Functional Characterisation of Perovskite Films for Solar Cell Applications

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A thesis submitted in partial fulfilment of the requirements of the degree of Doctor of Philosophy

July 28th, 2020
Declaration

I, Robert John Eric Westbrook, confirm that the work presented in this thesis is my own.

Where information has been derived from other sources, I confirm this has been indicated in the work.
Abstract

The world is currently faced with an energy dilemma; as global demand for power continues to soar, pressure is mounting to move away from fossil fuels towards low-carbon alternatives. In this setting, highly efficient, low-cost photovoltaics, which turn solar photons into electricity offer an attractive solution. The efficiency of such photovoltaics is essentially underpinned by the competition between extraction and recombination of photogenerated charges. In this thesis, we use a combination of transient optical, structural and device characterisation techniques to elucidate the key factors governing these two processes in perovskite solar cells.

In Chapter 3, we address the issue of charge extraction at perovskite|hole transport layer interfaces. We find that a remarkably small driving energy ($\Delta E \sim 0.1$ eV) between the perovskite valence band and the highest occupied molecular orbital (HOMO) of the hole transport layer is required to induce efficient hole injection ($>75\%$). We also find that the rate of recombination of injected holes in $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{PbI}_3$ systems is slower compared to $\text{MAPbI}_3$.

In Chapter 4, we show that passivation of perovskite with phenethylammonium iodide results in an enhancement of the efficiency from 12.95% to 16.73% and an improvement in stability – taken as the time for efficiency to drop to 80% of its initial value – from a few hours to over 21 days. Optical characterisation reveals that a bilateral passivation mechanism is behind these improvements, where iodide anions fill iodide vacancies and the phenethylammonium cation induces a 2D heterostructure.

Finally, we bring these two strands of research together in Chapter 5 by correlating the extent of passivation from transport layers with an enhancement in the interfacial charge injection yield.

Throughout, we make constant reference to the impact of our findings on perovskite solar cell device parameters and set out design rules for their optimum efficiency and stability.
Impact Statement

Climate change is the most immediate challenge facing society. In light of this, world leaders met in 2015 to sign the Paris Agreement that aims to halt global warming to 1.5 °C on pre-industrial levels. In order to achieve this, current CO₂ emissions must be cut by almost half over the next decade. This extraordinary challenge has left governments stuck between climate catastrophe and energy crisis due to the dearth of low-carbon alternatives to fossil fuels. Consequently, interest in photovoltaics has intensified given that the sun offers an essentially limitless source of energy.

The work in this thesis comprises three studies that set about understanding and optimising photovoltaic activity in hybrid organic-inorganic perovskites, an emerging family of cost-effective optoelectronic materials. In particular, we establish design rules that, along with other work in the field, will aid the development of this potentially disruptive technology towards market. This will have several important economic, social and environmental impacts in both the Global North and South. Firstly, the potential for cheap, on-grid centralized power generation that could undercut the fossil fuel market will reduce CO₂ emissions in the Global North and mitigate global warming. Furthermore, this will aid low-carbon economic development in the Global South. Notably, the development of an easy-to-deploy photovoltaic technology holds promise to provide decentralized power in rural areas of the Global South, where 840 million people still have intermittent or zero access to electricity.

Moreover, the rapid development of perovskite solar cells over the last decade has benefitted from knowledge gained from their predecessors. In the same way, we expect contemporary findings on perovskite solar cells to accelerate the development of next-generation technologies, such as tandem solar cells. Finally, while our results have been framed primarily in the language of solar cells, we expect their impact to span several related applications including perovskite light-emitting diodes (PeLEDs). In this way, our research could aid both low-carbon energy consumption, as well as production, given the promise that PeLEDs hold for energy-efficient lighting and display applications.
Acknowledgements

Firstly, I would like to give my strongest thanks to Prof Saif Haque for his mentorship, expertise and for giving me the freedom to pursue my own research interests. Saif has also been a great friend with which to discuss the diabolical developments of the British political landscape over the last half-decade, amongst other things. I would further like to thank Dr Tracey Clarke in equal parts for her expertise in spectroscopy and her forensic critique of papers, both of which have been instrumental in writing this thesis. For this final submission, huge thanks must also go to Prof David Scanlon and Dr Samuel Stranks for the engaging discussion during my PhD viva and their valuable insights, which have no doubt improved this thesis.

The work on these pages was supported by EPSRC through the Centre for Doctoral Training in Advanced Characterisation of Materials (EP/L015277/1). Here, my thanks go especially to Prof Neil Curson, Prof Stephen Skinner and Dr Camille Petit for their support and encouragement. It has been a pleasure to be part of a dynamic, talented and convivial CDT cohort, with such a broad range of perspective across materials science.

My thanks go to all of the members of the Haque group past and present. It really has been a dream to work with such a talented, dedicated and passionate team of researchers whose dynamic has been as strong in the lab as in the Karaoke bar. Special thanks go to Jose – who taught me everything I know about transient absorption spectroscopy (and Andalucian slang, which I shan’t repeat here); to Irene – for passing on a huge amount of knowledge and skill in my first year and her fantastic company; to Luis – an incredible talent and great friend with a contagious enthusiasm for perovskite photovoltaics; to Bowon and Dong – for their experimental assistance and friendship; and to Tom - for his kind mentorship and unparalleled skill with device fabrication. I also note here my huge appreciation for the support staff at ICL and UCL: Steve Atkins, Martyn Towner, Martin Vickers, Stefanos Karapanagiotidis and especially Xiaoe Li, whose assistance was invaluable during the South Kensington-White City laboratory move.

I am also indebted to Prof James Durrant for his – and his student Weidong Xu’s – insight into my PhD research as well as his kind advice and support with next steps in academia. Massive thanks go also to Prof Prashant Kamat, who kindly agreed to the invitation of a PhD student to deliver some fantastic talks at Imperial. I also thank Dr Anna Demming for the opportunity to contribute/edit at Physics World, a welcome respite from PhD work.
I sincerely thank Charlie Turner at Bluecoat School, Coventry – the kindest and most enthusiastic chemistry teacher I had, who got a distracted Year 9 student to concentrate.

On a personal note, I owe everything to my parents, who have supported me in all conceivable ways over the last twenty-seven years. Thanks also to Rachel and Rosemary for their encouragement throughout. I’m incredibly fond of Tom, Lew, Rav, Dan, Henry, Elliot, Jord, Quinn and friends on Median, Rendlesham and Lynmouth Rds for all the welcome distractions over the years.

Above all, thank you Maud, for solace and your singular ability to make light of life both academic and otherwise.
Publications

Robert J. E. Westbrook, Dr Irene Sanchez-Molina, Dr Jose Manuel Marin-Beloqui, Dr Hugo Bronstein, Dr Saif A Haque*, Effect of Interfacial Energetics on Charge Transfer from Lead Halide Perovskite to Organic Hole Conductors, J. Phys. Chem. C., 2018, 122(2), 1326


Alex Aziz, Nicholas Aristadou, Xiangnan Bu, Robert J. E. Westbrook, Saif A. Haque*, Saiful M. Islam*, Understanding the Enhanced Stability of Bromide Substitution in Lead iodide Perovskites, Chemistry of Materials, 2020, 32(1) 400-409


Robert J. E. Westbrook*, Weidong Xu, Xinxing Liang, Bu Xiangnan, Saif A Haque*, Control of Layered Perovskite Growth Drives Performance Enhancements in Lead Halide Perovskites Passivated with Bulky Iodide Salts, In Submission
# Table of Contents

## 1 Introduction

1. 1. Global Warming ........................................................................................................... 2
1. 2. Solar Energy .................................................................................................................... 3
1. 3. Solar Harvesting: Inspiration from Nature ....................................................................... 4
1. 4. Photovoltaic Energy Conversion ......................................................................................... 6
   1. 4. 1. First-Generation Solar Cells .................................................................................. 6
   1. 4. 2. Second-Generation Solar Cells ............................................................................ 6
1. 5. Perovskite Solar Cells .................................................................................................... 8
   1. 5. 1. Perovskite Solar Cell Architecture ........................................................................ 9
      1. 5. 1. 1. nip Perovskite Solar Cells ........................................................................... 9
      1. 5. 1. 2. pin Perovskite Solar Cells ......................................................................... 10
   1. 5. 2. Perovskite Active Layer ......................................................................................... 10
      1. 5. 2. 1. Methylammonium Lead Triiodide ................................................................. 10
      1. 5. 2. 2. Mixed ion Perovskites .............................................................................. 13
      1. 5. 2. 3. Layered Perovskites ................................................................................ 14
   1. 5. 3. Charge Transfer Mechanism in Perovskite Solar Cells ........................................ 16
1. 6. Challenges Facing Perovskite Solar Cells ..................................................................... 20
   1. 6. 1. Toxicity ................................................................................................................... 20
   1. 6. 2. Stability of MAPbI$_3$ and related perovskites ...................................................... 21
      1. 6. 2. 1. Ion Migration and J-V Hysteresis ................................................................ 21
      1. 6. 2. 2. Oxygen-Mediated Degradation .................................................................. 22
   1. 6. 3. Efficiency in MAPbI$_3$-based solar cells ............................................................. 23
      1. 6. 3. 1. Open-Circuit Voltage ............................................................................... 23
1. 7. In the Next Chapters ..................................................................................................... 25
1. 8. References ...................................................................................................................... 26

## 2 Experimental Materials & Methods

2. 1. Sample Preparation ....................................................................................................... 41
   2. 1. 1 Materials ................................................................................................................ 42
   2. 1. 2. Preparation of Perovskite layer ........................................................................... 42
      2. 1. 2. 1. Methylammonium lead triiodide ................................................................. 42
      2. 1. 2. 2. Cs-FA-MA “Triple-Cation” perovskite ......................................................... 42
3. Effect of Interfacial Energetics on charge transfer to organic charge transport layers 67

3.1. Abstract .................................................................................................................68
3. 2. Introduction ........................................................................................................... 69
3. 3. Materials & Methods .......................................................................................... 71
   3. 3. 1. Sample and Device preparation ................................................................. 71
   3. 3. 2. Characterisation techniques ...................................................................... 72
3. 4. Results .................................................................................................................. 73
   3. 4. 1. Interfacial Energetics .............................................................................. 73
   3. 4. 2. Transient Absorption Spectroscopy .......................................................... 75
   3. 4. 3. Steady-State Photoluminescence ............................................................... 78
   3. 4. 4. Time-Resolved Photoluminescence ............................................................ 81
   3. 4. 5. Overview of Charge Transfer Dynamics in the TiO₂|MAPbI₃|HTL System .... 84
   3. 4. 6. Consistency with Other Perovskite Systems ............................................ 86
3. 5. Implications for Device Design ........................................................................ 88
3. 6. Conclusions and Outlook ................................................................................... 90
3. 7. References ......................................................................................................... 92

4 Passivation of Perovskite Surfaces with Bulky Iodide Salts for Enhanced Efficiency & Stability

4. 1. Abstract .............................................................................................................. 102
4. 2. Introduction ....................................................................................................... 103
4. 3. Materials & Methods ...................................................................................... 104
   4. 3. 1. Sample Preparation .................................................................................. 104
   4. 3. 2. Device Fabrication .................................................................................... 105
   4. 3. 3. Superoxide Measurements ..................................................................... 106
   4. 3. 4. Ageing Conditions .................................................................................... 106
   4. 3. 5. Spectroscopy & Diffraction .................................................................... 106
4. 4. Results .............................................................................................................. 107
   4. 4. 1. Film Characterisation .............................................................................. 107
   4. 4. 2. Hole injection at the MAPbI₃|(PEA)₂MAₓ₋₃PbₓI₃₋₁|HTL Interface ............ 113
4. 5. Implications for Device Design ........................................................................ 119
4. 6. Mechanism of PhEtNH₂| Passivation .............................................................. 121
4. 7. Conclusions & Outlook .................................................................................. 123
4. 8. References ..................................................................................................... 124

5 Passivation-Mediated Charge Transfer at Lead Halide Perovskite Heterojunctions

5. 1. Abstract ............................................................................................................ 132
5. 2. Introduction ..................................................................................................... 133
5. 3. Materials & Methods .................................................................................... 134
List of Figures

Figure 1-1: World energy consumption (total: 583.90 EJ) by fuel and average CO₂ emissions per capita by country (tonnes per year).

(2)

Figure 1-2: Comparison of cumulative grid connected capacity of solar PV with the total costs for PB installation and fossil fuels.

(4)

Figure 1-3: Illustration of natural photosynthesis, artificial photosynthesis and photovoltaics.

(5)

Figure 1-4: Schematic illustrating the operating mechanism of a dye-sensitized solar cell (DSSC)

(7)

Figure 1-5: Schematic illustrating some of the different material properties of perovskite solar cells

(9)

Figure 1-6: Perovskite crystal structure, trap formation energies and ionisation levels.

(11)

Figure 1-7: Demonstration of band-gap tunability from UV-Vis spectroscopy in MAPb(IₓBr₁₋ₓ)₃ films.

(13)

Figure 1-8: Structure and charge transport in (RA)₂MAₙ₋₁PbₙI₃n+₁ layered perovskites.

(15)

Figure 1-9: Illustration of the key kinetic processes governing charge extraction and recombination at the electron transport layer|perovskite and perovskite|hole transport layer interfaces.

(16)

Figure 1-10: Illustration of (a) trap-mediated, (b) radiative and (c) Auger recombination. (d) Recombination rate as a function of carrier density in MAPbI₃.

(17)

Figure 1-11: (a) Schematic illustrating adiabatic electron transfer and the Marcus inverted region.

(19)

Figure 1-12: Summary of key processes involved in ion migration.

(22)

Figure 1-13: Schematic illustrating the reaction of O₂ with MAPbI₃.

(22)
Figure 1-14: Progress towards the radiative limit of $V_{OC}$ in perovskite solar cells (PSCs) and schematic illustrating $V_{OC}$ loss pathways.

Fig 2-1: Schematic illustrating the make-up of a typical $nip$ film used for the spectroscopic investigations in this thesis.

Fig 2-2: Schematic illustrating the make-up of a typical $pin$ film used for the spectroscopic investigations in this thesis.

Fig 2-3: Schematic outlining the scattering processes at the sample surface in an absorption spectroscopy measurement.

Fig 2-4: Extinction coefficient of MAPbI$_3$ in the visible range. Inset describes the attenuation of the excitation beam in the MAPbI$_3$ layer.

Fig 2-5: Schematic illustrating the rough time scale of photoinduced processes in perovskite solar cells. The electron and hole recombination processes relevant to $\mu$s-TAS are highlighted.

Fig 2-6: Microsecond transient absorption spectroscopy set-up.

Fig 2-7: Example transient absorption spectroscopy trace for a TiO$_2$|MAPbI$_3$|PTB1 film. The relative injection yield, $\Delta O_{D_{max}}$ and recombination time, $\tau_{rec,h}$ are indicated. (b) absorptance of our 400 nm MAPbI$_3$ film.

Fig 2-8: (a) Transient spectrum as a function of time for a TiO$_2$|MAPbI$_3$|F8T2 film pumped at 510 nm (fluence: 10 $\mu$J cm$^{-2}$). (b) The simple 2D spectrum taken at $10^{-6}$ s for the same sample.

Fig 2-9: Schematic demonstrating how electronic processes in the sample translate to photoinduced absorption (PIA) & ‘bleaching’ in the transient absorption spectrum.

Fig 2-10: An example measurement of the recombination rate constant, $k_{rec,h} = 1/\tau_{rec,h}$ for a TiO$_2$|perovskite|P3HT film (perovskite = MAPbI$_3$, BA$_{0.09}$MA$_{0.91}$PbI$_3$).

Fig 2-11: Photoluminescence (PL) spectroscopy set-up.

Fig 2-12: Comparison of MAPbI$_3$ and BA$_{0.09}$MA$_{0.91}$PbI$_3$ photoluminescence, excited at 510 nm.
Fig 2-13: Photoluminescence spectra of MAPbI₃ and MAPbI₃|PTB1. Inset: schematic describing the key kinetic processes occurring in the MAPbI₃|PTB1 film: radiative recombination (\(k_r\)); non-radiative recombination (\(k_{nr}\)); and injection (\(k_{inj}\)).

Fig 2-14: Time-Correlated Single Photon Counting Set-Up.

Fig 2-15: (a) Schematic outlining the key kinetic processes occurring in time-correlated single photon counting experiments and this technique is used to understand passivation and interfacial injection.

Fig 2-16: Example J-V curve for an ITO|SnO₂|MAPbI₃|PTAA|Au device.

Fig 2-17: Example of intensity dependent \(J_{SC}\) and \(V_{oc}\) measurements for an ITO|SnO₂|MAPbI₃|PTAA|Au device.

Fig 2-18: Illustration of the architecture of an X-ray photoelectron spectroscopy measurement.

Fig 2-19: Schematic illustrating interference of light fringes between two crystal planes distance, \(d\) apart (for X-ray diffraction).

Fig 3-1: Relation of the interfacial energy offset, \(\Delta E\) between the highest occupied molecular orbital (HOMO) of the hole transport layer & the valence band of MAPbI₃ and the quasi-Fermi level splitting (QFLS) at a perovskite|HTL heterojunction.

Fig. 3-2: (a) Structures of all polymeric HTLs used herein.

Fig. 3-3: Transient absorption spectra of Al₂O₃|MAPbI₃, TiO₂|MAPbI₃, Al₂O₃|MAPbI₃|HTL and TiO₂|MAPbI₃|HTL films.

Fig 3-4: (a) Contour plot depicting the decay of the TiO₂|MAPbI₃|F8T2 TA spectrum. b) TAS decay kinetics for TiO₂|MAPbI₃|HTL samples. (c) Interfacial recombination time, \(\tau_{rec,h}\) extracted from the TiO₂|MAPbI₃|F8T2 spectrum in the F8T2⁺ and TiO₂⁻ regions of the spectrum. (d) Maximum of TAS trace, \(\Delta OD_{max}\) as a function of \(\Delta E\).

Fig 3-5: Steady-state photoluminescence spectra for MAPbI₃ and MAPbI₃|HTL films. (b) Effect of \(\Delta E\) on the quenching efficiency, \(\eta\). Fitted lines indicate the inhomogeneous model calculations for \(\sigma = k_bT\) and \(\sigma = 1.2\ eV\).
Fig 3-6: (a) Photoluminescence (PL) decay kinetics for MAPbI$_3$ and MAPbI$_3$|HTL films. (b) hole injection time constant, $\tau_{inj}$, for MAPbI$_3$|HTL samples as a function of $\Delta E$.

Fig 3-7: PL decay kinetics for MAPbI$_3$|PTAA samples in which the MAPbI$_3$ layer was treated with increasing [PhEtNH$_3$I].

Fig 3-8: Summary of calculated and literature time constants at TiO$_2$|MAPbI$_3$|HTL interfaces.

Fig 3-9: Time-resolved single photon counting (TCSPC) traces for a MAPbI$_3$ (black) and Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$PbI$_3$ (red) film. Films were excited at 635 nm and probed at 760 nm to capture the MAPbI$_3$ emission.

Fig 3-10: Comparison of injection and recombination at the perovskite|HTL interface (perovskite = MAPbI$_3$, Cs$_{0.5}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$PbI$_3$).

Fig 3-11: Summary of experimental and literature values for the band-gap normalised $V_{oc}$ ($qV_{oc}/E_g$) versus $\Delta E$.

Fig 4-1: Schematic describing the concept of MAPbI$_3$ passivation with bulky iodide salts.

Fig 4-2: Effect of CH$_3$NH$_3$I and PhEtNH$_3$I passivation on stability and charge generation in MAPbI$_3$.

Fig 4-3: Relative hole injection yield from MAPbI$_3$ to PTPD after treatment of MAPbI$_3$ with and without various bulky iodide salts.

Fig 4-4: Evidence for 2D layer formation after treatment of MAPbI$_3$ with PhEtNH$_3$I.

Fig 4-5: Assignation of the MAPbI$_3$:PhEtNH$_3$I transient absorption spectrum, including further proof for 2D layer formation.

Fig 4-6: Hole injection in MAPbI$_3$:PhEtNH$_3$I|HTL films investigated by transient absorption and time-correlated single photon counting.

Fig 4-7: Illustration of the two possible mechanisms for hole injection at the MAPbI$_3$:PhEtNH$_3$I|HTL interface. (i) Mediated hole injection; (ii) tunnelling injection.
Fig 4-8: Ultrafast transient absorption spectroscopy of MAPbI$_3$ versus MAPbI$_3$:PhEtNHI.

Fig 4-9: Model of charge injection at the MAPbI$_3$:PEA$_2$Pb$_4$ interface.

Fig 4-10: Device characterisation of efficiency and stability of FTO$|$compact-TiO$_2$$|$mesoporous-

Fig 4-11: Proposed mechanism for PhEtNHI passivation.

Fig 5-1: Chemical structures and highest occupied molecular orbital energies of PTAA, PTPD and

Fig 5-2: Evidence for passivation of MAPbI by charge transport layers.

Fig 5-3: Comparison of the PL decay dynamics for MAPbI$_3$ and MAPbI$_3$:3-Hexylthiophene films.

Fig 5-4: C 1s, N 1s and S 2p X-Ray Photoelectron spectra of MAPbI$_3$$|$HTL (HTL = PTAA, PTPD, P3HT) films.

Fig 5-5: An example set of TAS traces for a TiO$_2$|MAPbI$_3$|PTPD sample where the excitation fluence

Fig 5-6: Relative hole injection yield, $\Delta D_{max}$ versus the initial carrier density, $n_0$ in the MAPbI$_3$ layer

Fig 5-7: Relative hole injection yield, $\Delta D_{max}$, as a function of the initial carrier density, $n_0$ in the

Fig 5-8: (a) Interfacial recombination time, $\tau_{rec,h}$ and (b) rate, $k_{rec,h}$ as a function of the initial carrier-

Fig 5-9: Relative hole injection yield, $\Delta D_{max}$ versus the recombination time, $\tau_{rec,h}$ for all MAPbI$_3$$|$HTL

Fig 5-10: Model of charge injection at the MAPbI$_3$:PEA$_2$Pb$_4$ interface.

Fig 5-11: Proposed mechanism for PhEtNHI passivation.
Fig 5-10: Steady-state photoluminescence spectra for MAPbI₃ and BA₀.₀₉MA₀.₉₁PbI₃.

Fig 5-11: Effect of perovskite trap density on hole injection. (a-c) Relative hole injection yield, $\Delta OD_{max}$, as a function of the initial carrier density, $n_0$ in the MAPbI₃ layer for TiO₂|MAPbI₃|HTL and TiO₂|BA₀.₀₉MA₀.₉₁PbI₃|HTL films (HTL = PTAA, PTPD or P3HT).

Fig 5-12: Interfacial recombination rate constant, $k_{rec,h}$ taken as $1/\tau_{rec,h}$ as a function of initial carrier density in the perovskite layer, $n_0$ for perovskite|P3HT (perovskite = MAPbI₃, BA₀.₀₉MA₀.₉₁PbI₃) films.

Fig 5-13: Characterisation of ITO|SnO₂|MAPbI₃|HTL|Au (HTL = PTAA, P3HT) devices: (a) current-voltage (J-V) characteristics of a doped PTAA-based device. (b) J-V characteristics of undoped devices containing PTAA, PTPD and P3HT. Intensity dependence of (c) the short-circuit current ($J_{SC}$) and (d) the open-circuit voltage ($V_{OC}$).

Fig 5-14: Extension to other HTLS. (a) The chemical structures of PTB1 and spiro-OMeTAD. Dependence of the (b) recombination rate constant, $k_{rec,h}$ and (c) relative hole injection yield, $\Delta OD_{max}$ as a function of the initial carrier density, $n_0$ in the MAPbI₃ layer. Inset: DFT-calculated highest occupied molecular orbital (HOMO) map of spiro-OMeTAD.

Fig 5-15: (a-b) Relative hole injection yield, $\Delta OD_{max}$ as a function of the initial carrier density, $n_0$, in the MAPbI₃ layer for nip (TiO₂|MAPbI₃|HTL) and pin (HTL|MAPbI₃|PCBM) films (HTL = PTAA & P3HT).

Fig 5-16: (a) Structures of the PCBM, IPH and PTEG and their associated energetics. (b-d) transient absorption spectra of MAPbI₃|ETL (ETL = PCBM, IPH, PTEG) films.

Fig 5-17: The recombination rate, $k_{rec,h}$ for injected electrons in MAPbI₃|ETL films (ETL = PCBM, IPH, PTEG), as a function of the initial carrier density in the MAPbI₃ layer, $n_0$. 

Fig 5-18: Electron transfer yield (%) as a function of irradiance for MAPbI₃|ETL (ETL = PTEG, IPH, PCBM) films. 1 Sun is indicated by the red line.
List of Tables

Table 3-1: Reference ($E_n$) and mean ($E_{HOMO/VB}$) energies for the MAPbI$_3$ valence band edge and HTL HOMO.

Table 3-2: Summary of the biexponential fitting ($y(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$) for the PL decay of MAPbI$_3$ and MAPbI$_3$|HTL films in Fig 3-6a.

Table 3-3: Bi-exponential fitting parameters for time-resolved single photon counting (TCSPC) traces in Fig. 3-7b. The half-life of the unquenched MAPbI$_3$:PhEtNH$_3$I film, $\bar{\tau}_{rec,M}$ is also given for reference.

Table 3-4: Summary of the key results found for the MAPbI$_3$|HTL samples investigated: PL quenching efficiency, $\eta$, TAS injection yield, mΔOD$_{max}$, injection time, $\tau_{inj}$ and interfacial recombination time, $\tau_{rec,h}$.

Table 4-1: Biexponential fitting ($y(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$) parameters for the time-resolved single photon counting (TCSPC) decays given in Fig.6c-e. We note that $\tau_1 = \tau_{inj}$ for HTL-coated samples.

Table 4-2: Initial device performance parameters of FTO|compact-TiO$_2$|mesoporous-TiO$_2$|perovskite (iodide salt)|spiro-OMeTAD|Au devices based on various concentrations of PhEtNH$_3$I coated on MAPbI$_3$ perovskite films.

Table 5-1: Parameters from XPS spectra. Binding energies ($E_b$) are for N 1s (PTAA and PTPD) and S 2p$_{3/2}$ (P3HT). $\Delta E_b$ is the difference between $E_b$ measured for the 30 nm and < 10 nm films.

Table 5-2: J-V parameters for the ITO|SnO$_2$|MAPbI$_3$|HTL|Au (HTL = P3HT, PTAA) cells in Fig 5-13.
Chapter 1

Introduction
1. 1. Global Warming

At present, annual world primary energy consumption is close to 584 exajoules, with carbon-based sources, i.e. coal, oil and natural gas, accounting for 84% (492.34 EJ) of the total (Fig 1-1, top panel).\(^1\) The associated trajectory of greenhouse gas emissions and global warming could see Arctic permafrost eradicated by 2050\(^2\) and glacial ice in the Himalayas cut to just two thirds by 2100.\(^3\) Besides disruption to the two billion users of Himalayan water stores,\(^3\) this would have several catastrophic global impacts: (i) melting land ice will cause sea levels to rise, putting low-lying areas at risk;\(^4\) (ii) loss of arctic and glacial permafrost will lower the Earth’s albedo – essentially reflectivity – inducing a positive feedback loop of further warming;\(^5\) (iii) disruption of the Atlantic Meridional overturning circulation (AMOC) current has already begun to induce extreme weather in Western Europe and will intensify as the ice caps continue to melt.\(^6\) Ironically, these impacts disproportionately affect the Global South where 840 million people still do not have access to electricity.\(^7\) Indeed, Fig 1-1 (bottom panel) demonstrates the clear disparity between the Global North and South on CO\(_2\) emissions.

Fig 1-1: World energy consumption (total: 583.90 EJ) by fuel. Source: BP Statistical review, 2020.\(^1\) Average CO\(_2\) emissions per capita by country (tonnes per year). Source: OWID based on CDIAC; Global Carbon project; Gapminder & UN; OurWorldInData.org/co2-and-other-greenhouse-gas-emissions/• CC-BY.
World leaders responded to this crisis in 2015 with the Paris agreement, pledging to halt global warming ‘to well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C’. This goal represents the level of climate change that governments agreed would mitigate the worst effects of global warming, while minimising harm to world economies and food production. The agreement has galvanized some promising signs, with the UK, California and 75 other parties committing to carbon neutrality before 2050. However, over the last five years, nations have consistently failed to meet emissions targets that were arguably already too lax to satisfy the Paris Agreement. Consequently, in order to satisfy the Paris Agreement, CO₂ emissions must be cut by 46% over the next decade on current levels, which amounts to a staggering 19 EJ hole in world energy production. Moreover, world energy consumption is expected to increase by 28% over the next twenty years with much of the growth coming from developing countries according to the US Energy Information Administration. Therefore, a complete overhaul of the world energy paradigm is required in order to solve this paradox.

1. 2. Solar Energy

Solar energy perhaps offers one of the most viable alternatives to fossil fuels, as the sun beats down around 417 EJ of energy to the Earth’s surface every year and will continue to do so for the next five billion years. Therefore, enough solar energy is incident on the Earth’s surface in 17 days to fill the 19 EJ gap in energy production required to satisfy the IPCC’s scenario for limiting global warming to 1.5 °C. Furthermore, solar power is far more versatile than the traditional coal power plant allowing for large centralized farms or de-centralized rooftop panels. This opens up the possibility of electrifying even the most rural communities that cannot be reached by conventional grid systems. However, for wide-scale use to be economically viable, installation costs must be competitive with fossil fuels.

It is encouraging then that solar is the leading source of renewable energy in terms of investments, with $133.5 billion injected into the market last year. This is largely due to the plummeting cost of module prices, plant costs and installation fees for photovoltaics, the largest sub-sector across the renewable sector (Fig 1-2, purple circles). Notably, the total

* Intergovernmental panel on climate change (IPCC) have stated that CO₂ emissions must be cut by 41% on 2010 over the next decade to meet the 1.5 °C target. Based on BP figures for that year (31086 x 10⁹ Kg) and this year (34169 x 10⁹ Kg), this amounts to an overall reduction in CO₂ emissions of 15829 x 10⁹ Kg. Assuming energy production is the primary target of reducing emissions and considering current usage of natural gas, coal and oil and their respective CO₂ conversion coefficients (0.184, 0.322, 0.268 Kg CO₂ (kWh)⁻¹; Carbon Trust), this amounts to a 19 EJ reduction in world energy production.
installed cost per kWh for solar PV generation are now competitive with conventional fossil fuels (Fig 1-2).

