment and interface processes of the dye were studied. Finally, Paper V compares different methods to study the energy alignment and surface dipoles of dyes adsorbed to mesoporous TiO$_2$ films.

The following chapters will provide background reading to the papers, a summary of the results and an outlook for future work:

- The properties and problems of solid state DSCs, and in particular the interface processes which were studied will be introduced in Chapter 2.
- I will summarise the requirements for properties of organic dyes used in DSCs and I will introduce the dyes studied here in Chapter 3.
- Chapter 4 will describe the treatment of electric fields in DSCs, introduce the Stark effect and ways to measure it.
- In Chapter 5, I will describe the methods used in this work and the theory required for applying them.
- Chapter 6 will summarise some of the results from my papers regarding the study of energy alignment and interface processes in solid state DSCs.
- Finally, I will summarise the implications of my results for the measurement and development of solid state DSCs and provide an outlook for future work (Chapter 7).
2. Solid state dye-sensitized solar cells

The development of solid state alternatives to the liquid electrolyte in DSCs began in order to avoid solvent evaporation or leakage which might occur in liquid electrolyte DSCs. One approach to this problem was to replace organic solvents in the liquid electrolyte by ionic liquids\textsuperscript{16} or polymers.\textsuperscript{17} The other approach was to completely replace the iodide/tri-iodide redox couple by solid state hole conductors. Both inorganic\textsuperscript{18,19} and organic\textsuperscript{12,20,21} hole conductors have been tested for this purpose. In a recent publication, an impressive 6\% efficiency were achieved with in situ polymerised poly(3,4-ethylenedioxythiophene) (PEDOT) as a hole conducting material.\textsuperscript{22} The most widely used hole conductor is the organic hole conductor spiro-MeOTAD (2,2’7,7’-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobifluorene)\textsuperscript{12} (Figure 2.1b) and work in this thesis focuses solely on this material.

Figure 2.1a shows a schematic diagram of a solid state DSC. Fabricating the devices is usually started by preparing a dense TiO\textsubscript{2} blocking layer on the FTO substrate for the working electrode by spray pyrolysis.\textsuperscript{23} This blocking layer prevents a direct contact between the hole conductor and the FTO, which would short-circuit the cell. The mesoporous TiO\textsubscript{2} film is applied on top of the blocking layer by doctor blading, screenprinting or spin-coating of a colloidal TiO\textsubscript{2} paste. The commercially available TiO\textsubscript{2} paste DSL 18NR-T from Dyesol was used in this thesis work. The films are then sintered at 450 - 500 °C. For optimised solid state devices, the resulting film thicknesses are around 2 µm. After a sensitising step, spiro-MeOTAD is applied to the films by spin-coating from solution. Typical spin-coating solutions consist of 150 - 200 mg spiro-MeOTAD per ml of chlorobenzene and the additives LiTFSI (typically 15 mM) and tBP (typically around 60 mM) (Figure 2.1c,d). The solution fills the pores and during spin-coating the solvent evaporates, leaving spiro-MeOTAD in the pores and an overstanding layer of spiro-MeOTAD on top of the TiO\textsubscript{2} film.

LiTFSI reduces recombination in the cell\textsuperscript{24} and increases the conductivity of spiro-MeOTAD.\textsuperscript{25,26} Initially, also N(PhBr)\textsubscript{3}SbCl\textsubscript{6} was added to the spiro-MeOTAD solution to chemically dope the semiconductor but it was found that this was not necessary.\textsuperscript{25} tBP has been used to improve the open-circuit voltage of the liquid electrolyte DSCs by causing a favourable upward shift in the TiO\textsubscript{2} conduction band and by reducing recombination.\textsuperscript{27} It was found to work similarly in the solid state DSC when added to the spiro-MeOTAD solution.\textsuperscript{24}
Solid state DSCs are completed by evaporation of a metal back contact. Both gold and silver have been shown to work well. Silver offers the additional advantage of being more reflectant than gold and can help to enhance photocurrents. \(^{28}\)

### 2.1 Interface reactions in solid state DSC

Of particular interest for this thesis work were the interface properties and processes of the solid state DSC, which involve the sensitiser. The interface reactions in DSCs can be grouped into two categories: the favourable forward reactions and the unwanted backward reactions. Figure 2.2 shows energy diagrams where the reactions are summarised.

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**Figure 2.1:** a) Schematic diagram of a solid state DSC. Molecular structure of b) spiro-MeOTAD, c) LiTFSI, and d) 4-tertbutylpyridine (tBP).

**Figure 2.2:** a) Forward (black arrows) and backward reactions (red arrows) in a solid state DSC following the conventional reaction scheme in DSCs. b) Alternative reaction scheme, where sensitiser reduction precedes electron injection.
The first reaction always has to be the excitation of the sensitisier by absorp-
tion of a photon:

\[ D + h\nu \rightarrow D^* \]  

(2.1)

The excited dye molecule will then inject an electron into the TiO\(_2\) so that the
sensitiser is oxidised (Equation 2.2). The oxidised sensitiser can then receive
an electron from the hole conductor so that the sensitiser is regenerated and a
hole is created in the hole conductor (Equation 2.3).

\[ D^* \rightarrow D^+ + e^- \]  

(2.2)

\[ D^+ \rightarrow D + h^+ \]  

(2.3)

This reaction scheme is equivalent to the one observed in liquid electrolyte
DSCs. For solid state DSCs, one can also consider that the excited sensitisier
might be reductively quenched by the hole conductor creating the reduced
sensitiser and a hole in spiro-MeOTAD (Equation 2.4).\(^{29}\) This option will be
discussed in more detail in Chapter 6.4 and in Paper IV. The reduced sensitisier might then inject its electron into the TiO\(_2\) completing charge separation
(Equation 2.5).

\[ D^* \rightarrow D^- + h^+ \]  

(2.4)

\[ D^- \rightarrow D + e^- \]  

(2.5)

Recombination reactions are possible after each step of charge generation:

\[ D^* \rightarrow D(\pm h\nu) \]  

(2.6)

\[ D^+ + e^- \rightarrow D \]  

(2.7)

\[ D^- + h^+ \rightarrow D \]  

(2.8)

\[ e^- + h^+ \rightarrow \]  

(2.9)

If one of the forward reactions is not efficient, charge carriers will recom-
bine. A forward reaction should therefore be faster than the backward reac-
tion of the previous step. For example, regeneration of oxidised dye molecules
(Reaction 2.3) should be faster than recombinations of oxidised dye molecules
and electrons (Reaction 2.7). Finally, the recombinations of electrons in the
TiO\(_2\) and holes in spiro-MeOTAD (Equation 2.9) competes with the charge
transport to the contacts.
2.2 Differences between spiro-MeOTAD and a redox electrolyte

Comparing the properties of spiro-MeOTAD to the properties of a redox electrolyte, it is immediately obvious that the charge transport mechanism of positive charge carriers is different in solid state and liquid electrolyte DSCs. In the liquid electrolyte case, the redox mediator diffuses in a liquid medium while in the solid state case, the holes move in a solid medium. The ratio of tri-iodide and iodide in the liquid electrolyte cells is about 1 to 10 and both are present in large quantities. In the solid state DSCs considered here, spiro-MeOTAD is not actively doped and the concentration of holes might be very low. There is some evidence that spiro-MeOTAD can become oxidised in the presence of oxygen and LiTFSI and that this improves device performances.

Considering the interface reactions discussed in the previous section, it is clear that all reactions involving spiro-MeOTAD will be different to the equivalent reactions in the liquid electrolyte DSC. In the latter, iodide has to diffuse to the oxidised dye molecule, while in the solid state DSC, a spiro-MeOTAD molecule is either present close to the dye molecule or not. If it is, then the regeneration reaction might be expected to occur much faster than in the liquid electrolyte DSC. Regeneration in the picosecond time scale has indeed been observed with spiro-MeOTAD.

The recombination between tri-iodide and electrons in the liquid electrolyte DSC (the equivalent of Reaction 2.9) is slow, as iodide/tri-iodide is a two electron redox couple. Faster recombination has been observed in solid state DSCs.

Finally, the energy level / redox potential of spiro-MeOTAD is different from the redox potential of iodide/tri-iodide. Iodide/tri-iodide has a redox potential of approximately -0.32 V vs. Fc/Fc+ while the redox potential of spiro-MeOTAD has been determined to be 0.12 V vs. Fc/Fc+ in solution and 0.15 V vs. Fc/Fc+ in a solid film (Paper I). Therefore solid state DSCs can give higher voltages and have a potential for higher efficiencies than liquid electrolyte DSCs.

2.3 Performance limitations of solid state DSCs

As mentioned above, the highest efficiencies in solid state DSCs have been achieved using approximately 2 µm thick TiO2 films. This is much lower than optimised film thicknesses of liquid electrolyte DSCs. Light harvesting, especially in the red part of the solar spectrum, is often not complete when using such thin films. In order to improve the efficiencies of solid state DSCs further, it is important to understand the cause of the low optimal film thickness. One needs to determine which processes work well in the cell and which processes are limiting.
Another way to improve the light harvesting in thin films is to use organic dyes with high extinction coefficients.\textsuperscript{36–38} This was also the motivation for using organic dyes in this thesis work and design principles and properties of such dyes are discussed in the next chapter.

Difficulties in filling the pores of mesoporous TiO\(_2\) have been viewed as one of the reasons for the limitations in the TiO\(_2\) film thickness.\textsuperscript{20,31} One should distinguish here between the contacting of the dye molecules by the hole conductor and the actual filling of all pores of the titanium dioxide. On the one hand, if some dye molecules are not contacted by the hole conductor, they might not be regenerated. On the other hand, incomplete filling of the pores could lead to difficulties in transporting holes out of the spiro-MeOTAD film. Recent studies have shown that filling fractions can be very high for thin TiO\(_2\) films and might be as high as 60\% for 7 \(\mu\)m thick TiO\(_2\) films.\textsuperscript{39,40} In Paper I, I tried to study the pore filling by studying the regeneration of oxidised dye molecules at different spiro-MeOTAD concentrations. This method examines the contact behaviour rather than the actual pore filling.

Another reason for the lower efficiencies of solid state DSCs seems to be that the electron diffusion length close to open-circuit conditions is close to the optimum film thickness.\textsuperscript{33,34,39} Other studies have suggested that the electron diffusion length is sufficiently long for complete charge collection under short circuit conditions.\textsuperscript{39,41} The diffusion length can be either improved by decreasing the transport times or by decreasing recombination. It has been suggested that the electron transport in the TiO\(_2\) is limiting rather than the hole transport in spiro-MeOTAD.\textsuperscript{28} Therefore, one might be able to improve the devices by employing more ordered TiO\(_2\) structures with better transport properties.

Recombination in solid state DSCs has been inhibited by adding tBP to the spiro-MeOTAD solution.\textsuperscript{24} Another approach has been to protect the TiO\(_2\) surface by using small organic molecules as co-adsorbers\textsuperscript{42} or by coating the TiO\(_2\) surface with an insulating oxide layer prior to dye adsorption.\textsuperscript{43,44} While this latter approach is very efficient in reducing recombination, it can also block electron injection and therefore does not always improve efficiencies. The largest improvements in efficiency have come from employing dyes with long alkyl chains, which can reduce recombination at the TiO\(_2\)/spiro-MeOTAD interface.\textsuperscript{14,28,36} This indicates the central role the dye and the TiO\(_2\)/dye/spiro-MeOTAD interface play in understanding and optimising the properties of solid state DSCs.
3. Organic dyes for solid state dye-sensitized solar cells

One of the components of the dye-sensitized solar cell, which is easiest to vary, is the sensitising dye and many different dyes have been synthesised for DSCs and tested in functional devices. The most successful devices still use ruthenium sensitisers but efficiencies of up to 10% have been obtained using organic sensitisers in liquid electrolyte DSCs. Organic dyes have some advantages over ruthenium dyes. They exhibit higher extinction coefficients and therefore do not need as thick mesoporous TiO$_2$ films as ruthenium sensitisers for complete light harvesting. They can be relatively easily modified to tune their properties.

In general, dyes for DSCs should fulfil the following properties to be successfully used in devices:

1. The dye should have at least one anchoring group to bind to the TiO$_2$ surface.
2. The excited state of the dye must be high enough in energy and long-lived enough to allow for electron injection into the TiO$_2$.
3. The highest occupied molecular orbital (HOMO) of the dye should be low enough to allow for regeneration.
4. The dye should have a high extinction coefficient over a large region of the solar spectrum.
5. The dye should be photo-, thermally and electrochemically stable.
6. The dye should form a densely packed monolayer on the TiO$_2$ surface.

3.1 Donor-linker-acceptor dyes

A common line of development for organic dyes in DSCs is to synthesise so-called D-π-A dyes, consisting of an electron donor (D), a conjugated linker (π) and an electron acceptor (A). The idea behind this concept is that in such molecules most electron density of the HOMO will be located on the donor, while most density of the lowest unoccupied molecular orbital (LUMO) will be located on the acceptor. The dyes therefore show intramolecular charge transfer (ICT) from the donor to the acceptor upon excitation.

For typical n-type dyes used in standard DSCs, the anchoring group is located close to or is even part of the acceptor. This ensures that the excited
state of the dye is located closer to the TiO₂ surface than the hole remaining on the dye after electron injection. This should help supressing recombination between electrons and oxidised dye molecules and make the hole easily accessible for the redox mediator, which is beneficial for regeneration. A variation of this theme is employed in p-type DSCs, which use a p-type semiconductor (NiO) as a photocathode.⁴⁹,⁵⁰ In these DSCs, a hole is injected into the semiconductor and therefore the anchoring group will now be on the donor of the sensitisier, facilitating hole injection.

The donor, acceptor and linker of the molecule can then be independently varied to tune the properties of the molecules.⁵¹,⁵² Typically used donors are triphenylamine, indoline or coumarin units. Examples of acceptors, which include anchoring groups, are cyanoacrylic acid and rhodanine-3-acetic acid. Figure 3.1a shows the n-type dye, D149,⁵³,⁵⁴ and the p-type dye, P1, which were used in Paper II.⁵⁰ D149 uses an indoline donor and a rhodanine acceptor. P1 uses a triphenylamine donor and dicyanovinyl groups as electron acceptors.

\[ \text{Figure 3.1: a) Molecular structures of D-π-A dyes used in this thesis work. b) Molecular structures of the perylene dyes, ID28 and ID176 and of the terylene dye, ID1. Structures were drawn and geometry optimised in Avogadro.}^{55} \text{ The structures represent possible geometries and not fully optimised geometries of minimal energy.} \]
Another modification often made to organic dyes is to introduce alkyl chains to the linker or donor part of the molecule. These can prevent formation of dye aggregates and/or inhibit electron and hole recombination by protecting the TiO$_2$ surface. An example of such a dye based on a triphenylamine donor is D35$^{56,57}$ (Figure 3.1a), which has been successfully employed in liquid electrolyte as well as solid state DSCs. This dye was used for the comparison of measurements on complete solid state devices to liquid electrolyte devices here (Chapter 5.2).