Although solar power only makes a modest contribution (1.2%) to world power generation at present, it is the fastest growing renewable energy sector (Fig 1-2, 24.3% per year). Countries in the Global South have demonstrated the most rapid growth, with heavy investments from China, India and Brazil while the NOORo solar thermal farm project is set to contribute 300 MW to Morocco’s plans for 50% clean energy production by 2050. This is a promising sign as mitigating global warming will rely heavily on low-carbon economic growth in the Global South.

![Cumulative grid connected capacity of solar PV (bar chart, left axis) overlaid with the global weighted average total costs for PV installation (purple circles, right axis). The purple shaded area indicates the fossil fuel cost range (right axis). Source: IRENA, 2019 (CC-BY).](image)

**Fig 1-2: Cumulative grid connected capacity of solar PV (bar chart, left axis) overlaid with the global weighted average total costs for PV installation (purple circles, right axis). The purple shaded area indicates the fossil fuel cost range (right axis). Source: IRENA, 2019 (CC-BY).**

### 1. 3. Solar Harvesting: Inspiration from Nature

In answer to the question of how to harness this unlimited source of energy, scientists have historically turned to nature. In particular, plants have developed sophisticated solar harvesting mechanisms through millions of years of natural selection. In green plants, natural photosynthesis (NPS) is described by the Z-scheme, presented in Fig 1-3a. Briefly, chloroplasts absorb light via photosystem II (PS II), which results in the formation of an electron-hole pair. The holes are then used to oxidise water into molecular oxygen in the oxygen evolving centre (OEC). Meanwhile, the electrons are transported through a second photosystem (PS I) where they catalyse the conversion of CO₂ to various carbohydrates.
Fig 1-3: Natural and Artificial light harvesting systems. (a) Z-scheme for natural photosynthesis. (b) operation of an artificial water-splitting device. (c) operation of an artificial solar cell device. Modified with permission from [20].

Aspects of NPS were first used by Fujishima and Honda to kick-start the field of artificial photosynthesis (APS) in 1971, using photoinduced holes on TiO₂ to drive the production of H₂ fuel from water (“water splitting”, Fig 1-3b). Since then, APS has blossomed into an active field of research, with solar fuel production being demonstrated in other metal oxides, dyes and semi-artificial systems involving PS II.

However, solar-driven water-splitting is not without its disadvantages. Many of its limitations stem from the fact that multiple energy conversion processes (e.g. light to electron, electron to H₂) must be achieved for them to function. In particular, the oxidation and reduction reactions required to form H₂ are:

\[
2H_2O + 4h^+ \rightarrow O_2 + 4H^+, \quad E_{ox}^0 = -1.23 \text{ V vs NHE} \tag{1.1}
\]

\[
4H^+ + 4e^- \rightarrow 2H_2, \quad E_{red}^0 = 0 \text{ V vs NHE} \tag{1.2}
\]

Where \(E_{ox}^0\) and \(E_{red}^0\) are the standard potential versus a standard hydrogen electrode (NHE). It is noteworthy that four holes are required to produce two H₂ molecules, making the reaction energetically costly, as implied by the large, 1.23 V potential barrier to drive equation 1.1. This sets a theoretical limit to the performance of water splitting devices,
depending on their band-gap e.g. 15.4% for state-of-the-art $\alpha$-Fe$_2$O$_3$, without taking into account inevitable losses associated with light absorption, charge separation and interfacial injection processes.$^{24}$

1.4. Photovoltaic Energy Conversion

Photovoltaic energy conversion provides a more direct path to solar power generation. As outlined in Fig 1-3c, electron-hole pairs are separated via layered architectures, similar to NPS. However, rather than being stored as fuel, the generated charges are immediately extracted to the external circuit. Although the immediacy of this process means that power generation is at the whim of the variations in incident light – e.g. cloud cover, day/night, seasonal - and therefore macroscale implementation must rely on high energy density battery storage, much larger efficiencies (e.g. 33%) are possible with this simplified harvesting mechanism.

1.4.1. First-Generation Solar Cells

The photovoltaic effect was first discovered by Alexandre-Edmond Becquerel in 1839, through his experiments on platinum electrodes in electrolyte solutions under solar illumination.$^{25}$ It wasn’t until 1954, however, that Bell laboratories achieved the first efficient 6% power conversion efficiency (PCE) - solar cells using silicon,$^{26}$ kick-starting the contemporary field of solar cell research. Since then, three key types of silicon cell have emerged: high-cost monocrystalline Si (record research efficiency 26.1 %), slightly cheaper polycrystalline (23.3%) & “heterojunction with intrinsic thin layer” (HIT) (26.7%) Si; and relatively cheap amorphous Si:H (14.0 %)$^{27}$ While crystalline silicon cells represent 85% of the commercial market, efforts are underway to advance the cheaper alternatives. The first-generation concept has extended to encompass other photovoltaics including gallium arsenide (GaAs; 29.1%)$^{27}$ indium phosphide (InP; 24.2%)$^{28}$ and gallium indium phosphide (GaInP, 22.4 %).$^{29}$ However, their extremely high production costs make them suitable mainly for concentrator and space applications.$^{30}$

1.4.2. Second-Generation Solar Cells

Motivated by the high cost of commercial Si solar cells at the time (10 times that of conventional power sources), in 1991 O’Reagan and Grätzel developed the first efficient (8%) dye-sensitized solar cells (DSSCs).$^{31}$ Notably, this was achieved with cheap, Earth abundant materials. As we showed in Fig 1-2, since then the cost of Si-based PV (0.7 USD/kWh) has become competitive with fossil fuels in certain countries (0.05 – 0.17 USD/kWh).$^7$ Nevertheless, in a paper that has been cited over 30,000 times, O’Reagan and
Grätzel seeded the growth of numerous 2nd generation PV technologies, which have several unique advantages over their predecessors. 2nd generation photovoltaics are often compatible with low temperature processing and thus lightweight, flexible plastic substrates. This produces a wider range of deployment settings (e.g. cars, weak roofs) and cheaper manufacturing processes (e.g. roll-to-roll). Moreover, the strong absorption coefficient ($\varepsilon \sim 10^5 \text{cm}^{-1}$) and tunability across the visible spectrum commonly exhibited by this class of materials, makes them more suited to application as semi-transparent windows than e.g. silicon cells ($\varepsilon \sim 10^4 \text{cm}^{-1}$), which are often hidden away on rooftops due to their opacity and unattractive blue hue. The more appealing aesthetics of 2nd generation materials open up an opportunity for greater coverage of buildings (i.e. facades as well as roofs) and thus additional solar harvesting.\textsuperscript{32–34}

![Diagram](image)

**Fig 1-4:** Schematic illustrating the operating mechanism of a dye-sensitized solar cell (DSSC). (a) Illustration of cell architecture. (b) Energetic scheme at the TiO$_2$|dye|electrolyte interface. Adapted with permission from [31] and [35].

The operating mechanism of a DSSC is outlined in Fig 1-4. The mesoporous titanium dioxide (TiO$_2$) layer (thickness $\sim 10 \mu$m) provides the electron conducting skeleton for the device. This layer is deposited on a transparent conducting oxide (TCO) such as fluorine-doped tin oxide (FTO). Sunlight is then allowed to enter the device and excite an ultrathin layer of dye, which is anchored to the TiO$_2$ surface. Photoexcitation of the dye produces an electron-hole pair, which is quickly separated by electron injection from the lowest occupied molecular orbital (LUMO) of the dye into the TiO$_2$ conduction band. The remaining hole in the highest occupied molecular orbital is then reduced after electron transfer from the iodide/triiodide ($I^-/I_3^-$) redox electrolyte. The I$_3^-$ ions formed after oxidation of I$^-$ diffuse 50 $\mu$m through the electrolyte to the cathode, where the platinum catalyst reduces I$_3^-$ back to I$^-$.\textsuperscript{35}

Although the efficiency of DSSCs has remained fairly modest (record, 13%),\textsuperscript{36} this concept has inspired a number of other efficient solar cell systems with different sensitizers: quantum dots (QDSCs, 16.6%),\textsuperscript{37–39} CZTSSe (12.6%)\textsuperscript{27} and organic polymer blends (OSCs, 17.6%).\textsuperscript{40}
While OSCs in particular hold great commercial promise on account of their excellent cost to efficiency ratio, they are beyond the scope of this thesis. We point the interested reader to review articles outlining their fundamental spectroscopy, solar cell design and stability for more information.41–43

1. 5. Perovskite Solar Cells

Perhaps the most promising second-generation photovoltaic technology is perovskite solar cells (PSCs), which have rapidly developed from 3% to 25.2% PCE over the last decade,27,44 a remarkable achievement considering they are radiatively limited to 30% (Figure 1-5a). PSCs were first established practically by Tsutomu Miyasaka in 2009,44 building on a number of pioneering fundamental studies that revealed their high conductivity and unique optical properties.45–49

This early PSC prototype, where the only deviation from Grätzel’s DSSC was the replacement of the sensitizer dye with methylammonium lead triiodide (MAPbI$_3$), achieved a respectable 3.81%.44 However, hole transport was still conducted via a liquid electrolyte meaning that device performance was degraded in minutes. These issues were alleviated in 2012 by the incorporation of solid-state HTLs.50–53 This sparked great excitement within the area of second-generation photovoltaics as it was quickly found that relatively stable PSCs could be deployed using the cheap solution process of DSSCs, but with much enhanced semiconductor properties, outlined in the following.

In a landmark study, Stranks et al found that the electron-hole diffusion length in MAPbI$_3$ and related perovskites can be as high as 1 µm.54 In parallel, Xing et al showed that such transport is independent of the charge carrier, with both electrons ($L_D = 130$ nm) and holes ($L_D = 110$ nm) having similar diffusion lengths, $L_D$.55 The implied excellent charge transport properties can be traced back to the remarkably low rate of non-radiative recombination of photogenerated carriers. Moreover, the mobility of hybrid organic-inorganic perovskites is also high, which can be attributed in part to the steep dispersion of their electronic band-structure and the associated low effective mass of electrons and holes (Fig 1-5b).56–59

Additionally, MAPbI$_3$ and related perovskites have a low exciton binding energy ($E_b = 16$ meV) on account of their large dielectric constant, such that charge transport is dominated by free-carriers at room temperature (Fig 1-5c).60–63 Finally, unlike silicon semiconductors, which have an indirect band-gap, the absorption transition in PSCs is direct, more akin to GaAs. This results in a large extinction coefficient ($\sim 10^5$ cm$^{-1}$).64 Important design outcomes of this are that PSCs are generally thin (> 1 µm) and can also be made to be semi-transparent (Fig 1-5d).55–68
Fig 1-5: (a) Shockley-Queisser limit to solar cell efficiency as a function of band-gap in relation to the AM 1.5 solar spectrum. Top efficiencies for MAPbI$_3$ (red star), gallium arsenide (GaAs, green square) and crystalline silicon (c-Si, purple circle) also shown. (b) illustration of perovskite band-structure indicating the relation between dispersion and effective mass. (c) illustration of thermalisation of free-carriers from excitons in MAPbI$_3$. (d) Comparison of extinction coefficient of MAPbI$_3$ (red), GaAs (green) and c-Si (purple). (e-g) Perovskite solar cell mesoscopic (e), planar (f) and nip (g) architectures. (g) also shows an example of a flexible perovskite solar module, made possible by the low-temperature compatibility of the pin architecture. (a), (b) and (d, left panel) were reprinted with permission from [111]; (d, right panel) from [66]; and (g, top panel) from [65].

1.5.1. Perovskite Solar Cell Architecture

1.5.1.1. nip Perovskite Solar Cells

As a consequence of these remarkable properties, the architecture of PSCs started to evolve from that of their DSSC predecessors. Firstly, the high charge-carrier mobility of the perovskite meant that thicker layers could be used, such that the perovskite fills the mesoporous TiO$_2$ but also leaves a capping layer of pure perovskite between the TiO$_2$ and HTL. This ‘mesoscopic’ architecture is presented in Fig 1-5e. Moreover, Lee et al showed...
that mesoporous, insulating Al₂O₃ provides an effective support for PSCs, where the electron transport is carried by the MAPbI₃ layer itself.⁶⁹

Secondly, the high mobility of the perovskite layer means that the requirement for a mesoscopic framework can be relaxed completely to make planar PSCs (Fig 1-5f). A number of other metal oxides e.g. ZnO (E₉ = 3.3 eV)⁷⁰ and SnO₂ (E₀ = 3.6 eV)⁷¹ as well as planar (anatase) TiO₂ (E₉ = 3.2 eV)⁷² have been widely adopted in this architecture.⁵³,⁷³,⁷⁴ Of these, SnO₂ has the most favourable properties: (i) better conduction band alignment with MAPbI₃;⁷⁵ (ii) order of magnitude larger mobility relative to TiO₂; (iii) reduced parasitic absorption, which improves J_SC.⁷⁶

A wide selection of HTLs (commonly known by their abbreviations) have been developed for nip PSCs over the last decade including inorganics,⁷⁷–⁷⁹ small-molecules⁵³,⁸⁰,⁸¹ and polymers.⁸²–⁸⁶ The deployment of inorganic HTLs has so far been limited due to the partial dissolution of the MAPbI₃ layer with the required solvents. However, some success has been observed with CuSCN (18.57%)⁸⁷ and Cu₂O (13.4%).⁸⁸ On the other hand, numerous organic HTLs have been implemented in PSCs to yield efficiencies of larger than 20%, including: spiro-OMeTAD,⁸⁹ FDT,⁸⁰ PTAA,⁹⁰ and P3HT⁹¹ despite their generally lower mobility. This is partly thanks to effective p-doping strategies using additives such as LiTFSI,⁹² F4CTNQ⁹³ and FK209.⁹⁴ Remarkably, spiro-OMeTAD has remained the best-performing HTL since its first use in 2012. This has been attributed to its twisted spiro-centre that reduces the MAPbI₃/spiro-OMeTAD coupling and thus interfacial recombination.⁹⁵ We explore the role of state-of-the-art HTLs on charge injection yield and device performance in chapters 4 and 6.

1. 5. 1. 2. pin Perovskite Solar Cells

Finally, the architecture can be reversed such that the substrate becomes the transparent p-type CTL (e.g. PEDOT:PSS, PTAA, PTPD)⁹⁶–¹⁰⁰ with the perovskite active layer then being capped by the ETL (e.g. PCBM, C₆₀).¹⁰¹–¹⁰⁶ Such ETLs have the advantage of functioning without the large temperatures associated with the processing of TiO₂. This is what makes pin PSCs compatible with flexible substrates and more complex architectures e.g. tandem cells (Fig 1-5g).¹⁰⁷,¹⁰⁸ Thus far, the most promising candidate for mesoscopic inverted cells remains to be NiOₓ, with top efficiencies close to 17%.¹⁰⁹

1. 5. 2. Perovskite Active Layer

1. 5. 2. 1. Methylammonium Lead Triiodide

Hybrid organic-inorganic perovskites have formula ABX₃ where traditionally A (= CH₃NH₃⁺, HC(NH₂)₂⁺, Cs⁺) and B (= Pb²⁺, Sn²⁺) are cations and X (= Br⁻, Cl⁻, I⁻, SCN⁻) is an anion.
Additionally, double perovskites of formula $A_2B'B'^{III}X_6$ allow for exploration of a wider array of potential occupants of the B-site as one mono- and one tri-valent cation are used instead of two Pb$^{2+}$ or Sn$^{2+}$ ions.\textsuperscript{110–112} However, methylammonium lead triiodide (MAPbI$_3$) represents the simplest perovskite absorber that leads to high efficiency PSCs. Therefore, although multi-ion PSCs - e.g. (CsPbI$_3$)$_{0.05}$[(FAPbI$_3$)$_{0.83}$(MAPbBr$_3$)$_{0.17}$]$^{0.05}$ - produce higher efficiencies by alloying the A and X-site alloys, MAPbI$_3$ provides a simple archetypal perovskite with which to conduct fundamental studies. As such, it is the most widely studied perovskite absorber and is the most commonly referred to in this thesis.

![Diagram of MAPbI$_3$ structure and defect formation energies](image)

**Fig 1-6:** (a) The crystal structure of MAPbI$_3$. Defect formation energies (b) and ionisation levels (c) relative to the perovskite valence and conduction bands. Reprinted with permission from [123].

The structure of MAPbI$_3$ (Fig 1-6a) was first characterised by Weber et al in 1978.\textsuperscript{113} They found that MA$^+$ ions fill the interstitial space between eight corner-sharing PbI$_6$ octahedra. Moreover, the structure transforms from orthorhombic to tetragonal (161.4 K) to cubic (330.4 K) as a function of temperature. More recently, it has been shown that although MAPbI$_3$ is
nominally cubic (on average) above 330.4 K, the perovskite forms a tetragonal structure on sub-ps timescales relevant to light absorption.\textsuperscript{114}

Generally, the possibility of forming a cubic perovskite structure is determined by the Goldschmidt factor, $t$.

$$t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}$$  \hspace{1cm} (1.3)

where $r_A$, $r_X$ and $r_B$ are the radii of the A, X and B ions respectively, satisfies $0.8 < t < 1$.\textsuperscript{115,116} We note that a more careful revision of Equation 1.3 that reflects greater covalency in metal halide bonds was later developed by Travis \textit{et al.}\textsuperscript{117} By their method, the MAPbI\textsubscript{3} structure falls well within the acceptable range, with $t = 0.95$ (the value is 0.91 via the uncorrected method). However, the deviation to a significantly lower value than 1 means that there is a significant degree of octahedral distortion.\textsuperscript{118}

MAPbI\textsubscript{3} is formed after donation of three electrons from MA and Pb to I, forming MA\textsuperscript{+}, Pb\textsuperscript{2+} and 3I\textsuperscript{-}. The strong bonding in the PbI\textsubscript{6} octahedra dominates the formation of the electronic structure, with the valence band maximum (VBM) formed from a combination of Pb $s$ and I $p$ orbitals and the conduction band minimum (CBM) formed of empty Pb $p$ orbitals.\textsuperscript{47,119–121} This is in line with the formal electronic configuration: [Xe] 4f\textsuperscript{14} 5d\textsuperscript{10} 6s\textsuperscript{2} 6p\textsuperscript{2} of Pb. The dominance of I$^-$ in the VBM and Pb\textsuperscript{2+} in the CBM is evidence of the strong ionic character in this system.

The interruption of crystal symmetry at the film surface, grain boundaries and bulk defect sites can lead to the formation of trap-states. The formation energies and ionization levels of key defects in MAPbI\textsubscript{3} are given in Fig 1-6b and 1-6c respectively. Fig 1-6b suggests that traps associated with Pb, MA and I interstitials (Pb\textsubscript{i}, MA\textsubscript{i}, I\textsubscript{i}) and Pb vacancies are most prevalent, given their low formation energy. A significant density of iodide vacancies (V\textsubscript{I}) is also expected given that the formation energy in this case is only slightly higher.

As shown in Fig 1-6c, many of the most prevalent bulk defects in MAPbI\textsubscript{3} do not contribute directly to charge trapping as their energies lie close to or within the CB or VB.\textsuperscript{122} This may be due to the strong antibonding coupling between the fully occupied Pb $s$, and I $p$ orbitals, which makes the upper-valence bands dispersive. Moreover, many of the defects that could form deep traps (e.g. V\textsubscript{MA}, I\textsubscript{MA}) have relatively high activation energies (Fig 1-6b).\textsuperscript{122–124}

On the other hand, V\textsubscript{Pb} and I\textsubscript{i} present potential sites for charge trapping. However, V\textsubscript{Pb}(0/2-) and V\textsubscript{Pb}(-, 2-) require two holes to form and thus have a vanishingly small hole capture cross section, while V\textsubscript{Pb}(0/-) is inactive due to the instability of V\textsubscript{Pb} at the Fermi level (Fig 1-6b).
Therefore, given the combination of a low activation energy, relative stability and mid-band gap presence, $I^+$, $I^0$ and $I^-$ are the most common sources of trapping in MAPbI$_3$.\textsuperscript{123,124}

Chemically benign defects can also indirectly induce active defects such as $I^-$. A key example of this is iodide vacancies ($V_I$), which are generally thought to occupy electronic states close to or within the conduction band of MAPbI$_3$ and therefore should not contribute directly to charge trapping.\textsuperscript{119,124} However, in order to preserve charge neutrality in the presence of the positively charged $V_I$ sites, additional negatively charged defects must arise. This has been shown to lead to the formation of $I_I$ sites via Frenkel pairs, which form active traps within the band-gap.\textsuperscript{125}

1.5.2. Mixed ion Perovskites

Miyasaka showcased MAPbI$_3$ and its bromide containing counterpart MAPbBr$_3$ in the first practical PSC paper back in 2009. The lower efficiency from MAPbBr$_3$ (3.13 \%) compared to MAPbI$_3$ (3.81 \%) in that work follows from its wider band-gap (2.2 eV vs 1.6 eV), which is less suited to the solar spectrum (optimum 1.4 eV). In 2013, Noh et al. filled the gaps between these two types of perovskite, by characterising MAPb(I$_x$Br$_{1-x}$)$_3$.\textsuperscript{126} Moving from $x = 0$ to $x = 1$ increases the band-gap from around 1.6 to over 2.2 eV and tunes the colour from dark brown to yellow (Fig 1-7a and b).\textsuperscript{126} This is due to the smaller size of the Br ion, which shrinks the lattice constant and increases the dispersion of the electronic structure.\textsuperscript{49}

**Fig 1-7:** (a) Demonstration of band-gap tunability from UV-Vis spectroscopy in MAPb(I$_x$Br$_{1-x}$)$_3$ films and (b) their corresponding colours. Reprinted with permission from [126].
The A-cation has also been the subject of optimisation over the last decade, particularly given the thermal and chemical instability of the MA cation. This has led to the development of FAPbI$_3$-based PSCs, which have a narrower band-gap (1.48 eV) compared to MAPbI$_3$ (1.6 eV). This shift in band-gap occurs due to the reduction of octahedral character in the crystal ($t = 1.03$), that ultimately increases the I-Pb-I bond angle. As such, their band-gap is closer to the maximum of the solar spectrum (~1.4 eV) and the resultant enhanced light absorption leads to greater J$_{SC}$ (~26 mA cm$^{-2}$) than MAPbI$_3$-based cells (~23 mA cm$^{-2}$). However, purely FA-based perovskites must be stabilised with Cs (5 mol%) in order to ensure the formation of the photoactive $\alpha$-phase over the non-perovskite $\delta$-phase. Device performance has been improved further by the addition of other A cations including Rb, which was initially thought to intercalate into the perovskite structure despite its insufficient ionic radius to satisfy the Goldschmidt factor. However, recent work by Abdi-Jalebi et al on K$^+$ incorporation in perovskite absorbers, as well as studies conducted on Rb$^+$ and K$^+$ elsewhere, suggest that the addition of alkali metals smaller than caesium contribute to device performance via a passivation effect instead.

Critically, the ease and breadth of band-gap tunability in (Cs)FA$_{1-y}$MA$_y$Pb(I$_x$Br$_{1-x}$)$_3$ perovskites has opened the door for application in tandem with CIGS, other perovskites and silicon, where the top cell must have a wide band-gap ($E_g > 1.6$ eV) and silicon. Such cells hold great promise for over-30% efficient cells (current record 28%) in the near future and we point the reader to a review for more information on the topic.

1.5.2.3. Layered Perovskites

If bulkier A cations such as butylammonium (BAI) or phenethylammonium (PEAI) are used, formation of the 3D perovskite becomes sterically forbidden and instead layered (RA)$_2$A$_n$Pb$_n$I$_{3n+1}$ (n = number of layers) perovskites can be produced. Indeed, even ethylammonium iodide (EAI) is known to produce such layered structures making the window of suitable A-cations for the formation of 3D perovskites quite narrow.

This sub-set of perovskite structures was first explored by Mitzi et al in 1994. Generally, (RA)$_2$A$_{1-n}$B$_n$I$_{3n+1}$ layered perovskites consist of conducting A$_{1-n}$B$_n$I$_{3n+1}$ domains separated by insulating RA organic spacers (Fig 1-8a). Therefore, a 2D quantum well is formed with width increasing by ~12 Å for each integer increase in n. As such, upon decreasing the number of layers from n = $\infty$ to n = 1 the band-gap of MAPbI$_3$ shifts from 1.6 eV to 2.24 eV (Fig 1-7b) due to quantum confinement. Concomitant with this is an increase in exciton binding energy, moving from ~ 16 meV in MAPbI$_3$ to > 300 meV in (PEA)$_2$PbI$_4$, and a decrease in charge carrier mobility from 25 to 1 cm$^2$ V$^{-1}$ s$^{-1}$. 
Fig 1-8: Structure and charge transport in (RA)$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ layered perovskites. (a) illustration of the change in layered structure upon increasing n. (b) Charge transfer cascade mechanism. (c) Energy transfer from low n to high n perovskite.

On the other hand, stability improves dramatically as n decreases, which has been attributed to a six-fold reduction in the A-cation (e.g. MA) desorption rate, associated with the increased Van der Waal interactions from the bulky cations. Therefore, researchers have probed intermediate-n systems to learn the best trade-off between excellent electronic & photovoltaic properties and chemical stability. To this end, Quan et al found that the ideal balance between stability and photovoltaic performance should be found in the range, 40 < n < 60 through a combined DFT and experimental study.

This study inspired the more recent trend of 3D-2D perovskites, in which largely 3D perovskites with a small amount of 2D character have shown great promise. Indeed, in 2017 Grancini et al reported on 3D-2D (HOOC(CH$_2$)$_4$NH$_3$)$_2$PbI$_4$/MAPbI$_3$ perovskites that were stable for one year although less efficient than the MAPbI$_3$ control. Later that year, Wang et al demonstrated that the efficiency could also be improved with the 3D-2D concept, most likely due to mitigation of non-radiative recombination via passivation.

Finally, the energetic landscape at the 3D-2D graded interface is complex relative to purely 3D perovskite and only a few studies have addressed charge transfer in this system. Interestingly, mixed-n systems have been found to spontaneously separate electrons and holes given the decrease in both the CB and VB with n (Fig 1-8b). Moreover, energy transfer – where an electron-hole pair is transported through the film via photon emission
and reabsorption - between low-\( n \) and high-\( n \) regions is also possible (Fig 1-8c).\(^{161}\)

Therefore, despite these 3D-2D systems providing some of the best PSC efficiencies, more needs to be done to understand the fundamental mechanisms of charge separation for further optimisation. We document our contribution towards this goal in Chapter 5.

1.5.3. Charge Transfer Mechanism in Perovskite Solar Cells

**Fig 1-9:** Illustration of the key kinetic processes governing charge extraction and recombination at the electron transport layer|perovskite and perovskite|hole transport layer interfaces. (0) light absorption; (1) electron injection; (2) hole injection; (3) radiative recombination; (4) non-radiative recombination; back transfer of injected (5) electrons and (6) holes.

The charge transfer mechanism in PSCs was first elucidated in full by Marchioro et al.\(^{163}\) although many other studies have focused on this topic.\(^{164–169}\) Generally, electrons and holes are formed in the CB and VB after absorption of a photon with energy larger than the band-gap (Fig 1-9, 0). We present the main subsequent charge transfer processes at the ETL/perovskite/HTL interface in Fig 1-9. Interfacial charge injection ensues via:

\[
e^{-}\text{(perovskite)} \rightarrow e^{-}\text{(TiO}_2\text{)} \quad (i)
\]

\[
h^{+}\text{(perovskite)} \rightarrow h^{+}\text{(HTL)} \quad (ii)
\]

Meanwhile, electrons and holes in the perovskite layer can also recombine radiatively (iii) and non-radiatively (iv) through:

\[
e^{-}\text{(perovskite)} + h^{+}\text{(perovskite)} \rightarrow hv \quad (iii)
\]

\[
e^{-}\text{(perovskite)} + h^{+}\text{(perovskite)} \rightarrow \nabla \quad (iv)
\]

where \( \nabla \) and \( hv \) indicate the emission of heat or light after mono- or bimolecular recombination respectively. Finally, back electron or hole transfer of injected charges is also possible, i.e.:

\[
e^{-}\text{(TiO}_2\text{)} + h^{+}\text{(perovskite)} \rightarrow \nabla, hv \quad (v)
\]

\[
h^{+}\text{(HTL)} + e^{-}\text{(perovskite)} \rightarrow \nabla, hv \quad (vi)
\]
In section 1.5.3.1 and 1.5.3.2 we outline in detail the key parameters that determine the rates of recombination and interfacial injection.

1.5.3.1. Recombination

Recombination in the perovskite active layer can be modelled by the following rate equation:

\[- \frac{dn}{dt} = an + bn^2 + cn^3\]  

(1.4)

where \(n\) is the carrier density of free electrons or holes and \(a\), \(b\) & \(c\) are the first, second & third order rate coefficients. It is assumed that the concentration of electrons and holes are the same i.e. \(n_e = n_h = n\). Each term in equation 1.4 denotes a specific recombination process: (a) non-radiative recombination via trap-states within the band-gap; (b) radiative recombination of CB electrons with VB holes; (c) Auger recombination of two electrons (holes) with one hole (electron). These processes are shown in Fig 1-10a-c.

**Fig 1-10**: Recombination processes. (a) trap-mediated recombination; (b) radiative recombination between electron and hole; (c) Auger recombination between two electrons and one hole. (d) Recombination rate, \(\frac{dn}{dt}\) versus carrier density, \(n\) in MAPbI\(_3\). Reprinted with permission from [173].

Non-radiative recombination occurs in two steps. Firstly, a CB electron (VB hole) is rapidly trapped (~ 1 ns) by a mid-gap trap-state e.g. an iodide interstitial (I\(_I\), see 1.5.1.1).\(^{170}\) The trapped electron (hole) is then either re-excited to the conduction (valence) band with a probability that decreases exponentially with energy, or de-excited to the valence (conduction) band. Motti et al showed that the de-excitation process occurs on much longer timescales for electrons (> 100 ns) than for holes (~ 1ns) in MAPbI\(_3\),\(^{124}\) which could be due to the larger lattice reorganisation energy associated with the former.

Richter et al and others have explored the carrier density dependence of the recombination rate implied by Equation 1.4 as shown in Fig 1-10d.\(^{58,171-173}\) They found for a typical MAPbI\(_3\) film that the charge-carrier recombination dynamics are dominated by Auger processes at \(n > 10^{18}\) cm\(^{-3}\), radiative recombination between \(10^{16} < n < 10^{18}\) and non-radiative recombination for \(n < 10^{16}\). Such a transition is indicative of the trap-state density in MAPbI\(_3\).
\( n_t \sim 10^{16} \text{ cm}^{-3} \) as above this value of \( n \) all of the trap-states are filled and radiative recombination ensues.

Interestingly, Wheeler et al found that under 1 Sun illumination conditions (0.1 W cm\(^{-2}\)) the carrier density in their MAPbI\(_3\) films was \( n \sim 10^{15} \text{ cm}^{-3} \). This relatively low carrier density and its similarity with \( n_t \) has several important implications. Firstly, Auger recombination can be ruled out in conventional solar cells operating at 1 Sun. Secondly, 1 Sun (\( n \sim 10^{16} \text{ cm}^{-3} \)) conditions lies close to the transition between unwanted, fast (~ 1 ns) trapping processes associated with non-radiative recombination (\( n < 10^{16} \text{ cm}^{-3} \)) and the desired slow (10 – 1000 ns) dynamics associated with radiative recombination (\( n < 10^{16} \text{ cm}^{-3} \)). This was summed up most elegantly by DeQuillettes et al who showed that bright and dark regions of MAPbI\(_3\) films under fluorescence microscopy at 1 Sun were associated with trap densities of < 1 x 10\(^{15}\) and 4 x 10\(^{16}\) cm\(^{-3}\) respectively. Consequently, the efficiency of PSCs is highly sensitive to the trap density in the perovskite absorber.

As a result, an intense research effort has developed over the last five years to identify and optimise strategies to lower the trap-state density in PSCs. Most notably, Noel et al showed in 2014 that Lewis bases such as pyridine could be used to form dative bonds with unsaturated Pb\(^{2+}\) at the perovskite surface. Notably, their as-prepared perovskite had a trap density of 3.5 x 10\(^{-16}\) cm\(^{-3}\), which was reduced by over an order of magnitude to 0.2 x 10\(^{-16}\) cm\(^{-3}\) after the pyridine treatment. As a consequence, device efficiency improved from 13% to 16.5%, which was remarkably efficient for that time. Explicit in these results is the fact that shifting the trap-density below the carrier density offered at 1 Sun (~10\(^{16}\) cm\(^{-3}\)) results in the filling of traps, suppression of non-radiative recombination and ultimately improvements in device performance. Since this pioneering study, myriad other passivating agents have been developed in order to reduce the trap density in the perovskite layer.

As the community begins to understand the nuances of trap-state passivation, more sophisticated multi-functional passivation strategies have arisen. For example, Abdi-Jalebi et al demonstrated such a mechanism passivating (Cs\(_{0.06}\)FA\(_{0.79}\)MA\(_{0.15}\))Pb(I\(_{0.85}\)Br\(_{0.15}\))\(_3\) with KI. They propose that the I\(^-\) ion targets V\(_t\) sites while K\(^+\) rich areas within the passivated film attract interstitial halides (I\(_i\)). Moreover, K\(^+\) selectively extracts Br from the perovskite grains, allowing for use of the positive effects of Br in film formation but removing the negative effects of Br on film mobility. We outline our contribution to this field in Chapter 4 and 5 where we look at passivation of MAPbI\(_3\) with bulky iodide salts and CTLs respectively.

1. 5. 3. 2. Interfacial Injection

If the perovskite is interfaced with an \( n \) or \( p \) type CTL capable of extracting electrons or holes, Equation 1.3 can be modified to:
\[- \frac{dn}{dt} = an + bn^2 + cn^3 + Xn \quad (1.5)\]

where the \(Xn\) term describes the first-order rate of transfer into the CTL.

The modern story of electron transfer began in the 1950s with Rudolph A. Marcus’ experiments on outer shell electron transfer.\(^\text{186}\) He built on Eyring’s transition state theory, but with one key development: the thermally induced reorganisation of the reactants and solvent create the required reaction geometry prior to electron transfer. As such, the reactant and product remain weakly coupled (non-adiabatic) as opposed to Eyring’s theory (adiabatic), where they become increasingly linked via an intermediate reaction complex. Marcus theory was then extended by N. S. Hush to the adiabatic case in 1960.\(^\text{187}\)

**Fig 1-11:** (a) Schematic illustrating non-adiabatic electron (●) transfer. (b) Charge transfer rate as a function the free energy change, \(\Delta G^0\) between biphenyl ions and the eight acceptors (A) shown in eight molecules with general structure given in the inset. Reprinted with permission from [190].

Marcus theory states that the free energy of activation, \(\Delta G^*\) of an electron transfer reaction is dependent on the free energy change \(\Delta G^0\) between donor and acceptor (Fig 1-11a) as follows,

\[
\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \quad (1.6)
\]

where \(\lambda\) is the reorganisation energy (Fig 1-11a), associated with the distortion of the acceptor structure to form that of the donor in its relaxed state or vice versa.\(^\text{186}\) This means that the rate of electron transfer, \(k_{et}\) is then defined by:

\[
k_{et} \propto \exp(-\beta r) \exp\left(\frac{(\lambda + \Delta G^0)^2}{4\lambda k_b T}\right) \quad (1.7)
\]

where \(\hbar, k_b\) and \(T\) are the Planck constant, Boltzmann constant and temperature respectively. \(\beta\) (Fig 1-11a) describes the mixing of the donor and acceptor wavefunctions,
where $\beta$ depends on the medium between donor and acceptor (28 nm$^{-1} < \beta < 35$ nm$^{-1}$ in vacuum and $\beta \sim 9$ nm$^{-1}$ through a covalent bond). Equation 1.7 identifies two important parameters that could impact charge transfer between perovskite and CTL: (i) $\Delta G^0$ between perovskite and CTL; (ii) the strength of overlap between their wavefunctions (signified by $\beta$). We address issue (i) and (ii) in Chapters 3 and 5 of this thesis respectively. Furthermore, a striking outcome of Equation 1.6 is that the parabolic nature of the exponent means that, contrary to basic chemical intuition, the rate of reaction decreases for $\Delta G^0 > \lambda$. Although predicted in 1954, this 'Marcus inverted region' was not established experimentally until 1984, by Miller et al.\cite{Miller1984} We discuss the Marcus inverted region in relation to charge transfer in 3D-2D perovskite systems in Chapter 4.

### 1.6. Challenges Facing Perovskite Solar Cells

As we have shown in the previous sections, PSCs exhibit comparable efficiencies to silicon but with much less intensive processing techniques. Therefore, although commercial silicon technology has reached parity with conventional fossil fuels, PSCs offer the potential to provide even cheaper power. Moreover, options for flexible, semi-transparent and colour-tuneable devices open up a host of commercial applications unavailable for dull, black, rigid silicon. However, key challenges remain associated with (i) the toxicity of lead, (ii) the unstable nature of the most efficient perovskite absorbers and (iii) the potential to further improve the efficiency towards the radiative limit of 30%.

#### 1.6.1. Toxicity

Solving the toxicity issue of Pb-based PSCs is paramount to their future commercialisation, but beyond the scope of this thesis. Briefly, researchers have set out to address this by replacing Pb with less-toxic elements,\cite{Snaith2014} with the most viable alternative so far being Sn.\cite{Snaith2014_Sn} May 2014 saw two pivotal works on Sn-based perovskite solar cells published in quick succession from the Snaith and Kanatzidis groups.\cite{Snaith2014_Sn, Kanatzidis2014} Notably, Noel et al. reported a high-efficiency (> 6%) $\text{MASnI}_3$ photovoltaic cell with a remarkably small $V_{oc}$ deficit of 350 mV.\cite{Noel2014} They highlighted the short electron-hole diffusion length ($\sim 30$ nm) and instability as key areas to improve, which are both linked to p-doping associated with the ready oxidation of Sn$^{2+}$ to Sn$^{4+}$. Based on this blueprint, a combined research effort spanning a number of groups has pushed the efficiency of $\text{MASnI}_3$-based solar cells to over 13%.\cite{Snaith2014_Sn, Kanatzidis2014, Gao2015} Meanwhile, significant enhancements in efficiency have also been obtained through the incorporation of additives and mixed 3D-2D systems.\cite{Snaith2014_Sn} In the next two sections we give a more in-depth view into the state-of-the-art in addressing stability and efficiency.
1. 6. 2. Stability of MAPbI\textsubscript{3} and related perovskites

MAPbI\textsubscript{3} and related perovskites suffer from severe instability on two fronts: (i) inherent instability associated with migration of ions under applied voltage and (ii) instability to external entities e.g. H\textsubscript{2}O or the combination of O\textsubscript{2} and light. While the moisture degradation pathway is an important one, it is beyond the scope of this thesis. However, this topic has been well-covered in the literature and we point the reader to a number of key publications.\textsuperscript{129,180,198–202} In the following, we address ion migration and O\textsubscript{2}/light degradation.

1. 6. 2. 1. Ion Migration and J-V Hysteresis

Current-voltage hysteresis – where the current response to a voltage sweep is dependent on the sweep direction (Fig 1-12a) – has consistently been an issue over the last decade of PSC research, with the consensus being that it is associated with the migration of ions.\textsuperscript{203–208} In particular, Weber \textit{et al} gave a detailed account in 2018, which we summarise in the following and in Fig 1-12b-e.\textsuperscript{204}

During the upward scan of voltage, the electric field in the device drives electrons and holes to the opposite electrode and the extraction efficiency (thus $J_{SC}$) is low. Simultaneously, mobile iodide (I\textsuperscript{-}) anions migrate towards the HTL interface, leaving behind static positive (V\textit{I}) sites at the ETL interface (Fig 1-12b and c). Importantly, the adsorption and complexation of mobile anions at the HTL interface fixes the charge distribution such that when the field is reversed an extra push is given to the electrons and holes to reach their respective electrodes thus increasing $J_{SC}$ (Fig 1-12d and e).

The activation energies for migration of Pb\textsuperscript{2+} (2.31 eV), MA\textsuperscript{+} (0.84 eV) and I\textsuperscript{-} (0.58 eV) in MAPbI\textsubscript{3} films were elucidated by Eames \textit{et al.}\textsuperscript{209} As such, I\textsuperscript{-} anions are widely thought to be the main proponent of ion migration. The migration occurs either via V\textit{I} sites at the MAPbI\textsubscript{3} grain boundaries (Fig 1-12f),\textsuperscript{209–213} or through I\textit{i} sites.\textsuperscript{212} As such, passivation (of e.g. V\textit{I}, I\textit{i}) has come to the fore as an effective strategy to mitigate hysteresis.\textsuperscript{103,183,214–216}
Fig 1-12: Summary of key processes involved in ion migration. (a) Example J-V curve exhibiting hysteresis. (b-f) Hysteresis mechanism: (b) the perovskite layer is in equilibrium in the absence of an electric field; (c) In the presence of an electric field, electrons and holes are driven towards the cathode and anode respectively. Simultaneously, mobile iodide ions (I⁻) native to the perovskite are driven from the ETL interface towards the HTL where they form complexes X⁺·I⁻ or are adsorbed. The drifting ions begin to screen the external voltage. (d) The adsorption/complexation at the cathode interface depletes the perovskite of mobile anions and positive ions at the anode interface are compensated by electrons from the ETL. These charges now screen the entire electric field and the potential is flat across the perovskite layer. (e) Upon switching off the field, the slow release of separated charges at the interfaces keeps a reverse electric field in the perovskite layer. This contributes to pushing electrons towards the anode and holes to the cathode. (f) possible mechanism for iodide anion migration. (a-e) and (f) were reprinted with permission from [204] and [213].

1. 6. 2. 2. Oxygen-Mediated Degradation

Fig 1-13: Schematic illustrating the reaction of O₂ with MAPbI₃. (a) O₂ diffuses into the lattice and docs at an iodide vacancy (V_I); (b) MAPbI₃ receives a photon to create electrons and holes; (c) O₂ reacts with an electron to form superoxide (O₂⁻); and (d) degradation to layered PbI₂, H₂O, I₂ and CH₃NH₂. Adapted with permission from [218].

Several works have outlined the mechanism of oxygen induced degradation in hybrid organic-inorganic perovskite films.²¹⁷⁻²²⁴ Briefly, atmospheric oxygen adsorbs to the perovskite surface at a halide vacancy (V_halide) site.²¹⁸ There, the oxygen receives an electron from the perovskite conduction band to form superoxide (O₂⁻):
\[ \text{O}_2 + \text{e}^- \rightarrow \text{O}_2^- \]  

(1.8)

They calculate the associated formation energy of \( \text{O}_2^- \) as -1.19 eV in the case of iodide vacancies (\( \text{V}_i \)). The next step in the reaction sequence is for \( \text{O}_2^- \) to react with photo-oxidized \( \text{CH}_3\text{NH}_3\text{PbI}_3^* \) to produce \( \text{PbI}_2, \text{I}_2, \text{H}_2\text{O} \) and \( \text{CH}_3\text{NH}_2 \) according to the following reaction (Fig 1-13):

\[ 4\text{CH}_3\text{NH}_3\text{PbI}_3^* + \text{O}_2^- \rightarrow 4\text{PbI}_2 + 2\text{I}_2 + 2\text{H}_2\text{O} + 4\text{CH}_3\text{NH}_2 \]  

(1.9)

Under illumination, Reaction 1.9 was calculated to have an enthalpy, \( \Delta H_{\text{deg}} \) of -1.40 eV per \( \text{O}_2 \) molecule, making the degradation reaction highly favourable relative to the unilluminated case (+ 1.60 eV). While a wide range of values for \( \Delta H_{\text{deg}} \) have been reported in the literature depending on model specifics, there is broad agreement that degradation of MAPbI\(_3\) in the presence of \( \text{O}_2^- \) proceeds via Equation 1.9 with a negative reaction enthalpy. The rate of degradation is therefore likely to be highly dependent on (i) the concentration of electrons in the MAPbI\(_3\) conduction band and (ii) the nature of the halide vacancy. Consequently, better electron extraction, \( \text{V}_i \) passivation and switching iodine to bromine all have a marked effect on enhancing stability.

1.6.3 Efficiency in MAPbI\(_3\)-based solar cells

The open-circuit voltage (\( V_{\text{OC}} \)), together with the short-circuit current (\( J_{\text{SC}} \)) and fill factor (FF) determine the power conversion efficiency (PCE) of a solar cell:

\[ \text{PCE} = V_{\text{OC}}J_{\text{SC}}FF \]  

(1.10)

The \( J_{\text{SC}} \) is related to the number of charges extracted from the solar cell and some of the parameters that underpin its value were outlined in Section 1.5.3.2. Moreover, the FF describes the ideal-ness of the J-V curve. This is therefore a reflection of the bias dependence of the photocurrent and is therefore closely related to the series (e.g. due to layer conductivity) and shunt resistances (e.g. short-circuits) of the solar cell stack. In the following, we discuss the origin of the \( V_{\text{OC}} \), which Tress has shown (Fig 1-14a) to be closely related to the remarkable increase in the PCE of PSCs over the last decade.

1.6.3.1 Open-Circuit Voltage

Rau defined the radiative limit of the \( V_{\text{OC}} \) for a given solar cell as:

\[ V_{\text{OC,rad}} = \frac{k_bT}{e} \ln \left( \frac{J_{\text{SC}}}{J_{\text{em},0}} \right) \]  

(1.11)

where \( J_{\text{SC}} \) is the short-circuit current and \( J_{\text{em},0} \) is the emission current. \( J_{\text{em},0} \) can be obtained by considering the reciprocity of absorption and emission (i.e. detailed balance):
Here $\Phi_{em,0}$ is the photon flux associated with $J_{em,0}, \varphi_{BB}(E)$ represents the black body spectrum and $a(E)$ is the absorbance of the film as a function of energy. This therefore sets a fundamental, unavoidable loss to the $V_{OC}$ associated with radiative recombination.

\[
J_{em,0} = e\Phi_{em,0} = e \int a(E)\varphi_{BB}(E) \, dE
\]  

(1.12)

Fig 1-14: (a) development of power conversion efficiency (black circles) and open-circuit voltage (white crosses) of PSCs over the last decade. The data for (a) came from [44], [230] [234] and [235]. (b) Relationship between $V_{OC}$ and band-gap across the literature. Blue and red stars indicate the $V_{OC}$ in MAPbI$_3$-based PSCs at the start and end of the PhD period documented in this thesis. The surface plot indicates the theoretically determined $V_{OC}$ for an external quantum efficiency of $10^0 - 10^6$ calculated with a step-function like absorptance. Adapted with permission from [232]. (c-f) Different $V_{OC}$ loss pathways: (c) ideal case; (d) band-gap; (e) charge-trapping; (f) interfacial injection into CTLs.

For MAPbI$_3$, assuming $a(E)$ is a step function rising at the band-gap (1.6 eV), a theoretical limit can be obtained for the $V_{OC}$ as 1.32 V.$^{231-233}$ Remarkably, during the period of work set out in this thesis, the record $V_{OC}$ in PSCs has moved from 1.1 V (2015) to 1.26 V (2019) as shown in Fig 1-14a and b.$^{234,235}$ However, record $V_{OC}$ values still trail below the radiative limit due to losses including non-radiative recombination. One way of rationalising this is that $a(E)$ is never a step function due to an exponential density of traps at the band-edges.$^{234}$

Alternatively, Rau expressed the loss in $V_{OC}$ due to non-radiative recombination as:$^{228}$

\[
V_{OC} = V_{OC,rad} - \frac{k_b T}{e} \ln \left( EQE_{EL}^{-1} \right)
\]  

(1.13)
where $E_{QE_{EL}}$ is the external quantum efficiency of the solar cell operating as an electroluminescent LED with injection current set to $J_{SC}$, and therefore describes the ratio of radiative to total recombination. Equation 1.13 can be re-written as:

$$eV_{OC} = E_g - k_b T \ln \frac{N_C N_V}{n p}$$  \hspace{1cm} (1.14)

where $E_g$ is the band-gap, $k_b$ is the Boltzmann constant, $T$ is the temperature, $N_C$ & $N_V$ are the density of conduction and valence band states and $n$ & $p$ are the carrier densities of free conduction band electrons and valence band holes.

When considering the physical origin of such losses, it is useful to view the $V_{OC}$ in relation to the electronic structure of the solar cell (Fig 1-14). Würfel was the first to rationalise the $V_{OC}$ as the quasi-Fermi level splitting (QFLS) between electrons and holes under illumination. Therefore, Equation 1.14 has several important implications: (i) the $V_{OC}$ is directly related to the band-gap of the solar absorber, with $eV_{OC} = E_g$ at absolute zero (Fig 1-14a and b); and (ii) the deviation of $V_{OC}$ away from ideality increases for decreasing $n$ and $p$. We identify the key loss pathways in Figure 1-14c-f: (i) non-radiative recombination via bulk and interfacial trap-states; (ii) energetic misalignment at the perovskite|CTL interfaces. Therefore, key strategies for improving the $V_{OC}$ of PSCs are mitigation of trap-states via passivation,\textsuperscript{99,155,237–239} and incorporation of CTLs that minimise interfacial overpotential.\textsuperscript{100,240–243}

### 1.7. In the Next Chapters

Disruptive photovoltaic technologies such as PSCs will be instrumental in the rapid decarbonisation required to satisfy the Paris Agreement, but as outlined in Section 1.6 progress has been hampered by instability and sub-optimal efficiency. Therefore, after setting out our experimental process in \textbf{Chapter 2}, in \textbf{Chapters 3, 4 and 5} we document our progress towards understanding and solving these issues.

Ultimately, the power conversion efficiency of solar cells is driven by the victory of charge extraction over recombination. Therefore, in \textbf{Chapter 3} we focus on how the interfacial energy offset between hybrid inorganic-organic perovskites and their hole transport layers impacts the yield of hole injection. We then focus on the other aspect of this equation in \textbf{Chapter 4}, where we elucidate strategies to mitigate non-radiative recombination and instability via passivation. Finally, in \textbf{Chapter 5}, we bring these two strands of research together to show how passivating interactions at the top-interface between the perovskite and its charge transport layers in both \textit{pin} and \textit{nip} architectures mediate interfacial injection.
1.8. References


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Chapter 2

Experimental Materials & Methods
2. 1. Sample Preparation

2. 1. 1. Materials

All materials were purchased and used as received. Glass microscope slides were obtained from VWR. PbI\(_2\) was purchased from Alpha Aesar; mp-TiO\(_2\), methylammonium iodide (MAI), Formamidinium iodide (FAI) & cesium iodide (CsI) from Dyesol; Butylammonium iodide (BAI), phenylammonium iodide (PAI), phenethylammonium iodide (PMAI), phenethylammonium iodide (PEAI), ammonium iodide (AI), mp-\(\text{Al}_2\text{O}_3\), anhydrous dimethylsulfoxide (DMSO), anhydrous \(\gamma\)-butyrolactone (GBL), anhydrous chlorobenzene & F8T2 (\(M_W = 63,525\)) from Sigma Aldrich; TFB (\(M_W = 40,000\)), PTAA (\(M_W = 14,000\)), PTPD (\(M_W = 80,000\)), P3HT (\(M_W = 24,480\)) PCBM & IPH from Ossila; PTEG from Solenne BV; and PFN, PTB1 (\(M_W = 48 \text{kDa}\)) & F8BT (\(M_W = 50 \text{kDa}\)) from 1 material. Spiro-OMeTAD was kindly provided by Prof Neil Robertson, University of Edinburgh. Devices in sections 3. 4. 1 & 4. 4. 1 and section 5. 4. 1 were kindly fabricated by Dr Xiangnan Bu and Dr Thomas J MacDonald respectively.

2. 1. 2. Preparation of Perovskite layer

2. 1. 2. 1. Methylammonium lead triiodide

The method for deposition of methylammonium lead triiodide (MAPbI\(_3\)) employed herein was adapted from that first reported by Jeon et al.\(^1\) Briefly, PbI\(_2\) and CH\(_3\)NH\(_3\)I were mixed together in a 1:1 ratio at a concentration of 1.2 M in GBL and DMSO (3:7). After solvation, the solution was filtered with a 200 nm PTFE filter and spin-coated on top of the relevant substrate in a three step program: sequentially at 1000 rpm (10 s), 5000 rpm (30 s) and 6000 rpm (20 s). Crucially, 800 \(\mu\)L of toluene antisolvent was drop-casted onto the spinning film after 25 s to aid crystallisation. The film was then annealed at 100 °C for 10 minutes. The antisolvent treatment resulted in a colour change from pale yellow to pale brown, while annealing resulted in a dark brown film. This produced a 400 nm thick perovskite layer.

2. 1. 2. 2. Cs-FA-MA “Triple-Cation” perovskite

The method for Cs-FA-MAPbI\(_3\) deposition employed herein was adapted from that first reported by Saliba \textit{et al.}\(^2\) Briefly, CsI, PbI\(_2\) and CH\(_3\)NH\(_3\)I were mixed together to achieve the desired stoichiometric ratio at a concentration of 1.2 M in DMF:DMSO (1:4). This layer was then deposited via the same method as with MAPbI\(_3\), but with a diethyl ether (Sigma) antisolvent.
2. 1. 3. *nip Films*

![Fig 2-1: Schematic illustrating the make-up of a typical *nip* film used for the spectroscopic investigations in this thesis. (1) Glass substrate; (2) 200 nm of mesoporous titanium or aluminium oxide; (3) 400 nm thick MAPbI$_3$ layer, infiltrated into the 200 nm mesoporous framework and leaving a 200 nm overlayer; (4) 30 nm Hole transport layer (HTL).]

A typical *nip* film is presented schematically in Fig 2-1. The film consists of a MAPbI$_3$ layer (3) infiltrated into 200 nm of mesoporous TiO$_2$ (mp-TiO$_2$; 2) on a glass substrate (1). A 200 nm overlayer of pure MAPbI$_3$ lies above the infiltrated mp-TiO$_2$. The film is capped with a 30 nm hole transport layer (4; HTL). We note that electron-conducting TiO$_2$ can be swapped for insulating Al$_2$O$_3$ in experiments where only the p-type interface is of interest.

2. 1. 3. 1. Metal Oxide Substrate

Glass microscope slides were washed in deionised water, acetone and isopropanol (IPA) for 15 minutes followed by O$_2$ plasma treatment. Al$_2$O$_3$ substrates were prepared by making up a 6.67 wt% solution of Al$_2$O$_3$ nanoparticles (Sigma) in IPA and spin-coating at 6000 rpm immediately after O$_2$ plasma treatment. TiO$_2$ substrates were prepared by making up a 2:7 (weight) solution of TiO$_2$ paste (18NR-T, Dyesol) in EtOH, spin-coating on the glass immediately after plasma treatment, drying at 90 °C for 10 minutes and annealing at 450 °C for 45 minutes. The result was a 200 nm thick mp-TiO$_2$ layer.

2. 1. 3. 2. Hole transport Layer

Polymeric HTL solutions at 10 mg/mL were spin-coated on top of the perovskite film at a speed which ensured all HTL layers were 30 ± 5 nm thick. For spiro-OMeTAD, 1 mL of 72 mg/mL solution in chlorobenzene was prepared, (optionally) doped with 17 µL of 520 mg/mL lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) & 28.8 µL of tert-butyl-pyradine (tBP) and spin-coated at 4000 rpm.
2. 1. 4. **pin Films**

![pin Films](image)

**Fig 2-2:** Schematic illustrating the make-up of a typical *pin* film used for the spectroscopic investigations in this thesis. (1) Glass substrate; (2) 20 nm hole transport layer (HTL); (3) ultrathin (< 10 nm) layer of PFN; (4) 400 nm MAPbI$_3$ layer; (5) 50 nm electron transport layer (ETL).

A typical *pin* film is presented schematically in Fig 2-2. The film consists of a 400 nm thick perovskite layer (4) on top of a 20 nm HTL (e.g. P3HT, PTAA, 2) supported by a glass substrate (1). In order to improve the wetting of the perovskite on the polymeric HTL, an ultrathin (< 10 nm) layer of PFN (3) was placed between them. The film is then completed with a 50 nm thick ETL layer (e.g. PCBM, IPH, PTEG).

### 2. 1. 4. 1. Hole Conducting Substrates

Glass microscope slides were washed in deionised water, acetone and isopropanol (IPA) for 15 minutes followed by O$_2$ plasma treatment. Hole conducting substrates were then prepared by first depositing the HTL onto the glass at 0.25 wt% in chlorobenzene so as to form a 20 nm thick layer. Next, 0.05 wt% PFN in MeOH was spin-coated at 4000 rpm (45s) to provide a thin interlayer that ensures decent wetting of the MAPbI$_3$ layer.

### 2. 1. 4. 2. Electron Transport Layer

ETL (PCBM, PTEG, IPH) solutions were prepared in chlorobenzene at 23 mg/mL and stirred at 40 °C for 1 hour and filtered with a 200 nm PTFE filter before use. These solutions were spin-coated on top of MAPbI$_3$ film at 2000 rpm (30 s) to produce a 50 nm thick film.

### 2. 1. 5. Passivation Treatments

Iodide salt coatings were added directly to the MAPbI$_3$ layer once they had cooled to room temperature. This was done via the method first reported by Aristidou *et al.* Briefly, solutions...
were prepared by dissolving the iodide salt (ammonium iodide, methylammonium iodide, n-butylammonium iodide, phenylammonium iodide, phenylmethylammonium iodide, phenylethylammonium iodide) in a 1:4 solvent mixture of IPA to chlorobenzene (CB) at the desired concentration. 100 µL of this solution was then dripped onto pre-deposited perovskite films with a 20 s loading time before spinning at 4,000 rpm and annealing at 100 °C for 5 min. This was followed by a washing step, in which the film was treated with 100 µL of the 1:4 IPA:CB mixture and spin-coated at 4,000 rpm.

2. 2. Absorption Spectroscopy

2.2.1. Description of Set-Up

In this thesis, absorbance data was collected with a Shimadzu UV-2600 spectrophotometer with a wavelength resolution of 0.5 nm and a scan rate of 1 nm/s. This model uses an integrating sphere to capture the absorbance of the sample.

![Fig 2-3: Schematic outlining the scattering processes at the sample surface in an absorption measurement.](image)

The various scattering processes of light upon incidence with a surface are outlined in Fig 2-3. Scattering at a perfectly smooth surface ensues via specular reflectance, i.e. the incident and reflected light beams are normal to each other. However, if the sample is rough then the normal angle is not constant across the breadth of the sample and light is scattered in all directions, this is called diffuse reflectance. An issue with measuring the absorption properties of perovskite films which have a smooth surface, on substrates such as mesoporous TiO₂, which are necessarily rough, is that diffuse reflectance becomes significant. This would ultimately limit the light-collection efficiency at the detector and ultimately the sensitivity of a conventional spectrophotometer. However, an integrating sphere is designed to collect diffusely reflected light and focus it on the detector. The walls of the sphere consist of highly reflective barium sulphate, meaning that light incident on any
point on the inner surface is equally distributed to all other points. As such, all of the scattered light can be detected, and the sensitivity remains high.

2. 2. 2. Absorption Spectroscopy in this thesis

2. 2. 2.1. Excitation of Samples in Pump-Probe Measurements

![Fig 2-4: Extinction coefficient of MAPbI₃ in the visible range. Taken with permission from [5]. Inset describes the attenuation of the excitation beam in the MAPbI₃ layer.](image)

In this thesis we carry out pump-probe spectroscopy measurements on multi-layer - e.g. TiO₂|MAPbI₃|HTL – films. Therefore, in experiments where we only want to excite the MAPbI₃ layer, careful consideration of the excitation wavelength and fluence must be carried out. Fig 2-4 shows the MAPbI₃ extinction coefficient as a function of wavelength. Typically, we excite films at 510 nm to avoid the absorption of TiO₂ (onset: 388 nm).