### 3.2 Dipole moments in ground and excited states

The donor-acceptor nature of the D-π-A dyes causes them to have strong dipole moments in both ground and excited state (a distribution of electron density across the molecule). Dipole moments are defined to point from the negative charge ($\delta^-$) to the positive charge ($\delta^+$). For D-π-A dyes in their ground-state, this usually means that the dipole moment ($\vec{\mu}_{\text{ground}}$) points from the acceptor to the donor (Figure 3.2), i.e. there is more electron density on the acceptor than on the donor. This is due to the fact that the acceptor consists of electron withdrawing groups while the donor consists of groups donating electron density into the molecule. When the dye molecules adsorb to a TiO$_2$ surface, they often align in such a way that their dipole moments point away from the surface. This can cause a favourable upward shift of the TiO$_2$ conduction band which improves the $V_{OC}$ of the device.$^{58}$

![Figure 3.2: Schematic diagram of a D-π-A dye with the direction of the dipole moments in ground and excited state and their difference indicated.](image)

In their excited state, the molecules have even more electron density on the acceptor leading to a dipole moment ($\vec{\mu}_{\text{ex}}$) pointing in approximately the same direction as before but with a higher magnitude. The change in dipole moment upon excitation ($\Delta\vec{\mu}$) is defined as

$$\Delta\vec{\mu} = \vec{\mu}_{\text{ex}} - \vec{\mu}_{\text{ground}}$$ (3.1)
This quantity gives information about the magnitude of the intramolecular charge transfer upon excitation and is therefore an important parameter in the characterisation of D-π-A dyes.

For p-type dyes like P1, the dipole moments typically point in the opposite direction relative to the binding group and the semiconductor surface than for n-type dyes.

3.3 Rylene dyes

A different category of organic dyes which have been tested in DSCs are rylene dyes and a summary of their application in DSCs (and other types of solar cells) can be found in a recent review paper. Rylene dyes consist of naphthalene units connected in the peri position. Two such units make up a perylene, three units a terrylene, and so on. With increasing size, the energy gap between the HOMO and the LUMO of the dyes decreases, and they absorb light at longer wavelengths.

A terrylene sensitiser, called ID1 or TMIMA (Figure 3.1b) was used in Paper V. This dye is more symmetrical than other dyes and shows almost no ICT character. However, the terrylene chromophore has a very high extinction coefficient in the red part of the solar spectrum, which complements the absorption spectra of many, more blue-absorbing, organic sensitisers. ID1 showed good photocurrents in liquid electrolyte DSCs but efficiencies were low as voltage improving additives such as tBP could not be used as they decreased the photocurrents dramatically.

A common development strategy for application of rylene dyes in DSCs was to functionalise the highly stable perylene chromophore by adding different substituents. It was found that by adding electron donors to the perylene core, efficient sensitisers with ICT character could be obtained. These sensitisers were usually bound to the TiO$_2$ surface by ring-opening of an anhydride group. The structure of ID28, the sensitiser of this type used in this thesis work (Papers I and V), is shown in Figure 3.1b. This dye has shown an efficiency of 3.9 % in liquid DSCs. A closely related sensitiser, ID94, showed an efficiency of 6.8 % in liquid electrolyte DSCs, which is the highest efficiency of perylene sensitisers reported to date. Adsorption of ID28 and ID94 to the TiO$_2$ surface leads to a large spectral blue shift of their absorption spectra due to a decrease in the effective π-conjugation length.

ID176 is a modification of ID28, where the anhydride anchoring group has been replaced by a carboxylic acid attached to a perylene monoimide (Figure 3.1b). The absorption spectrum of this dye does not change much upon attachment to TiO$_2$ as there is no ring-opening, and ID176 showed a broad absorption spectrum when adsorbed to TiO$_2$. ID176 worked well in solid state but not in liquid electrolyte DSCs (Paper III). A large part of this thesis work was dedicated to understanding this unusual behaviour (Paper IV).
4. Electric fields in DSCs and the Stark effect

4.1 Energetics and electric fields at the TiO$_2$ surface

Anatase titanium dioxide, which is used in the dye-sensitized solar cell, is a n-type semiconductor (Figure 4.1a), as it has oxygen vacancies. When the surface of a bulk anatase crystal is brought into contact with a redox electrolyte, this leads to charge transfer from TiO$_2$ to the electrolyte in order to equilibrate the Fermi levels of the two materials. The semiconductor becomes depleted of charges close to the interface, which leads to an upward bending of the energy levels (Figure 4.1b) and the presence of an electric field within the semiconductor. This field enables electron transport away from the semiconductor/electrolyte interface. If a negative potential is applied to the titanium dioxide, eventually a potential will be reached at which the bands are flat again, the flat-band potential ($U_{fb}$). This potential is closely related to the conduction band energy of the titanium dioxide.

The potential drop between the semiconductor and the electrolyte is expected to be mostly located within the Helmholtz layer, a layer of the ions closest to the titanium dioxide surface. The conduction band position can be shifted by 59 mV per pH unit in an aqueous solution due to the adsorption and desorption of protons from the surface.$^{65,66}$ In an organic electrolyte solution, the conduction band position is determined by the solvent and often by the size of the cations present in the solution.$^{67,68}$ Lithium ions shift the conduc-

---

**Figure 4.1:** a) Energy levels of the surface of a bulk TiO$_2$ crystal. b) Equilibrium energy levels after bringing the surface of the TiO$_2$ in contact with a redox electrolyte. c) Representation of the shift in TiO$_2$ bands at the surface depending on the cations present in a contacting electrolyte.
tion band downwards in energy compared to the bulky TBA ions, as they can adsorb directly to the TiO$_2$ surface (Figure 4.1c). When the cations are adsorbed closer to the surface it becomes easier to inject an electron into the TiO$_2$ and harder to remove one, as the counter charge is closer to the electron. In a similar way, also the dipole moments of a molecules adsorbed to the TiO$_2$ surface can change the conduction band position. Dipole moments pointing towards the TiO$_2$ surface shift it to more positive potentials while dipole moments pointing away from the TiO$_2$ surface shift it to more negative potentials. An example of this is the use of rBP as an additive to liquid electrolytes or to spiro-MeOTAD to shift the conduction band to more negative potentials and to improve the open-circuit voltage of DSCs.

In mesoporous TiO$_2$ films, band bending of the TiO$_2$ bands is not considered to play a role. The particles become essentially depleted of conduction band electrons upon contact with the redox mediator. As the particles are small (20 nm in diameter), the potential drop within the particles is only estimated to be about a few meV.$^{66,69}$ Charges therefore travel within and between the particles by diffusion rather than by the drive of an electric field. Furthermore, in the consideration of the DSC energetics, it is not just the conduction band position, which is important but also the density of trap states in the band gap.$^{70}$ The density of states is expected to decrease exponentially below the conduction band edge. The density of states in the TiO$_2$ has been probed by electrochemistry in this thesis work and the density of surface trap states has been measured by photoelectron spectroscopy (Chapter 6.2 and Paper IV).

In DSCs, dye molecules are present at the TiO$_2$ surface. These dye molecules might be closer adsorbed to the TiO$_2$ surface than any of the ions in the electrolyte and therefore be located within the Helmholtz layer. In such a case, their potentials have been observed to follow the potential of the TiO$_2$ surface.$^{71,72}$ Alternatively, if the dye molecules are located outside the Helmholtz layer, the potentials of the dye molecules will not follow those of the TiO$_2$. $^{71}$ This might be the case for large dye molecules, or if the ions in the electrolyte are small and can adsorb closer to the TiO$_2$ surface than the dye molecules, shielding the dye molecules from the potential at the TiO$_2$ surface.

In this thesis work, a shift to longer wavelengths of the absorption spectra was observed for dye molecules adsorbed to TiO$_2$ in presence of lithium ions (Figures 4.6a and 5.1b). It was found that the oxidation potentials of dyes were essentially unchanged in presence of different cations, while their excited state potential and their reduction potential followed the potential of the titanium dioxide (Chapter 6.2 and Paper IV).

Photo-induced electron injection into the TiO$_2$ leads to an increased amount of charge present in the semiconductor. These charges are thought to be screened by the shell of adsorbed ions around the TiO$_2$. This is also considered to be the case in solid state DSCs, where LiTFSI has been added to the spiro-MeOTAD matrix. However, if dye molecules are located within
the Helmholtz layer, they may be exposed to an increased potential drop upon electron injection. This effect was observed in this thesis work (Paper II) and simultaneously by Meyer and co-workers.\textsuperscript{73} Photo-induced electron injection was found to cause a Stark shift in the ground-state absorption spectra of dye molecules adsorbed to the TiO\textsubscript{2} surface.

4.2 The Stark effect

Electric fields can induce a change in the transition energies of molecules ($\Delta E$).\textsuperscript{74–76} This effect is called Stark effect, electroabsorption or electrochromism.\textsuperscript{i} In very general terms the change in transition energy due to an external electric field ($\overrightarrow{F}$) is given by:\textsuperscript{ii}

$$\Delta E = -\Delta \mu \cdot \overrightarrow{F} - \frac{1}{2} \overrightarrow{F} \cdot \Delta \alpha \cdot \overrightarrow{F}$$  \hspace{1cm} (4.1)

where $\Delta \alpha$ is the change in polarisability due to the transition. This equation is valid for electronic transitions as well as for other transitions. One distinguishes the first order Stark effect, which is linear in the electric field, and the second order Stark effect, which is quadratic in the electric field.

Considering dye-sensitized solar cells, we are interested in how the Stark effect affects electronic transitions of dye molecules which are adsorbed to titanium dioxide surfaces. The effect will be induced by electrons injected into the titanium dioxide. We can define a main direction of the electric field, which is normal to the titanium dioxide surface, assuming, for simplification, that the positive counter charges are uniformly distributed at a certain distance away from the TiO\textsubscript{2} particle (Figure 4.2a). On average, dye molecules adsorbed to the surface should therefore experience an almost uniform electric field in one direction (Figure 4.2b), and we can rewrite Equation 4.1 in a one-dimensional form (chosen to be along the $z$-axis here):

$$\Delta E = -\Delta \mu_z \cdot F_z - \frac{1}{2} \Delta \alpha \cdot F_z^2$$  \hspace{1cm} (4.2)

However, it is the change in absorbance ($\Delta A$) due to an electric field rather than the change of transition energy which is of practical interest. An expression for $\Delta A$ can be derived from a Taylor expansion of $A$ around $E$ at $F_z = 0$:

$$\Delta A = A(E, F_z) - A(E, F_z = 0) = \frac{dA}{dE} \Delta E + \frac{1}{2} \frac{d^2A}{dE^2} \Delta E^2 + ...$$  \hspace{1cm} (4.3)

\textsuperscript{i}I will refer to the effect as Stark effect here and will call one of the methods to measure it electroabsorption spectroscopy.

\textsuperscript{ii}In Paper II, these Equations were written in terms of frequency, and the electric field was called $\overrightarrow{E}$. I found it more practical to write about transition energies here and I termed the electric field, $\overrightarrow{F}$, to distinguish it from $E$ for energy.
Substituting $\Delta E$ from Equation 4.2 into this equation, one can obtain an expression for the terms of $\Delta A$ linear and quadratic with the electric field:

$$\Delta A = -\frac{dA}{dE}\Delta \mu_z F_z + \frac{1}{2} \left( \frac{d^2A}{dE^2} \Delta \mu_z^2 - \frac{dA}{dE} \Delta \alpha \right) F_z^2$$  \hspace{1cm} (4.4)

Figure 4.2: a) Electric field direction outside a titanium dioxide particle with a 20 nm diameter into which electrons have been injected. A dye molecule with a length of 2 nm and a width of 1 nm is included. b) Enlargement of the dye molecule on the surface. The electric field lines around the dye molecule are almost parallel. c) Representation of the first order Stark shift when $\Delta \mu_z$ is anti-parallel to $F_z$ and when $\Delta \mu_z$ is parallel to $F_z$. 

Organic dyes used in DSCs are usually designed to have a large change in dipole moment upon excitation and should therefore show a first order Stark effect, given by the linear term of Equation 4.4. A representation of this first order Stark effect is shown in Figure 4.2c. For D-$\pi$-A dyes designed for n-type DSCs, $\Delta \mu_z$ usually points away from the TiO$_2$ surface. The transition energies are therefore expected to increase upon electron injection into the TiO$_2$ and the absorption spectrum is expected to shift to shorter wavelengths.

In this thesis work, I observed the Stark effect in three different types of measurements:

- in photo-induced absorption measurements, where the Stark effect of ground-state dye molecules was observed both in absence and presence of a redox mediator after photo-induced electron injection,
- in electroabsorption measurements where an external electric field was applied to a mono-layer of dye molecules adsorbed to a flat TiO$_2$ substrate, and
- in spectroelectrochemistry, where charges were injected into a dye-coated mesoporous TiO$_2$ film surrounded by a supporting electrolyte by applying a negative potential to the film.
The Stark effect in photo-induced absorption spectroscopy

Photo-induced absorption spectroscopy (PIA) will be described in detail in Chapter 5.1.3. In this section, the influence of the Stark effect on photo-induced absorption spectra will be explained. Absorption spectra of D149 and P1 adsorbed to mesoporous TiO$_2$ and their derivatives with respect to frequency are shown in Figure 4.3a. PIA spectra measured in absence and in presence of a redox electrolyte containing TBAI and I$_2$ are shown in Figure 4.3b. It can be seen that PIA spectra of D149 show a bleach at about 600 nm, which is at roughly the same position as the minimum in the derivative of the absorption spectrum. This feature is due to the Stark shift of ground-state D149 induced by electrons injected into the TiO$_2$. In absence of redox electrolyte, the positive charges are located on oxidised dye molecules, and in presence of redox electrolyte, the counter charges are located in the electrolyte.iii

![Figure 4.3: a) Absorption spectra (black, dashed) and derivatives of absorption spectra with respect to frequency multiplied by \(-5 \cdot 10^{13} \text{ s}^{-1}\) (grey) of D149 and P1 adsorbed to mesoporous TiO$_2$ films. b) PIA spectra of the D149 and P1 films in absence (black) and presence of redox electrolyte (grey, dashed). Figure adapted from Paper II.](image)

For P1, a peak is observed at 560 nm in both PIA spectra, which is at the same position as the minimum in the derivative spectrum. This peak is also due to the Stark effect. The sign of the Stark effect is reversed for P1 compared to D149 as $\Delta \mu_z$ points in opposite directions relative to the TiO$_2$ surface for the two sensitisers (see Chapter 3.2 and Paper II). The peak at 630 nm observed in absence of electrolyte is due to the absorbance of oxidised dye molecules.iii

iiiA more detailed discussion of the PIA spectra of D149 and P1 can be found in Paper II.
Stark shifts were also observed in PIA spectra of all other dyes used in this thesis work and in femtosecond transient absorption measurements (Paper IV).