While most of the HTLs used in this thesis (e.g. F8T2, TFB, PTAA, PTPD, spiro-OMeTAD) do not absorb at 510 nm due to their blue-shifted absorption, a few HTLs (P3HT, PTB1) do have overlapping absorption. In order to minimise direct excitation of these HTLs at 510 nm, we excite the MAPbI₃ film via the glass|TiO₂ substrate. The maximum excitation fluence used in any of the pump-probe techniques documented herein is 25 µJ cm⁻² (for µ-TAS). At 510 nm this corresponds to an initial carrier concentration \( n (cm^{-2}) = 6.4 \times 10^{13} \) cm⁻² in the MAPbI₃ film at the TiO₂|MAPbI₃ interface. Given the large (~ 2 \times 10^5 m⁻¹) extinction coefficient of MAPbI₃ at 510 nm (Fig 2-5) and a MAPbI₃ film thickness of 400 nm, \( n (cm^{-2}) \) at the HTL is typically 2.15 \times 10^{10} cm⁻². Therefore, assuming 100% absorption at the HTL and given the respective film thickness of the MAPbI₃ (400 nm) and HTL (30 nm) layers, \( n (cm^{-3}) \) is 1.83 \times 10^{18} cm⁻³ and 7.16 \times 10^{15} cm⁻³ respectively. Therefore, the carrier density in the HTL layer is around 0.4% that of the MAPbI₃ allowing us to consider it negligible. In reality, the value of \( n_{o,HTL} \) is likely much lower than this considering absorptance of e.g. P3HT is less than 30% for a 30 nm film.
2. 3. Transient Absorption Spectroscopy

2. 3. 1. Brief Introduction and description of set-up

Transient absorption or flash photolysis spectroscopy was first demonstrated by Lord George Porter and Ronald George Wreyford Norrish in 1950 as a novel method for studying free radical reactions. The resolution in their experiment was around $10^{-4}$ s, associated with the high pressure gas-filled discharge tube excitation source, a biproduct of aerial photography cameras developed during World War II. This pioneering research led them to share the 1967 Nobel Prize in Chemistry 1967 with Manfred Eigen for their contributions towards the studies on “extremely fast chemical reactions”. Since then, progress in the development of ever faster excitation sources e.g. Ti:sapphire lasers has allowed the resolution of TAS to reach femtosecond timescales.

![Fig 2-5: Schematic illustrating the rough time scale of photoinduced processes in perovskite solar cells. The electron and hole recombination processes (6, 7) relevant to µs-TAS are highlighted.](image)

The kinetic processes that drive charge separation in solar cells occur on timescales that range from less than femtoseconds to milliseconds (Fig 2-5). However, recombination of electrons and holes from the relevant charge transport layers tends to occur on timescales longer than $10^{-6}$ s. Therefore, microsecond TAS ($\mu$-TAS) is an ideal probe of the yield and recombination dynamics of this injected population, as it does not capture the much faster processes – e.g. recombination in the perovskite layer – that could complicate the TA signal.
µ-TAS is a pump-probe technique that operates on the idea that photogenerated charges change the optical density (OD) property of semiconductors. An initial ‘pump’ laser pulse, with energy larger than the band-gap, is used to excite electrons from $\psi_0$ to $\psi_1$ (Fig 2-6, 1). Subsequently, a second beam probes the absorbance of $\psi_1$, effectively by exciting it to $\psi_2$. Given that the change in optical density, $\Delta OD$ is proportional to the concentration, $n_1$, of $\psi_1$ by the Beer-Lambert law, $(\Delta OD = \varepsilon_1 \cdot n_1 \cdot l)$ where $\varepsilon_1$ and $l$ are the extinction coefficient of the excited state and path length respectively, it is possible to track the evolution of $\psi_1$.

Our TAS set-up is outlined schematically in Fig 2-6. Briefly, we held our sample films (2) in a sealed cuvette (3) under a steady purge of N$_2$ (4). We then exposed the sample to the pulsed (3 Hz) pump (blue) and continuous probe (red) beams. The probe beam was generated by a 100 W tungsten lamp (5, Bentham IL 1) and filtered by a monochromator (6, OBB-2001, Photon technology international) and a long-pass filter (7) before it was collimated and focused on the sample (8). On a separate optical axis, the pump beam was generated by a tuneable dye laser (9b, Photon Technology International Inc. GL-301; pulse width ~ 1.6 ns, 10) that was itself excited by a N$_2$ laser (9a, Photon Technology International Inc. GL-3300). We controlled the laser fluence (maximum: 25 µJ cm$^{-2}$) by inserting neutral
density (ND) filters at 11. The transient changes in the absorption of the sample were detected by a silicon photodiode (12, Hamatsu Photonics, S1722-01) after filtering with more long-pass filters in order to remove the contribution from the sample PL. The signal was then amplified (Costronics Electronics) and finally interpreted by a digital oscilloscope (Tektronics DPO3012) to produce the output signal at the PC (13).

2.3.2. Signal conversion to ∆OD

The change in optical density (∆OD) is calculated from the light intensity change with and without excitation, measured at the photodiode. Beer-Lambert law defines the optical density (OD) as,

$$OD_{\lambda,t} = -\log(T_{\lambda,t}) = -\log\left(\frac{I_{\lambda,i}}{I_{\lambda,f}}\right) = \varepsilon_{\lambda} c_t l \quad (2.1)$$

Where $T_{\lambda,t}$ is the transmittance through the sample, $I_{\lambda,i}$ is the intensity incident on the sample, $I_{\lambda,f}$ is the transmitted intensity, $\varepsilon_{\lambda}$ and $c_t$ are the extinction coefficient and concentration of the species in question and $l$ is the path length. The measured $I_{\lambda,f}$ changes upon laser excitation due to the presence of transient species, such that under monochromatic illumination:

$$\Delta OD_t = -\log\left(\frac{I_t}{I_{f,t}}\right) + \log\left(\frac{I_t}{I_{f,t0}}\right) = \log\left(\frac{I_{f,t}}{I_{f,t0}}\right) \quad (2.2)$$

Where $I_{(f,t0)}$ and $I_{(f,t)}$ are the transmitted intensity before the excitation pulse and at time, $t$ after it. Given that $I_{(f,t)}$ is equivalent to $I_{(f,t0)} + \Delta I_{f,t}$, where $\Delta I_{f,t}$ is the intensity change in the transmitted light, this can be rewritten as:

$$\Delta OD_t = \log\left(\frac{I_{f,t0} + \Delta I_{f,t}}{I_{f,t0}}\right) = \log\left(1 + \frac{\Delta I_{f,t}}{I_{f,t0}}\right) \quad (2.3)$$

$\Delta I_{f,t}$ is proportional to the change in voltage, $\Delta V_t$ measured at the photodiode. Therefore, Equation 2.3 can be rewritten in terms of the photodiode voltage, as:

$$\Delta OD = \log\left(1 + \frac{\Delta V_t}{V_0}\right) \quad (2.4)$$

2.3.3. µ-TAS in this thesis

At a maximum fluence of 25 µJcm$^2$, TAS represents the highest intensity laser spectroscopy technique used in this thesis. We note that even at these relatively high fluences, the TAS trace remained stable over a maximum measurement window of four hours, suggesting minimal beam induced transient species or damage.
2. 3. 3. 1. The Transient Absorption Trace

An example µs-TAS trace is given in Fig 2-7 for a TiO$_2$|MAPbI$_3$|PTB1 film. The trace can be fitted to a stretched exponential,

$$\Delta OD \propto \exp\left[-\left(\frac{t}{t_0}\right)^\alpha\right]$$ (2.5)

where $\alpha$ is the stretching factor, $t$ is the time and $t_0$ is the time taken for $\Delta OD$ to reach 1/e of its original value. The stretched exponential shape derives from the fact that recombination occurs over a wide distribution of energies and distances. Given that the overall lifetime of the stretched exponential can be fitted with multiple combinations of $t_0$ and the stretching factor, $\alpha$ we avoided extracting quantitative information from the fit itself. Instead, we use the fit as a guide to assign an approximate lifetime $\tau_{rec,h}$ as the time taken for $\Delta OD$ to reach half the initial intensity, $\Delta OD_{max}$. Both of these parameters are indicated on the example trace in Fig 2-7a. Therefore, from the µ-TAS trace we can obtain information about the yield ($\Delta OD_{max}$) and recombination lifetime ($\tau_{rec,h}$) of injected charges at the perovskite|CTL interface in PSCs. We note that all TAS traces presented herein are normalised by their absorptance (Fig 2-7b):

$$\text{absorptance} = 100 - T - R$$ (2.6)

where T and R are the transmittance and reflectance measured via UV-Vis absorption.

**Fig 2-7:** Example transient absorption spectroscopy (TAS) trace for a TiO$_2$|MAPbI$_3$|PTB1 film fitted to a stretched exponential - $\Delta OD \propto \exp\left[-\left(\frac{t}{t_0}\right)^\alpha\right]$ (red line). The relative injection yield, $\Delta OD_{max}$ and recombination time, $\tau_{rec,h}$ are indicated. (b) absorptance of our 400 nm MAPbI$_3$ film.

Moreover, the raw change in optical density, $\Delta OD_{max}$ obtained from TAS measurements for MAPbI$_3$|CTL films can be converted into the electron (hole) injection yield, via the Beer-Lambert law:
\[ Yield = \frac{n_{+/\text{H}}}{n_0} = \frac{\Delta OD_{\text{max}} \cdot N_A}{1000 \cdot \varepsilon_{+/\text{H}} / n_0} \]  

(2.7)

where \( n_{+/\text{H}}, n_0, \varepsilon_{+/\text{H}} \) and \( N_A \) are the area density of hole (electron) polarons in the HTL (ETL) (cm\(^2\)), area density of photoexcited electrons in the MAPbI\(_3\) layer (cm\(^2\)), extinction coefficient of the hole (electron) polaron in the HTL (ETL) and Avogadro’s constant respectively. We obtain \( \Delta OD_{\text{max}} \) as the value of \( \Delta OD \) at 1 \( \mu \text{s} \) in the raw transient absorption spectra and \( n_0 \) by assuming that every photon absorbed by the perovskite is converted to an electron/hole pair.

2.3.3.2. Transient Absorption Spectra

![Figure 2-8](image)

**Fig 2-8:** (a) Transient spectrum as a function of time for a TiO\(_2\)|MAPbI\(_3\)|F8T2 film pumped at 510 nm (fluence: 10 \( \mu \text{J cm}^{-2} \)). (b) The simple 2D spectrum taken at 10\(^{-6}\) s for the same sample.

Moreover, if multiple TAS traces such as that in Fig 2-7a are taken as a function of the probe wavelength, \( \lambda \), a transient spectrum can be obtained similar to the one in Fig 2-8a. Given that each excited state will have different TA responses in both the time and wavelength domains, such spectra can give information about the presence of different excited species in a given film. This can also be presented as in Fig 2-8b by a simple 2D transient spectrum, taken 10\(^{-6}\) s after excitation (i.e. \( \Delta OD_{\text{max}} \) as a function of wavelength). The example given in Fig 2-8 is for a TiO\(_2\)|MAPbI\(_3\)|F8T2 film, where the contribution from F8T2 hole polarons (\( \sim 750 \) nm) and free electrons in TiO\(_2\) (1100-1600 nm) are distinguishable.
Fig 2-9: Schematic demonstrating photoinduced absorption (PIA) and ‘bleaching’. The two panels on the left hand side show the possible absorption processes (red arrows) before and after the excitation pulse. The panel on the right shows how these processes translate to the ground state absorption (dashed line) and difference spectrum after the pulse (solid line).

Generally, two types of TA features are observed after excitation of a sample, outlined in Fig 2-9: (i) a positive signal corresponding to the appearance of a newly accessible absorption band originated by the excited state. This is often termed photoinduced absorption (PIA). (ii) a negative signal associated with the loss of absorption in the ground state due to excitation-induced depopulation. This is usually called ‘bleaching’.

2. 3. 3. 3. Order of recombination from TA

Fig 2-10: An example measurement of the recombination rate constant, $k_{rec,h} = (1/\tau_{rec,h})$ for a TiO$_2$perovskite|P3HT film (perovskite = MAPbI$_3$, BA$_{0.09}$MA$_{0.91}$PbI$_3$).

TAS can also give us information about the order of recombination and thus the trap density at the perovskite|CTL interface. At the low fluences probed here (i.e. without Auger processes), the recombination rate at the MAPbI$_3$|HTL interface can be modelled by:
\[-\frac{dn_+}{dt} = An_+ + Bn_+n \]  \hspace{1cm} (2.8)

where \(n_+\) is the density of holes on the HTL, \(n\) is the density of electrons in the perovskite layer and A & B are the 1\textsuperscript{st} and 2\textsuperscript{nd} order recombination rate coefficients.

Equation 2.8 can be simplified in two limiting cases. Firstly, if \(n < n_{\text{trap}}\), the trap-state density in the MAPbI\(_3\) layer, then the \(Bn_+n\) term vanishes as there is negligible free electron density in the MAPbI\(_3\) layer to induce bimolecular recombination. As such, Equation 2.8 can be simplified to,

\[-\frac{dn_+}{dt} = An_+ \]  \hspace{1cm} (2.9)

Equation 2.9 tells us that recombination should ensue via first order recombination kinetics and that \(\tau_{\text{rec,h}}\) and \(k_{\text{rec,h}}\) should be intensity independent.\(^{12}\)

On the other hand, if \(n > n_{\text{trap}}\), there is a non-negligible electron density in the MAPbI\(_3\) layer and therefore bimolecular recombination cannot be ignored. In this case, recombination ensues via a two-body bimolecular recombination scheme, where \(\tau_{\text{rec,h}}\) and \(k_{\text{rec,h}}\) are intensity dependent. We can therefore obtain information about the trap-density at the MAPbI\(_3\)|HTL interface given the close relationship between \(n\) and \(n_{\text{trap}}\).

Finally, an analogous expression can be developed for electron recombination at the MAPbI\(_3\)|ETL interface, where \(n_+\) is swapped for \(n_-\), which describes the electron density on the ETL:

\[-\frac{dn_-}{dt} = An_- + Bn_-n \]  \hspace{1cm} (2.10)

Information can then be obtained about the trap density at MAPbI\(_3\)|ETL interfaces following the same logic.

In Fig 2-10 we give the example of P3HT on MAPbI\(_3\) and BA\(_{0.09}\)MA\(_{0.91}\)PbI\(_3\). We find that in the case of MAPbI\(_3\) \(k_{\text{rec,h}}\) is not intensity dependent suggesting monomolecular recombination kinetics. However, a clear dependence of \(k_{\text{rec,h}}\) on light intensity is observed in the case of BA\(_{0.09}\)MA\(_{0.91}\)PbI\(_3\), suggesting that recombination ensues via a two-body recombination mechanism. This is important because it suggests a greater density of traps in the MAPbI\(_3\) compared to the BA\(_{0.09}\)MA\(_{0.91}\)PbI\(_3\) film.
2. 4. Steady-State Photoluminescence Spectroscopy

2. 4. 1. Brief Introduction & Description of Set-Up

Fig 2-11: Photoluminescence (PL) spectroscopy set-up. (1) Schematic demonstrating energetic processes in the sample; (2) white light source; (3) Excitation monochromator; (4) Sample; (5) Sample chamber; (6) Long-pass filter; (7) Emission monochromator; (8) photomultiplier detector; (9) Output (PL spectrum).

The principle of photoluminescence is illustrated in Fig 2-11 (1). Briefly, if a semiconductor absorbs a photon of greater energy than its band-gap an electron will be excited into the conduction band, leaving behind a hole. The electrons and holes will then rapidly cool to their respective band edges and some of them will recombine bimolecularly, producing a photon. In order to capture this process experimentally, we used a Fluorolog 1039 fluorescence spectrometer (Horiba). This system consists of a white light source (Fig 2-11, 2; Intensity 260 mW cm⁻²), which is filtered with a monochromator (3) to produce a single excitation wavelength (510 nm unless otherwise stated) and made incident on the sample (4, 5). This induces the sample emission, which is filtered (6) and monochromated (7) before being detected at the photomultiplier detector (8). The processes associated with 6-8 are rapidly repeated at each probe wavelength to build up the output spectrum (9).
2. 4. 2. Steady-State Photoluminescence in this Thesis

2. 4. 2. 1. Relation of Intensity to Trap-Density

![Comparison of MAPbI₃ and BA₀.₀₉MA₀.₉₁PbI₃ photoluminescence, excited at 510 nm.](image)

The relative PL intensity of a set of samples can give information about the trap-density in the respective films. This is of paramount importance for solar cells as charge-trapping ultimately limits the efficiency. The PL intensity is related to the photoluminescence quantum yield, \( \phi_{PL} \), given by:

\[
\phi_{PL} = \frac{k_r n}{k_r n + k_{nr}}
\]

(2.11)

where \( k_r \) and \( k_{nr} \) are the radiative and non-radiative decay rate coefficients and \( n \) is the carrier density, which is assumed to be sufficiently low as to forbid Auger recombination. \( \phi_{PL} \), and thus the observed PL intensity, is then essentially a measure of the ratio between \( k_r \) and \( k_{nr} \) in a sample. Therefore, given that the presence of trap-states results in non-radiative recombination, the PL intensity is ultimately a measure of the relative trap-density. We see this in the comparison between MAPbI₃ and its highly passivated counterpart, BA₀.₀₉MA₀.₉₁PbI₃, presented in Fig 2-12. The lower trap-density in the BA₀.₀₉MA₀.₉₁PbI₃ film shifts \( \phi_{PL} \) towards higher values and is ultimately manifest in its larger PL intensity.

2. 4. 2. 2. Relation of Intensity to Charge Injection

If the photoluminescent film is interfaced with a charge acceptor, or ‘quencher’, equation 2.11 can be modified as:

\[
\phi_{PL} = \frac{n k_r}{n k_r + k_{nr} + k_{inj}}
\]

(2.12)

where \( k_{inj} \) is the 1st order rate constant of injection into the quencher, illustrated in Fig 2-13. This is because electron (or hole) injection into the quencher effectively reduces the number
of holes (or electrons) in the photoluminescent layer for bimolecular recombination. Therefore, the PL intensity before and after the addition of a quencher gives direct information about the extent of interfacial charge injection.

![Photoluminescence spectra of MAPbI\textsubscript{3} and MAPbI\textsubscript{3}|PTB1, excited at 510 nm. Inset: schematic describing the key kinetic processes occurring in the MAPbI\textsubscript{3}|PTB1 film: radiative recombination (\(k_r\)); non-radiative recombination (\(k_{nr}\)); and injection (\(k_{inj}\)).](image)

In this thesis, we define the photoluminescence quenching yield, \(\eta\) as:

\[
\eta = \frac{PL - PL_Q}{PL}
\]

where PL and PL\textsubscript{Q} are the initial PL intensity of the unquenched perovskite film and PL\textsubscript{Q} is the PL intensity of the same film after deposition of the quencher. It is assumed that the addition of the quencher does not alter the trap density in the perovskite. In Fig 2-13 we give the example of MAPbI\textsubscript{3}|PTB1, which quenches the original MAPbI\textsubscript{3} PL such that \(\eta = 0.92\).

**2. 5. Time-Correlated Single Photon Counting**

**2. 5. 1. Brief Introduction & Description of Set-Up**

Time-correlated single photon counting (TCSPC) is essentially the transient analogue of the ss-PL technique outlined in **Section 2. 4.** As such, we use TCSPC to obtain the kinetics of the various processes occurring in the film. Briefly, a film is excited with a short laser pulse (IRF = 100 ps; \(\lambda_{ex} = 635\) nm; fluence = 0.11 nJ cm\textsuperscript{-2} unless otherwise stated). The detector then picks up all photons emitted by the sample. Consequently, the TCSPC trace picks up any process that depopulates the emissive population of electrons, this could be direct e.g. radiative recombination or indirect e.g. charge trapping.
Our commercial DeltaFlex (Horiba Scientific) TCSPC set-up is outlined in Fig 2-14. We achieve excitation with a 635 nm diode laser (1; NanoLED, N-02B, Horiba Scientific) with a 100 ps pulse duration and a 1 MHz rep-rate. The pulse passes through a monochromator (2) before it reaches the sample (5). The emission is then collected along a different optical axis, passing through another monochromator (3) before hitting the single photon counting detector (4; PPD-900, Horiba Scientific). The time between excitation and detection is correlated via a time digitizer (6) such that time bins associated with detection of photons at time $t$ are created. The output (7) is effectively a histogram with the number of photons recorded for time bins spaced 0.025 ns apart, accounting for the PL dynamics.

**2. 5. 2. TCSPC in this Thesis**

The relaxation rate of the excited electron population – carrier density, $n$ – can be modelled by the following rate equation:

$$- \frac{dn}{dt} = k_{nr}n + k_r n^2 + k_A n^3 + k_{inj} n$$  \hspace{1cm} (2.14)

where $k_{nr}$, $k_r$, $k_A$ and $k_{inj}$ are the rate coefficients for non-radiative recombination, radiative recombination, Auger recombination and interfacial charge injection. Given the low fluence (0.11 nJ cm$^{-2}$) of our TCSPC set-up, we assume $k_A n^3$, $k_r n^2 \ll k_{nr} n$ and Equation 2.14 becomes:
\[
\frac{dn}{dt} = k_{nr}n + k_{inj}n
\]  

(2.15)

Here, \( k_{nr} \) may represent multiple trapping processes (\( k_{nr} = k_{nr,1} + k_{nr,2} + \ldots \)). As such, the overall rate of decay of \( n \) is related to the rates of non-radiative recombination and injection in the presence of a quencher. Given the first order nature of these processes, the carrier population, \( n \) varies with time, \( t \) as:

\[
n(t) = n_0\left(e^{-k_1t} + e^{-k_2t}\right)
\]

Where in unquenched films, \( k_1 \) and \( k_2 \) represent two trapping processes (e.g. surface and bulk) and in a quenched film, they represent a trapping process and an injection process. Therefore, in both cases the PL intensity varies as:

\[
PL(t) = k_r n^2 = k_r n_0\left(e^{-2k_1t} + e^{-2k_2t}\right)
\]

This ultimately means that TCSPC data in the fluence regime covered here can be fitted to a biexponential decay. The dependence of PL on (i) \( k_{nr} \) and (ii) \( k_{inj} \) leads to the two key functions of TCSPC in this thesis: (i) evaluation of the trap-density in films and (ii) investigation of interfacial charge injection.

**Fig 2-15:** Use of time-correlated single photon counting (TCSPC) in this thesis. (a) schematic outlining the key kinetic processes observable in TCSPC: radiative recombination, \( k_r \); charge trapping (\( k_{nr} \)); and charge injection in the presence of a quencher (\( k_{inj} \)). (b) Comparison of photoluminescence dynamics captured by TCSPC for MAPbI\(_3\) (black) and MAPbI\(_3\) passivated with 20 mM PhEtNH\(_3\)I (red) films. (c) demonstration of PL quenching through comparison of a MAPbI\(_3\) (black) and MAPbI\(_3\)|PTAA (blue) film.

We give an example of (i) in Fig 2-15b where we compare the PL dynamics in a MAPbI\(_3\) before (black) and after (red) treating it with the passivating agent PhEtNH\(_3\)I. The PL decay
can be fitted to a biexponential, which accounts for a fast trapping process \( (k_{nr,1}; \text{Fig 2-15a, b}) \), associated with surface states, and a slower trapping process \( (k_{nr,2}; \text{Fig 2-15a, b}) \), associated with bulk states.\textsuperscript{15–17} We see that in the pure MAPbI\textsubscript{3} film, \( \tau_1 = 0.732 \text{ ns} \) and \( \tau_2 = 5.28 \text{ ns} \). Upon treatment with PhEtNH\textsubscript{3}, both of these parameters increase to \( \tau_1 = 1.22 \text{ ns} \) and \( \tau_2 = 17.76 \text{ ns} \). This therefore implies that the trap density is significantly reduced in the passivated film.

Additionally, we demonstrate the use of TCSPC to address (ii) in Fig 2-15c by comparing the PL dynamics of MAPbI\textsubscript{3} and MAPbI\textsubscript{3}|PTAA. The introduction of this HTL results in the acceleration of the MAPbI\textsubscript{3} PL decay due to rapid hole injection. The PL decay of MAPbI\textsubscript{3}|HTL samples can be fitted to a biexponential, with a fast component indicative of hole transfer to the HTL\textsuperscript{18–20} and a slow component due either to surface\textsuperscript{21} or bulk\textsuperscript{22} recombination in the MAPbI\textsubscript{3} layer. We note that an alternative explanation could be that the slow component is due to monomolecular radiative recombination of the excess electrons in the MAPbI\textsubscript{3} layer, which has been depleted of its hole population, as in doped semiconductors.\textsuperscript{23} However, given the low fluences used, we deem it more likely that this component is due to trapping.

In our example, the unquenched MAPbI\textsubscript{3} time constants are \( \tau_1 = 0.732 \text{ ns} \) and \( \tau_2 = 5.28 \text{ ns} \). Upon addition of the quencher, we obtain \( \tau_1 = 0.303 \text{ ns} \) and \( \tau_2 = 1.30 \text{ ns} \), suggesting that \( \tau_{inj} = 0.303 \text{ ns} \). We note that the accuracy of this method relies on interfacial charge injection being rate-limiting i.e. \( k_{inj} \gg k_{nr} \).

### 2.6. Current-Voltage Characteristics

#### 2.6.1. Description of set-up

The ultimate method for determining the viability of a solar cell stack under working conditions is by measuring its current-voltage (J-V) characteristics. In this measurement, the cell is illuminated with a calibrated lamp (Oriel Instruments) that imitates the intensity (100 mW cm\textsuperscript{-2}) and spectrum (i.e. AM 1.5) of the sun at the Earth’s surface. Under illumination, a source meter (Keithley 2400) applies a voltage and simultaneously measures the current response. In order to universalise the current output of solar modules with different area, the current is divided by the device area to obtain the current density, \( J \).
2. 6. 2. The J-V Curve

An example J-V curve is given in Fig 2-16, from which there are four key parameters that can be extracted.

- **Open-circuit voltage** ($V_{OC}$). This parameter is defined as the voltage required to equalise the potential of the anode and cathode, and thus reduce the current to zero. The $V_{OC}$ can be extracted from the x-intercept of the J-V curve.

- **Short-circuit current** ($J_{SC}$). This is the current that the cell produces when no voltage is applied. The $J_{SC}$ can be extracted from the y-intercept of the J-V curve.

- **Fill factor (FF)**. The FF is related to the “squareness” of the J-V curve i.e. the ratio between the measured maximum power ($P_{max} = J_{FF}V_{FF}.A$) and the maximum theoretical power ($P_T = J_{SC}V_{OC}.A$).

- **Power Conversion Efficiency (PCE)**. The overall efficiency of the cell,

\[
PCE \, (\%) = \frac{I_{FF}V_{FF}}{P_{in}}
\]

(2.16)

where $P_{in}$ is the incident power and $I_{FF}$ ($= J_{FF}.A$) & $V_{FF}$ are the current and voltage at the maximum power point respectively.

Fig 2-16: Example J-V curve for an ITO|SnO$_2$|MAPbI$_3$|PTAA|Au device.
2. 6. 3 Intensity Dependence of the J-V Curve

Fig 2-17: Example of intensity dependent J-V measurements for an ITO|SnO₂|MAPbI₃|PTAA|Au device. (a) Raw J-V curve as a function of intensity (1 Sun = 100 mW cm⁻²). (b) log-log plot of $J_{SC}$ versus intensity. (c) semi-logarithmic plot of $V_{OC}$ versus intensity.

By mounting neutral density between the light source and the cell, it is possible to alter the intensity of illumination. Fig 2-17a shows the intensity dependence of the J-V curve, taking the specific example of an ITO|SnO₂|MAPbI₃|PTAA|Au device. A log-log plot of $J_{SC}$ versus light intensity is given in Fig 2-17b, which follows $J_{SC} = LI^\alpha$, where LI is the light intensity. When $\alpha = 1$, it is implied that negligible non-linear losses are occurring at short-circuit. This is a precondition for conducting further measurements.²⁴,²⁵

Fig 2-17c displays the relationship between $V_{OC}$ and LI. An expression for the $V_{OC}$ as a function of LI can be obtained from the ideal diode equation:

$$dV_{OC} = \frac{k_B T}{q} \cdot d\ln(LI) \quad (2.17)$$

Where $k_B$ is the Boltzmann constant, $T$ is the temperature and $q$ is the elementary charge. In the case of pure bimolecular recombination, the slope of the semi-logarithmic plot should be equal to the thermal voltage, $k_B T/q$.²⁴ However, in the presence of trap-mediated recombination, the slope deviates towards steeper values, with a value of $2k_B T/q$ being the fingerprint of pure monomolecular recombination.²⁶ Therefore Equation 2.17 can be modified to reflect departures from ideality as:

$$dV_{OC} = n_{ID} \cdot \frac{k_B T}{q} \cdot d\ln(LI) \quad (2.18)$$

where $n_{ID}$ is the ideality factor. When $n_{ID} = 1$, we have pure bimolecular recombination, but when $n_{ID} = 2$, we have pure non-radiative recombination. Intermediate situations with
\( n_{ID} \cdot k_b T / q \) (1 < \( n_{ID} < 2 \)) can then be assessed by their ideality factor, \( n_{ID} \).\(^{25}\) In Fig 2-17c our example ITO/SnO\(_2\)/MAPbI\(_3\)/PTAA/Au device has \( n_{ID} = 1.45 \), which might suggest mixed non-radiative and radiative recombination. We use this technique to study recombination in MAPbI\(_3\)|HTL films in Section 5.4.1.4.