The Stark effect in electroabsorption spectroscopy

In electroabsorption spectroscopy, the Stark effect is measured by applying an external electric field to a sample and measuring the resulting change in absorbance. To measure the first order Stark effect, dye molecules were adsorbed to flat TiO$_2$ surfaces so that electric fields could be applied normal to the dye layer. Details of the set-up and samples used for electroabsorption measurements can be found in Chapter 5.1.4. Electroabsorption spectra of D149 and P1 can be seen in Figure 4.4a. A voltage of 20 V with the negative pole on the titanium dioxide side of the sample was applied to the samples for these measurements. The spectra have a similar shape as the derivatives of the absorption spectra, and the same sign as the Stark shifts observed in the PIA spectra (Figure 4.3).

\[
\Delta A = -\frac{dA}{dE} \Delta \mu \frac{V_{\text{mod}}}{l}
\]  

(4.5)

where $V_{\text{mod}}$ is the voltage difference applied to the electrodes. Figure 4.4b shows the dependence of $\Delta A$ on $V_{\text{mod}}$. It is linear for both dyes in good agreement with Equation 4.5. The gradient of the plots can be used to determine
\( \Delta \mu_z \) if the magnitude of \( \frac{dA}{dE} \) is known. For D149, \( \Delta \mu_z \) was estimated to be approximately 1 Debye (Paper II).

The Stark effect in spectroelectrochemistry

The Stark effect can also be observed in spectroelectrochemistry. This was already shown in Paper I, even though the effect was not identified as the Stark effect there. Details of the experimental set-up for spectroelectrochemistry of dyes adsorbed to mesoporous TiO\(_2\) can be found in Chapter 5.1.2. When applying a negative potential to a TiO\(_2\) film, charges are injected into band gap states in the TiO\(_2\) and at sufficiently negative potentials also into the conduction band. The counter ions of these charges are cations in the supporting electrolyte. The electrons injected into the TiO\(_2\) can cause a Stark shift of the adsorbed dye molecules in a similar manner to photo-injected electrons in photo-induced absorption spectroscopy.

Figure 4.5a compares the charge passed at a TiO\(_2\) electrode dyed in ID28 upon scanning towards negative potential to the change in absorbance of ID28 at 550 nm. The supporting electrolyte used here was 0.1 M TBAClO\(_4\) in MPN. The change in absorbance is proportional to the charge rather than to the voltage applied at the electrode (Figure 4.5b). The magnitude of the potential drop the dye experiences therefore depends on the amount of charges in the TiO\(_2\). Assuming an average distance \( l \) between the injected electrons and their counter charges in the electrolyte and electric field lines similar to those depicted in Figure 4.2, one can rewrite Equation 4.5 as:

\[
\Delta A = -\frac{dA}{dE} \Delta \mu_z \frac{Q}{C_H l}
\]

where \( C_H \) is the capacity of the Helmholtz layer. This treatment assumes that dye molecules are located within the Helmholtz layer.

In order to compare Stark shifts of different dye molecules or the magnitude of Stark shifts in different electrolytes, we can divide \( \Delta A \) by \( \frac{dA}{dE} \) and by \( Q \). Such a comparison is shown for ID28 in different electrolytes here and a comparison for different dyes can be found in Paper V.

Figure 4.6a shows the ground-state absorption spectra of ID28 adsorbed to TiO\(_2\) immersed in 0.1 M TBAClO\(_4\) or 0.1 M LiClO\(_4\) in MPN. The spectrum is shifted to slightly longer wavelengths in presence of lithium ions. The Stark shifts obtained by spectroelectrochemistry normalised to the maximum gradient of the absorption spectrum and to the charge are shown in Figure 4.6b. It can be seen that the observed Stark shift is much smaller in LiClO\(_4\) electrolyte than in TBAClO\(_4\) electrolyte. Lithium ions seem to shield the dye molecules from the potential drop at the TiO\(_2\) surface, as they are able to approach closer to the TiO\(_2\) surface than the TBA ions.

In further experiments, the study of the Stark shift should be extended to include more parameters, such as the dye coverage and the pH at the TiO\(_2\)
surface. Such studies are likely to provide new insights into the properties of the TiO$_2$/dye/electrolyte interface in functional DSCs.

Figure 4.5: a) Charge passed at working electrode and change in absorbance of a TiO$_2$ electrode dyed in ID28 as a function of applied potential in TBAClO$_4$ supporting electrolyte. b) Change in absorbance of the electrode as a function of charge. The solid line indicates a linear to fit to the data below -0.02 mC cm$^{-2}$.

Figure 4.6: a) Absorption spectra of ID28 adsorbed to TiO$_2$ films in 0.1 M TBAClO$_4$ or 0.1 M LiClO$_4$ electrolyte. b) Change in absorbance of the same films during a scan towards negative potentials normalised to the amount of charge passed at the working electrode and to the maximum of the derivative of the absorption spectra with respect to energy.
5. Characterisation techniques

This chapter describes the different techniques used for characterisation of dye-sensitized solar cells throughout my PhD studies. The techniques can be divided into two sub-categories, where one focuses on mainly spectroscopic techniques which are applied to components of the solar cell and the second on electrical measurements of complete devices.

5.1 Characterisation of components

5.1.1 UV-visible spectroscopy

One of the nice aspects of working with dyes is the use of colourful samples (Figure 5.1). Visual inspection of samples can often give a first indication of samples changing. Figure 5.1 shows two examples of colours and colour changes of dyes adsorbed to TiO$_2$. Photographs and UV-visible spectra of TiO$_2$ films dyed in ID28, ID176, and ID1 can be seen in Figure 5.1a. ID28 absorbs mainly in the blue and green part of the solar spectrum resulting in its reddish colour. ID176 absorbs at most visible wavelengths with a maximum absorption at green wavelengths leading to its purple colour. ID1 absorbs strongly in the red region of the solar spectrum resulting in its blue colour.

The second example shows the colour change of ID176 upon addition of a drop of LiClO$_4$ solution on the dyed TiO$_2$ surface. Lithium ions red-shift the absorption spectrum of ID176 leading to a more bluish colour (Figure 5.1b).

UV-visible spectra presented in this thesis were recorded on a HR-2000 Ocean Optics fiber optics spectrophotometer in transmission mode. The spectrometer was usually calibrated against air and background correction was carried out separately. The absorbance, $A$, of a sample was automatically calculated by the Ocean Optics software according to:

$$A = - \log_{10} T$$  \hspace{1cm} (5.1)

This calculation ignores any losses of transmission due to reflectance. Where used for further calculations, $A$ was background corrected by subtracting a baseline at the relevant wavelength or by subtracting the absorbance of a blank sample (e.g. the absorbance of the solvent or of a blank TiO$_2$ film, $A = A_{\text{sample}} - A_{\text{baseline}}$). When measuring absorbances on relatively thin TiO$_2$
Figure 5.1: a) Photograph of TiO$_2$ films dyed in ID28, ID176 and ID1 (from right to left) and corresponding UV-visible absorption spectra. b) Photograph of TiO$_2$ film dyed in ID176 with a drop of 0.1 M LiClO$_4$ solution added to the bottom half of the film and corresponding UV-visible absorption spectra.

Figure 5.2: UV-visible absorption spectra of 1.8 µm thick, dyed TiO$_2$ films and of a blank TiO$_2$ film. Slightly different interference patterns are observed for all films.

films, interference fringes are sometimes observed. As these are sensitive to the exact thickness of the TiO$_2$ film, it is hard to correct for them (Figure 5.2).
A is related to the extinction coefficient ($\varepsilon$) of the examined species by:

$$A = \varepsilon \cdot C \cdot l$$  \hspace{1cm} (5.2)

where $C$ is the concentration of the species in solution and $l$ is the path length. Using this equation, extinction coefficients of dye molecules in solution can be determined.

For quantification of other experiments (e.g. fluorescence spectroscopy, IPCE), the percentage of light absorbed at each wavelength is needed, i.e. the light harvesting efficiency (LHE), which can be calculated from $A$ by:

$$\text{LHE}(\lambda) = 1 - 10^{-A(\lambda)}$$  \hspace{1cm} (5.3)

### 5.1.2 Spectroelectrochemistry

Electrochemistry of molecules in solution is one of the standard characterisation techniques used for dye molecules and will be found in most papers publishing new dyes for DSCs. Here, I will focus on describing electrochemistry of mesoporous semiconductor films and of dyes adsorbed to these films carried out in combination with UV-visible spectroscopy (spectroelectrochemistry).

Electrochemistry of mesoporous semiconductor films is one method to study the density of states in these films (Paper IV). Electrochemistry of dyes adsorbed to semiconductor films can be used to determine redox potentials of dyes in surroundings similar to solar cell conditions (all Papers). Only a small amount of material is required for these studies and dye molecules do not need to be soluble in the supporting electrolyte. The absorption spectra measured during the electrochemical experiment can help to identify the oxidation or reduction processes occurring and can give information about the reversibility of the electrochemical reaction. Absorption spectra of oxidised or reduced dye molecules can be used to identify species observed in photo-induced absorption spectroscopy (Papers I, II and IV). In an optimal case, even the extinction coefficients of the electrochemically created species can be obtained.

#### Experimental set-up

Electrochemical measurements presented in this thesis were mostly performed on a CH Instruments 660 potentiostat with a 3-electrode set-up, i.e. with a working electrode (WE), a reference electrode (RE) and a counter electrode (CE). Between 6 and 15 mm wide FTO (TEC 8) working electrodes were used, where approximately the bottom centimeter was coated with the mesoporous semiconductor film to be measured. The films were covered with supporting electrolyte (Figure 5.3). The most common supporting electrolytes used were 0.1 M lithium perchlorate or 0.1 M tetrabutylammonium perchlorate in acetonitrile (MeCN) or methoxypropionitrile (MPN). For
these four electrolytes, an Ag wire in a Teflon tube with a porous tip containing a matching electrolyte solution with an additional 10 mM of AgNO₃ added was used as pseudo reference electrode. For all other electrolytes, including ionic liquids, an Ag/AgCl electrode in LiCl saturated ethanol was used as reference. The system was always internally calibrated by measuring a cyclic voltammogram of ferrocene (Fc) in the same electrolyte before and after the other measurements. Where applicable, potentials were converted to potentials versus the normal hydrogen electrode (NHE) by using \( U^0'(\text{Fc/Fc}^+) = 0.63 \text{ V vs. NHE} \). ¹² A platinum working electrode was used in this calibration. For all measurements, a platinum wire counter electrode was used. A schematic diagram of the set-up is shown in Figure 5.3. The electrochemical experiments were carried out in a cuvette so that the working electrode could be aligned perpendicular to the beam of the fiber optics spectrophotometer.

**Cyclic voltammetry**

The main electrochemical technique used in this thesis was cyclic voltammetry (CV). In this measurement, the voltage is continuously increased to a certain potential and then decreased back to the original potential, while the current is measured (Figure 5.4a). ¹³ The main input parameters are therefore the initial and final voltage and the scan rate. The main output parameters are the voltages at which peaks occur and the peak currents. In electrochemical experiments, current flows due to two types of processes: charging processes and Faradaic processes. The latter are oxidation or reduction processes of analytes at the working electrode. The magnitude of charging currents should be linearly dependent on the scan rate, while faradaic currents should increase
with the square root of the scan rate, if the analytes travel to and from the working electrode by diffusion.

Figure 5.4: a) Applied voltage versus time in CV scans with different scan rates: 0.01 V s\(^{-1}\) (solid), 0.02 V s\(^{-1}\) (dashed), 0.05 V s\(^{-1}\) (dotted), and 0.1 V s\(^{-1}\) (dott-dashed). b) Cyclic voltammograms at the different scan rates of a TiO\(_2\) film dyed in ID176 in 0.1 M LiClO\(_4\) in MPN as supporting electrolyte. A repetition of the scan at 0.01 V s\(^{-1}\) after all other scans is shown in grey.

Figure 5.4b shows cyclic voltammograms of ID176 dye bound to mesoporous TiO\(_2\) in 0.1 M LiClO\(_4\) in MPN as supporting electrolyte. The scans were started close to 0 V vs. Fc/Fc\(^+\). Early in the scan almost no current flowed. At approximately 0.45 V vs. Fc/Fc\(^+\) an anodic current started flowing due to the oxidation of ID176 to ID176\(^+\). The current increased as the rate of change of ID176 concentration at the FTO electrode increased. Some way past the redox potential of ID176/ID176\(^+\)\(U_0^\text{redox}\), ID176 was depleted close to the electrode and the current decreased. The scans therefore showed an oxidation (anodic) peak at potential, \(U_{pa}\). Upon reversal of the scan, re-reduction of ID176\(^+\) started and a reduction (cathodic) peak was formed somewhere past \(U_{\text{redox}}^0\) at potential \(U_{pc}\).

For a fully reversible electrochemical reaction of dissolved redox species at a metal electrode, the peak potentials should be independent of scan rate and separated by approximately 59 mV for a one electron oxidation at 298 K.\(^{83}\) For this system, the separation of the peaks was larger than 59 mV at the lowest scan rate of 0.01 V s\(^{-1}\) and increased with scan rate (Figure 5.5a). However, the average potential of the peaks, \(U_{1/2}\), which is closely related to \(U_{\text{redox}}^0\), was independent of scan rate. The redox potential of ID176 adsorbed to TiO\(_2\) could therefore be determined from the cyclic voltammograms at different scan rates.
Figure 5.5: Peak analysis of cyclic voltammograms of ID176 (Figure 5.4b) at different scan rates. a) Peak voltages: $U_{pa}$ (squares), $U_{pc}$ (circles), $U_{1/2}$ (crosses) and average of $U_{1/2}$ (dotted line). b) Peak currents of oxidation (anodic) peaks (squares) and fit against the square root of the scan rate (dashed line).

The peak currents for the anodic peaks, as determined by the CH Instruments software, are shown in Figure 5.5b. It can be seen that they vary linearly with the square root of the scan rate, which is similar to the behaviour of dissolved redox species at metal electrodes. These results show that charge transport for this dye attached to a mesoporous TiO$_2$ electrode has to be by diffusion, i.e. by a hole transfer mechanism (hole hopping) between neighbouring dye molecules, as the TiO$_2$ is insulating at the potentials used here.

**Differential pulse voltammetry**

For some dyes, cyclic voltammetry might not be as reversible as for ID176 (Figure 5.6). Either the anodic or the cathodic peak or even both might not be well resolved. In such cases, differential pulse voltammetry (DPV) might offer a better resolution. In this method, a voltage pulse with a certain peak amplitude ($\Delta V$) and pulse width is applied after a wait time. The current is measured directly before applying the pulse and at the end of the pulse. The potential is then stepped to the next base potential and the measurement is repeated (Figure 5.7) until a final voltage is reached.

For a reversible electrochemical reaction, a peak should form at a potential, $U_p$, which is related to $U_{1/2}$ determined in CV, by:

$$U_p = U_{1/2} - \frac{\Delta V}{2} \quad (5.4)$$

In all DPV experiments presented in this thesis, a pulse amplitude of 0.05 V, a pulse width of 0.06 s and a pulse period of 0.2 s were used. As can be seen
Figure 5.6: Cyclic voltammogram and differential pulse voltammogram of ID176 (a) and ID1 (b) in 0.1 M TBAClO$_4$ in MPN as supporting electrolyte. Peak positions of the DPV scan is indicated for both dyes (grey dashed line). For ID176, additionally $U_{1/2}$ from CV is indicated (black, solid line).

Figure 5.7: Applied voltage as a function of time in a typical DPV measurement. The current is sampled immediately before and at the end of each voltage pulse.

in Figure 5.6a, DPV of ID176 shows a peak at approximately 0.03 V lower potential than $U_{1/2}$ determined from cyclic voltammetry, in good agreement with Equation 5.4. For the oxidation of ID1 (Figure 5.6b), the cyclic voltammogram shows only an anodic peak. From DPV, a peak could be resolved at 0.50 V vs. Fc/Fc$^+$. As the reaction was not reversible, the redox potential of ID1/ID1$^+$ could not be determined with high certainty but an indication of its position was obtained with DPV.
Multiple potential steps

Another method used in this thesis was the multiple potential steps method. In this method, the potential is stepped to different values and held there for a certain period of time, while the current is measured. This can be useful for spectroelectrochemistry when there are several processes happening at potentials close to each other and one wishes to monitor a particular process (Paper I). The measured current can be converted into the charge, \( Q \), accumulated during the measurement:

\[
Q = \int J \, dt = \sum J \cdot \Delta t
\]  

(5.5)

Usually, the potential is first held at a potential where no faradaic process occurs for several seconds and then stepped to a potential at which the faradaic process occurs.

Relating electrochemistry and absorption

The oxidised or reduced forms of dye molecules usually have distinctly different absorption spectra from the ground-state species. Therefore, the formation of oxidised or reduced dye molecules during an electrochemical experiment can also be monitored by the change in UV-visible absorption. Doing so can help identifying if a Faradaic process is occurring. The spectra can give information about the reversibility of the electrochemical process as the recovery of ground-state dye molecules can be monitored.

As \( A \) is proportional to the concentration of a species (Equation 5.2), the change in \( A \) is proportional to the charge passed at the working electrode due to Faradaic processes. Neglecting the influences of charging processes, one can write for a one electron reaction:

\[
\Delta A(\lambda, t) = \frac{\Delta \varepsilon(\lambda)}{F} \cdot Q(t)
\]  

(5.6)

where \( \Delta \varepsilon(\lambda) \) is the change in extinction coefficient between oxidised and the reduced form of the analyte and \( F \) is the Faraday constant. \( \frac{\Delta \varepsilon(\lambda)}{F} \) is called the colouration efficiency (\( CE(\lambda) \)). Alternatively, one can relate the derivate of \( A \) to the current:

\[
\frac{\delta A(\lambda, t)}{\delta t} = CE(\lambda) \cdot J(t) \quad \text{or} \quad \frac{\delta A(\lambda, V)}{\delta V} = CE(\lambda) \cdot J(V)
\]  

(5.7)

A plot of \( \frac{\delta A(\lambda, t)}{\delta t} \) vs. \( t \) can be useful when absorbances have been measured in combination with cyclic voltammetry and peaks should be identified.

As can be seen from Equation 5.6, spectroelectrochemical measurements can be used to determine differences in extinction coefficients between the oxidised and ground-state species of a compound from the gradient of a plot of \( A \) vs. \( Q \). It is important for this determination that the electrochemical and the
spectral measurements have a common time zero. Ideally, both experiments should be started simultaneously automatically. This was not possible with the equipment used in this thesis work and time axes were aligned manually.

Difficulties arise when a plot of $A$ vs. $Q$ is not linear throughout the measurement range. This can be due to $Q$ being influenced by charging currents, due to products reacting or due to spectral features varying with concentration. In Paper I, a potential step experiment was used to determine $\Delta \varepsilon$ for spiro-MeOTAD and for ID28. For spiro-MeOTAD, $A$ vs. $Q$ was linear, while for ID28 the gradient decreased throughout the measurement.

![Graph](image.png)

**Figure 5.8:** a) Change in absorbance at 700 nm and 780 nm plotted against anodic charge accumulated during cyclic voltammetry of ID176 on TiO$_2$ in 0.1 M LiClO$_4$ in MPN as supporting electrolyte. Grey regions indicate example fit intervals and linear fits used to determine extinction coefficients. The entire fit region is indicated by vertical dashed lines. b) Extinction coefficient of oxidised – ground-state ID176. Extinction coefficients were determined for 45 mV (or 4.5 s) intervals between 0.47 and 0.71 V vs. Fc/Fc$^+$ in steps of 0.01 V (from black to grey).

Figure 5.8a shows the change in absorbance of ID176 at two different wavelengths during the oxidation process in cyclic voltammetry. It can be seen that $A$ vs. $Q$ is linear for short intervals but that the gradient of $A$ vs. $Q$ changes throughout the experiment. Figure 5.8b shows $\Delta \varepsilon$ values determined by fitting 45 mV wide intervals of the data in steps of 10 mV. The shape of the determined extinction coefficient spectra depends strongly on the interval of the fit. However, the magnitude of the extinction coefficients is affected to a lesser extent.

Spectroelectrochemistry can therefore give a good indication of the magnitude of the extinction coefficient of oxidised dye molecules attached to TiO$_2$ surfaces but great care has to be taken in the fitting process.
5.1.3 Photo-induced absorption spectroscopy

Transient absorption spectroscopy (TAS) is a common tool for the study of the kinetics of dye-sensitized solar cells.\textsuperscript{31,84–89} Usually, the change in absorption of a visible probe light by a dyed TiO\textsubscript{2} film is measured as a function of time following excitation of the dye by a short laser pulse (the pump). This technique is also referred to as laser flash photolysis and kinetics can be measured on different time scales depending on the equipment and the laser pulse length. In femtosecond TAS, a femtosecond laser pulse is split into a pump and probe pulse of which one can be delayed to reach the sample at a different time. Kinetics in the femto- and picosecond time scales can be resolved (electron injection and regeneration in the solid state DSCs). Results of such measurements are presented in Paper IV.\textsuperscript{1} When lasers with nanosecond long pulses are used, the probe light is often supplied by a separate lamp and kinetics on the nano- and microsecond time scales can be resolved (regeneration in liquid electrolyte DSCs and recombination). In order to create a detectable concentration of transient species, TAS often requires the use of high light intensities in the pump.

In this thesis work (in Papers I, II, IV, and V), photo-induced absorption spectroscopy (PIA)\textsuperscript{90,91} was mostly used instead of laser flash photolysis. In PIA, the difference in absorption between a pump light being on and off is measured as a function of modulation frequency and probe wavelength. As the on-time of the pump is relatively long in these experiments (55 ms at a 9 Hz modulation), light intensities similar to the light intensities under operating conditions of the solar cell can be used.

The PIA set-up

A schematic diagram of the PIA set-up is shown in Figure 5.9. A white probe light, provided by a 20 W tungsten-halogen lamp, was focused onto the sample by a series of optics. Superimposed at the sample was the pump light used for excitation. Typical excitation intensities at the sample were between 8 and 25 mW cm\textsuperscript{-2}, and typical probe intensities were between 10 \% of 1 sun and 40 \% of 1 sun. The pump light could be chosen between a blue LED (Luxeon Star, 1 W, Royal Blue, 460 nm), a green LED-pumped laser at 530 nm, or a red-diode laser at 640 nm. The pump light was square-wave modulated (on/off) with a function generator (HP 33120A) at a frequency, \( f = \frac{\omega}{2\pi} \). After transmission through the sample the probe light was focused onto a monochromator (Acton Research Corporation SP-150) and detected by a UV enhanced silicon photodiode, allowing for measurements between 400 and 1100 nm. The detector was connected to a current amplifier and a lock-in amplifier (Stanford Research Systems models SR570 and SR830, respectively). The lock-in amplifier was locked to the modulation frequency, such that \( \Delta T / T \) in phase with the modulation frequency (the “real” part of \( \Delta T / T \), \( \text{Re}(\Delta T / T) \)) and \( \Delta T / T \)

\textsuperscript{1}Femtosecond TAS measurements were carried out by Amanda Smeigh.
out of phase with the modulation frequency (the “imaginary” part of $\Delta T/T$, $\text{Im}(\Delta T/T)$) were measured. In this way only signals occurring at the modulation frequency are detected, which greatly enhanced the signal to noise ratio. $\Delta A$ is then given by:

$$\Delta A \cdot \ln(10) = -\text{sgn}\{\text{Re}(\Delta T/T)\} \cdot \sqrt{\text{Re}(\Delta T/T)^2 + \text{Im}(\Delta T/T)^2} \quad (5.8)$$

The set-up therefore allows the measurement of $\Delta A$ at different wavelengths, resulting in the measurement of a photo-induced absorption spectrum at a given frequency, and the measurement of $\Delta A$ at different frequencies (frequency-resolved PIA at a given $\lambda$). Additionally, $\Delta A$ could also be measured as a function of time, i.e. individual time traces following the rise and decay of $\Delta A$ could be obtained.

The theory of PIA

The PIA signal (as a function of wavelength and angular frequency$^\text{ii}$) can be viewed as the sum of the absorbances of the different transient species:

$$\Delta A_{\text{PIA}}(\lambda) = \sum \Delta A_s(\lambda) = \sum [s] \Delta \varepsilon_s(\lambda) + \Delta A_{\text{Stark}}(\lambda) \quad (5.9)$$

where $[s]$ is the number of moles of transient species $s$ per unit area. As discussed in Chapter 4, the Stark effect of dye molecules has to be considered in PIA and therefore a term for this is included in Equation 5.9. Considering the possible transient species present in a solid state DSC, one can write:

$$\Delta A_{\text{PIA}}(\lambda) = [D^+] \{\varepsilon_{D^+}(\lambda) - \varepsilon_D(\lambda)\} + [D^-] \{\varepsilon_{D^-}(\lambda) - \varepsilon_D(\lambda)\} + [e^-] \varepsilon_e(\lambda) + [h^+] \varepsilon_h(\lambda) + \Delta A_{\text{Stark}}(\lambda) \quad (5.10)$$

$^\text{ii}$To decrease the length of equations, the frequency dependence is not included in all equations.
This equation allows for the calculation of the PIA signal from spectra of the individual components, which can, for example, be obtained by spectro-electrochemistry (an example of such a calculation can be found in Paper I). Considering now the case of dye molecules attached to a TiO$_2$ surface in absence of spiro-MeOTAD or redox electrolyte, this equation reduces to:

$$\Delta A_{\text{PIA}}(\lambda) = [D^+e^-] \Delta \varepsilon(\lambda) + \Delta A_{\text{Stark}}(\lambda)$$  \hspace{1cm} (5.11)

where $\Delta \varepsilon(\lambda) = \{\varepsilon_D(\lambda) + \varepsilon_e(\lambda) - \varepsilon_D(\lambda)\}$. An equation for $[D^+,e^-]$ can be found considering the generation and recombination rates ($G$ and $R$) of the transient species:

$$G = \Phi_{\text{inj}} \cdot \frac{I_0}{N_A} \cdot \text{LHE}$$  \hspace{1cm} (5.12)

$$R = k_{\text{rec}} \cdot [D^+,e^-]^\beta$$  \hspace{1cm} (5.13)

where $\Phi_{\text{inj}}$ is the quantum efficiency of photo-induced electron injection, $I_0$ is the incident photon flux, $N_A$ is Avogadro’s constant and LHE is the light harvesting efficiency of the sample at the pump wavelength, and $k_{\text{rec}}$ is the rate constant of recombination and $\beta$ is a constant, related to the recombination order. $\beta$ is included as the kinetics of recombination observed in PIA are seldom simply first order.

Under steady-state illumination (or when frequencies used are significantly lower than $k_{\text{rec}}$), equilibrium is reached so that $R = G$, and the steady-state concentration, $[D^+,e^-]_{\text{SS}}$, can be found:

$$[D^+,e^-]_{\text{SS}} = \left(\frac{1}{k_{\text{rec}}} \cdot \Phi_{\text{inj}} \cdot \frac{I_0}{N_A} \cdot \text{LHE}\right)^{1/\beta}$$  \hspace{1cm} (5.14)

Substituting this expression into Equation 5.11, one obtains an expression for $\Delta A_{\text{SS}}$:

$$\Delta A_{\text{SS}}(\lambda) = \Delta \varepsilon(\lambda) \cdot \left(\frac{1}{k_{\text{rec}}} \cdot \Phi_{\text{inj}} \cdot \frac{I_0}{N_A} \cdot \text{LHE}\right)^{1/\beta} + \Delta A_{\text{Stark}}(\lambda)$$  \hspace{1cm} (5.15)

This equation makes it in principle possible to determine $\Phi_{\text{inj}}$ from PIA measurements: The recombination order can be determined from the gradient of a plot of $\log \Delta A_{\text{SS}}$ vs. $\log I_0$, and $\Delta A_{\text{SS}}$ and $k_{\text{rec}}$ can be obtained from either a frequency-resolved PIA measurement or a time-resolved PIA measurement. I will only provide a description of frequency-resolved PIA here as this is also relevant for spectral PIA measurements. A description of time-resolved PIA can be found elsewhere.$^{91}$

The frequency dependence of the PIA signal is given by:

$$\Delta A(\omega) = \frac{\Delta A_{\text{SS}}}{1 + (i\omega \tau_f)^\alpha}$$  \hspace{1cm} (5.16)
where \( i = \sqrt{-1} \), \( \tau_f \) is the time constant obtained from this measurement, which can be equated to \( \frac{1}{k_{rec}} \), and \( \alpha \) a constant, which is equal to 1 for first order recombination and smaller than 1 for dispersive recombination (when there is a distribution of lifetimes).\(^9\) Substituting \( i^\alpha = \cos(\alpha \frac{\pi}{2}) + i \sin(\alpha \frac{\pi}{2}) \), expressions for the real (in-phase) and imaginary (out-of-phase) parts of Equation 5.16 can be found:

\[
\text{Re}(\Delta A) = \frac{\Delta A_{SS} \cdot \left\{ 1 + (\tau_f \omega)^\alpha \cdot \cos \left( \alpha \frac{\pi}{2} \right) \right\}}{1 + 2(\tau_f \omega)^\alpha \cdot \cos \left( \alpha \frac{\pi}{2} \right) + (\tau_f \omega)^{2\alpha}} \quad (5.17a)
\]

\[
\text{Im}(\Delta A) = \frac{-\Delta A_{SS} \cdot (\tau_f \omega)^\alpha \cdot \sin \left( \alpha \frac{\pi}{2} \right)}{1 + 2(\tau_f \omega)^\alpha \cdot \cos \left( \alpha \frac{\pi}{2} \right) + (\tau_f \omega)^{2\alpha}} \quad (5.17b)
\]

For \( \alpha = 1 \), these expressions simplify to the following expressions, which users of impedance spectroscopy may recognise from the analysis of a circuit element consisting of a capacitor and a resistor in parallel:

\[
\text{Re}(\Delta A) = \frac{\Delta A_{SS}}{1 + (\tau_f \omega)^2} \quad (5.18a)
\]

\[
\text{Im}(\Delta A) = -\frac{\Delta A_{SS} \tau_f \omega}{1 + (\tau_f \omega)^2} \quad (5.18b)
\]

Plots of \( \text{Re}(\Delta A) \) and \( \text{Im}(\Delta A) \) are therefore also similar to those found in impedance spectroscopy of a capacitor and a resistor in parallel (Figure 5.10), and values for \( \Delta A_{SS} \) and \( \tau_f \) can be found by fitting PIA data in an impedance fitting program.