2.7. X-Ray Photoelectron Spectroscopy

![Illustration of the architecture of the X-ray photoelectron spectroscopy measurement.](image)

A schematic of the XPS measurement is given in Fig 2-18. Photons (1) of energy, \( h\nu \) are made incident on the sample (3) and ionise an electron from a core level to beyond the vacuum level \((E_{\text{vac}})\). The resulting kinetic energy \( E_K \) of the emitted electron (2) can be obtained with an electron analyser & detector (4, 5) and can be related to its binding energy, \( E_b \) by the Einstein equation:

\[
E_K = h\nu - E_b - WF
\]  
(2.19)

Where WF is the work function of the sample. Given that the binding energy of a specific orbital in a specific element tends to be unique, XPS spectra (6) can be used to identify the constituent elements at the surface of a sample. Moreover, the chemical shift in \( E_b \) can give insight into the chemical environment around the core-level electron in question.\(^{27}\) We use this principle in Section 5.4.1.2 to probe binding interactions at MAPbI\(_3\)|CTL interfaces.

Our XPS measurements were obtained in MultiLab 2000 with the X-ray source provided by monochromated Al K \( \alpha \) X-ray photons \((h\nu = 14.9 \text{ keV})\). The core level spectra were performed with pass energy of 20 eV and step size of 0.05 eV.
2. 8. X-Ray Diffraction

![Fig 2-19: Schematic illustrating interference of light fringes between two crystal planes distance, $d$ apart. $\theta$ describes the angle between the incident light beam and the crystal plane. Only when $n\lambda = d\sin\theta$ can constructive interference occur.](image)

Diffraction occurs when a wave-front reaches an aperture of comparable width to its wavelength. For crystals, which have typical dimensions of a few angstroms, X-rays (i.e. $\lambda \sim \text{Å}$) are required to produce diffraction. As described in Fig 2-19, in the event that two beams with identical wavelength and phase are scattered off consecutive planes in a crystal, the lower beam traverses an extra length of $2d\sin\theta$. Indeed, constructive interference can only ensue when this length is equal to an integer multiple of the wavelength of the radiation ($n\lambda$). This can be modelled by Bragg’s condition:

$$n\lambda = 2d\sin\theta \quad (2.19)$$

where $\lambda$ is the wavelength of light, $n$ is the order of diffraction, $d$ is the lattice spacing and $\theta$ is the angle between the incident light beam and the plane of the lattice. In Section 4. 4. 1 of this thesis, we use XRD to identify the formation of 2D (PhEtNH$_3$I)$_2$PbI$_4$ perovskite on 3D MAPbI$_3$, made possible by the fact that the dominant phases in the two crystals have distinctly different $d$.

XRD patterns in this thesis were recorded using a Bruker D8 Discover X-ray diffractometer using monochromatic Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ radiation of wavelengths 1.54056 and 1.54439 Å, respectively.
2. 9. References


Chapter 3
Effect of Interfacial Energetics on charge transfer to organic charge transport layers
3. 1. Abstract

The control and optimisation of interfacial charge transfer processes is crucial to the design of efficient perovskite solar cells. Herein, we measure the yield and kinetics of hole transfer across methylammonium lead triiodide perovskite|polymeric hole transport layer heterojunctions, as a function of the interfacial energy offset, $\Delta E'$, between the highest occupied molecular orbital of the hole transport layer and the valence band edge of the perovskite. A combination of steady-state and time-resolved photoluminescence, along with transient absorption spectroscopy, revealed that only a small driving energy ($\Delta E \sim 0.1$ eV) is required to induce highly efficient hole transfer yields (> 75%). We also show that this trend holds for $\text{Cs}_{0.5}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{PbI}_3$|HTL interfaces, implying that this is a general trait of hybrid-organic inorganic perovskites.

We also assessed the injection and recombination kinetics at the MAPbI$_3$|HTL interface, finding that recombination is at least $10^5$ times slower than injection for MAPbI$_3$|HTL interfaces with $\Delta E > 0$ eV. Additionally, we assigned a recombination time of 0.1 ms to the TiO$_2$|MAPbI$_3$ interface. Moreover, interfacial recombination was found to be even slower in $\text{Cs}_{0.5}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{PbI}_3$|HTL films, which we show is due to a lower interfacial trap density in this perovskite.

We finally demonstrate correlation between $\Delta E$ and the open-circuit voltage ($V_{OC}$) through an extensive survey of 104 perovskite|HTL combinations from the literature and our own measurements. Our findings give insight into the success of certain HTLs with deep lying HOMO energies such as PTAA, PTPD & TFB and ultimately set out an important design rule for the design of next-generation HTLs: $0 < \Delta E < 0.2$ eV.

Most of the results in this chapter are included in the following publication:

3. 2. Introduction

The incorporation of the first solid-state hole transport layers (HTLs) for PSCs in 2012, enhanced their efficiency from 6.5% to 9.7% and sparked an active sub-field of perovskite research. Since then, the design and development of HTLs has been an integral part of the global research effort that has driven efficiencies to the current record of 25.2% and yielded over 30,000 peer-reviewed journal articles. However, despite this intensive research, concrete design rules for optimum charge transfer yields at perovskite|HTL interfaces are still lacking.

Much of the early work in this regard set about assigning time constants to the key charge transfer processes at the perovskite|HTL interface. In 2013, Marchioro et al found that hole transfer to the current state-of-the-art HTL spiro-OMeTAD occurs on a picosecond timescale. Importantly, hole transfer was found to be much faster than the subsequent recombination back across the interface, a prerequisite for sustained charge separation. A later study by Brauer et al, suggested that hole transfer into polymeric HTLs is slower, typically on the order of nanoseconds.

Fig 3-1: Illustration of the interfacial energy offset, $\Delta E$ and quasi-Fermi level splitting (QFLS) at a perovskite|HTL heterojunction. The energetic driving force for hole transfer can be approximated as, $\Delta E = E_{HOMO} - E_{VB}$, where $E_{HOMO}$ and $E_{VB}$ are the ionisation potentials of the HTL and perovskite valence band. Ideally, the quasi-Fermi energy of electrons ($E_{F,n}$) and holes ($E_{F,p}$) should be located at the band-edges of the MAPbI$_3$ layer. However, partial hole injection into the HTL, increases $E_{F,p}$ to an extent that is dependent on $\Delta E$. This reduces the QFLS and ultimately the $V_{OC}$.

As we saw in Section 1. 5. 3. 2, Marcus theory states that the rate of electron/hole injection is related to the Gibbs Free energy change between the donor and acceptor levels. Therefore, the interfacial energy offset, $\Delta E$, between the HTL HOMO and perovskite valence band (VB; Fig. 3-1) is the primary driving force for hole transfer. However, in contrast to the

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1 Google scholar, Feb 2020; Search terms: ‘perovskite solar cell’ AND ‘novel hole transport layer’
adjacent fields of organic and dye-sensitized solar cells (OSC and DSSC), in which the relationship between $\Delta E$ and charge separation has been well covered,\textsuperscript{15-17} research on this topic in PSCs has been limited. Ishida \textit{et al} made some ground in this regard by studying the hole transfer process for HTLs with different HOMO energies in devices using time-resolved microwave conductivity (TRMC).\textsuperscript{18} However, while TRMC is an excellent probe of working devices, it is unable to distinguish between the different charge carriers and interfaces of the cell. There have so far been no studies addressing the effect of $\Delta E$ on hole yield at the perovskite|HTL heterojunction with optical techniques such as transient absorption spectroscopy (TAS), which offer a direct and interface-specific probe of hole transfer.

Such a study would have important implications for device open-circuit voltage ($V_{oc}$) – defined as the quasi-Fermi level splitting (QFLS) of electrons and holes under illumination. As described in Fig 3-1, in ideal circumstances, where recombination occurs purely between the electron and hole population at the band edges, and taking methylammonium lead triiodide (MAPbI$_3$) perovskite as an example, $eV_{oc}$ should be equal to 1.32 V after consideration of detailed balance.\textsuperscript{19-21} In reality, several phenomena including interfacial recombination,\textsuperscript{22} phase separation\textsuperscript{23} and – most notably for the present study - imbedded ‘overpotential’ ($\Delta E$) at the interfaces with CTLs limit the $V_{oc}$.\textsuperscript{24} Indeed, typical voltages for MAPbI$_3$-based cells still lie at around 1.1 V.\textsuperscript{25-27} Some smart defect management strategies have led to impressive voltages e.g. 1.13 V, but this is still 14% away from the theoretical maximum of 1.32 V.\textsuperscript{28}

It is therefore surprising that little attention has been paid to the role of $\Delta E$ in determining the $V_{oc}$, illustrated in Fig 3-1. Theoretically, at open-circuit, holes should occupy states in the HTL to an extent that depends on $\Delta E$. Given the resulting upward shift of the quasi-Fermi energy, the QFLS, and ultimately $V_{oc}$ would be reduced. Some studies have questioned this effect, usually on the grounds that injection cannot occur at $V_{oc}$, or that ion migration effects shield the overpotential related to $\Delta E$.\textsuperscript{29-31} However, a recent study by Stolterfoht \textit{et al} has proved the relationship between $\Delta E$ and $V_{oc}$ across a number of perovskite|CTL combinations, building on circumstantial evidence from many other publications over the last decade of PSC research.\textsuperscript{25,32-35} Therefore, given the delicate balance between $\Delta E$ and $V_{oc}$, a better understanding of charge separation in MAPbI$_3$|HTL systems could benefit the future optimisation of PSCs.

In this work, we investigate the effect of $\Delta E$ on the yield and kinetics of hole injection at perovskite|HTL (perovskite = MAPbI$_3$, Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$PbI$_3$) heterojunctions through steady-state and time-resolved photoluminescence (ss-PL and TRPL) along with microsecond transient absorption spectroscopy (TAS), allowing for an interface-specific
probe of hole transfer and recombination. The resulting investigation revealed that hole injection into the HTLs is possible even at $V_{OC}$ and shows that a remarkably small $\Delta E$ (0.1 ± 0.1 eV) is required to drive large hole transfer yields (77%) and ultrafast (< 1 ns) hole injection. We also show that recombination of holes at the MAPbI$_3$|HTL interface is typically $10^5$ slower than the initial injection process allowing for sustained charge separation. Finally, we present an extensive survey of over 100 perovskite|HTL devices across the literature and our own measurements, confirming some correlation between $\Delta E$ and $V_{OC}$. The findings herein have important implications for the design of PSCs, as we provide strong evidence that careful consideration of $\Delta E$ could further increase their $V_{OC}$.

3. 3. Materials & Methods

3. 3. 1. Sample and Device preparation

Glass slides were cut to 1x1 cm and washed in detergent, acetone, water and isopropanol sequentially. Mesoporous TiO$_2$ substrates were prepared by spin-coating commercial TiO$_2$ paste (Dyesol), diluted in ethanol 2:7 (paste: ethanol), at 6000 rpm for 30 s onto the clean glass slides. They were then annealed at 500 °C for 45 minutes. Mesoporous Al$_2$O$_3$ substrates were fabricated by spin-coating commercial Al$_2$O$_3$ paste (Sigma) at 6 wt% in isopropanol at 6000 rpm for 30 s onto clean glass slides. They were then dried at 150 °C for 1 hour. The MAPbI$_3$ deposition method was adapted from that of Seok et al.\textsuperscript{36} The MAPbI$_3$ precursor solution contained a 1:1 molar ratio of PbI$_2$ (Sigma) and CH$_3$NH$_3$I (Sigma) at a concentration of 1.2 M in a mixture of γ-Butyrolactone and dimethyl sulfoxide (ratio 3:7). Once properly mixed, the resulting solution was spin-coated onto the relevant substrate in a 3-step program at 1000, 5000 and 6000 rpm for 10, 30 and 20 s respectively. Importantly, between the second and third step, 300 µL of toluene was drop casted onto the spinning film to aid crystallisation. After the spin-coating program, the film was dried on a 100 °C hotplate for 10 minutes. The formation of the perovskite was indicated by a colour change from pale yellow to dark brown. HTL solutions at 10 mg/mL could then be spin-coated on top of the MAPbI$_3$ film at a speed which ensured all HTL layers were 30±5 nm thick. P3HT and PTAA were purchased from Sigma-Aldrich, F8T2 and TFB from Osilla and all other polymers from 1m mater.

Device Preparation: FTO-coated glass substrates (100 x 25 mm, 2.3 mm thick TEC15, Pilkington) were cut to 25 x 25 mm after etching with Zn powder and aqueous hydrochloric acid (37%). They were then sequentially cleaned in acetone, distilled water and IPA with sonication for 10 min per cycle. The compact TiO$_2$ precursor was made from 350 mL titanium isopropoxide (Aldrich), 35 ml hydrochloric acid (37%) and 5 ml anhydrous ethanol.
This was then spin-coated at 5000 rpm for 30 s and sintered at 160 °C for 5 min and then 500 °C for 45 min. The mesoporous TiO$_2$ layer was prepared by diluting the titania paste (18NR-T, Dyesol) in ethanol (2:7 mass ratio) and was deposited on the blocking layer. The layer was then dried on a hotplate at 80 °C for 10 min and subsequently sintered at 500 °C for 45 min. The MAPbI$_3$ layer was prepared using a one-step deposition as mentioned in the film fabrication. Hole transport layers were spin coated on top of the MAPbI$_3$ from a solution of 10 mg/mL in anhydrous chlorobenzene. Finally, a 100 nm thick gold contact was evaporated under vacuum (~10$^{-6}$ Torr at a rate of 0.2 nm/s) with an active pixel area of 0.12 cm$^2$.

3.3.2. Characterisation techniques

Photoluminescence Studies: Steady-state photoluminescence spectroscopy was performed with a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer at an excitation of 510 nm and a slit width of 5 nm. Time resolved photoluminescence spectroscopy was undertaken with a Horiba Deltaplex modular fluorescence lifetime system that uses a PPD 900 detector. Excitation of the sample was achieved with a 635 nm LED (Horiba N-635L) at a rate of 1MHz and a fluence (power density) of 0.13 nj/cm$^2$. The half-life of the prompt pulse was 100 ps.

Transient Absorption Spectroscopy: Samples for microsecond transient absorption spectroscopy measurements were taken in a sealed quartz cuvette from the nitrogen-filled glovebox where they had been prepared and excited with a dye laser (Photon Technology International Inc. GL-301) with fluence (power density) 10 µJ cm$^2$ (10$^4$ W cm$^{-2}$). The dye laser was itself pumped by a N$_2$ laser (Photon Technology International Inc. GL-3300). The transient changes in the absorption of the sample were captured with a 100 W tungsten lamp (Bentham IL 1) on an orthogonal optical axis to the excitation beam. The probe wavelength was adjusted by a monochromator (OBB-2001, Photon technology international). This probing beam was detected by a silicon photodiode (Hamatsu Photonics, S1722-01) before being filtered and amplified (Costronics Electronics) and finally interpreted by a digital oscilloscope (Tektronics DPO3012).

Device Characterisation: The J-V measurements were taken using a Keithley 2400 source meter with the samples under AM 1.5 radiation from a solar simulator (Oriel Instruments). The calibration was performed with a silicon photodiode. The scan-rate was 0.125 V s$^{-1}$ for both forward scan (from $J_{SC}$ to $V_{OC}$) and backward scan (in the opposite direction). Cells were placed unmasked under continuous 1 sun illumination during aging and were masked during each scan to ensure the active area (0.12 cm$^2$) remained the same for all measured devices.
3. 4. Results

3. 4. 1. Interfacial Energetics

![Interfacial Energetics Diagram]

**Fig. 3-2:** (a) Structures of all polymeric HTLs used herein. Note that each polymer is referenced by a unique symbol. (b) HOMO energies, $E_{HOMO}$ of all HTLs shown relative to the MAPbI$_3$ valence band energy, $E_{VB}$ (-5.4 eV). Conduction band energy of the TiO$_2$ ETL also shown.$^{37}$

The following HTLs were used for the study (see Fig. 2a for structures): poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT), poly[[2,2′-bithiophene]-5,5′-diyl(9,9-dioctyl-9H-fluorene-2,7-diyl)] (F8T2), Poly(9,9-dioctyfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), poly[N,N′-bis(4-butylphenyl)-N,N′-bisphenylbenzidine] (PTPD), Poly(3-hexylthiophene-2,5-
diyl) (P3HT) or poly((4,8-bis(octyloxy)benzo(1,2-b:4,5-b’))dithiophene-2,6-diyl)(2-((dodecyloxy)carbonyl)thieno(3,4-b)thiophenediyl)) (PTB1).

Incorporating these HTLs in prototype PSCs gave rise to the average MAPbI₃-HTL interface energetics as shown in Fig 3-2. The energies for the MAPbI₃ valence band (Eᵥ_b) edge and HTL HOMO levels (E_HOMO) were obtained by averaging the values reported over many literature works (details in Table 3-1). It is important to note that the HOMO energy acquired from different methods (e.g. Ultraviolet photoelectron spectroscopy, cyclic voltammetry, Kelvin probe) can vary considerably. Therefore, we ensured that all of the values for the different polymeric HTLs were acquired via cyclic voltammetry. We note that the uncertainty of the CV technique (± 0.1 eV) is somewhat higher than that of e.g. UPS. However, CV was the only method common to all HTL layers in the literature and we considered the error associated with the technique to be smaller than the error associated with deriving HOMO energies from a variety of techniques. Moreover, we note that contacting the individual layers will alter the absolute values of the HOMO and band energies of MAPbI₃ and HTL to a degree. However, it has been shown that the relative trend in ΔE between isolated and contacted perovskite and HTL layers (HTL = PTAA, PTPD and P3HT) remains roughly the same. By changing the HTL at the interface, the approximate ΔE could be modulated from 0.5 ± 0.2 eV to -0.5 ± 0.1 eV (hereafter uncertainties omitted).

Table 3-1: Reference (Eᵥ_b) and mean (E_HOMO/V_b) energies for MAPbI₃ valence band edge and HTL HOMO. The MAPbI₃ and HTL values were obtained via photoelectron spectroscopy and cyclic voltammetry respectively. We also include the interfacial energy offset, ΔE ± s = E_HOMO ± s_HOMO - Eᵥ_b ± sᵥ_b, where s denotes the propagation of the standard deviation of the values for E_HOMO and Eᵥ_b. To our knowledge, only one literature value exists for PTB1⁴⁹ and so we add an uncertainty of ± 0.1 eV in this case, which is the error associated with the cyclic voltammetry technique.

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<th>Desc.</th>
<th>E₁ (eV)</th>
<th>E₂ (eV)</th>
<th>E₃ (eV)</th>
<th>E₄ (eV)</th>
<th>E₅ (eV)</th>
<th>E₆ (eV)</th>
<th>E_HOMO/V_b (eV)</th>
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<td>-5.¹⁴⁸</td>
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<td>-5.⁵ ± ⁰.⁰³</td>
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3.4.2. Transient Absorption Spectroscopy

![Diagram of energetic picture in different films]

**Fig. 3-3:** (a-d) Energetic picture in the (a) Al₂O₃|MAPbI₃, (b) TiO₂|MAPbI₃, (c) Al₂O₃|MAPbI₃|HTL and (d) TiO₂|MAPbI₃|HTL films. (e-j) Transient absorption spectra of Al₂O₃|MAPbI₃ (wine), TiO₂|MAPbI₃ (black), Al₂O₃|MAPbI₃|HTL (coloured solid lines) and TiO₂|MAPbI₃|HTL (coloured dashed lines) measured 1 µs after excitation at 510 nm. Each figure is denoted with the corresponding HTL.

We first investigated the yield and recombination dynamics of injected holes at the MAPbI₃|HTL interface with microsecond transient absorption spectroscopy (µ-TAS). An overview of the TAS technique is given in **Section 2.3** and details specific to this chapter in **Section 3.3.3**. Furthermore, samples were excited at 510 nm via the glass substrate, such that the direct excitation density in the HTL layer was small (> 1%) compared to that in the MAPbI₃ layer (See **Section 2.2.2**).

The TA spectra of all TiO₂|MAPbI₃|HTL samples (Fig 3-3, dashed lines) after excitation of the MAPbI₃ layer at 510 nm contained broad features across the near-infra red (NIR; 800 – 1600 nm). Therefore, in order to deconvolute and assign the features, we carried out control spectra on several films: (a) Al₂O₃|MAPbI₃ – where charge carriers can only be located in the MAPbI₃ layer (Fig 3-3a) due to the shallow conduction band of Al₂O₃; (b) TiO₂|MAPbI₃ –
where electrons can be injected into the TiO$_2$ but holes remain in the MAPbI$_3$ layer (Fig 3-3b); and (c) Al$_2$O$_3$|MAPbI$_3$|HTL – where holes can be injected into the HTL but electrons remain in the MAPbI$_3$ layer (Fig 3-3c). Therefore, comparing the spectra in these three cases with those of the TiO$_2$|MAPbI$_3$|HTL films, in which both electron and hole injection may occur (Fig 3-3d), would elucidate which layers dominate the spectrum.

The resulting spectra are given in Fig 3-3e-j. Firstly, the Al$_2$O$_3$|MAPbI$_3$ control (Fig 3-3e-j, wine lines) shows negligible signal across the studied range, which agrees with the rapid (< 1 µs) recombination typical of MAPbI$_3$ films. For the TiO$_2$|MAPbI$_3$ film (Fig 3-3e-j, black lines) we observe a weak contribution increasing towards the infra-red. Moreover, the Al$_2$O$_3$|MAPbI$_3$|HTL (Fig 3-3e-j, solid coloured lines) films generally give intense TA spectra in the infra-red. The new features in the TiO$_2$|MAPbI$_3$ and MAPbI$_3$|HTL films could be for two reasons: (i) charge injection to CTLs increases the lifetime of trap-states in the MAPbI$_3$ film; or (ii) TAS intensity is due to the injected charges themselves. Given that the spectra when MAPbI$_3$ is interfaced with TiO$_2$ or a HTL agree well with literature reports of free electrons in TiO$_2$ and hole polarons in the HTLs respectively, we assign the transient features to (ii).

The P3HT$^+$, PTB1$^+$ and F8T2$^+$ spectra contain a single contribution in the NIR, with respective maxima at 950 nm, 1100 nm and 775 nm respectively. This is in good agreement with values obtained in the literature, for single polarons formed in the HTLs. In contrast, the triarylamine (TFB, PTAA, PTPD) TA spectra contain multiple peaks with significantly red-shifted maxima of 1500, 1500 and 1600 nm, which agree well with previous reports. Generally, the accordance between the MAPbI$_3$|HTL spectra on TiO$_2$ and Al$_2$O$_3$ suggests that the TA spectrum of TiO$_2$|MAPbI$_3$|HTL films is dominated by the HTL polaron (i.e. $\Delta OD_{\text{HTL}}^{\text{max}} > \Delta OD_{\text{TiO}_2}^{\text{max}}$). However, we note that in the specific case of TiO$_2$|MAPbI$_3$|F8T2, $\Delta OD$ for F8T2$^+$ is only double that of TiO$_2^-$, most likely due to the low hole injection yield in this energetically unfavourable ($\Delta E \sim -0.1$ eV) case. Serendipitously, the features associated with F8T2$^+$ ($\lambda \sim 950$ nm) and TiO$_2^-$ ($\lambda > 1100$ nm) can be easily distinguished.

Having assigned the spectra, we could next monitor the population of holes in the different MAPbI$_3$|HTL combinations, by probing the maximum of the respective TA bands as a function of time after excitation. Fig 3-4a depicts the decay of the TiO$_2$|MAPbI$_3$|F8T2 TA spectrum, chosen because of the clear distinction between the F8T2$^+$ ($\lambda \sim 750$ nm) and TiO$_2^-$ ($\lambda > 1000$ nm) features. Here, we find the decay dynamics of F8T2$^+$ and TiO$_2^-$ to be significantly different, which adds weight to our assignation that the two features emanate from different species.
Fig 3-4: (a) Contour plot depicting the decay of the TiO$_2$|MAPbI$_3$|F8T2 TA spectrum. b) TAS decay kinetics for TiO$_2$|MAPbI$_3$|HTL samples probed at the peak wavelength of the polaron TA. (c) The values for $\tau_{rec}$ measured as the time taken for $\Delta$OD to reach 50% of its original value - extracted from the TiO$_2$|MAPbI$_3$|F8T2 spectrum in the F8T2$^+$ (blue) and TiO$_2^-$ (black) regions of the spectrum between 750-800 and 950-1600 nm respectively. (d) Maximum of TAS trace, $\Delta OD_{max}$ normalised for the ground-state absorbance of MAPbI$_3$, taken at 3 μs for all HTLs probed in this study. In all cases, the films were excited at 510 nm under a fluence of 20 μJ cm$^{-2}$ via the substrate.

In order to quantify the recombination time constants in each TiO$_2$|MAPbI$_3$|HTL system, we fitted the relevant TAS traces with a stretched exponential: $\Delta OD \propto e^{-\left(\frac{t}{t_0}\right)^\alpha}$. This function accounts for the non-exponential recombination dynamics typical of systems that contain a significant amount of disorder. In this case, the stretched exponential could signify the energetic disorder of the HTL as well as recombination over a broad range of distances. Given that the overall lifetime of the stretched exponential can be fitted with multiple combinations of $t_0$ and the stretching factor, $\alpha$ we avoided extracting quantitative information from the fit itself. Instead, we approximated the recombination lifetime of the species in question with, $\tau_{rec}$ as the time taken for the signal to drop to 50% of its original value. Fitted traces for all of the TiO$_2$|MAPbI$_3$|HTL films are given in Fig. 3-4b and the time constants for recombination of the injected holes at the MAPbI$_3$|HTL interface, $\tau_{rec}$ are given in Table 3-4 (vide infra). We found that in all cases where $\Delta E > 0$ eV, $\tau_{rec}$ was remarkably slow, between 0.1 – 1 ms.
In the case of F8T2 ($\Delta E < 0$ eV), we calculate $\tau_{rec,h}$ as 0.02 ms. This faster decay is most likely due to the favourable energy offset for back electron transfer at the MAPbI$_3$|F8T2 interface. Indeed, it is likely that a portion of the decay occurs within the instrumental response and as such this value for $\tau_{rec,h}$ should be viewed as an upper limit. Moreover, the blue-shifted TA of F8T2 in TiO$_2$|MAPbI$_3$|F8T2 films, allowed us to isolate the decay kinetics of TiO$_2^{-}$ (Fig. 3-4c), $\tau_{rec,e} = 0.1 \pm 0.013$ ms.

Moreover, the different time constants of F8T2$^+$ ($\tau_{rec,h} = 0.015$ ms) and TiO$_2^{-}$ ($\tau_{rec,e} = 0.1$ ms) decay reflect something about device architecture. In the early days of perovskite research, cells were based on their dye-sensitized precursors, in which both the active layer and HTL were infiltrated into the mesoporous TiO$_2$ (mp-TiO$_2$) layer. In this ‘perovskite-sensitized’ system, $\tau_{rec}$ for HTL$^+$ and TiO$_2^{-}$ were similar, signifying that the majority of recombination occurs between the two CTL layers. However, in the present system, the MAPbI$_3$ layer entirely fills the mp-TiO$_2$ and forms an overlayer above it. As such, no direct interface between ETL and HTL is formed, meaning that the TAS dynamics are due to recombination of the injected charges with their opposite number in the MAPbI$_3$ layer.

In Fig 3-4d we plot the maximum of the transient absorption trace, $\Delta \OD_{max}$, corrected for the MAPbI$_3$ ground-state absorption, versus $\Delta E$. $\Delta \OD_{max}$ is related to the concentration of photogenerated transient species and so the yield of hole transfer. Therefore, this data suggests that the hole injection yield increases with $\Delta E$. However, we stress that in order to obtain an absolute yield from TAS, the signal must be corrected for the extinction coefficient of the oxidised polymer in accordance with the Beer-Lambert law.

3. 4. 3. Steady-State Photoluminescence

A complimentary technique with which to assess the extent of hole transfer is photoluminescence quenching. Here, we selectively excite the MAPbI$_3$ layer at 510 nm and monitor its photoluminescence yield in the presence of the different HTLs. This situation can be modelled by the rate equation:

$$\frac{dn}{dt} = G - k_{inj}n - An - Bn^2$$

(3.1)

where $n_y$ and $n$ are the concentration of incident photons and photo-induced holes respectively, $G$ is the charge generation rate, $k_{inj}$ the hole injection rate constant and $A$ & $B$ are the first-order and second-order recombination rate constant for the MAPbI$_3$ layer. At the low fluences associated with this experiment we excluded the contribution of Auger recombination. As modelled by the $k_{inj}n$ term, hole transfer provides a competing pathway
for relaxation of the MAPbI$_3$ excited state. Therefore, quenching of the MAPbI$_3$ fluorescence is directly related to the yield of hole transfer.

We note that while this method has been part of the basic toolkit for characterising charge transfer in OPV, DSSC and PSC systems for many years, some recent studies have questioned the relevance of charge injection in films (i.e. at $V_{OC}$), on the basis that net extraction is, by definition, zero. However, our TAS measurements (Fig 3-3) prove that while there may be no net extraction from the film, there is a significant population of holes in the HTL. We therefore attribute the quenching in the MAPbI$_3$|HTL samples in Fig 3-5a to hole injection from the MAPbI$_3$ valence band into the HOMO level of the HTL.

![Fig 3-5: ss-PL spectra for MAPbI$_3$ compared with MAPbI$_3$|HTL samples excited at 510 nm. (b) Effect of $\Delta E$ on the quenching efficiency, $\eta$. The fitted lines indicate the model calculations following Equation 1.3 for $\sigma = k_B T$ (dashed line) and $\sigma = 1.2$ eV (solid line).](image)

The resulting spectra of the MAPbI$_3$ and MAPbI$_3$|HTL samples are displayed in Fig. 3-5a. MAPbI$_3$ exhibited an intense narrow emission at 770 nm due to the near-band-edge recombination between electrons and holes across its 1.6 eV band gap. As shown in Fig. 5a the MAPbI$_3$ emission was quenched significantly in the presence of all of the HTLs, except for F8BT, which imposes a 0.5 eV barrier to hole transfer.