\( \text{Re}(\Delta A) \) is very small at high frequency, then increases until it becomes equal to \( \Delta A_{SS} \) at low frequencies (Figure 5.10a). \( \text{Im}(\Delta A) \) shows a maximum at an angular frequency, \( \omega_{\text{max}} = \frac{1}{\tau_f} \). The magnitude of \( \Delta A \) is similar to \( \text{Im}(\Delta A) \) at high frequencies and similar to \( \text{Re}(\Delta A) \) at low frequencies, where it approaches \( \Delta A_{SS} \) (Figure 5.10a). Nyquist plots of PIA signal, i.e. plots of \( \text{Im}(\Delta A) \) vs. \( \text{Re}(\Delta A) \), describe a semi-circle which becomes increasingly depressed as \( \alpha \) becomes smaller than one (Figure 5.10b). The maximum of this semi-circle lies at \( \omega_{\text{max}} = \frac{1}{\tau_f} \). If \( \alpha \) equals one, \( \text{Re}(\Delta A) \) and \( \text{Im}(\Delta A) \) are equal at \( \omega_{\text{max}} \). If \( \alpha \) is smaller than one, they are equal at a higher frequency. A user of PIA should consider this, when measuring a PIA spectrum at one frequency. If \( \text{Im}(\Delta A) \) is larger than \( \text{Re}(\Delta A) \), then \( \Delta A_{SS} \) is at the least 1.4 times higher than the measured \( \Delta A \). On the other hand, the ratio \( \frac{\text{Im}(\Delta A)}{\text{Re}(\Delta A)} \) can also be used to obtain a rough estimate of \( \tau_f \) under the assumption \( \alpha = 1 \):

\[
\tau_f = -\left( \frac{\text{Im}(\Delta A)}{\text{Re}(\Delta A)} \right) \cdot \frac{1}{2\pi f} \quad (5.19)
\]
Implications for the measurement of dye-sensitized solar cells

Reconsidering Equation 5.15 and the equations relating the PIA signal to the measurement frequency (Equations 5.16-5.18b), what does the time constant dependence of the PIA signal mean for the measurement of dye-sensitized solar cells? Equations 5.16-5.18b show that time constants, which are much smaller than the measurement frequencies, cannot be resolved in PIA measurements. From Equation 5.15, it follows that the magnitude of the PIA signal depends on the recombination time constant of the process measured, i.e. if $k_{\text{rec}}$ is very large, $\Delta A_{\text{SS}}$ becomes very small. A result of this is that only processes with a relatively long lifetime (milliseconds to seconds) can be resolved with PIA. A sample of dyed TiO$_2$ therefore only shows a signal of oxidised dye molecules, if recombination times are sufficiently long. This is often the case$^{89,92,93}$ and PIA can show if effective injection is happening.$^{61}$

When a redox electrolyte or spiro-MeOTAD are added to such a sample and the regeneration of oxidised dye is fast and efficient, the “lifetime” of the oxidised dye becomes very short. Consequently, the concentration of oxidised dye is decreased by many orders of magnitude and the PIA signal of oxidised dye will be negligible. Instead a signal due to holes and electrons will be observed, which can be written in the form:

$$\Delta A_{\text{PIA}}(\lambda) = [e^-, h^+] \{ \epsilon_{e^-}(\lambda) + \epsilon_{h^+}(\lambda) \} + \Delta A_{\text{Stark}}(\lambda)$$  \hspace{1cm} (5.20)

PIA can therefore show if the regeneration of oxidised dye molecules is efficient, and if it is, Equation 5.20 can be used to determine the concentration
of photo-generated holes and electrons and therefore the amount of charge in the TiO$_2$.

A conclusion one might draw from the above equations is that using PIA for quantification of the injection and regeneration efficiencies ($\Phi_{\text{inj}}$ and $\Phi_{\text{reg}}$) is very difficult. First, one needs to choose a wavelength, at which the Stark effect of the dye is not observed. Then, one needs to determine the rate constant of recombination and the order of recombination by measuring and fitting frequency-resolved PIA at different light intensities. Finally, any values of $\Phi_{\text{inj}}$ and $\Phi_{\text{reg}}$ will include any recombination, which occurs on faster time scales than the PIA measurement.

In this thesis, PIA was therefore mainly used for qualitative studies of the effectiveness of injection and regeneration processes and to determine time scales of recombination processes. I would like to conclude this section by summarising the advantages of PIA: PIA can be measured over a large wavelength range, which can even be extended by using a different detector. PIA measurements can be carried out under illumination intensities similar to solar conditions. Finally, PIA measurements are relatively fast (acquisition of a spectrum often takes only 10 minutes) and very easy to set-up and use.

5.1.4 Electroabsorption spectroscopy

Electroabsorption spectroscopy (EA) was one of the methods used to determine the Stark effect of dye molecules adsorbed to TiO$_2$ (Papers II and IV). This technique is closely related to photo-induced absorption spectroscopy but instead of modulating a light source, an electric field is modulated across the sample. The same equipment was used for these measurements as for PIA measurements. The only difference was that the frequency generator was connected directly to the sample instead of to a light source, thereby modulating a voltage directly across the sample. In the lock-in detection, only the in-phase part of the signal was used as change in absorbance in electroabsorption measurements is instantaneous and therefore not frequency dependent:

$$\Delta A_{EA} \cdot \ln(10) = -\text{Re}(\Delta T/T)$$  \hspace{1cm} (5.21)

Equations relating to the $\Delta A$ to the electric field can be found in Chapter 4. An important consideration for this technique was what type of samples to use in order to be able to measure the first order Stark effect, which is relevant for DSCs. Electroabsorption spectroscopy has mostly been measured on disordered samples where only the second order effect is observed,\textsuperscript{76,94} but there are also a few examples where electroabsorption was measured on ordered Langmuir-Blodgett films, where both the first and second order effect could be observed.\textsuperscript{95,96}

For our experiments, we chose to use samples where the dye molecules are attached to a flat TiO$_2$ film, which was prepared on an FTO substrate by spray
Figure 5.11: Schematic diagram of the samples used for electroabsorption measurements (adapted from Paper II).

pyrolysis\textsuperscript{23} (Figure 5.11). The monolayer of dye molecules should have a main direction of orientation relative to the TiO$_2$ surface, and an electric field could be applied normal to this surface. Samples were completed by spin-coating a poly(methyl methacrylate) (PMMA) in dichloromethane (DCM) solution onto the dye layer forming a PMMA spacer layer. Back contacts were prepared by evaporating semi-transparent silver contacts of a few nanometer thickness. This way, samples were prepared, in which an ordered monolayer of dye molecules could be placed perpendicular to the field lines of a parallel plate capacitor (the FTO and the silver acted as the capacitor plates).

A disadvantage of these devices was that only one monolayer of dye molecules was present resulting in very low optical densities. UV-visible characterisation to determine the absorbance of the dye layer was not possible, and only low $\Delta A$ signals were obtained with the voltage range available from the frequency generator (the maximum amplitude was 20 V).

5.1.5 Fluorescence spectroscopy

Steady-state fluorescence spectroscopy measures the photons emitted following monochromatic excitation of a sample as a function of wavelength. Fluorescence spectra were used in this thesis together with absorption spectra of dyes to determine the energy difference between the relaxed ground-state and the relaxed excited state of dye molecules, $E_{0-0}$ (Paper III and IV). Relative fluorescence quantum yields of ID176 adsorbed to TiO$_2$ were determined under different conditions in the following way (Paper IV): fluorescence and absorption spectra of films were measured at the same location on the film. The integrated fluorescence counts were divided by the light harvesting efficiency at the wavelength of excitation. This parameter was divided by the same parameter measured for a film of the dye dispersed in PMMA to obtain quantum yields relative to this reference. The yields reflect indirectly on the injection efficiencies although also other non-radiative processes can quench the excited state.
5.1.6 Photoelectron spectroscopy

Photoelectron spectroscopy (PES) is a surface sensitive technique in which atoms eject electrons after absorbing X-ray photons of known energy, and the kinetic energy of the ejected electrons is measured. The binding energy of the ejected electrons is determined from the difference between the energy of the absorbed photons and the kinetic energy of the ejected electrons. In a PES spectrum, the number of detected electrons is plotted against the binding energy. The spectrum can be divided into two regions of interest: core electrons (atomic orbitals) are measured at high binding energies and valence electrons (molecular orbitals) are measured at low binding energies.

PES was measured on samples of dyes adsorbed to mesoporous TiO$_2$ substrates and the spectra were energy calibrated relative to the titanium dioxide core levels and Fermi level (Papers IV and V). More details of the theory of PES and of experimental set-ups can be found in PhD theses dedicated to the study of dye-sensitized TiO$_2$ interfaces by photoelectron spectroscopy.$^{97,98}$

5.2 Characterisation of complete devices

I will describe the characterisation of complete devices using a liquid electrolyte and a solid state DSC with D35 as the sensitiser as an example.$^{iii}$ The cells were built with the same type of working electrodes: 1.8 $\mu$m thick TiCl$_4$-treated mesoporous TiO$_2$ films screenprinted on dense TiO$_2$ blocking layers. The electrolyte concentrations were 0.05 M I$_2$, 0.5 M LiI and 0.5 M tBP in MPN, while the spiro-MeOTAD solution used for spin-coating consisted of 150 mg spiro-MeOTAD per ml of chlorobenzene with 15 mM LiTFSI and 60 mM tBP added.

5.2.1 Current-voltage measurements

Current-voltage measurements (IV-measurements) under illumination are used to determine the efficiencies of solar cells. A lamp with a spectrum very similar to the solar AM1.5 spectrum (Figure 1.2) is used for illumination and calibrated to an intensity of 1000 W m$^{-2}$ for measurements at 1 sun intensity. A Newport solar simulator of class B was used here. A voltage is then applied between the working and counter electrode of the solar cell and the current output is measured. The voltage range should include the voltage at which the current is zero (the open-circuit voltage, $V_{OC}$) and 0 V, at which the short-circuit current density ($J_{SC}$) is measured. The scan rate should be sufficiently slow so that the solar cell has time to adjust. The resulting current-voltage curve is usually referred to as an IV-curve.

---

$^{iiii}$The liquid electrolyte DSC was assembled by Dr. Halina Dunn and the solid state DSC by Lei Yang.
Figure 5.12: a) IV-curves of a solid state DSC (grey) and a liquid electrolyte DSC (black) with D35 as sensitisier under 1 sun illumination (solid line) and in the dark (dashed line). b) Consecutive measurements of the solid state DSC under illumination.

Measurements can also be carried out in the dark, and the measured data is accordingly called a dark current curve. Figure 5.12a shows an example of IV-curves under illumination and in the dark for the solid and the liquid electrolyte cell with D35. Figure 5.12b shows how the IV-curves of the solid state DSC change when the measurement under illumination is repeated.

The efficiency of a solar cell, \( \eta \), is given by:

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{(J \cdot V)_{\text{max}}}{P_{\text{in}}} \quad (5.22)
\]

where \( P_{\text{in}} \) is the illumination intensity and \( P_{\text{max}} \) is the maximum power output of the solar cell at this light intensity. Figure 5.13 shows the power output as a function of potential of the solid state DSC. It can be seen that both the potential at which the maximum power occurs and the maximum power increase in consecutive measurements. In order to describe the efficiency of a solar cell in terms of \( V_{\text{OC}} \) and \( J_{\text{SC}} \), a quantity called the fill factor is introduced, which relates \( P_{\text{max}} \) to \( V_{\text{OC}} \) and \( J_{\text{SC}} \):

\[
\text{ff} = \frac{(J \cdot V)_{\text{max}}}{J_{\text{SC}} \cdot V_{\text{OC}}} \quad (5.23)
\]

The efficiency can then be written as:

\[
\eta = \frac{J_{\text{SC}} \cdot V_{\text{OC}} \cdot \text{ff}}{P_{\text{in}}} \quad (5.24)
\]

The efficiency, the short-circuit current, the open-circuit voltage and the fill factor are shown in Table 5.1 for the example of D35 used here. It should be noted that the solid state DSC has a higher \( V_{\text{OC}} \) than the liquid electrolyte DSC, which is the reason for the higher efficiency of the solid state DSC.
in the first measurement, where the short-circuit currents are equal. The fill factor of the liquid electrolyte DSC is relatively low here as the solar cell was not optimised. In consecutive scans, the short-circuit current of the solid state cell decreases, while the fill factor and the overall efficiency increase. This time dependence of $IV$-measurements has to be considered when determining efficiencies of solid state DSCs and has been studied elsewhere.\textsuperscript{30}

Table 5.1: Solar cell performances of the two DSCs with D35.

<table>
<thead>
<tr>
<th></th>
<th>$V_{OC}$ / V</th>
<th>$J_{SC}$ / mA cm$^{-2}$</th>
<th>ff</th>
<th>$\eta$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid electrolyte DSC</td>
<td>0.77</td>
<td>7.0</td>
<td>0.54</td>
<td>2.94</td>
</tr>
<tr>
<td>Solid state DSC, scan 1</td>
<td>0.93</td>
<td>7.0</td>
<td>0.55</td>
<td>3.61</td>
</tr>
<tr>
<td>Solid state DSC, scan 2</td>
<td>0.94</td>
<td>6.5</td>
<td>0.65</td>
<td>3.95</td>
</tr>
<tr>
<td>Solid state DSC, scan 3</td>
<td>0.95</td>
<td>6.1</td>
<td>0.71</td>
<td>4.12</td>
</tr>
</tbody>
</table>

By subtracting the dark current curve from the $IV$-curve under illumination, the photocurrent ($J_{PH}$) can be determined as a function of potential. For an ideal solar cell the photocurrent should be constant and independent of potential. Figure 5.13b shows that for the solid state DSC measured here the photocurrent decreases towards $V_{OC}$.

5.2.2 Incident photon to current conversion efficiency

The incident photon to current conversion efficiency (IPCE), sometimes also called the external quantum efficiency of the solar cell, describes how many of the incoming photons at one wavelength are converted to electrons:

$$\text{IPCE}(\lambda) = \frac{\text{electrons}_{\text{out}}(\lambda)}{\text{photons}_{\text{in}}(\lambda)} = \frac{hc}{e \cdot \lambda \cdot P_{\text{in}}(\lambda)} \cdot J_{\text{PH}}(\lambda)$$

(5.25)
The constants in this equation (the Planck’s constant \((h)\), the speed of light \((c)\) and the elementary charge \((e)\) can be summarised as 1240 V nm\textsuperscript{iv}.

IPCE spectra are obtained by illuminating a solar cell with light of a specific wavelength and known intensity and measuring the resulting current. Usually, this is done under short-circuit conditions but the measurement can also be carried out at an applied potential. An additional white bias light can be used to create an illumination intensity similar to the one used in IV-measurements. This can be useful if the photocurrent of the solar cell does not scale linearly with light intensity.

The magnitude of the IPCE spectrum depends on how much light is absorbed by the solar cell, and how much of the absorbed light is converted to electrons, which are collected:

\[
\text{IPCE} = T \cdot \text{LHE} \cdot \Phi_{\text{inj}} \cdot \Phi_{\text{reg}} \cdot \eta_{\text{cc}} \quad (5.26)
\]

where \(\eta_{\text{cc}}\) is the charge collection efficiency and where the transmission term \(T\) accounts for reflection losses at the front electrode and absorbances by other species than the dye, e.g. by spiro-MeOTAD. \(\Phi_{\text{inj}}\) and \(\Phi_{\text{reg}}\) are the effective injection and regeneration efficiencies. This means that they will be decreased by any recombination occurring on very fast time scales.

IPCE spectra of the two D35 cells are shown in Figure 5.14. The spectra are slightly different in shape although the same TiO\textsubscript{2} thickness and the same dye were used. The spectrum of the solid state DSC is lower at around 380 nm and higher at the red edge of the spectrum than the spectrum of the liquid electrolyte DSC. These differences can be explained with Equation 5.26: At around 380 nm, spiro-MeOTAD absorbs strongly decreasing \(T\) at this wavelength in the solid state device compared to the liquid electrolyte DSC and therefore decreasing the IPCE. LHE at the absorption maximum of D35 was close to one for the devices resulting in IPCE maxima of 80 %. However, at longer wavelengths light harvesting was incomplete. In the solid state DSC, the reflecting back contact increased the light harvesting at these wavelengths and therefore also the IPCE.

A useful quantity in the analysis of performances is the absorbed photon to current conversion efficiency (APCE), which should be equal to one for an ideal solar cell:

\[
\text{APCE} = \frac{\text{IPCE}}{T \cdot \text{LHE}} = \Phi_{\text{inj}} \cdot \Phi_{\text{reg}} \cdot \eta_{\text{cc}} \quad (5.27)
\]

The short-circuit current of a solar cell can be calculated by integrating over the product of the IPCE and the solar spectrum (Figure 1.2), and was determined to be 7.75 mA cm\textsuperscript{-2} for the solid state DSC and 7.4 mA cm\textsuperscript{-2} for the liquid electrolyte cell. These currents are higher than the currents determined

\textsuperscript{iv}This conversion factor is also frequently used to convert from the wavelength to the energy of a photon in units of eV.
5.2.3 “Toolbox” techniques

The name “Toolbox” is often used as a summarising term for techniques which study the properties of dye-sensitized solar cells under operating conditions. A good summary of these methods can be found in a recent review paper on dye-sensitized solar cells.\(^6\) The techniques allow for the study of transport, recombination and TiO\(_2\) conduction band positions in the DSC. As a final result the electron diffusion length under operating conditions can be determined. Alternative methods for determining the diffusion length are electrochemical impedance spectroscopy and front and back IPCE measurements. In all cases, the determination of the electron diffusion length requires extensive modelling of the dye-sensitized solar cell and the correct model for liquid electrolyte DSCs has recently been under debate.\(^99–103\) The determination of the electron diffusion length will not be discussed here but determinations of the electron diffusion length of solid state DSCs can be found in literature.\(^33,34,39,41\)

I will describe some “Toolbox” techniques and explain, using the example of the D35 cells illuminated with a white LED, how the results and underlying equations vary for solid state and liquid electrolyte DSCs.

**Photovoltage and photocurrent as a function of light intensity**

The short-circuit current and open-circuit voltage of a DSC can be determined as a function of light intensity. Ideally, the short-circuit current should increase linearly with light intensity. Considering Equation 5.26, this will be the case if the effective injection efficiency, regeneration efficiency and collection efficiency are independent of light intensity. Plots of \(J_{SC}\) vs. light intensity for the
example cells are shown in Figure 5.15a. The gradient of the log-log plot was 1.07 for the solid state cell and 0.99 for the liquid electrolyte cell, showing that the currents increased almost linearly with light intensity.

\[ J_{\text{SC}} = B \cdot P_{\text{in}} \]

\[ V_{\text{OC}} = C \cdot \ln \left( 1 + \frac{D}{E} \right) \]

![Figure 5.15: Light intensity dependence of \( J_{\text{SC}} \) (a) and \( V_{\text{OC}} \) (b) for the two DSCs. Dashed lines indicate fits to the data.](image)

If the contacts in a DSC are ohmic, the open-circuit is given by the difference between the Fermi level of the TiO\(_2\) \( (E_{\text{F,TiO}_2}) \) and the Fermi level of the redox electrolyte or hole conductor \( (E_{\text{F,redox}}) \):

\[ eV_{\text{OC}} = E_{\text{F,TiO}_2} - E_{\text{F,redox}} \] (5.28)

In the dark, \( E_{\text{F,TiO}_2} \) and \( E_{\text{F,redox}} \) are equal and the voltage is zero. The Fermi level of the TiO\(_2\) under illumination is given by:

\[ E_{\text{F,TiO}_2} = E_{\text{CB}} + k_B T \ln \left( \frac{n_{\text{CB}}}{N_{\text{CB}}} \right) \] (5.29)

where \( E_{\text{CB}} \) is the conduction band edge, \( n_{\text{CB}} \) is the density of conduction band electrons and \( N_{\text{CB}} \) is the density of states in the conduction band. \( n_{\text{CB}} \) increases with light intensity. If recombination is first order, then it does so linearly.

The redox Fermi level can be determined from the Nernst equation\(^\text{vi}\) written in the energy scale for a one-electron redox couple:\(^6\)

\[ E_{\text{F,redox}} = E_{\text{F,redox}}^{0'} - k_B T \ln \left( \frac{C_{\text{ox}}}{C_{\text{red}}} \right) \] (5.30)

\(^\text{vi}\)The energy level of spiro-MeOTAD is also treated by the Nernst equation here. Alternatively, one might describe spiro-MeOTAD as a p-type semiconductor.
where $E_{F,\text{redox}}^{0'}$ is the formal redox energy of the redox system, and $C_{\text{ox}}$ and $C_{\text{red}}$ are the concentrations of the oxidised and reduced redox species, respectively. For the liquid electrolyte cell, the concentrations in the electrolyte do not vary significantly between the dark condition and under illumination and therefore $E_{F,\text{redox}}$ can be treated as a constant (a typical value for iodide/tri-iodide is 0.31 V vs. NHE). The voltage change at different illumination intensities therefore only depends on $\ln n_{\text{CB}}$. If $n_{\text{CB}}$ increases linearly with light intensity, the voltage should increase by 59 mV per decade of increase in light intensity at 298 K. In the example shown here (Figure 5.15b), the slope of a plot of $V_{\text{OC}}$ vs. log $P_{\text{in}}$ is indeed 60 mV.

In the case of solid state DSCs, the relative concentrations of oxidised spiro-MeOTAD and ground-state spiro-MeOTAD are not as well known as the ratio of $\text{I}_3^-$ and $\text{I}^-$ in the liquid electrolyte. Therefore, $E_{F,\text{redox}}$ in the dark is not as well known as for the liquid electrolyte cell. If $C_{\text{ox}}$ is very small, then the concentration of holes injected under illumination ($C_{\text{h,inj}}$) might significantly influence the $E_{F,\text{redox}}$ of spiro-MeOTAD and therefore $V_{\text{OC}}$. Substituting into Equation 5.28, the open-circuit voltage in a solid state DSC can therefore be written as:

$$eV_{\text{OC}} = E_{\text{CB}} - E_{F,\text{redox}}^{0'} + k_{\text{B}} T \left( \ln \frac{n_{\text{CB}}}{N_{\text{CB}}} + \ln \frac{C_{\text{ox}} + C_{\text{h,inj}}}{C_{\text{red}}} \right) \quad (5.31)$$

It should be noted here that $n_{\text{CB}}$ and $C_{\text{h,inj}}$ are not the same quantity as $n_{\text{CB}}$ only refers to the conduction band electrons and does not include trapped electrons while $C_{\text{h,inj}}$ is the concentration of all injected holes. A graphical representation of Equation 5.31 and the energy levels relevant for the open-circuit voltage can be found in Figure 5.16.

The slope of a plot of $V_{\text{OC}}$ vs. log $P_{\text{in}}$ for the solid state cell (Figure 5.15b) was 80 mV. This higher value could be due to an effect of $c_{\text{h,Inj}}$ on the concentration of oxidised spiro-MeOTAD and on the open-circuit voltage.

**Figure 5.16:** Representation of the energy levels relevant for the voltage determination of a solid state DSC in the dark and under illumination.
Photocurrent and photovoltage response times

Information about the transport and lifetimes of charge carriers in the DSC can be obtained by monitoring the current and voltage transients following a small modulation of the light intensity. Figure 5.17a shows normalised photocurrent transients of the solid state DSC and the liquid electrolyte DSC measured under short-circuit conditions at the same bias light intensity. Due to the small amplitude of the modulation, the transients can be reasonably well fitted by a single exponential decay:

\[ J(t) = J_{\text{SC}} + \Delta J \cdot e^{-t/\tau_{\text{resp}}} \]  

(5.32)

where \( \tau_{\text{resp}} \) is the characteristic time constant of the decay. A plot of \( \tau_{\text{resp}} \) measured at different bias light intensities can be seen in Figure 5.17b. The photocurrent response times of the solid state DSC are significantly faster than the corresponding time constants for the liquid electrolyte DSC at the same short-circuit current.

![Figure 5.17](image)

Figure 5.17: a) Normalised current decays of the two DSCs at the same bias light intensity (560 W m\(^{-2}\)) following a small downward modulation of the light intensity. b) Photocurrent response times obtained from fits at different light intensities as a function of \( J_{\text{SC}} \). Dashed lines indicate a log-log fit to the data.

The time constant of the current decay depends on how fast the system adjusts to the decreased injection of charges into the TiO\(_2\). It therefore depends on the recombination rate and on the rate at which charge carriers can be transported out of the cell. Considering that both holes and electrons have to be transported out of the cell independently, it will depend on the limiting one of these two types of charge transport. For a liquid electrolyte DSC, this is the electron transport in the TiO\(_2\). The transport of I\(_3^-\) to the counter electrode can usually be ignored, as an excess of I\(_3^-\) is available in the electrolyte. \( \tau_{\text{resp}} \) can then be related to the transport time of electrons in the TiO\(_2\) (\( \tau_{\text{tr}} \)) and to the
electron lifetime ($\tau_e$) by:

$$\frac{1}{\tau_{resp}} = \frac{1}{\tau_{tr}} + \frac{1}{\tau_e}$$  \hspace{1cm} (5.33)

For optimised liquid electrolyte cells under short-circuit conditions, $\tau_e$ is much larger than $\tau_{tr}$ and the photocurrent response time becomes a direct measure of the electron transport time in the TiO$_2$.

For a solid state DSC, it seems possible that the charge transport could be limited by the transport of holes to the back contact if the concentrations of oxidised spiro-MeOTAD is very low. However, in such a case an increase in $\tau_{resp}$ would be expected compared to a comparable liquid electrolyte DSC.

The electron lifetime can be determined relatively easily from photovoltage transients under open-circuit conditions. The decay of the photovoltage following a small downward modulation in light intensity is measured and fitted to a single exponential decay in an equivalent way to the fitting of the photocurrent responses. As no charges are extracted from the cell under open-circuit conditions, the response time is equal to the electron lifetime. In such a way, $\tau_e$ could be determined for the two example cells as a function of open-circuit voltage and light intensity. However, considering the difference of $U_{\text{redox}}$ for the solid state DSC and the liquid electrolyte DSC, a comparison of $\tau_e$ at the same open-circuit voltage is not meaningful as $\tau_e$ should depend on the concentration of electrons in the TiO$_2$. Instead, a comparison of the lifetimes plotted against $U_{\text{redox}} - V_{OC}$ is shown in Figure 5.18a. For the liquid electrolyte cell, this latter quantity corresponds to the Fermi level in the TiO$_2$ (Equation 5.28). For the solid state DSC, this quantity also depends on the concentration of holes in spiro-MeOTAD, as $U_{\text{redox}}$ was unknown and $U'_{\text{redox}}$.

\[\begin{array}{c}
\text{a)}
\text{b)}
\end{array}\]

$\tau_e / \text{ms}$

$U_{\text{redox}} - V_{OC} / \text{V vs. NHE}$

$P_{in} / \text{W m}^{-2}$

$\tau_e / \text{ms}$

solid

liquid

Figure 5.18: Electron lifetimes of the DSCs obtained from fits to voltage transients at different light intensities: a) as a function of $U_{\text{redox}} - V_{OC}$, b) as a function of light intensity. Dashed lines indicate fits to the data.
(=0.78 V vs. NHE) was used in the calculations instead. It can be seen that in this comparison, $\tau_e$ is much larger for the liquid electrolyte DSC.

The electron lifetimes can also be compared at the same light intensities. This comparison makes sense if similar amounts of charge are injected into the TiO$_2$ at one light intensity. This is the case here, as the cells have similar short-circuit currents at the same light intensity (Figure 5.15a) and a plot of $\tau_e$ vs. light intensity is shown in Figure 5.18b. This representation also shows that electron lifetimes in the solid state DSC are much shorter than in the liquid electrolyte DSC.

In order to use $\tau_e$ to determine $\tau_{tr}$, the electron lifetime and the photocurrent response time should be measured under the same conditions. However, the electron lifetime has been found to increase with decreasing potential$^{39}$ and therefore $\tau_e$ measured under open-circuit conditions can be seen as a minimum estimate for $\tau_e$ under short-circuit conditions. Figure 5.19a shows $\tau_e$ measured under open-circuit conditions and $\tau_{resp}$ measured under short-circuit conditions as a function of light intensity. Figure 5.19b compares $\tau_{tr}$ estimated using Equation 5.33 to $\tau_{resp}$. It can be seen that the difference between $\tau_{tr}$ and $\tau_{resp}$ is negligible for the liquid electrolyte DSC. For the solid state DSC, the transport time estimated this way remains shorter than the transport time of the liquid electrolyte DSC.

In conclusion, both lifetimes and transport times determined for the solid state DSC are shorter than those determined for the liquid electrolyte DSC. The shorter lifetimes can be explained by faster recombination of electrons in TiO$_2$ with holes in spiro-MeOTAD than with tri-iodide. The reason for the shorter transport times is unclear.

---

**Figure 5.19:** a) Electron lifetimes (solid state DSC = grey dots, liquid electrolyte DSC = black squares) determined under open-circuit conditions compared to photocurrent response times (solid state DSC = grey crosses, liquid electrolyte DSC = black circles) determined under short-circuit conditions. b) $\tau_{tr}$ (dashed lines) estimated from values in (a) compared to $\tau_{resp}$ (solid lines).
Open circuit charge extraction

It is often desirable that comparisons of for example transport and electron lifetimes are carried out at the same electron concentrations in the titanium dioxide. A variety of methods to determine electron concentrations in the TiO$_2$ have been successfully applied to liquid electrolyte DSCs. Such methods include near-infrared transmission,$^{104}$ determinations of the capacity of the TiO$_2$, $^{105}$ and charge extraction methods.$^{106,107}$ In liquid electrolyte DSCs, determinations of the electron concentrations at open-circuit can be used to compare the conduction band positions of different cells according to Equations 5.28 and 5.29.$^{27}$ For solid state DSCs, such a comparison is more difficult as $U_{\text{redox}}$ is not always well known and might also vary between cells. In the following, I will describe the open-circuit charge extraction method and its limitations for solid state DSCs.

In open-circuit charge extraction measurements, the DSC is illuminated under open-circuit conditions with a certain light intensity for a certain period of time (10 s in this example). At the same time as switching off the illumination light, the cell is switched from open-circuit to short-circuit conditions and the current transient is measured. By integrating the current over time, the charge is determined. The experiment can be repeated at different light intensities to determine the charge at different open-circuit voltages.