Interestingly, we find that the MAPbI$_3$ photoactive layer is more emissive in the presence of F8BT relative to the pristine sample. This can be attributed to either (i) better passivation of surface defects or (ii) injection of photoexcited electrons and holes from F8BT into the MAPbI$_3$ layer (Fig 3-5a inset). The fact that we also observe this effect with insulating poly(methyl methacrylate) (PMMA; Fig 3-5a, dashed line) and that the MAPbI$_3$ film is consistently excited via the glass (penetration depth ~ 90 nm at 510 nm) to avoid direct excitation of the HTL, we can confidently confirm that this is a passivation effect. Indeed, such passivation from insulating polymers has been reported widely in the literature.
This finding poses some important questions – if non-injecting polymers can effectively triple the MAPbI$_3$ PLQY, are CTLs with $\Delta E > 0$ eV also capable of this effect? And if such interactions exist, are they involved in the charge transfer mechanism at the PSC interfaces? Indeed, this initial finding was the inspiration for the work in chapter 5 (vide infra), where we outline the critical role that such interactions play in charge transfer at MAPbI$_3$|CTL interfaces.

Fig 3-5b shows the effect of $\Delta E$ on the quenching efficiency, $\eta$, which we define as,

$$\eta = \frac{PL - PL_Q}{PL}$$

(1.2)

where $PL$ and $PL_Q$ are the intensities of each of the MAPbI$_3$|HTL samples before and after addition of the HTL. As the level of quenching is directly related to the concentration of holes removed from the perovskite valence band, $\eta$ is an indicator of relative hole yield. Here we assume that the addition of the HTL does not alter the trap density in the perovskite layer. We further note that $\eta$ is taken to be zero for MAPbI$_3$|F8BT as there is no evidence of hole injection from PL or the TAS measurements in Fig 3-4.

As expected, a higher yield of hole transfer is observed as $\Delta E$ is progressively increased. However, what is most striking here is the sharpness of this trend. For example, TFB provides a driving energy of $\Delta E \sim 0.1$ eV, but quenches 77% of the original MAPbI$_3$ PL. A further increase of $\Delta E$ to 0.5 eV in the case of PTB1 results in a relatively small increase in $\eta$, to 93%. This means that large charge transfer yields are possible at remarkably low levels of ‘overpotential’. The origin of this low-cost, high yield hole injection is in the small exciton binding energy ($E_b = 16$ meV = 0.6$k_bT$) of MAPbI$_3$, which means that the MAPbI$_3$ layer consists of free-carriers at room temperature. Therefore, in contrast to e.g. organic solar cells (OSCs) where exciton binding energies can be more significant, the HTL does not need to provide extra potential to drive the separation of excitons.

Surprisingly, despite a hole transfer barrier of $\Delta E \sim -0.1$ eV, F8T2 still produces a $\eta$ of 15.6%. The apparent interfacial barrier in this case is too large for hole transfer to occur via thermal excitation alone ($k_bT = 0.026$ eV at 298 K) and so another factor must be influencing the hole transfer process in this system. In explanation of this phenomenon, we turn to the work of Haque et al on DSSCs. They found that the relationship between hole yield and $\Delta E$ could be modelled by an error function,

$$yield = A \int_{\Delta E}^{\infty} \exp\left[-\left(\frac{E^2}{2\sigma^2}\right)\right] dE$$

(1.3)
where $A$ is a constant and $\sigma$ is the standard deviation of the Gaussian distribution ($\sigma \gg k_B T$). They rationalised the use of this model due to the inhomogeneous broadening of $\Delta E$ at the interface. By applying such a model to our PL data, we obtain a good fit for $\sigma = 0.12$ eV (FWHM = 0.28 eV; Fig 3-5b, solid line), suggesting a significant amount of energetic disorder around five times the thermal energy (0.026 eV at 298 K; Fig 3-5b, dashed line). Such inhomogeneous broadening can be explained by the high level of structural disorder inherent to polymeric materials, which results in a broad distribution of energies around the quoted HOMO level. Consequently, even though the HOMO of F8T2 appears to be situated below the MAPbI$_3$ valence band, the energetic disorder produces tail states that lie at a favourable energy for hole transfer. The energetic disorder we find here ($\sigma = 0.12$ eV; FWHM = 0.28 eV) is consistent with that observed in other hybrid systems e.g. metal-organic interfaces.

Additionally, it is noteworthy that the value for $\sigma$ found here for PSCs is significantly less than that observed for DSSCs ($\sigma = 0.19$ eV). This follows from the fact that in the latter case both donor and acceptor are organics with the propensity for significant disorder, whereas in the former only the hole acceptor is disordered with the perovskite being a relatively ordered crystalline donor. We note that another factor in the inhomogeneous broadening observed herein could be the shift of $\Delta E$ upon contacting the HTL and perovskite, as the quoted value is based on their respective ionisation potentials in isolation.

3.4.4. Time-Resolved Photoluminescence

We next probed the real-time dynamics of hole transfer for the MAPbI$_3$|HTL samples using time-resolved photoluminescence (TRPL), with the results presented in Fig 3-6a. The decay of the pristine MAPbI$_3$ sample was fitted to a bi-exponential which accounted for a fast ($\tau_1$) and slow component due to charge trapping at the surface and in the bulk respectively. The introduction of an HTL in all cases except F8BT resulted in the acceleration of the MAPbI$_3$ PL decay. The literature comprises two competing explanations for such behaviour: (i) rapid hole injection; (ii) enhanced interfacial recombination introduced by the HTL, as hole injection, it is argued, shouldn’t be possible at open-circuit. Given that transient absorption spectroscopy (TAS) data categorically proves hole injection (Fig 3-4), we attribute this quenching effect mainly to (i). Moreover, the decay was found to accelerate when $\Delta E$ was increased, with both $\tau_1$ and $\tau_2$ decreasing.

As shown in Fig 3-6a, the PL decay of MAPbI$_3$|HTL samples can be fitted to a biexponential, with a fast component indicative of monomolecular hole transfer to the HTL and a slow component due either to surface or bulk monomolecular recombination in the MAPbI$_3$.
The details of the fitting can be found in Table 3-2. We note that in the case of F8BT, the lifetime is slower than the recombination within the MAPbI₃ layer and therefore cannot be a valid indicator of hole injection. In fact, this provides further evidence that polymeric materials can effectively passivate the MAPbI₃ surface.

**Table 3-2:** Summary of the biexponential fitting ($y(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$) for the photoluminescence decay of MAPbI₃ and MAPbI₃|HTL films in Fig 3-6a. The values are displayed as the average over three repeats with the standard deviation given as the uncertainty.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>0.68 ± 0.03</td>
<td>436 ± 46.7</td>
<td>0.32 ± 0.03</td>
<td>2540 ± 258</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>F8BT</td>
<td>0.69 ± 0.09</td>
<td>557 ± 132</td>
<td>0.31 ± 0.09</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>F8T2</td>
<td>0.66 ± 0.054</td>
<td>347 ± 23.4</td>
<td>0.34 ± 0.052</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>TFB</td>
<td>0.60 ± 0.041</td>
<td>331 ± 68.3</td>
<td>0.40 ± 0.041</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>PTAA</td>
<td>0.83 ± 0.077</td>
<td>314 ± 60</td>
<td>0.17 ± 0.077</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>PTPD</td>
<td>0.90 ± 0.093</td>
<td>278 ± 7</td>
<td>0.097 ± 0.093</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>P3HT</td>
<td>0.87 ± 0.028</td>
<td>208 ± 10</td>
<td>0.13 ± 0.028</td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>PTB1</td>
<td>0.94 ± 0.071</td>
<td>178 ± 7</td>
<td>0.064 ± 0.071</td>
</tr>
</tbody>
</table>

In all other cases when MAPbI₃ was coated with an HTL, the value for $\tau_1$ was smaller than in MAPbI₃, suggesting hole injection begins to become rate limiting. As such, in these cases we assign $\tau_1 = \tau_{inj}$, reflecting the injection kinetics into the HTL. In Fig 3-6b, we show that $\tau_{inj}$ decreases as a function of $\Delta E$. Upon raising the driving energy from $\Delta E \sim -0.5$ eV to $\Delta E \sim 0.1$ eV, the PL decay became dominated by hole transfer with $\tau_{inj} = 331$ ps for the
MAPbI₃–TFB sample. This suggests that hole transfer occurs on a sub-nanosecond timescale at a driving energy of just 0.1 eV. We note that all observed values for $\tau_{inj}$ were found to be much larger than the instrumental response half-life of 100 ps, allowing for the accurate assignation of these PL decay dynamics.

**Fig 3-7:** PL decay kinetics for MAPbI₃|PTAA samples in which the MAPbI₃ layer was treated with 2.5, 5 and 10 mg mL⁻¹ PhEtNH₃I. Excitation fluence: 0.11 nJ/cm².

**Table 3-3:** Bi-exponential fitting parameters for time-resolved single photon counting (TCSPC) traces in Fig. 3-7. The half-life of the unquenched MAPbI₃:PEAI film, $\bar{\tau}_{rec,M}$ is also given for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{\tau}_{rec,M}$ (ps)</th>
<th>$A_1$</th>
<th>$\tau_1 = \tau_{HT}$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_{rec}$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>PTAA</td>
<td>453</td>
<td>0.894</td>
<td>399</td>
<td>0.106</td>
</tr>
<tr>
<td>MAPbI₃:PEAI-2.5</td>
<td>PTAA</td>
<td>660</td>
<td>0.672</td>
<td>399</td>
<td>0.328</td>
</tr>
<tr>
<td>MAPbI₃:PEAI-5</td>
<td>PTAA</td>
<td>708</td>
<td>0.950</td>
<td>399</td>
<td>0.05</td>
</tr>
<tr>
<td>MAPbI₃:PEAI-10</td>
<td>PTAA</td>
<td>1060</td>
<td>0.683</td>
<td>399</td>
<td>0.317</td>
</tr>
</tbody>
</table>

The accuracy of our assessment of the injection time, $\tau_{inj}$ with TCSPC (Fig 3-6) is predicated by $\tau_{inj}$ being much faster than the recombination processes in the perovskite i.e. the combination of $\tau_1$ and $\tau_2$ (hereafter denoted by $\bar{\tau}_{rec,M}$). However, $\tau_{inj}$ and $\bar{\tau}_{rec,M}$ are on the same order of magnitude in our MAPbI₃-HTL films which led us to question the reliability of our value for $\tau_{inj}$. The value for $\bar{\tau}_{rec,M}$ in the MAPbI₃ films was essentially limited by the relatively low fluence (0.11 nJ cm⁻²) of the excitation source in our commercial TCSPC set up. At these low fluences, the PL dynamics exhibited by MAPbI₃ are dominated by rapid trapping most likely at the surface and grain boundaries ($\tau_1 \sim 1$ ns). With no option to increase the excitation fluence, we had to find an alternative route to decreasing the trap density in the MAPbI₃ film. We show in Chapter 4 that treatment of the MAPbI₃ surface with phenethylammonium iodide (PEAI) can effectively suppress non-radiative recombination and
increase $\bar{\tau}_{\text{rec},M}$. Therefore, we decided to check our measured values for $\tau_{\text{inj}}$ as a function of $\bar{\tau}_{\text{rec},M}$ after passivation with PEAI.

Fig 3-7 and Table 3-3 show for the example of PTAA that even as the PL half-life, $\bar{\tau}_{\text{rec},M}$ of MAPbI$_3$ is increased through PEAI passivation, the hole injection kinetics ($\tau_1 = \tau_{\text{inj}}$) remain constant with the difference in overall lifetime accommodated by $\tau_2$. This adds weight to our use of $\tau_{\text{inj}}$ as an approximate measure of hole transfer time in the other MAPbI$_3$|HTL samples covered in Fig 3-6 and Table 3-2.

In the case of the HTLs that satisfy $\Delta E < 0$ eV, we concede that no reliable value for $\tau_{\text{inj}}$ can be produced. To obtain an accurate value for HTLs in which the injection dynamics are similar to, or slower than, the MAPbI$_3$ decay, TCSPC studies could be carried out on MAPbI$_3$ films that have a lower effective trap density. This would be best achieved by carrying out the measurements at slightly higher fluence (e.g. 0.03 $\mu$J cm$^{-2}$),$^{89}$ as passivation treatments could affect the hole transfer process.

Another factor affecting the value for $\tau_{\text{inj}}$ is the instrumental response time (~100 ps) of our TCSPC system. It is possible that some of the photoluminescence decay occurs within this time-frame. However, we accounted for this in the following ways. Firstly, we carried out measurements such that photons were collected over the same time for the quenched samples as for the control. Assuming the addition of the CTL does not alter the trap density at the MAPbI$_3$ surface, injection on <100 ps timescale would then be indicated by an attenuation of the initial signal. However, we observed no such effect. Secondly, the ratio of the integrated area under the TCSPC trace in the quenched and unquenched case matched closely with the quenching efficiency garnered from steady-state PL in Fig 3-5. Finally, our values match well with the injection timescales of 0.1-1 ns reported for other CTLs.$^{94,95}$ These points strengthen our argument that the dynamics occur on a >100 ps timescale.

### 3. 4. 5. Overview of Charge Transfer Dynamics in the TiO$_2$|MAPbI$_3$|HTL System

The key findings from the transient optical characterisation so far are summarised in Fig 3-8 and Table 3-4. This allows us to describe the photo induced charge separation processes in MAPbI$_3$-based cells from start to finish. (1) Photon absorption occurs rapidly (< 100 fs), followed by cooling of charge-carriers to the band edges (~100 fs).$^{94}$ (2) Recombination ensues in the MAPbI$_3$ layer either via trap-mediated ($\tau_1 \sim 1$ ns) or radiative ($\tau_2 \sim 10$-100 ns) recombination. The dominant recombination mechanism is governed by the trap-density in the MAPbI$_3$ layer. (3) Electrons are injected into the TiO$_2$ layer on a timescale reported by Xing et al to be 400 ps.$^{94}$ (4) Simultaneously, holes are injected into the HTL on a sub-nanosecond timescale in situations where $\Delta E > 0$ eV. (5) Injected electrons in TiO$_2$
recombine via traps at the MAPbI₃|ETL interface (~ 0.1 ms, Fig 3-4c). (6) Injected holes recombine at the MAPbI₃|HTL interface (0.1 - 1 ms).

**Fig 3-8:** Summary of calculated and literature time constants at TiO₂|MAPbI₃|HTL interfaces. (1) Electrons (holes) are generated in the conduction (valence) band and rapidly cool to the band edges;⁸⁴ (2) radiative/non-radiative recombination in the MAPbI₃ layer;⁸⁴,⁹⁴,⁹⁶ (3) electron injection into TiO₂;⁹⁴ (4) hole injection into HTL; (5) recombination of electrons in TiO₂ via interfacial traps; (6) recombination of holes in the HTL via interfacial traps. Red and green arrows indicate recombination and injection respectively. The values for (1), (2) and (3) were obtained from the literature.

**Table 3-4:** Summary of the key results found for the MAPbI₃|HTL samples investigated: PL quenching efficiency, η, TAS injection yield, m∆OD_{max}, injection time, τ_{inj} and interfacial recombination time, τ_{rec,h}.

<table>
<thead>
<tr>
<th>HTL</th>
<th>ΔE (eV)</th>
<th>η</th>
<th>m∆OD_{max}</th>
<th>τ_{inj} (ps)</th>
<th>τ_{rec,h} (ms)</th>
<th>τ_{rec,h}/τ_{inj} (×10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F8BT</td>
<td>0.5</td>
<td>0</td>
<td>0.00710</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F8T2</td>
<td>0.1</td>
<td>0.156</td>
<td>0.0141</td>
<td>347</td>
<td>0.0143</td>
<td>0.0412</td>
</tr>
<tr>
<td>TFB</td>
<td>0.1</td>
<td>0.770</td>
<td>0.0419</td>
<td>294</td>
<td>0.160</td>
<td>0.544</td>
</tr>
<tr>
<td>PTAA</td>
<td>0.2</td>
<td>0.832</td>
<td>0.100</td>
<td>285</td>
<td>0.1</td>
<td>0.278</td>
</tr>
<tr>
<td>PTPD</td>
<td>0.2</td>
<td>0.870</td>
<td>0.0468</td>
<td>278</td>
<td>0.360</td>
<td>1.29</td>
</tr>
<tr>
<td>P3HT</td>
<td>0.5</td>
<td>0.912</td>
<td>0.139</td>
<td>208</td>
<td>1.21</td>
<td>5.82</td>
</tr>
<tr>
<td>PTB1</td>
<td>0.50</td>
<td>0.927</td>
<td>0.0907</td>
<td>178</td>
<td>0.453</td>
<td>2.54</td>
</tr>
</tbody>
</table>

Ultimately, the efficiency of perovskite solar cells is predicated by the victory of charge generation & extraction (Figure 3-8; 1, 3 and 4) over recombination (Figure 3-8; 2, 5 and 6). Focusing on the perovskite|HTL interface, a large ratio between the time constants for extraction and recombination (τ_{rec}/τ_{inj}) is important for sustained charge separation in a solar cell. We can write a rate equation for the injected hole population perovskite|HTL films as,
\[
\frac{dn_+}{dt} = k_{inj}n - k_{rec,h}n_+
\] (1.4)

where \(n_+\) is the concentration of injected holes, \(n\) is the number of photoexcited holes in the MAPbI\textsubscript{3} layer, \(k_{inj}\) is the rate constant for injection and \(k_{rec,h}\) is the rate of recombination of injected holes. We have shown here that \(k_{rec,h}\) for all cases where \(\Delta E > 0\) eV is \(\times 10^5\) slower than \(k_{inj}\) (Table 3-4). This is only an order of magnitude less than for the state-of-the-art HTL spiro-OMeTAD.\textsuperscript{12} We have therefore established that kinetic competition between charge injection (\(k_{inj}\)) and recombination (\(k_{rec,h}\)) should not be device-limiting. We note that the role of process (2) and processes (3, 4, 5 and 6) are explored in more detail in chapters 4 and 5 of this thesis respectively.

Finally, in a device setting, an additional parameter must be considered: the hole mobility, \(\mu_h\) in the HTL. Having established \(k_{rec,h}\) we can make a rough estimate of the minimum value of \(\mu_h\), under the assumption that injected holes must traverse the 30 nm HTL film to the anode in \(t < 0.1\) ms. This allows us to estimate the diffusion constant, \(D\) as \(9 \times 10^{-8}\) m\(^2\) s\(^{-1}\). This in turn can then be converted to \(\mu_h\) via the Einstein relation,

\[
\mu_h = \frac{De}{k_B T}
\] (1.5)

where \(e\) is the elemental charge and \(k_B T\) is the thermal voltage. Via this rudimentary method we obtain \(\mu_h < 1 \times 10^{-2}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), which is reasonable when considering the mobilities of successful HTLs in MAPbI\textsubscript{3}-based solar cells. For example, while HTLs such as spiro-OMeTAD have typical \(\mu_h\) of \(10^{-5}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), they need to be doped considerably in order to work. As reported by Hawash \textit{et al}, \(\mu_h\) of spiro-OMeTAD increases to \(1.5 \times 10^{-2}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) upon doping, satisfying our roughly estimated requirement.

3.4.6. Consistency with Other Perovskite Systems

The introduction of ever more complex mixtures of A, B and X ions has been central to the drive forward in ABX\textsubscript{3} hybrid organic-inorganic perovskite efficiency over the last decade. Of these, Cs\(_{0.5}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.99}\text{PbI}_3\) (CsFAMAPbI\textsubscript{3}) perovskite, in which the A-site is alloyed with Cs and FA (formadinium) is one of the most prominent.\textsuperscript{97-99} When incorporated into PSCs, CsFAMAPbI\textsubscript{3} exhibits enhanced efficiency compared to MAPbI\textsubscript{3} due in part to its lower trap-state density.\textsuperscript{98,100,101} Therefore, we found it important to demonstrate that the results found in this chapter are consistent with the wider perovskite family and whether differences in charge injection and recombination could be in part responsible for the improved device performance in CsFAMAPbI\textsubscript{3}.
We first looked to ascertain what impact the addition of Cs and FA cations has on the trap-state density in the perovskite. Fig 3-9 shows that both perovskites have nanosecond decay lifetimes, consistent with trapping of photoexcited charges. However, the significantly slower lifetime in the case of CsFAMAPbI\(_3\) suggests that its trap-density is significantly lower. This is in good agreement with other reports in the literature that suggest the alloying of the A-site reduces the trap density.\(^{98,101,102}\)

Next, we conducted ss-PL, TCSPC and TAS measurements on CsFAMAPbI\(_3\) in order to extract \(\eta\), \(\tau_{\text{inj}}\) and \(\tau_{\text{rec},h}\) and compare to the MAPbI\(_3\)|HTL films characterised earlier in this chapter. Fig 3-10a and b show that the yield, \(\eta\) and rate of hole injection at the CsFAMAPbI\(_3\)|HTL interface have the same sharp increasing trend with \(\Delta E\) as observed with MAPbI\(_3\)-based films. Interestingly, the values for \(\eta\) are almost identical and \(\tau_{\text{inj}}\) deviates no more than 18% between the two perovskite types. The close agreement between the values for \(\eta\) and \(\tau_{\text{inj}}\) independent of the two perovskite types suggests that injection at the perovskite|HTL interface is similar. Moreover, this adds weight to the assertion that the findings herein should be relevant to other perovskite systems e.g. state-of-the-art multication systems and emerging Sn- and QD-based perovskites, provided they consist of free carriers rather than bound excitons at operation temperatures.
We next investigated the recombination of injected holes across the perovskite|HTL (HTL = PTAA, P3HT, PTB1) interface with TAS, results in Fig 3-10c-e. Surprisingly, we find that recombination is consistently slower in the case of CsFAMAPbI₃ compared to MAPbI₃. Notably, Hu et al found that the trap density decreases from \( n_T = 2.5 \times 10^{15} \text{ cm}^{-3} \) to \( n_T = 8 \times 10^{14} \text{ cm}^{-3} \) upon addition of 5% Cs to FAMAPbI₃. Therefore, we suggest that the lower \( n_T \) in CsFAMAPbI₃ compared to MAPbI₃ reduces interfacial recombination at the perovskite|HTL interface, accounting for the longer-lived TAS decays. Such suppression of interfacial recombination would be reflected in an increase in the \( V_{oc} \) and may be a factor in the enhanced performance observed in CsFAMAPbI₃-based devices.

### 3.5. Implications for Device Design

A key finding of this chapter has been that a remarkably small \( \Delta E \sim 0.1 \text{ eV} \) is required to drive highly efficient (> 75%) injection yields. We ascribe this to the large dielectric constant of MAPbI₃ that reduces the exciton binding energy, \( E_b \), to around 16 meV (0.6\( k_B T \)), relaxing the requirement for the interface to drive exciton splitting. This puts PSCs in the same bracket as other high-performance inorganic solar cell materials such as GaAs (\( E_b \sim 0.2k_B T \)),...
Si ($E_b \sim 0.4k_BT$), CdSe ($E_b \sim 0.4k_BT$) and CdS ($E_b \sim k_BT$), which share this attribute. Therefore, in contrast to other thin-film photovoltaic technologies in which $E_b > k_BT$ at operational temperatures - e.g. some types of dye-sensitized and organic solar cells – ∆$E$ can be minimised in PSCs as no extra energy is required to drive exciton separation. In the following, we explore the implications of this for the $V_{OC}$ in PSCs.

As outlined in the introduction, the impact of ∆$E$ at the perovskite|HTL interface is hotly debated in the literature. On the one hand, a few reports have demonstrated little dependence of device $V_{OC}$ on HOMO energy with the suggestion that no hole injection can occur at $V_{OC}$ or that mobile ions in the perovskite layer screen the associated overpotential. On the other, researchers say that the partial occupation of the HTL HOMO level increases the quasi-Fermi level of holes, $E_{f,p}$ above the MAPbI$_3$ valence band edge. This should serve to decrease the quasi-Fermi level splitting and ultimately the $V_{OC}$ to an extent that depends on ∆$E$ (Fig 3-11a).

In this chapter, we have contributed to this debate with correlated TAS and PL measurements that show significant hole injection to the HTL even at $V_{OC}$. This idea is supported by Fig 3-11b and c, in which we analysed the $V_{OC}$ to band-gap ratio ($qV_{OC}/E_g$) for 104 perovskite|HTL combinations as measured in our lab (Fig 3-11b, stars; J-V curves in Fig 3-11c) and in the literature. However, the heavily scattered nature of the trend implies that the relationship is not trivial. We therefore assert that ∆$E$ plays a role in determining the $V_{OC}$ in PSCs but that competing processes - e.g. the ion migration effects put forward by Belisle et al - cloud this picture.

We have shown here that highly efficient hole extraction at the MAPbI$_3$|HTL interface is possible at ∆$E \sim 0.1$ eV. Moreover, at this value of ∆$E$, hole extraction is on the order of $10^5$ times faster than the subsequent electron-hole recombination across the heterojunction. With this in mind, future PSCs could be enhanced by exploring HTLs with ∆$E$ in the range 0 < ∆$E$ < 0.2 eV, thus reaching the optimum balance between high hole transfer yields and minimum voltage loss. This has important implications for the power conversion efficiency ($PCE \propto V_{OC}J_{SC}$) of PSCs as devices are able to achieve large $J_{SC}$ and $V_{OC}$ simultaneously. This goes some way to explaining the success of HTLs with deep-lying HOMO levels such as PTAA, TFB, KR131 and TPA-CN, which all lie within the 0 < ∆$E$ < 0.2 eV range.
Fig 3-11: (a) illustration explaining the effect of injection on the electron and hole Fermi energies ($E_{f,n}$ and $E_{f,p}$), the quasi-Fermi level splitting (QFLS) and the open-circuit voltage ($V_{OC}$). (b) The band-gap normalised $V_{OC}$ ($qV_{OC}/E_g$) for perovskite|CTL systems as found in the literature. $^{11,76-105}$ (c) Device characteristics for an illustrative set of MAPbI$_3$|HTL combinations, corresponding to the stars in (b). Our J-V data was collected by Bu Xiangnan (dashed lines) and Dr Thomas McDonald (solid lines).

Since the completion of this work in 2017, research regarding the optimisation of $V_{OC}$ has intensified. A key driver for this was the 2018 publication from Braly et al, which showed that the internal QFLS in MAPbI$_3$ without any contacts can be as high as 1.28 V, with the implication being that the CTLs impart significant losses to the $V_{OC}$. $^{20}$ By optimising the perovskite|CTL interfaces, research across several groups has recently culminated in a record $V_{OC}$ of 1.26 V in MAPbI$_3$ cells, just 60 mV away from the radiative limit. $^{22,25,130}$ Instrumental in this progress was the 2018 paper from Stolterfoht et al, who optimised the energetic alignment at the perovskite|CTL interface to minimise the $V_{OC}$ loss associated with $\Delta E$. $^{25}$ Incidentally, their best performing HTLs with the least $V_{OC}$ loss fell within the ideal $0 < \Delta E < 0.2$ eV range established herein. $^{25}$

3. 6. Conclusions and Outlook

In summary, we have employed transient and steady-state optical spectroscopy to probe hole extraction at the MAPbI$_3$|HTL interface. PL spectroscopy illuminated the steep trend between the hole injection yield, $\eta$ and the interfacial energy offset, $\Delta E$ with $\eta = 77\%$ and hole injection on the sub-nanosecond scale at $\Delta E \sim 0.1$ eV. Further increases in $\Delta E$ beyond this value resulted in relatively small improvements in extraction. We attribute this
observation to the relaxed requirement for a large $\Delta E$ to drive the splitting of excitons as well as the low level of disorder at the perovskite|HTL interface.

In addition, hole transfer has been observed to occur even through an energetic barrier of $\Delta E \sim -0.1$ eV, which has been attributed to energetic disorder at the MAPbI$_3$|HTL heterojunction. The findings of the PL study have been supported by TAS measurements, which proved the full transfer of holes from the MAPbI$_3$ valence band to the HTL. Moreover, TAS measurements demonstrated that the recombination of holes in the HTL typically occurs at least 200,000 times slower than the initial hole transfer.

We also generalised these results to another perovskite type, namely Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$PbI$_3$. We found that the yield and kinetics of hole injection at the perovskite|HTL interface is similar in both cases. However, interfacial recombination is markedly slower in Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$PbI$_3$, which we attribute to the lower trap-density in this perovskite. The implications of these findings for the $V_{OC}$ of PSCs have been highlighted, and we suggest that further gains could be made by using HTLs with $0 < \Delta E < 0.2$ eV in future PSCs.
3. 7. References


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Chapter 4

Passivation of Perovskite Surfaces with Bulky Iodide Salts for Enhanced Efficiency & Stability
4.1. Abstract

Organic–inorganic halide perovskite materials have emerged as attractive alternatives to conventional solar cells, but device stability remains a concern. Here, we present phenethylammonium iodide as an effective agent for treating iodide vacancies and reveal its bilateral passivation mechanism in full through a mixture of transient and steady-state optical studies as well as optoelectronic device characterisation. We find that the iodide anion fills iodide vacancies that would otherwise contribute to instability and non-radiative recombination. Meanwhile, the phenethylammonium cation targets V\textsubscript{MA} sites at the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} surface, forming layered \((\text{PhEtNH}\textsubscript{3})\textsubscript{2}(\text{MA})\textsubscript{1-n}\text{Pb}\textsubscript{n}I\textsubscript{3n+1}\) heterostructures. We show that controlling the growth of this layer is critical to the improvements observed with this passivation technique, with \(n = 1\) yielding enhancements in hole injection and ultimately efficiency, but \(n > 1\) hindering hole injection and worsening efficiency. Optimised \textit{nip} photovoltaic cells exhibit an efficiency of 16.73%, retain 80% of this after a remarkable 21 days and exhibit much reduced hysteresis. This compares favourably to the control devices that only yielded 12.95% and lost 80% of this within hours.

Most of the results in this chapter are included in the following publications:


- “Bilateral Passivation Mechanism of Perovskite Films with Bulky Iodide Salts”, Manuscript in Preparation
4.2. Introduction

Many of the short-comings of PSCs can be traced back to structural defects. Remarkably, harmful bulk defects that form electronic states within the band-gap – i.e. traps – are found at relatively low concentrations in hybrid perovskites compared to other solution processed technologies. However, the termination of crystal symmetry at the surface and grain boundaries inevitably leads to a significant population of traps at the interfaces with the CTLs. Such traps limit the open-circuit voltage ($V_{OC}$) in MAPbI$_3$ to below the theoretical maximum of 1.32 V.

Moreover, the stability of this class of materials is of critical concern, with the best performing MAPbI$_3$, FAMAPbI$_3$- and CsFAMAPbI$_3$-based PSCs all suffering from degradation and ion-migration-induced hysteresis under working conditions. We recently showed that MAPbI$_3$ is rapidly degraded by superoxide ($O_2^-$) after ambient oxygen interacts with photoexcited electrons at iodide vacancies ($V_I$). Meanwhile, extensive work has been done elsewhere in the literature to understand and mitigate ion-migration-induced hysteresis, with the consensus that this process is mediated by those same $V_I$ sites at the surface and grain-boundaries of the perovskite. Consequently, passivation – the science of eliminating trap states or otherwise rendering them electronically inert – of $V_I$ and other defects has come to the fore as an effective strategy to improve both the stability and efficiency of PSCs.

In 2014, Noel et al showed that Lewis bases (e.g. pyridine) could eliminate the traps associated with Pb$^{2+}$ ions (i.e. iodide vacancies) by forming coordinate bonds with them. Since then, this principle has been expanded to include other small molecules, reduced graphene oxide and inert polymers as passivating agents. This active sub-field has also successfully developed passivation strategies for other defects such as undercoordinated I$^-$, PbI$_2$- antisites and A cation (MA$^+$, FA$^+$, Cs$^+$) vacancies with myriad molecules including caffeine. More recently, researchers have begun to establish the nuances of such passivation. W. Xu et al showed that careful control of the electron density at the passivating moiety determines whether coordination ensues with the (desirable) under-coordinated Pb$^{2+}$ ions or (undesirable) NH$_3^+$ ions. G. Xu et al built on this by showing how tuning molecule dimensions can initiate several simultaneous and synergic passivating interactions. On this basis, Zwitterions make particularly effective passivating agents, and have been shown to simultaneously target positively and negatively charged traps.

Another important passivation method is the use of bulky iodide salts (RNH$_3$I) – which here means those AX salts that cannot be incorporated into a 3D ABX$_3$ perovskite lattice. These include phenethylammonium iodide (PhEtNH$_3$I) and n-butylammonium iodide (BAI), which have been shown to passivate MAPbI$_3$ and related compounds by forming layered...
(RNH₃)₂PbI₄ heterostructures at the surface and grain boundaries.²⁸–³² This has been achieved either via including RNH₃I in the precursor solution,²⁸,²⁹ or application as a post-treatment.³⁰–³² Treatment of MAPbI₃ and related perovskites in this way has lead to significant improvements in efficiency and huge leaps forward in stability, with Grancini et al reporting up to one-year stable CsFAMA-based devices.²⁹ On the other hand, the picture of charge transport in such 3D-2D systems is a complex one, with energy cascades, excitonic effects and energy transfer all playing a role.³³–³⁷ Furthermore, the picture of hole injection and recombination at the MAPbI₃:(RNH₃)₂(MA)ₙ₋₁PbnI₃n⁺₁ HTL interface is even less plain. Firstly, it is unclear whether (RNH₃)₂(MA)ₙ₋₁PbnI₃n⁺₁ actively mediates hole injection as suggested by Cho et al³¹ or simply forms an electron-blocking tunnelling layer as proposed by Wang et al.²⁸ Secondly, little attention has been paid to the growth of the (RNH₃)₂(MA)ₙ₋₁PbnI₃n⁺₁ layer, especially in terms of how higher order (n > 1) structures impact charge separation. This is surprising given the potential for RNH₃⁺ to displace intrinsic MA⁺ in the MAPbI₃ layer. Finally, despite the presence of both positive (RNH₃⁺) and negative (I⁻) species, the potential for bilateral passivation remains unexplored.

Herein, we use a combination of transient and steady-state optical as well as device-based characterisation methods to elucidate the full scale of passivation in MAPbI₃ films treated with phenethylammonium iodide (PhEtNH₃I). Such passivation enhances the efficiency from 12.95% to 16.73% and the stability (t₈₀%) from a few hours to over 500, with a marked reduction in hysteresis. We show that these improvements are due to the simultaneous treatment of VₓI and VₓMA sites with the I⁻ and PhEtNH₃⁺ ions respectively. Moreover, we gain new insights into the charge separation mechanism at the 3D-2D MAPbI₃:(PhEtNH₃)₂(MA)ₙ₋₁PbnI₃n⁺₁ HTL interface: (i) hole injection ensues via a tunnelling mechanism; (ii) efficient hole injection is only possible for n = 1 and is significantly inhibited in systems where n > 1. These findings will aid the further development of intelligent passivation strategies for PSCs.

4. 3. Materials & Methods

4. 3. 1. Sample Preparation

Glass slides were cut to 1 x 1 cm and washed in detergent, acetone, water and isopropanol sequentially. Mesoporous titanium dioxide (mp-TiO₂) substrates were prepared by spin-coating commercial mp-TiO₂ paste (Dyesol), diluted in ethanol 2:7 (paste: ethanol), at 6000 rpm for 30 s onto the clean glass slides. They were then annealed at 500 °C for 45 minutes. Mesoporous aluminium oxide (mp-Al₂O₃) substrates were fabricated by spin-coating commercial Al₂O₃ paste (Sigma) at 6 wt% in isopropanol at 6000 rpm for 30 s onto clean glass slides. They were then dried at 150 °C for 1 hour. The MAPbI₃ deposition method was...
adapted from that of Jeon et al. The MAPbI$_3$ precursor solution contained a 1:1 molar ratio of PbI$_2$ (Sigma) and MAI (Sigma) at a concentration of 1.2 M in a mixture of γ-Butyrolactone and dimethyl sulfoxide (ratio 3:7). Once properly mixed, the resulting solution was spin-coated onto the relevant substrate in a 3-step program at 1000, 5000 and 6000 rpm for 10, 30 and 20 s respectively. 800 µL of toluene was drop casted onto the spinning film between the second and third step to aid crystallisation. After the spin-coating program, the film was annealed on a 100 °C hotplate for 10 minutes. The formation of the perovskite was indicated by a colour change from pale yellow to dark brown.

Once cooled, iodide salt coatings were added via the method first reported by Aristidou et al. Briefly, solutions were prepared by dissolving the iodide salt (ammonium iodide, methylammonium iodide, n-butylammonium iodide, phenylammonium iodide, phenylmethylammonium iodide, phenylethylammonium iodide) in a 1:4 solvent mixture of IPA to chlorobenzene (CB). One hundred microlitres of this solution was then dripped onto pre-deposited perovskite films with a 20 s loading time before spinning at 4,000 rpm and annealing at 100 °C for 5 min. This was followed by a washing step, in which the film was treated with 100 µL of the 1:4 IPA:CB mixture and spin-coated at 4,000 rpm.

HTLs, if relevant, were subsequently deposited via spin-coating such that a 30 ± 5 nm thick layer was formed. PTAA (M$_w$ = 28.422 kDa) and PTB1 (M$_w$ = 48 kDa) were deposited from 10 mg/mL solutions in CB and spin-coated at 5000 and 2500 rpm respectively. PTPD (M$_w$ = 80 kDa) was deposited from an 8 mg/mL solution in CB and spin-coated at 2000 rpm.

4. 3. 2. Device Fabrication

FTO-coated glass substrates (100 x 25 mm, 2.3 mm thick TEC15, Pilkington) were cut to 25 x 25 mm after etching with Zn powder and aqueous hydrochloric acid (37%). They were then sequentially cleaned in acetone, distilled water and IPA with sonication for 10 min per cycle. The compact TiO$_2$ precursor was made from 350 mL titanium isopropoxide (Aldrich), 35 ml hydrochloric acid (37%) and 5 ml anhydrous ethanol. This was then spin-coated at 5000 rpm for 30 s and sintered at 160 °C for 5 min and then 500°C for 45 min. The mp-TiO$_2$ and MAPbI$_3$ layers were then deposited as above. In instances where an iodide salt layer was used, 2.5, 5, 10, and 20 mM solution of phenethylammonium iodide (PhEtNH$_3$I) with isopropyl alcohol (IPA) were prepared, respectively. The solution was then spin coated onto the perovskite layer. The spiro-OMeTAD hole conductor layer was spin coated on top from a solution of 72.3 mg/mL 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) powder in 1 mL anhydrous chlorobenzene. The spiro-OMeTAD solution contained additives including 17.5 µL lithium bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) and 28.8 µL 4-tert-butylpyridine (tBP). Finally, a 100 nm thick gold contact was
evaporated under vacuum ($\sim 10^{-6}$ Torr at a rate of 0.2 nm/s) with an active pixel area of 0.12 cm$^2$.

4.3.3. Superoxide Measurements

A 0.317 mM solution of the hydroethidine (HE) probe was prepared; sonication was used to facilitate miscibility. Photoluminescence spectra were then recorded using an excitation wavelength of 520 nm and slit widths of 10 mm on a Horiba Yobin-Ybon Fluorolog-3 spectrofluorometer.

4.3.4. Ageing Conditions

Films were sealed in a nitrogen glovebox, and dry air was then gassed through for the duration of the degradation and illumination was provided by a tungsten lamp equipped with a UV-blocking filter as previously reported.$^{11,39,40}$

4.3.5. Spectroscopy & Diffraction

Transient absorption spectroscopy of MAPbI$_3$ films was done with a 510 nm excitation at an initial fluence of 10 µJ cm$^{-2}$, which was then damped with neutral density filters to achieve the operating range of 0.1 - 10 µJ cm$^{-2}$. A probe wavelength characteristic of the hole or electron polaron in the CTL was used to monitor charge injection. Details of our TAS set-up are given in Section 2.3. Steady-state photoluminescence was carried out with an excitation wavelength of 510 nm and samples were probed at 760 nm. TCSPC was carried out with the same probe wavelength at an excitation of 635 nm (0.11 nJ cm$^{-2}$). Details of out ss-PL and TCSPC set-up are given in Section 2.4 and 2.5. The XPS measurements were obtained in MultiLab 2000 with the X-ray source provided by monochromated Al K$\alpha$ X-ray photons (hv = 14.9 keV). The core level spectra were performed with a pass energy of 20 eV and step size of 0.05 eV.

XRD patterns were recorded using a Bruker D8 Discover X-ray diffractometer using monochromatic Cu K$_{\alpha1}$ and Cu K$_{\alpha2}$ radiation of wavelengths 1.54056 and 1.54439 Å, respectively. UV-Vis spectra were captured with a Shimadzu UV-2600 integrating sphere spectrophotometer.

Current-Voltage (J-V) Characteristics: The J-V measurements were taken using a Keithley 2400 source meter with the samples under AM 1.5 radiation from a solar simulator (Oriel Instruments). The calibration was performed with a silicon photodiode. The scan-rate was 0.125 V$^{-1}$ s$^{-1}$ for both forward scan (from $J_{SC}$ to $V_{OC}$) and backward scan (in the opposite direction). During the stability measurements, a slow scan rate (0.005 V$^{-1}$ s$^{-1}$) was used to minimize hysteresis effects encountered during the J-V scan. Cells were placed unmasked
under continuous 1 Sun illumination during aging and were masked during each scan to ensure the active area (0.12 cm²) remained the same for all measured devices.

4.4. Results

4.4.1. Film Characterisation

**Fig 4-1:** Passivation concept. (a) Illustration of iodide ion incorporation into vacancies at the perovskite surface from R-NH₃I. The right panel displays the structures of MAI and PhEtNH₃I. (b) schematic outlining the iodide salt treatment process: (i) perovskite precursor is spin-coated onto the substrate; (ii) MAPbI₃ formation after annealing; (iii) spin-coating iodide salt solution; and (iv) final formation of passivated film after second annealing step.

Our passivation technique is outlined in Fig 4-1. We selected CH₃NH₃I (MAI) and PhEtNH₃I (structures Fig 4-1a) as sources of iodide ions to passivate the halide vacancy sites in the CH₃NH₃PbI₃ (MAPbI₃) film. First, we deposited MAPbI₃ on a mesoporous substrate and controlled crystal growth via anti-solvent treatment before annealing at 100 °C as outlined previously. Once cooled, we applied the iodide salts to the film by spin-coating and further annealing at 100 °C. A more detailed outline of our processing method can be found in Section 4.3.1.

We first assessed the impact of the iodide salt treatment on MAPbI₃ film stability when exposed to oxygen and light. Fig 4-2a shows that the unpassivated MAPbI₃ films degrade completely within 4 days. We attribute this to the deprotonation of photoexcited MAPbI₃ by
superoxide (O$_2^-$) forming PbI$_2$, water, methyamine and iodine.$^{39,42}$ However, by treating MAPbI$_3$ with the iodide salts we markedly improved the film stability, with 90% of the original absorbance maintained after 5 days.

Fig 4-2: (a) Normalised absorbance at 750 nm over time for MAPbI$_3$ films as prepared and with 10 mM of CH$_3$NH$_3$I and PhEtNH$_3$I. (b) Relative superoxide yield $I_F(t)/I_F(0)$ for the same set of samples. The normalised fluorescence intensity increase of the hydroethidine probe at 610 nm (excitation at 520 nm), $I_F(t)$ is the fluorescence maximum at time t, while $I_F(0)$ is the background fluorescence intensity. The structures of hydroethidine and the 2-hydroxyethidium product formed after reaction with superoxide are given bottom right and top left of (b) respectively. In both (a) and (b) samples were kept under continuous illumination (25 mW cm$^{-2}$) and dry air flow. (c) Time-resolved single photon counting (TCSPC) decays of MAPbI$_3$ films with 4, 10 and 20 mM PhEtNH$_3$I (magenta) and MAI (gold). The control MAPbI$_3$ decay with no coating is given in black. Samples were excited with a pump wavelength of 635 nm at 0.11 nJ cm$^{-2}$ and probed at 760 nm. (d) Transient absorption spectroscopy (TAS) kinetic decays of TiO$_2$[MAPbI$_3$]spiro-OMeTAD films without any coating (black), with 10 mM PhEtNH$_3$I (magenta) and 10 mM CH$_3$NH$_3$I (gold) between the MAPbI$_3$ and spiro-OMeTAD layers. Samples were excited with a pump wavelength of 567 nm and an average pulse fluence of 25 μJ cm$^{-2}$. A probe wavelength of 1600 nm was used to probe the injected holes in spiro-OMeTAD. The data in (a) and (b) was collected by Dr Bu Xiangnan.

To gain mechanistic insight into this significant improvement, we next investigated the yield of superoxide produced by the films with a hydroethidine (HE) probe (Fig 4-2b, bottom right) as has been shown previously.$^{8,11,12,39}$ HE undergoes oxidation when exposed to O$_2^-$, forming 2-hydroxyethidium (2-OH-E$^+$) and the increase in conjugation during the reaction results in a
significant red-shift in the photoluminescence (PL) peak (see Fig 4-2b for structures). Consequently, qualitative information about the amount of O$_2^-$ produced by MAPbI$_3$ can be obtained by monitoring the increase of the peak at 610 nm over time.$^{43,44}$ From Fig 4-2b it is clear that O$_2^-$ production is greatly suppressed in the MAPbI$_3$ films that have undergone iodide salt treatment.

Next, we looked at how the iodide salts affect charge recombination within the MAPbI$_3$ film. Fig 4-2c shows the photoluminescence (PL) lifetime for MAPbI$_3$ films as prepared (black) and treated with 4, 10 & 20 mM PhEtNH$_3$I (magenta) and MAI (gold). Trap states such as iodide vacancies are responsible for a rapid decay process ($\tau \sim 1 \text{ ns}^{45,46}$) that is manifest in a short PL lifetime. Therefore, the rapid PL decay in the control MAPbI$_3$ sample suggests that recombination in this film is dominated by trap-mediated recombination. However, the lifetime of the PL decay is found to significantly increase upon passivation with PhEtNH$_3$I. Combined with the previous finding that superoxide production is significantly suppressed after passivation, we propose that PhEtNH$_3$I effectively targets and neutralises trap states including V$_I$ sites. Additionally, the large size of the PhEtNH$_3^+$ ion means that it is sterically hindered from entering the MAPbI$_3$ bulk, and therefore remains localised to the surface and grain boundaries where V$_I$ sites are most prevalent.$^{47}$ Surprisingly, the reverse is true for MAI passivation (Fig 4-2c, gold), where increasing concentration reduces the lifetime of photogenerated charges in MAPbI$_3$.

We next looked to see if the markedly different effects of the two iodide salts on charge generation in the MAPbI$_3$ layer manifested any changes in hole injection at the MAPbI$_3$|HTL interface. To do this we carried out microsecond transient absorption spectroscopy ($\mu$s-TAS) on MAPbI$_3$, MAPbI$_3$:MAI and MAPbI$_3$:PhEtNH$_3$I films interfaced with a spiro-OMeTAD HTL. Importantly, by Beer-Lambert law $\Delta OD$ is directly related to the concentration of the probed species. Therefore, by probing the films at 1600 nm - i.e. the maximum of spiro-OMeTAD hole polaron - we could build up a picture of how hole injection is affected after the different treatments.$^{48}$ Fig 4-2d shows that PhEtNH$_3$I passivation results in modest improvements in hole injection yield (6.5%) and lifetime (10%) relative to the untreated MAPbI$_3$ film. On the other hand, treatment with MAI results in greatly reduced hole injection yield (-36.8%) and lifetime (-86%).

All of this evidence points to the fact that MAI treatment deteriorates charge generation in the MAPbI$_3$ layer. We suggest that even though the I$^-$ ions can fill V$_I$ sites and suppress O$_2^-$ production - as evidenced by Fig 4-2b - the addition of MA$^+$ leaves the surface with poor stoichiometry. The resulting trap-states would result in the reduced lifetime of photogenerated charges in MAPbI$_3$ and injected charges in the HTL. All of this points to MAI
being a poor passivating agent for MAPbI$_3$ solar cells. Indeed, over-stoichiometric mixing of MAI and PbI$_2$ (i.e. over 1: 1.06) has been shown elsewhere to reduce PL lifetimes and ultimately degrade device performance.\textsuperscript{49}

**Fig 4-3:** (a) Intensity at $10^{-6}$ s of the transient absorption trace, $\Delta OD_{max}$ for MAPbI$_3$:R-NH$_3$I|PTPD samples, where R-NH$_3$ is ammonium (A), methylammonium (MA), butylammonium (BA), phenylammonium (PA), phenylmethylammonium (PMA) and phenethylammonium (PEA). The maximum of the transient absorption trace for a MAPbI$_3$|PTPD sample with no passivation treatment is given for comparison (black). The samples were excited with a wavelength of 510 nm, a pulse fluence of 10 $\mu$Jcm$^{-2}$ and probed at 1600 nm to identify injected holes in the PTPD HTL layer. The structures of the passivating agents surround (a); anti-clockwise: AI, MAI, BAI, PAI, PMAI and PEAI.

The comparison of MAI and PhEtNH$_3$I passivation raises some important questions. Both salts deliver the same amount of I$^-$ ions to V$_I$ sites in MAPbI$_3$ and therefore have an almost identical impact on stability. However, only PhEtNH$_3$I can improve charge separation within the MAPbI$_3$ layer and across the MAPbI$_3$|HTL interface. In stark contrast, MAI passivation has a destructive impact on charge separation within the film. We therefore posit that the size of the cation plays a critical role.

We further tested this hypothesis by measuring the relative hole injection yield i.e. $\Delta OD_{max}$ in the case of passivation with several more iodide salts: ammonium iodide (AI), Butylammonium iodide (BAI), phenylammonium iodide (PAI) and phenylmethylammonium iodide (PMAI). Strikingly, only the iodide salts with bulky cations i.e. those to the right of the control (black) film in Fig 4-3 can improve the hole injection yield to PTPD. In contrast, both AI and MAI passivation result in reduced hole injection yields. This is most likely because the
introduction of extra A$^+$ and MA$^+$ ions leaves the surface with poor stoichiometry. In the following, we outline our investigation into the mechanism of trap passivation with bulky cations, using PhEtNH$_3$I as an example.

Fig 4-4. (a) X-ray diffraction patterns for MAPb$_3$ films treated with 0, 4, 10, 20 and 40 mM PhEtNH$_3$I. (b) Change in the (110) peak from MAPb$_3$ (●) and the (002) peak from the (PhEtNH$_3$I)$_2$PbI$_4$ passivating layer (●) with [PhEtNH$_3$I]. (c) Steady-state photoluminescence spectra of the same set of samples. Inset: close-up view of the PL contribution between 500 and 575 nm. (d) Steady-state photoluminescence spectra of a MAPb$_3$:PhEtNH$_3$I sample measured with excitation (450 nm) at the film surface (solid line) and substrate (dashed line).

PhEtNH$_3$I is a well-known precursor to the so-called 2D, layered perovskites – (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ – because its bulky structure cannot be integrated into the traditional 3D lattice when combined with PbI$_2$. Therefore, we wanted to probe whether the more favourable passivation effect from this salt is due to the formation of a 2D perovskite layer at the MAPb$_3$ surface. Fig 4-4a presents XRD patterns for MAPb$_3$ films treated with increasing amounts of PhEtNH$_3$I. The strong diffraction peaks in the MAPb$_3$ pattern at 14.2, 28.5 and 32.5° are associated with the (110), (220) and (310) lattice orientations of tetragonal halide perovskite. Furthermore, another contribution at 5.4° becomes increasingly prevalent as the concentration of PhEtNH$_3$I is increased. This closely matches previously reported values for the (002) orientation of (PhEtNH$_3$I)$_2$PbI$_4$. Moreover, the growth of this 2D layer does not significantly impact the underlying 3D perovskite up to 20 mM PhEtNH$_3$I, as the intensity and position of the MAPb$_3$ (110) peak remains constant (Fig 4-4b). This suggests that the new 2D layer is formed separately to the MAPb$_3$ layer when
On the contrary, upon increasing [PhEtNH$_3$I] to 40 mM the (110) contribution becomes lower in intensity, suggesting significant damage to the underlying MAPbI$_3$ layer.

The XRD technique is limited by sensitivity on the order of one per-cent by mass. Therefore, we next turned to PL spectroscopy hoping that the orders of magnitude greater sensitivity of this technique could reveal more about the 2D character of the passivated films. Fig 4-4c shows two key contributions: (i) a peak at 760 nm due to bimolecular recombination of electrons and holes across the 1.6eV band-gap of MAPbI$_3$; (ii) a peak at 525 nm that we associate with recombination in (PhEtNH$_3$I)$_2$PbI$_4$. It is important to note that given the greater sensitivity of the PL technique we are able to resolve 2D contributions from films treated with 4 and 10 mM of PhEtNH$_3$I (Fig 4-4c, inset). Additionally, higher order (i.e. (PhEtNH$_3$I)$_2$(MA)$_{n-1}$PbI$_{3n+1}$, $n > 1$) layered structures begin to appear when [PhEtNH$_3$I] > 10 mM as evidenced by the contributions at 560 nm ($n = 2$) and 625 nm ($n = 3$).

Moreover, given the large extinction coefficient of MAPbI$_3$, excitation at 450 nm allows for interface selectivity, as the penetration depth is only 100 nm (film thickness, 350 nm). Fig 4-4d shows the PL spectra in the range relevant to (PhEtNH$_3$I)$_2$PbI$_4$ for MAPbI$_3$:PhEtNH$_3$I films excited from the film (solid line) and substrate (dashed line) faces. The much enhanced intensity of this contribution after excitation from the film face confirms that the 2D layer is formed at the top surface of the MAPbI$_3$ film, consistent with the idea that PhEtNH$_3^+$ ions cannot penetrate the bulk.

**Fig 4-5:** (a) Transient absorption spectra of MAPbI$_3$|P3HT, MAPbI$_3$:PhEtNH$_3$I|P3HT and (PhEtNH$_3$I)$_2$PbI$_4$|P3HT measured 1 µs after excitation at 450 nm (15 µJ cm$^{-2}$). (b) Illustration of TA redshift of (PhEtNH$_3$I)$_2$(MA)$_{n-1}$PbI$_{3n+1}$ for increasing values of $n$; evolution of the (PhEtNH$_3$I)$_2$(MA)$_{n-1}$PbI$_{3n+1}$ crystal structure (left) and energetics (right) with $n$. (c) Decay of the peaks at 970 nm and 1350 nm in the Al$_2$O$_3$|MAPbI$_3$:PhEtNH$_3$I films shown in (a).
The 2D character of the passivated films is further exemplified by the transient absorption spectroscopy (TAS) data in Fig 4-5. In Fig 4-5a we present the TA spectra after exciting MAPbl$_3$|P3HT, (PhEtNH$_3$I)$_2$Pbl$_4$|P3HT and MAPbl$_3$:PhEtNH$_3$I|P3HT ([PhEtNH$_3$I] = 40 mM) films at 450 nm, which have three key features.

Firstly, common to all films is a contribution at $\lambda < 1000$ nm, which we attribute to the hole polaron formed on P3HT (P3HT$^+$) after hole injection from the active layers. This assignation has been reported in this thesis (chapter 3, Fig 3-3) and elsewhere.$^{56}$ Secondly, the (PhEtNH$_3$I)$_2$Pbl$_4$|P3HT sample exhibits some TA in the 1000 nm $< \lambda < 1300$ nm region. We associate this feature with the excited (PhEtNH$_3$I)$_2$Pbl$_4$ film as there are no other TA-active species in the sample. This feature also appears – although at lower intensity – in the MAPbl$_3$:PhEtNH$_3$I film, suggesting that PhEtNH$_3$I passivation introduces some (PhEtNH$_3$I)$_2$Pbl$_4$ to the MAPbl$_3$ surface. A final contribution in the $\lambda > 1300$ nm region (Fig 4-5a, red) only appears in the MAPbl$_3$:PhEtNH$_3$I film. We associate this contribution with excited states of (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pbl$_3n+1$ (where the number of perovskite layers exceeds 1 ($n > 1$).

The explanation for the red shift in the TA as $n$ is increased is summarised in Fig 4-5b. As $n$ is increased, the number of perovskite unit cells between insulating PhEtNH$_3$I spacers increases (Fig 4-5b, left). The resulting delocalisation of photoexcited charges in the perovskite layer relaxes the valence and conduction band levels, ultimately narrowing the bandgap (Fig 4-5b, right). Assuming that the deep traps observed on these long timescales lie somewhere in the middle of the bandgap, the increase in $n$ should reduce $\Delta E_{pr}$ between the hole (electron) trap and the valence (conduction) band. Therefore, transient features of (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pbl$_3n+1$ ($n > 1$) should appear at more red-shifted positions in the spectrum.

The decay dynamics for the two features at 970 nm and 1350 nm are given in Fig 4-5c. It is clear from this data that the two features at 970 nm and 1350 nm emanate from separate species given the drastically different lifetime of 0.027 ms and 0.15 ms respectively. All of this serves to further confirm that PhEtNH$_3$I passivation introduces a new species to the perovskite surface, which we attribute to (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pbl$_3n+1$.

4.4.2. Hole injection at the MAPbl$_3$|(PEA)$_2$MA$_{n-1}$Pbl$_3n+1$|HTL Interface

The P3HT$^+$ TA signal observed in Fig 4-5 proves that some hole injection occurs across the MAPbl$_3$:PhEtNH$_3$I|HTL interface. Therefore, we next looked to quantify exactly how interfacial hole injection correlates with the growth of the (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pbl$_3n+1$ layer. In Fig 4-6a we summarise the evolution of (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pbl$_3n+1$ with [PhEtNH$_3$I] by tracking the $n = 1$, $n = 2$ and $n = 3$ contributions in the PL spectra at 525, 560 and 610 nm.
respectively. Interestingly, we find that the n = 2 feature for the [PhEtNH₃] ≤ 10 mM samples are small: 0% and 2% of the n = 1 contribution for 4 mM and 10 mM respectively. Notably, the contribution from the n = 2 structure increases with [PhEtNH₃] thereafter to 4% and 25% for 20 mM and 40 mM respectively. Additionally, a third contribution associated with the n = 3 structure is present at 5% in the PL spectrum of the 40 mM film.

**Fig 4-6**: Hole injection in MAPbI₃:PhEtNH₃ films. (a) Evolution of the (PhEtNH₃)₂(MA)ₙ₋₁ PbₙI₃n₊₁ photoluminescence peak in MAPbI₃:PhEtNH₃ films for n = 1 (purple), n = 2 (green) and n = 3 (red) at 525, 560 and 610 nm respectively. ΔODₘₐₓ – i.e. ΔOD from transient absorption spectroscopy (TAS) measured 1 µs after excitation - of MAPbI₃:PhEtNH₃|PTAA films with increasing [PhEtNH₃]. The films were excited at 510 nm (fluence: 1.5 µJ cm⁻²) and probed at 1500 nm, the maximum of the PTAA polaron. c-e) Time-resolved single photon counting (TCSPC) decays for MAPbI₃ (solid points) and MAPbI₃:PhEtNH₃ films (empty points) with and without PTAA (orange), PTPD (green) and PTB1 (blue). Films were excited at 635nm with a pulse fluence of 0.11 nJ cm⁻² and probed at 780 nm.

**Table 4-1**: Biexponential fitting (\(y(t) = A₁e^{-t/\tau₁} + A₂e^{-t/\tau₂}\)) parameters for the time-resolved single photon counting (TCSPC) decays given in Fig.6c-e. We note that \(\tau₁ = \tau_{inj}\) for HTL-coated samples.
In order to assess the impact of \((\text{PhEtNH}_3)_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}\) growth on hole injection, we deposited poly-(triarylamine) (PTAA) on the MAPb\(_3\):PhEtNH\(_3\)I samples and used transient absorption spectroscopy (TAS) to measure the relative yield of hole injection i.e. \(\Delta \text{OD}_{\text{max}}\). The results in Fig 4-6b show that the relationship between hole injection and [PhEtNH\(_3\)I] is non-trivial, reaching a maximum at 10 mM. Importantly, this is the concentration at which the largest amount of phase-pure \((\text{PhEtNH}_3)_2\text{PbI}_4\) (i.e. \(n = 1\)) layered perovskite is formed, with minimal formation of higher-order \(n > 1\) structures. Indeed, the formation of these higher order structures in the passivating layer is concomitant with a drop in the hole injection yield.