Current transients for the solid state and liquid electrolyte DSC are shown in Figure 5.20a. It can be seen that in the solid state DSC, the current decays much faster than in the liquid electrolyte DSC. This is unsurprising considering the faster time constants of the solid state DSC but also limits the accuracy.

Figure 5.20: a) Current traces of the two DSCs in the dark after illumination at 1800 W m$^{-2}$ (solid line) and at 18 W m$^{-2}$ (dashed) under open-circuit conditions. b) Charge integrated from the current traces for the solid state DSC. Black lines indicate a fit to the second half of the data. The extracted charge was determined from the $t = 0$ s intercept of these fit lines.
of the measurement. Most current flows in a time scale which is close to the switching time constant of the system. Any inaccuracies in switching times will therefore introduce large errors in the measurement. A large amount of charges may also be lost due to recombination. The integrated charge can therefore only provide a minimum estimate of the charge present under open-circuit conditions.

Further care has to be taken in correcting for small background currents. The charge will rise in a linear fashion at long times due to a background current (Figure 5.20b). Therefore, the absolute charge was therefore determined by fitting a straight line to the linear part of the charge vs. time plot and taking the intercept of this straight line at \( t = 0 \) (Figure 5.20b).

Graphs of \( \log Q_{OC} \) vs. \( V_{OC} \) are shown in Figure 5.21a. It can be immediately seen that the charges measured for the solid state DSC are much lower than the ones for the liquid electrolyte DSC, in agreement with the shorter electron lifetimes under open-circuit conditions. The slope of the plots are also different for the two solar cells. In order to come closer to comparing the charge at the same Fermi level of the TiO\(_2\), also a plot of \( \log Q_{OC} \) vs. \( U_{redox} - V_{OC} \) is shown (Figure 5.21b). However, as the concentration ratio of oxidised and ground-state spiro-MeOTAD was not known, a value of \( U_{redox}^{0} = 0.78 \) V vs. NHE was used for the solid state solar DSC (Paper I). In a true plot of \( \log Q_{OC} \) vs. \( E_{F, TiO_2} \) one can therefore imagine that the data points for the solid state DSC should be moved to the right due to \( U_{redox} \) being smaller than 0.78 V vs. NHE and upwards due to having underestimated the charge in the TiO\(_2\). As it is, the plot indicates that the conduction band position of both DSCs are similar but that the TiO\(_2\) has a much lower Fermi level in the solid state DSC.

![Figure 5.21: Extracted charge after illumination under open-circuit conditions: a) as a function of \( V_{OC} \), b) as a function of \( U_{redox} - V_{OC} \).](image)
6. Energy alignment and interface processes in solid state DSCs

6.1 DSC results with ID176

As discussed in previous sections, optimised liquid electrolyte cells usually show higher efficiencies than optimised solid state DSCs. For ID176, however, this situation is reversed. IPCE spectra and IV-curves of solid state and liquid electrolyte cells, which use ID176 as the sensitising dye, are shown in Figure 6.1. The cells “Solid 1” and “Liquid 1” did not contain the additive tBP but it was used in cells “Solid 2” and “Liquid 2”. The solid state cell without

![Figure 6.1: IPCE spectra (a) and IV-curves (b) of solid state and liquid electrolyte DSCs using ID176 as a sensitiser. Cells “Solid 1” and “Liquid 1” did not contain tBP while cells “Solid 2” and “Liquid 2” contained tBP as an additive to spiro-MeOTAD or to the redox electrolyte. Figure adapted from Paper III.](image)

$tBP$ showed the highest IPCE and efficiency, while the liquid electrolyte cell with $tBP$ showed a much lower IPCE and efficiency than the other cells. The solid state cell with $tBP$ and the liquid electrolyte cell without $tBP$ showed a similar $J_{SC}$ but the solid state cell had a higher efficiency due to a higher $V_{OC}$. $tBP$ is likely to lead to a decrease in electron injection as it raises the TiO$_2$ conduction band. The difference in the performances of the solid state DSCs and liquid electrolyte DSCs is surprising and we therefore examined the energy alignment and interface processes at the TiO$_2$/dye/spiro-MeOTAD interface more closely.
6.2 Energy alignment

In order to determine an accurate energy alignment of the TiO$_2$/dye/spiro-MeOTAD interface, energy levels (or redox potentials) of all cell components should be determined under solar cell conditions. Figure 6.2 shows a Gerischer diagram of the energetics of a dye-sensitized solar cell. Redox potentials indicated in the diagram can be determined by electrochemistry. Excited state potentials can be determined by subtracting $E_{0-0}$ from the redox potentials. Photoelectron spectroscopy (PES) can be used to estimate the position of the HOMO levels (D in the diagram) in relation to the states in the TiO$_2$ as only electronic relaxations are observed in PES. In this thesis work, I used electrochemistry to determine the energetics of the components in dye-sensitized solar cells. In Papers IV and V, the results from electrochemistry were compared to the results from PES.

Figure 6.2: Gerischer diagram for a solid state DSC adapted from literature.$^6,70$ Bandgap states of the titanium dioxide are indicated and spiro-MeOTAD is treated as a redox couple.

6.2.1 Redox potential of spiro-MeOTAD

The redox potential of spiro-MeOTAD was determined from cyclic voltammetry of a spiro-MeOTAD film on a FTO substrate (Figure 6.3). An ionic liquid was used as electrolyte in these measurements as it did not dissolve the spiro-MeOTAD film. The cyclic voltammogram was not very reversible when scanning from -0.4 V vs. Fc/Fc$^+$ to 0.6 V vs. Fc/Fc$^+$ and back but there were two distinct onsets of oxidation in the anodic scan (Figure 6.3a). The first onset occurred at 0.15 V vs. Fc/Fc$^+$ (see inset in Figure 6.3a) and the second onset occurred at 0.36 V vs. Fc/Fc$^+$. The first oxidation was assigned to the formation of spiro-MeOTAD$^{+}$ and the second oxidation to the formation of spiro-MeOTAD$^{4+}$ using evidence from UV-visible absorption spectra.
Figure 6.3b shows that the scan became more reversible if it was reversed at 0.3 V Fc/Fc\textsuperscript{+} before spiro-MeOTAD\textsuperscript{4+} was created. However, there were still no clear peaks from which the redox potential could be determined. Instead, the redox potential was determined from the onset of oxidation at 0.15 V vs. Fc/Fc\textsuperscript{+}. This potential is similar to the redox potential of spiro-MeOTAD in solution (0.12 V vs. Fc/Fc\textsuperscript{+}).\textsuperscript{35}

The redox potential of spiro-MeOTAD determined this way is important for determining the energy matching between a sensitisier and spiro-MeOTAD. However, it might not be the potential relevant for determining the voltage of a solid state DSC as the concentration of ground-state and oxidised spiro-MeOTAD are not equal in the cell (see Chapter 5.2.3).

6.2.2 Density of states in the titanium dioxide

It is not easy to determine exact conduction band positions of mesoporous TiO\textsubscript{2} films. A value often used in literature is -0.5 V vs. NHE, which is an estimation of the flat band potential of TiO\textsubscript{2} particles in aqueous solutions at pH 7.\textsuperscript{108,109} However, as discussed in Chapter 4.1, the conduction band position is dependent on the surface charge and might also not be well defined for mesoporous TiO\textsubscript{2} films.\textsuperscript{6,70} The density of states of the TiO\textsubscript{2} can be probed by cyclic voltammetry.\textsuperscript{79–81} The measured current is proportional to the capacitance, which can be directly related to the density of states in the TiO\textsubscript{2}. Figure 6.4 shows a cyclic voltammogram of a TiO\textsubscript{2} electrode in a LiClO\textsubscript{4} electrolyte scanning from 0.6 V vs. NHE to -0.6 V vs. NHE. There are states in the TiO\textsubscript{2} from about +0.2 V vs NHE onwards. One cannot distinguish, if the states lie in the conduction band or in the band gap of the TiO\textsubscript{2}. A clear onset defining the conduction band position was not observed.
Figure 6.4: Cyclic voltammogram of a TiCl$_4$-treated, 900 nm thick, mesoporous TiO$_2$ electrode in 0.1 M LiClO$_4$ in MPN as supporting electrolyte scanning from 0.6 V vs. NHE to -0.6 V vs. NHE and back with a scan rate of 0.05 V s$^{-1}$. Oxygen in the electrolyte was removed by bubbling with argon gas. Figure adapted from Paper IV.

Photoelectron spectra of a similar mesoporous TiO$_2$ film showed states throughout the band gap (Paper IV). A peak observed at around 1.4 eV binding energy was likely to be due to defects in the stoichiometry of the anatase TiO$_2$ (101) dominated surface. The states have a cut off positioning, which can be referred to as the Fermi energy position. This position determines an upper binding energy limit (a lower energy limit) for the conduction band edge.

6.2.3 Energetics of dye molecules adsorbed to TiO$_2$ surfaces

The energetics of ID176 were studied in Papers III-V. $E_{0-0}$ was determined from the cross-section of the normalised absorption and emission spectra of the dye in solution as well as adsorbed to TiO$_2$. $E_{0-0}$ was found to be 1.85 eV for the dye adsorbed to TiO$_2$ in absence of solvent and in presence of spiro-MeOTAD. In presence of MPN, $E_{0-0}$ was 1.83 eV. However, when lithium ions were added, $E_{0-0}$ decreased to 1.77 eV for all cases.

Redox potentials of ID176 were measured relative to an external reference (Fc/Fc$^+$) in different supporting electrolytes. The oxidation potential of ID176 adsorbed to TiO$_2$ was found to be 0.59 V vs. Fc/Fc$^+$ in LiClO$_4$ or in TBAClO$_4$ in MPN as electrolyte (Figure 6.5a) and a similar value was also found in MeCN electrolytes (Paper III). The reduction potential was much more negative in TBAClO$_4$ electrolyte than in LiClO$_4$ electrolyte (Figure 6.5b). Excited state potentials were calculated by subtracting $E_{0-0}$ from the oxidation potentials as depicted in Figure 6.2. One obtains a less negative excited state potential in presence of lithium ions than otherwise.

These measurements did not determine the excited state potentials relative to the states of the TiO$_2$. The HOMO level of ID176 was determined relative to the titanium dioxide levels with PES in absence and in presence of LiClO$_4$.
Figure 6.5: a) CV showing the oxidation of ID176 adsorbed to TiO₂ recorded with a scan rate of 0.01 V s⁻¹. Dashed line indicates $U_{1/2}$. b) DPV showing the reduction of ID176 adsorbed to Al₂O₃. Dashed lines indicate $U_p$ (b). Figures adapted from supporting information of Paper IV.

(Paper IV). An energy difference of 0.07 eV between the HOMO levels was found which is very similar to the difference in the measured $E_{0-0}$ values (0.08 eV). PES measurements therefore suggested that the excited state of ID176 is not shifted relative to the TiO₂ levels by the addition of lithium ions. It therefore seems that for ID176 attached to TiO₂, the excited state potential and the reduction potential are sensitive to the energetics of the TiO₂.

In order to understand, how the different techniques used for the determination of the interface energetics vary, we compared the results from electrochemistry and PES of three dyes: ID28, ID176 and ID1 (Paper V). Figure 6.6a summarises the redox potentials and $E_{0-0}$ of the dyes determined by electrochemistry. Values which were published in literature⁶¹,⁶³ as well as those values measured in Paper V are shown. The conduction band position of TiO₂ is indicated at the typical literature value of -0.5 vs. NHE. The oxidation potentials follow the ordering of ID28 < ID1 < ID176. The excited state potentials of ID176 and ID1 are similar while the excited state potential of ID28 is significantly more negative. Figure 6.6b summarises the energetics measured relative to the TiO₂ with PES. The Fermi level of an undyed TiO₂ film is indicated at 0 eV binding energy. In this case the ordering of HOMO levels (in binding energy) is ID1 << ID176 < ID28. We showed in Paper V that a reason for the lower HOMO of ID1 is that it has a different magnitude and direction of dipole moment than the other two dyes, which causes a positive shift in the energies of the titanium dioxide. According to this analysis, ID176 has a more positive excited state than ID1 and ID28, and therefore the least driving force for photo-induced electron injection. Why ID28 and ID176 showed such a different ordering of their oxidation potentials / HOMO levels in electrochemistry and PES remains unclear.
Figure 6.6: a) Potentials of ID28, ID176 and ID1 determined by electrochemistry. Literature values $^{61,63}$ are indicated by dashed lines. Absorption spectra were subtracted from $U_{ox}$ determined in this study. The conduction band of TiO$_2$ is indicated at -0.5 V vs. NHE. b) Energy levels of ID28, ID176 and ID1 determined by PES. The results were calibrated to the Fermi level of an undyed TiO$_2$ film placed at 0 eV binding energy. Absorption spectra were subtracted from the HOMO energy and dashed lines indicate the 10% onset of the absorption spectra. Figure adapted from Paper V.

6.3 Electron injection

Photo-induced electron injection into titanium dioxide was studied by PIA. Figure 6.7 shows PIA spectra of TiO$_2$ films dyed in ID28, ID176 and ID1 in absence of electrolytes or spiro-MeOTAD. The spectra of ID28 and ID1 show clear signals which are due to the presence of oxidised dye molecules, while for ID176, almost no signals are observed. This suggests that ID28 and ID1 are able to effectively inject electrons into the TiO$_2$ while ID176 is not, in agreement with the trends in excited state levels determined by PES.

For liquid electrolyte cells, supporting electrolytes are often used when measuring PIA spectra in order to mimic the dye surroundings in a working device. For solid state DSCs, this approach might not be as useful but ions are also present at the interface in these devices. To study injection relevant to solid state DSCs, we therefore added a LiClO$_4$ solution to the TiO$_2$ surface and measured the sample once the solvent had evaporated. PIA spectra of ID176 in different surroundings are shown in Figure 6.8. Clear signals of oxidised ID176 are observed when lithium ions are dry on the surface, while only very small signals are observed in presence of MPN.

This result shows that the solvent hinders electron injection and explains why ID176 worked poorly as a sensitisier for liquid electrolyte DSCs. This explanation was also supported by relative fluorescence quantum yields which were 4.3% in absence of solvent and ions, 3.2% in presence of 0.1 M LiClO$_4$ in MPN and 1.5% when LiClO$_4$ was dry on the surface (Paper IV). Femtosecond TAS of the same samples showed significant amounts of excited ID176
Figure 6.7: a) Photo-induced absorption spectrum of ID28 adsorbed to a 2 µm thick TiO$_2$ film measured with a blue LED as pump. Figure adapted from Paper I. b) Photo-induced absorption spectra of ID176 and ID1 adsorbed to a 1 µm thick TiO$_2$ film measured with a red laser as pump. Figure adapted from Paper V.

Figure 6.8: PIA spectra of ID176 adsorbed to TiO$_2$ in different surroundings. Excitation was provided by a green laser. Figure adapted from Paper IV.

decaying without injecting (Reaction 2.6) for all samples but the last one. Considering the energetics of ID176 relative to the TiO$_2$, it seems likely that injection occurs into band gap trap states rather than into the conduction band.$^1$

6.4 Regeneration

Regeneration was also studied by PIA. For dyes like ID28, which show clear oxidised dye signals in absence of spiro-MeOTAD (or a redox mediator), regeneration can be monitored by the disappearance of the oxidised dye features

$^1$Additional data and a more detailed discussion can be found in Paper IV.
in presence of spiro-MeOTAD. We studied the regeneration of ID28 for a variety of spiro-MeOTAD concentrations and at two TiO$_2$ film thicknesses (2 and 6 µm). The PIA spectra of the different samples are shown in Figure 6.9. All spectra show a bleach at 550 nm and a positive absorption with a maximum between 730 and 750 nm. The peak feature was assigned to the absorption of spiro-MeOTAD$^+$, which should peak at 510 and 700 nm (Paper I). The peak at 510 nm was not observed clearly as it was overlayed with the Stark shift of ground-state ID28. The red-shift of the 700 nm peak was assumed to be due a change in the absorption spectrum of oxidised spiro-MeOTAD when the holes are located close to the TiO$_2$/dye/spiro-MeOTAD interface. As no additional peak was observed at 790 nm, where the absorption maximum of oxidised ID28 occurs, the results suggest that spiro-MeOTAD was able to efficiently regenerate ID28 for the different spiro-MeOTAD concentrations and film thicknesses used. This means that spiro-MeOTAD was able to infiltrate even deep pores in the titanium dioxide, and that there should be no losses in a DSC due to non-contacted dye molecules. However, it is not clear from these measurements what fraction of the pores were filled with spiro-MeOTAD.

PIA shows qualitatively if oxidised dyes can be regenerated, but it does not give information about regeneration time constants. Femtosecond transient absorption spectroscopy was used in Paper IV to study the regeneration of ID176 by spiro-MeOTAD. In these measurements, we also included a sample where ID176 was dispersed in a film of spiro-MeOTAD to determine if the dye can be photo-reduced by spiro-MeOTAD (Reaction 2.4). Transient absorption spectra of this sample at different delay times after excitation with a

Figure 6.9: PIA spectra of ID28 adsorbed to 2 µm thick TiO$_2$ films (a) or 6 µm thick TiO$_2$ films (b) in presence of spiro-MeOTAD at different concentrations (given as mg/ml) of the spiro-MeOTAD solution used for spin-coating. A blue LED was used for excitation and the spectra were recorded by illumination from the substrate side. Figures adapted from Paper I.
femtosecond laser pulse are shown in Figure 6.10a. A peak at 510 nm and a broad positive absorption feature between 650 nm and 750 nm are observed. This latter feature was partially due to the excited state of ID176 and decreases in intensity with time. The peak at 510 nm increases in intensity from 0.5 to 6 ps. This feature was associated with the formation of ID176\(^{-}\) and spiro-MeOTAD\(^{+}\), which absorbs at 510 nm. A time constant of a slow component of the photo-reduction was found to be approximately 35 ps. This is much faster than the regeneration of oxidised dye molecules by iodide, which typically occurs on the nanosecond to microsecond time scale.\(^{89,112}\)

\[
\begin{array}{c}
\text{Spectra of a “complete” TiO}_2/\text{ID176/spiro-MeOTAD sample where LiTFSI was added to spiro-MeOTAD are shown in Figure 6.10b. This sample represents the conditions under which solid state DSCs with ID176 work well. The spectra show the Stark shift of ID176 at all delay times. As solar cells work well under the measured conditions, both injection and regeneration must happen but it is unclear from these spectra in which order. Kinetic traces at 540 and 640 nm show that the signals are largest after 1 ps and then decrease (Figure 6.11). This suggests that charge separation is complete after this time and that in presence of lithium ions both injection and regeneration are very fast.}
\end{array}
\]

6.5 Recombination

A consequence of the fast charge separation in solid state DSCs is that recombination will be dominated by recombination of electrons in the TiO\(_2\) and holes in spiro-MeOTAD (Reaction 2.9). Here, one might distinguish between
geminate recombination of an electron-hole pair and non-geminate recombination. In the latter case, the electron will travel in the TiO$_2$ before it finds a (different) hole to recombine with. This type of recombination can be measured on complete devices on the millisecond time scale and is light-intensity dependent. It has been shown that it is faster in solid state DSCs than in liquid electrolyte DSCs (see Chapters 2.2 and 5.2.3).

![Kinetic traces of ID176 adsorbed to TiO$_2$ in presence of spiro-MeOTAD and LiTFSI following excitation by a femtosecond laser pulse. Solid lines indicate multiexponential fits to the data from 5 ps to 7 ns. Figure adapted from Paper IV.](image)

*Figure 6.11:* Kinetic traces of ID176 adsorbed to TiO$_2$ in presence of spiro-MeOTAD and LiTFSI following excitation by a femtosecond laser pulse. Solid lines indicate multiexponential fits to the data from 5 ps to 7 ns. Figure adapted from Paper IV.

Geminate recombination is usually not considered for DSCs, as regeneration occurs long after electron injection in liquid electrolyte DSCs. However, in the solid state case, geminate recombination might play a role as electrons and holes seem to be created almost simultaneously. If injection occurs into band gap states at the TiO$_2$ surface, it might take some time before the electron moves to a different TiO$_2$ site and the electron might recombine with the hole created on an adjacent spiro-MeOTAD molecule. It has been observed that IPCEs of solid state DSCs usually have maxima of 60-70 % even when organic dyes with high extinction coefficients are used.$^{29,36,38}$ A study by Huang et al. showed that APCEs using the ruthenium dye, Z907, or the organic dye, D149, are approximately 60 %.$^{113}$ Geminate recombination might provide an explanation for these non-ideal APCE values.

The transient absorption signals of ID176 adsorbed to TiO$_2$ in presence of spiro-MeOTAD and LiTFSI decrease from 1 ps onwards (Figure 6.11). This is not direct evidence of recombination as the signals are due to a Stark shift. If charges and ions (Li$^+$) at the TiO$_2$ surface rearrange and this would lead to a decrease of the electric fields acting on the dye molecules, the signals would also decrease. However, it seems likely that some of the decrease in signals stems from recombination. This suggests that recombination in solid state DSCs with ID176 occurs on a fast time scale.
7. Conclusions and outlook

In this thesis work, I used and developed measurement techniques to study the properties and processes of solid state DSCs under conditions close the operating conditions of the solar cell. Electrochemistry and photoelectron spectroscopy were used to study the energy alignment at the TiO$_2$/dye/spiro-MeOTAD interface. Photo-induced absorption spectroscopy and femtosecond transient absorption spectroscopy were used to study the injection, regeneration and recombination processes across this interface. It was found that the results of the latter two techniques are strongly influenced by a Stark shift of the ground-state absorption spectra of dye molecules caused by electrons in the TiO$_2$. The Stark shift has the shape of the derivative of the absorption spectrum and depends on the size and magnitude of the change in dipole moment of the molecule normal to the TiO$_2$ surface.

The results of the measurements revealed some fundamental differences between solid state DSCs employing the hole conductor spiro-MeOTAD and conventional liquid electrolyte DSCs, which employ the iodide/tri-iodide redox couple. An organic dye (ID176) studied here was able to efficiently inject electrons into the TiO$_2$ in absence but not in presence of an organic solvent. As a consequence, liquid electrolyte DSCs using this dye showed poor performances, while the dye worked well in solid state DSCs. Regeneration by spiro-MeOTAD is very fast and can even preceed electron injection into the titanium dioxide. The dominating recombination reaction occurring in solid state DSCs is recombination between electrons in the TiO$_2$ and holes in spiro-MeOTAD, which is faster than recombination of electrons with tri-iodide. In addition to non-geminate recombination, also geminate recombination might cause losses in solid state DSCs.

Redox potentials and energy levels of dye molecules adsorbed to TiO$_2$ surfaces determined by electrochemistry and photoelectron spectroscopy can show different trends, as the redox potentials in electrochemistry are measured relative to an external reference and the energy levels in PES are measured relative to the levels of the TiO$_2$. Furthermore, dyes are in a solvent and ion environment in electrochemistry, which they are (usually) not in PES. PES might be better suited for predicting driving forces for electron injection, especially for solid state DSCs. For ID176, some evidence was found that it is not the conduction band of the TiO$_2$, which is important for electron injection, but rather the density of available states in the band gap of the TiO$_2$. 
The results of this thesis work show that it is important to consider the interplay and matching of all components of a DSC both when applying measurement techniques to the system and when replacing one of the components. This is in line with some of the recent successes in DSC research: alternative redox couples capable of replacing iodide/tri-iodide were successfully used in DSCs together with organic dyes,\textsuperscript{114,115} which were much better suited to these systems than the standard ruthenium complexes, such as N719, which had been used previously.

In the future, it will be interesting to apply new time-resolved techniques, such as time resolved vibrational spectroscopies, to the solid state DSC and to modify some existing techniques to come even closer to measuring the operating system. An example of the latter is to include ions, solvents and hole conductors in the interface measurements with photoelectron spectroscopy.

Studies of how negative the oxidation potential of dye molecules are allowed to be for efficient regeneration by spiro-MeOTAD might help improve solid state DSCs. In this way, the energy losses in the system could be minimised. Dyes which absorb in the near-infrared could be used to increase the light-harvesting in solid state DSCs – either on their own or as co-sensitisers together with organic dyes which absorb strongly in the visible part of the solar spectrum.

Recombination between electrons in the TiO\textsubscript{2} and holes in spiro-MeOTAD might be reduced by an optimised engineering of the interface: dyes which protect the surface such as D35 and also co-adsorbers could be used. Alternatively, an additional potential step could be included in the injection or regeneration process in order to separate the charges more effectively.\textsuperscript{44}

New hole conductors with more positive potentials or higher hole mobilities could replace spiro-MeOTAD. A new hole conductor should be doped by a known amount in order to obtain stable and predictable cell performances, and have minimal competitive absorption of its oxidised state with the absorption spectrum of the sensitisier. An alternative approach might be to use hole conductors, which absorb visible light in their ground-state and can contribute to the photocurrent by injecting electrons into the TiO\textsubscript{2}.\textsuperscript{116,117}
Sammanfattning

Inledning
Utveckling av energiproduktion från förnybara energikällor är viktigt av olika anledningar. Just nu behöver världens befolkning 15 TW effekt och man förväntar sig att det ska öka. Den största delen av energin är producerad från fossila bränslen, men reserverna av fossila bränslen är begränsad och tillgängligheten blir allt svårare. Samtidigt är det väldigt troligt att CO₂ som produceras i förbränningen av fossila bränslen påverkar jordens klimat på ett negativt sätt.


Av de förnybara energikällor som finns är solljuset det med den största potentialen: 10000 gånger mer än vad som skulle behövas, men att omvandla ljuset till ström är inte helt enkelt. Just nu är det bara 24 GW elektrisk effekt som kan produceras från solljuset och nästan allt är producerad med kiselsolceller eller med solvärmeanläggningar som omvandlar värme från solljuset till ström.

För att verkligen utnyttja den stora potentialen hos solljuset är det viktigt att utveckla många olika tekniker för att omvandla solljuset till ström eller bränsle. Solceller måste bli billiga att producera och vanligt förekommande material måste användas för att tekniken ska kunna ersätta andra energikällor.

Färgämnessensiterade solceller
En av de typer av solceller som utvecklas är färgämnessensiterade solceller (figur 1, också kallad för Grätzelssolceller efter Michael Grätzel som visade den första cellen med bra verkningsgrad).

det är ett material som kan ta emot elektroner med hög energi och att elektronerna kan röra sig fritt i materialet.


Fasta färgämnessensiterade solceller

I den här avhandlingen har jag jobbat med en variant av färgämnessensiterade solceller som använder en fast organisk hålledare i stället för en elektrolyt. Att
använda ett fast material i stället för en vätska kan vara bra i syfte att producera stabila solceller. Materialet som användes här heter 2,2’7,7’-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobifluorene (eller kortare spiro-MeOTAD) och sätts in i titandioxidens porer från ett lösningsmedel som sedan evaporeras bort och det fasta materialet stannar kvar i porerna. Ovanpå spiro-MeOTAD evaporeras en silver- eller guldkontakt (figur 1).

Spiro-MeOTAD kan ge elektroner till de oxiderade färgämnesmolekulerna och på så sätt generas positiva laddningar (hål) i spiro-MeOTAD som sedan kan transporteras till silverkontakten. Fasta färgämnensensiterade solceller har visat verkningsgrader upp till 6% vilket är ungefär hälften av verkningsgraden hos liknande solceller med jodidelektrolyt.

Syftet med det här arbetet var att undersöka olika organiska färgämnen och hur de fungerar i den fasta färgämnensensiterade solcellen. Ett av färgämnena visade dålig verkningsgrad i vanliga färgämnensensiterade solceller men bra verkningsgrad (runt 3%) i solceller med spiro-MeOTAD (Paper III). Med hjälp av olika karaktäriseringsmetoder visade det sig att färgämnets fungerade i fasta solceller och inte i vanliga solceller därför att det är lättare för färgämnets att ge elektroner till titandioxid när det inte är i kontakt med en vätska. Samtidigt kan också spiro-MeOTAD ge elektroner mycket snabbare till det oxiderade färgämnnet än vad jodid kan (Paper IV).

Photo-induced absorption spectroscopy och Starkeffekten

En av de metoder jag använde mest för karaktärisering var photo-induced absorption spectroscopy (PIA). PIA används för att undersöka om färgämnens kan ge elektroner till titandioxid och om oxiderade färgämnensmolekyler kan få elektroner tillbaka från jodid eller spiro-MeOTAD. I PIA mäts skillnaden i absorbtionsspektrum när färgämnensmolekyler på titandioxid har exciterats respektive inte. Om exciterade färgämnensmolekyler ger en elektron till titan- dioxide så blir molekulerna oxiderade och har ett annat absorbtionsspektrum än molekyler som är i grundtillstånd (figur 2a). När det även finns jodid eller spiro-MeOTAD på provet så kan de oxiderade molekulerna få en elektron tillbaka. Om det händer, så är molekyler inte längre i oxiderat tillstånd och signalen av oxiderade färgämnens försvinner (figur 2a).

I det här arbetet visade det sig att man mäter en signal till i PIA som kommer från en Starkeffekt av färgämnensmolekyler (Paper II). Elektroner i titandioxid kan orsaka ett elektriskt fält som påverkar färgämnensmolekyler som är i grundtillståndet. Det här fältet orsakar ett skift i färgämnens absorptionspektrum, ett Starkefält. Skiftet finns kvar i spektrummet även när jodid eller spiro-MeOTAD finns i provet eftersom fältet på färgämnnet är kvar (figur 2b).
Sammanfattningsvis är viktigt att förstå Starkeffekten för att kunna tolka sina experimentella resultat från PIA och andra mätningar på ett korrekt sätt.

Meine Doktorarbeit – ein klassisches Drama in fünf Akten

Liebe Leser,
ich möchte euch mit dieser Zusammenfassung zum einen mein Forschungsgebiet etwas näher bringen und zum anderen die Entstehungsgeschichte der Artikel in dieser Arbeit beleuchten.

Die Akteure


*Links:* Die flüssige Farbstoffsolarzelle, *rechts:* die feste Farbstoffsolarzelle.


**Erster Akt (August 2007 bis Anfang 2008)**


Zweiter Akt (Anfang 2008 bis Anfang 2009)


Dritter Akt (Anfang 2009 bis August 2009)

Vierter Akt (September 2009 bis Frühling 2010)


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References


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