PL decay dynamics for MAPb\(_3\)|HTL and MAPb\(_3\):PhEtNH\(_3\)I|HTL (10 mM) samples with PTAA, PTPD and PTB1 are given in Fig 4-6c-e. The PL decay of MAPb\(_3\) can be fitted to a biexponential with a fast (\(\tau_1\)) and slow (\(\tau_2\)) component indicative of charge trapping at the surface and bulk respectively.\(^{57-59}\) Upon addition of a HTL, the fast decay (\(\tau_{\text{inj}}\)) becomes indicative of hole injection and the slow component (\(\tau_2\)) is due to either unquenched charges that remain in the bulk,\(^{62}\) or surface recombination.\(^4\)

As discussed in detail in the Section 3.4.3, we observe sub-nanosecond hole injection in all cases where a HTL is interfaced with MAPb\(_3\). We find that the kinetics of hole injection to PTPD and PTAA are slower (~ 400 ps) than to PTB1 (185 ps) as expected given the greater energetic offset in the latter case. Importantly, the data can be fitted such that \(\tau_{\text{inj}}\) is independent of passivation (Table 4-1, bold). In other words, PhEtNH\(_3\)I passivation has little impact on the kinetics of hole injection at the MAPb\(_3\)|HTL interface. We can therefore explain the increased hole injection yield at [PhEtNH\(_3\)I] = 10 mM (Fig 4-6b) as a shift in the balance of the kinetic processes occurring in the film (Fig 4-6b, inset). Specifically, the hole injection rate constant, \(k_{\text{inj}}\) remains constant but that the recombination in the MAPb\(_3\) layer, \(k_{\text{rec,M}}\) becomes slower. Consequently, the overall yield of hole injection i.e. \(n_+\) increases.

The findings summarised in Fig 4-4, Fig 4-5 and Fig 4-6 prove that upon passivation of MAPb\(_3\) with 10 mM PhEtNH\(_3\)I: (i) a (PhEtNH\(_3\)I)_2PbI\(_4\) layer is formed; (ii) this layer is positioned at the MAPb\(_3\)|HTL interface; and (iii) hole injection is not impeded by the passivating layer. We therefore next looked to build a picture of the interfacial energetics to explain these observations.

The energetic structure of (PhEtNH\(_3\)I)_2PbI\(_4\) and related (e.g. (BA)_2PbI\(_4\); BA = C\(_4\)H\(_9\)NH\(_3\)) compounds has not been consistently reported in the literature. Cho et al report that the valence band (VB) energy of (PhEtNH\(_3\)I)_2PbI\(_4\) is similar to that in MAPb\(_3\), while the conduction band (CB) becomes significantly shallower.\(^{31}\) In contrast, Cao et al place the VB of pure (PhEtNH\(_3\)I)_2PbI\(_4\) at -4.55 eV, around 0.9 eV shallower than the VB of MAPb\(_3\).\(^{63}\) They also report a shallower CB in (PhEtNH\(_3\)I)_2PbI\(_4\): -2.13 eV compared to -3.94 eV in MAPb\(_3\).
Additionally, Wang et al model the 3D-2D interface on a type-I heterojunction, placing the VB of (BA)$_2$PbI$_4$ at a deeper energy than that of the MAPbI$_3$ VB.\textsuperscript{28}

![Diagram](image)

**Fig 4-7:** Illustration of the two possible mechanisms for hole injection at the MAPbI$_3$:PhEtNH$_3$I|HTL interface. (i) Mediated hole injection; (ii) tunnelling injection.

Given this information, two interfacial charge separation mechanisms are possible, as outlined in Fig 4-7. Firstly, if the VB of (PhEtNH$_3$I)$_2$PbI$_4$ lies between the VB of MAPbI$_3$ and HOMO of the HTL, it is likely that the interlayer mediates hole injection in a two-step mechanism (Fig 4-7a). Otherwise, if the VB of (PhEtNH$_3$I)$_2$PbI$_4$ lies either below the VB of MAPbI$_3$ (Fig 4-7b, solid line) or above both the VB of MAPbI$_3$ and the HOMO of the HTL (Fig 4-7b, dashed line), it is likely that hole injection occurs via a one-step tunnelling mechanism.

![Graphs](image)

**Fig 4-8:** Ultrafast transient absorption spectroscopy. Decay of (a) MAPbI$_3$ and (b) MAPbI$_3$:PhEtNH$_3$I spectra as a function of time. The steady-state spectrum of MAPbI$_3$ (a) and MAPbI$_3$:PhEtNH$_3$I & (PhEtNH$_3$I)$_2$PbI$_4$ (b) are overlaid. The two key features around 476 nm (blue) and 760 nm (red) are highlighted. The decay dynamics of the spectrum at 476 nm and 760 nm are shown in (c) and (d) respectively. Data collected by Weidong Xu.
In order to establish which of the two proposed mechanisms is at work, we conducted femtosecond-TAS (fs-TAS) studies on MAPbI$_3$ and MAPbI$_3$:PhEtNH$_3$I films, details in Fig 4-8. We probed the visible/near infra-red (400-800 nm) region after exciting the samples at 635 nm (fluence: 24 µJ cm$^{-2}$) and found two distinct bleaching peaks at ~476 nm (PB1) and ~760 nm (PB2). PB2 is assigned to the band edge transition of MAPbI$_3$ while the origin of PB1 is debated, but may be due to excitation from a deeper valence band. The broad positive band between 500-700 nm is assigned to excited state absorption.

We hypothesised that if the 2D layer plays an active role in mediating hole injection, TA features of the (PhEtNH$_3$I)$_2$PbI$_4$ ground-state bleach (GSB) would be present in the spectrum at time $t_{inj}$ after initial excitation. However, the shape of the MAPbI$_3$ (Fig 4-8a) and MAPbI$_3$:PhEtNH$_3$I (Fig 4-8b) spectra are strikingly similar, the only significant difference being the increased intensity of PB1 in the MAPbI$_3$:PhEtNH$_3$I sample. Given that PB1 (~ 476 nm) and the expected GSB of (PhEtNH$_3$I)$_2$PbI$_4$ (~ 525 nm) should lie at similar wavelengths, we decided to probe this blue-shifted peak in more detail.

First, we tracked the dynamics of the TA decay at 476 nm and 760 nm in the MAPbI$_3$ film (Fig 4-8c). The two contributions had different dynamics with the decays at 476 nm and 760 nm following mono- and bi-molecular kinetics respectively. Such a discrepancy has been observed elsewhere in the literature, with no clear explanation. We tentatively ascribe the mono-exponential decay of PB1 to the lower population of the deeper valence band involved in this transition, but further investigation is beyond the scope of this study. In agreement with our time-resolved PL studies we find an increased lifetime of photoexcited charges in the MAPbI$_3$:PhEtNH$_3$I samples (Fig 4-4d) compared to pure MAPbI$_3$.

 Crucially, the same trend was observed in the MAPbI$_3$:PhEtNH$_3$I system, suggesting that the contribution at 476 nm hails from photophysical phenomena in the MAPbI$_3$ layer. Combining this with the lack of new features observed in the MAPbI$_3$:PhEtNH$_3$I TA spectra, we have strong evidence that the (PhEtNH$_3$I)$_2$PbI$_4$ layer formed after PhEtNH$_3$I passivation does not accept holes from MAPbI$_3$ on the timescales studied (< 6 ns). Given that hole injection in the best-performing PSC devices occurs on faster timescales – often sub-nanosecond as observed in Fig 4-6b, chapter 3 and elsewhere – we can say with some certainty that the (PhEtNH$_3$I)$_2$PbI$_4$ layer in our MAPbI$_3$:PhEtNH$_3$I system does not actively mediate hole injection. Consequently, hole injection in PhEtNH$_3$I passivated films most likely occurs via a tunnelling mechanism.
Fig 4-9: A highly simplified model of charge transfer at the MAPbI$_3$(PEA)$_2$PbI$_4$ interface. Proposed potential energy parabolas of the MAPbI$_3$ (black) and (PEA)$_2$PbI$_4$ (purple) layers in two cases: (i) Normal Marcus region, where $\Delta G^0_1 < \lambda$ – here the rate of reaction increases with $\Delta G^0$; and (ii) the Marcus inverted region, where $\Delta G^0_2 > \lambda$ – here the rate of reaction decreases with $\Delta G^0$.

Without carrying out ultraviolet photoelectron spectroscopy (UPS) measurements to directly measure the interfacial energetics, we can only conjecture as to the origin of this phenomenon. One theory is that the VB of PhEtNH$_3$I lies at a deeper energy than MAPbI$_3$ as suggested by Wang et al. However, the overriding majority of literature reports place the VB of (PhEtNH$_3$)$_2$PbI$_4$ and related layered perovskites well above the VB of MAPbI$_3$. Therefore, on this basis we tentatively propose an explanation in the following discussion.

Marcus theory states that the free energy of activation, $\Delta G^*$ of an electron transfer reaction is dependent on the free energy change $\Delta G^0$ between the donor [(PhEtNH$_3$)$_2$PbI$_4$, $G^0_1$, $G^0_2$; Fig 4-9] and acceptor (MAPbI$_3$, $G^0_A$; Fig 4-9) as follows,

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^0}{\lambda}\right)^2$$

where $\lambda$ is the reorganisation energy, associated with the distortion of the acceptor structure to that of the donor or vice versa. An important outcome of this is that, contrary to basic chemical intuition, the rate of reaction does not increase monotonically with $\Delta G^0$, but rather decreases for $\Delta G^0 > \lambda$ (Fig 4-9).

This has been proven experimentally in a number of organic-organic systems, where $\lambda$ is usually found to be around 1 eV. It is therefore noteworthy that $\Delta G^0 \sim 1$ eV at the MAPbI$_3$(PEA)$_2$PbI$_4$ interface according to Cao et al. It is therefore possible that the observed slow ($\tau_{HT} > 6$ ns) hole injection kinetics at the MAPbI$_3$(PEA)$_2$PbI$_4$ interface are due to the over-large interfacial energy offset between them. We note that this would still likely
hold for mixed $(\text{PhEtNH}_3)_2\left(\text{MA}\right)_{n-1}\text{Pb}_n\text{I}_{3n+1}$ systems as it has been proven that the layers stack in order of increasing $n$ and so a MAPb$_3$(PEA)$_2$Pb$_4$ interface would still be present.\textsuperscript{33}

### 4.5. Implications for Device Design

![Fig 4-10: (a) Initial current–voltage measurements of devices without iodide salt coating (black), with 10 mM of PhEtNH$_3$I (magenta) and 10 mM of MAI (gold) salt coating. Devices were measured using a xenon lamp AM 1.5 simulated solar spectrum with a scan rate of 0.125 V s$^{-1}$. Both the illuminated (solid line) and dark current (dash line) were recorded. (b) Normalised efficiency loss for devices employing MAPb$_3$ without (black) and with 10 mM phenylethylammonium iodide (PhEtNH$_3$I) and methylammonium iodide (MAI) salt coating (dark yellow) for a period of 500 h. The temperature was constantly at 25 $^\circ$C. All devices were fabricated in FTO|compact-TiO$_2$|mesoporous-TiO$_2$|perovskite (iodide salt)|spiro-OMeTAD|Au architecture. Data gathered by Bu Xiangnan.]

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Fig 4-10a displays the optimised J-V curves for FTO|compact-TiO$_2$|mesoporous-TiO$_2$|perovskite|spiro-OMeTAD|Au samples where the perovskite was as prepared and treated with MAI and PhEtNH$_3$I. Upon treatment of MAPb$_3$ films with 10 mM of PhEtNH$_3$I, we see an improvement in device efficiency from 12.95% to 16.73%. Closer inspection of the
J-V curve reveals that this is achieved via increasing the short-circuit current ($I_{SC}$), open-circuit voltage ($V_{OC}$) and fill-factor (FF) by 14%, 7.0% and 6.3% respectively. In contrast, MAI passivation results in a reduction of device performance, which can be rationalised in terms of the deterioration of charge generation observed in Fig 4-2c and d. This underlines the fact that the formation of 2D layers at the perovskite surface is prerequisite to improved device performance.

The $I_{SC}$ reflects the total number of charges extracted from the device at the electrodes. We have presented two ways in which PhEtNH$_3$I passivation could enhance charge extraction through the course of this study: (i) suppression of non-radiative recombination within the MAPbI$_3$ layer, resulting in a significant enhancement in hole injection yield (Fig 4-6); (ii) insertion of a wide band-gap 2D layer at the MAPbI$_3$|HTL interface results in a 1.8 eV barrier to back electron transfer (Fig 4-2).

The $V_{OC}$ is defined as the splitting of the quasi-Fermi energies of electrons and holes after illumination. Trap states limit this splitting by allowing the electron and hole population to occupy states within the band-gap. Therefore, we attribute the improvement in $V_{OC}$ to the effective passivation of these states. This is likely to include iodide vacancies (V$_I$) given the correlation between the enhancement of PL and suppression of superoxide production. Although V$_I$ are generally thought to occupy electronic states within the conduction band of MAPbI$_3$ and therefore should not contribute directly to charge trapping,$^{79,80}$ there are several secondary pathways to this end. For example, the positively charged V$_I$ sites can couple to negatively charged defects that arise in order to preserve charge neutrality across the crystal bulk. A common example of this is the formation of iodide interstitials (I$_I$) via Frenkel pairs, which form deep traps in the MAPbI$_3$ band-gap.$^{79,81}$ Therefore, we expect that passivation of V$_I$ sites should reduce non-radiative recombination in some respect.

Moreover, it is well-known that cationic species such as K$^+$ and Na$^+$ are capable of passivating negatively charged traps such as undercoordinated I$^-$, PbI$_5^-$ antisites and MA$^+$ vacancies through ionic bonding.$^{82-84}$ It is therefore likely that the R-NH$_3^+$ cations herein are capable of passivating the same sites. However, the extent to which this happens is clouded by the concomitant formation of the layered (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ perovskite.

We also tested device stability by measuring J-V curves as a function of time under continuous illumination, Fig 4-10b. The MAPbI$_3$:PhEtNH$_3$I devices retain over 85% of their efficiency over a 20-day period. This compares favourably with the control MAPbI$_3$ devices, which degraded entirely within hours. The improvement shown here after our PhEtNH$_3$I post-treatment method agrees well with the work of Wang et al, who also prepared 3D-2D perovskites but by including small amounts of bulky butylammonium ions (0.09%) in the
precursor solution.\textsuperscript{28} This suggests that similar results can be obtained irrespective of whether the 2D quality is added during the precursor preparation or via a post-treatment. We have shown evidence herein that such improvements in stability mainly derive from suppressed $O_2^-$ production at $V_I$ sites. The fact that this mechanism occurs independently of 2D layer formation is confirmed by the improved stability after MAI passivation.

It is also clear from Table 4-2 that hysteresis is markedly reduced after the PhEtNH$_3$I treatment. Specifically, in the optimised device (10mM PhEtNH$_3$I) there is only a deviation of 0.72\% in the PCE between forward and backward scans compared to 4.6\% in the unpassivated control. The prevailing view in the literature is that hysteresis is due to the migration of halide ions via $V_{halide}$ at the surface and grain boundaries of the perovskite.\textsuperscript{85–89} Therefore, we attribute the mitigation of J-V hysteresis demonstrated herein to the effective passivation of $V_I$ sites.

4.6. Mechanism of PhEtNH$_3$I Passivation

The mechanism of PhEtNH$_3$I passivation is summarised in Fig 4-11. Firstly, the I\textsuperscript{-} anions target $V_I$ sites predominantly at the surface and grain boundaries (Fig 4-11a), given the larger activation energy for I\textsuperscript{-} diffusion in the bulk.\textsuperscript{13,14} By suppressing superoxide ($O_2^-$) production and non-radiative recombination – both of which occur at $V_I$ sites – the stability and efficiency of perovskite solar cells improves.

Simultaneously, the bulky PhEtNH$_3^+$ ions interact with the MAPbl$_3$ surface (Fig 4-11b) at MA\textsuperscript{+} vacancies ($V_{MA}$). If [PhEtNH$_3^+$] < 10 mM, the formation of pure (PhEtNH$_3$)$_2$Pbl$_4$ at the MAPbl$_3$ surface is favoured, with minimal disruption of the MA\textsuperscript{+} content in the MAPbl$_3$ bulk (Fig 4-11c). However, if [PhEtNH$_3$I\textsuperscript{+}] > 10 mM, a thicker (PhEtNH$_3$)$_2$(MA)$_{n-1}$Pbl$_{3n+1}$ layer ($n \geq 1$) is formed (Fig 4-11d) due to the displacement of intrinsic MA\textsuperscript{+} by PhEtNH$_3^+$. This would then produce a graded structure in which perovskite layers would be stacked with a tendency to small $n$ at the interface with MAPbl$_3$ and larger $n$ at the interface with the HTL.\textsuperscript{33} This, combined with the removal of MA\textsuperscript{+} from the MAPbl$_3$ bulk would serve to generate disorder.

Importantly, hole injection (Fig 4-6) and thus device efficiency (Table 4-2) are optimum at 10 mM PhEtNH$_3$I i.e. when the thin (PhEtNH$_3$)$_2$Pbl$_4$ layer is favoured. Here, the hole injection barrier is sufficiently thin that charge injection can proceed efficiently. On the contrary, in the case that [PhEtNH$_3$I\textsuperscript{+}] > 10 mM, we suggest that charge separation begins to be hindered by the thick, energetically disordered (PhEtNH$_3$)$_2$(MA)$_{n-1}$Pbl$_{3n+1}$ layer. Here, parasitic charge funnelling could occur into lower band-gap states of large $n$ ($n > 1$, $n \neq \infty$), effectively forming interfacial trap sites. It is also possible that unreacted PhEtNH$_3$I contributes to the obstruction of interfacial hole injection.
Fig 4-11: Proposed mechanism for PhEtNH$_3$I passivation. (a) I$^-$ ions neutralise iodide vacancies (V$_I$) at the surface and grain boundaries of MAPbI$_3$. (b) PhEtNH$_3^+$ ions bind to the perovskite surface at methylammonium vacancies (V$_{MA}$). (c) Over time MA$^+$ ions at the perovskite surface are displaced by PhEtNH$_3^+$ to form (PhEtNH$_3$)$_2$PbI$_4$. (d) At high concentrations, excess PhEtNH$_3^+$ combines with MA$^+$ from the MAPbI$_3$ bulk to form higher order (PhEtNH$_3$I)$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ (n > 1) layered structures.

Of the many literature reports dealing with bulky iodide salt passivation,$^{30-32,47,91-93}$ only a handful discuss the formation of 2D heterostructures at the MAPbI$_3$ surface.$^{31,32,45}$ Of these, none mention the presence of (PhEtNH$_3$I)$_2$(MA)$_{n-1}$Pb$_n$I$_{3n+1}$ (n > 1) structures and their negative impact on charge separation. Moreover, there has been little reporting on the positive effect on stability garnered by the presence of I$^-$. In this work we have added to this field of study on two fronts. Firstly, we show that precise control of the growth of the (PhEtNH$_3$I)$_2$MA$_{n-1}$Pb$_n$I$_{3n+1}$ layer is critical for improving device performance, with n = 1 yielding a significant improvement but n > 1 being detrimental for charge separation and device efficiency. Secondly, we have demonstrated the bilateral nature of PhEtNH$_3$I passivation, where PhEtNH$_3^+$ and I$^-$ simultaneously passivate V$_{MA}$ V$_I$ sites respectively.
4. 7. Conclusions & Outlook

In summary, we applied a combination of optical spectroscopy and photovoltaic device optoelectronic characterization to show that using PhEtNH$_3$I coatings enhances the efficiency and stability of PSCs. Moreover, we established the bilateral mechanism that underpins these improvements.

Firstly, iodide ions effectively target and passivate V$_I$ sites. We showed that this leads to a reduction of the superoxide yield and directly results in an increase in stability from a few hours in control devices to over 20 days in passivated devices. We also showed that the hysteresis effect is strongly suppressed in the passivated devices and related this to the mitigation of iodide ion migration by way of filling the V$_I$ sites that mediate this process.

Secondly, the importance of the bulky organic cation was revealed in detail. The solar cell efficiency of MAPbl$_3$:PhEtNH$_3$I devices (16.73%) exceeds those made with unpassivated MAPbl$_3$ (12.95%). We revealed that the bulky PhEtNH$_3^+$ targets the surface of MAPbl$_3$, where it most likely reacts with unsaturated PbI$_6$ octahedra at V$_{MA}$ sites to form a layered (PhEtNH$_3$)$_2$(MA)$_{n-1}$Pbl$_{3n+1}$ heterostructure. Control of the growth of this passivating layer was found to be critical to device performance with $n = 1$ yielding an improvement in efficiency and $n > 1$ degrading device efficiency. Notably, formation of this 2D heterostructure is critical to the improvements observed with iodide salt passivation. This was evidenced by the poor device efficiency (9.02%) of the MAI-passivated devices, in which a 2D layer cannot form. Ultimately, we have demonstrated the bilateral mechanism of trap passivation with bulky iodide salts. We expect that proper consideration and control of this principle in the design of future passivating agents could lead to further enhancements in the efficiency and stability of PSCs.
4.8. References


Chapter 5

Passivation-Mediated Charge Transfer at Lead Halide Perovskite Heterojunctions
5.1. Abstract

Understanding interfacial charge transfer processes such as trap-mediated recombination and injection into charge transport layers is crucial for the improvement of perovskite solar cells. Herein, we reveal that binding from charge transport layers to CH$_3$NH$_3$PbI$_3$ defect sites is an integral part of the interfacial charge injection mechanism in both nip and pin architectures. Specifically, we use photoluminescence and X-Ray photoelectron spectroscopy to show that binding interactions occur between electron donating moieties on hole transport layers and the CH$_3$NH$_3$PbI$_3$ surface. In particular, triarylamine-based HTLs such as PTAA and PTPD appear to bind much more strongly to the CH$_3$NH$_3$PbI$_3$ layer as compared to the thiophene-based P3HT.

Next, we correlated the extent of binding with an increase in both the yield and lifetime of injected holes with transient absorption spectroscopy. We also carried out an analogous experiment on pin cells incorporating fullerene derivative ETLs: PCBM, IPH and PTEG. Here again, we found that the better passivating capability of PTEG led to enhanced electron transfer yields and longer recombination lifetimes.

These fundamental studies were backed up with J-V measurements on ITO|SnO$_2$|CH$_3$NH$_3$PbI$_3$|HTL|Au devices (HTL = P3HT, PTAA), which produced 9.45% and 16.19% respectively. Further evidence for better defect passivation by PTAA vs P3HT was evidenced by the more favourable ideality factor of devices incorporating this HTL (1.45 vs 2.06). We attribute this, as well as better energy alignment to the CH$_3$NH$_3$PbI$_3$ valence band, to the enhanced open-circuit voltage in PTAA-based devices (1.07 V) compared to those incorporating P3HT (0.90 V). We also found that the short-circuit current density ($J_{SC}$) was much enhanced in the PTAA-based devices (22.35 vs 17.10 mJ cm$^{-2}$), which we attribute to the much enhanced hole transfer yield in this case.

Our results reveal for the first time the importance of passivation from the charge transport layers in perovskite solar cells and set out an important design rule for further enhancing the efficiency and stability of perovskite solar cells and LEDs.

Most of the results in this chapter are included in the following publication:

- “Passivation-Mediated Charge Transfer at Lead Halide Perovskite Heterojunctions”, Energy Environ. Sci., under revision
5.2. Introduction

The previous two chapters of this thesis have set out design rules for maximising charge separation in methylammonium lead triiodide (MAPbI\(_3\))-based perovskite solar cells (PSCs). In chapter 3, we showed that a remarkably small interfacial energy offset (\(\Delta E \sim 100\) meV) is required to drive efficient hole transfer at the MAPbI\(_3\)|hole transport layer (HTL) interface. We took a different direction in chapter 4, where we showed that passivating trap-states in MAPbI\(_3\)-based solar cells leads to significant enhancements in their efficiency (+ 30%) and stability (+ 2000%), and to markedly suppressed hysteresis. In this final chapter, we seek to weave these two strands of research together by investigating the role of passivating interactions between the charge transport layers (CTLs) themselves and MAPbI\(_3\).

Over the last decade, solution engineering strategies have led to highly crystalline, trap-free perovskite active layers in PSCs.\(^1\)\(^-\)\(^3\) As such, non-radiative recombination in the bulk of films tends to be orders of magnitude slower than at the interfaces where the bulk symmetry is interrupted.\(^4\) One of the most stark demonstrations of this was by Braley et al.,\(^5\) who treated the MAPbI\(_3\) surface with with tri-\(n\)-octylphosphine oxide (TOPO) and found that the resulting quasi-Fermi level splitting (QFLS) in the MAPbI\(_3\) film was 1.28 eV, just 50 meV away from the radiative limit of 1.32 eV.\(^5\)\(^-\)\(^7\)

Given that the open-circuit voltage (\(V_{OC}\)) is defined as the QFLS under 1 Sun illumination, this finding has two important implications: (i) the majority of voltage loss associated with the MAPbI\(_3\) film in PSCs occurs at the surface and (ii) careful management of interfacial defects could lead to open-circuit voltages approaching 1.28 V. Indeed, Wang et al. predicted that by reducing the surface recombination velocity at perovskite|CTL interfaces from \(10^4\) to \(10\) cm s\(^{-1}\), the \(V_{OC}\) could be increased from 1.1 to 1.3 V.\(^8\) As such, trap-state passivation – where external agents such as small molecules,\(^9\)\(^,\)\(^10\) polymers\(^11\)\(^,\)\(^12\) and heterocations\(^1\)\(^,\)\(^13\) are used to bond to trap sites and render them electronically inert - has emerged as an effective strategy to reduce interfacial recombination. This combined research effort has recently culminated in a record \(V_{OC}\) in MAPbI\(_3\)-based solar cells of 1.26 V, just 60 mV away from the radiative limit.\(^14\)

Despite the clear interplay between passivation and recombination at the perovskite|CTL interface and the observation that it is consistently the top perovskite|CTL interface in devices that is voltage-limiting,\(^15\) only a few groups report on the inherent passivation effects from the CTL layers themselves.\(^16\)\(^-\)\(^20\) Moreover, while these studies have demonstrated that passivation from CTLs can mitigate non-radiative recombination at the perovskite|CTL interface, no one has yet addressed the impact that such interactions have on charge injection to the CTLs.
As discussed in Section 1.5.3.2, An outcome of Marcus theory is that the rate of electron transfer is partly determined by the nature of the intervening medium between donor and acceptor. In other words, the rate of transfer through bonds far exceeds that through space. We therefore posit that dative bonds formed between CTLs and the perovskite surface should enhance interfacial charge injection. Although the important role of similar interactions was highlighted by Seok and co-workers in Sb$_2$S$_3$ quantum dots, few studies have broached this subject in the field of PSCs.

Brauer et al. suggested that the poor contact at the MAPbI$_3$|P3HT interface could limit hole transfer yields but didn't probe this specifically. More recently, Jung et al. achieved a remarkable efficiency of 22% in P3HT-based nip solar cells after functionalisation of (FAPbI$_{3-x}$(MAPbI$_3$)$_x$) with n-hexyl trimethyl ammonium bromide (HTAB). They attribute this improvement in part to the improved contact between perovskite|P3HT due to alkyl-alkyl Van der Waal interactions and the consequent enhanced hole transfer yields. Moreover, Bi et al. showed that the twisted structure of spiro-OMeTAD leads to reduced coupling with the perovskite, which in turn reduces the rate of interfacial recombination. However, they did not comment on how such coupling impacts the forward process of hole injection. Despite the excellent insights from these studies, the conclusions drawn tend to be from a narrow set of materials and based on macroscopic device performance, which cannot directly link absorber|CTL interactions with charge transfer yield.

Therefore, in this study we use a combination of transient absorption spectroscopy (TAS) and photoluminescence (PL) spectroscopy as an interface specific probe to show that binding interactions at MAPbI$_3$|CTL junctions mediate the charge separation process in both the nip and pin configurations, for eight MAPbI$_3$|CTL combinations. We show that such effects - while negligible at the high powers associated with TAS – are critical at the relatively low powers relevant to operational conditions of 1 Sun. This partially explains the success of commercial CTLs such as PTAA, spiro-OMeTAD and fullerene derivatives in contemporary PSCs and sets a precedent for the design of next-generation CTLs.

5.3. Materials & Methods

5.3.1. Film Processing

Glass slides were washed in deionised water, acetone and isopropanol (IPA) sequentially for 15 minutes followed by O$_2$ plasma treatment. Al$_2$O$_3$ substrates were prepared by making up a 6.67 wt% solution of Al$_2$O$_3$ nanoparticles in IPA and spin-coating at 6000 rpm immediately after O$_2$ plasma treatment. TiO$_2$ substrates were prepared by making up a 2:7 (weight)
solution of TiO\textsubscript{2} paste in EtOH, spin-coating on the glass immediately after plasma treatment, drying at 90 °C for 10 minutes and annealing at 450 °C for 45 minutes.

MAPbI\textsubscript{3} was deposited according to the method of Jeon et al.\textsuperscript{26} PbI\textsubscript{2} and CH\textsubscript{3}NH\textsubscript{3}I were mixed together in a 1:1 ratio at a concentration of 1.2 M in GBL and DMSO (3:7). After solvation, the solution was filtered with a 200 nm PTFE filter and spin-coated on top of the relevant substrate at 1000 rpm (10 s), 5000 rpm (30 s), 6000 rpm (20 s). Crucially, 800 µL of toluene antisolvent was drop-cast on the spinning film after 25 s to aid crystallisation. The film was then annealed at 100 °C for 10 minutes. This antisolvent treatment resulted in a colour change from pale yellow to pale brown, while annealing resulted in a dark brown film.

\textit{nip} films were made by depositing this layer on top of mesoporous TiO\textsubscript{2} and coating with a 10 mg/mL HTL solution. The spin-coating rotation speed was varied to ensure all HTL layers were 30 ± 5 nm thick. \textit{nip} films were prepared by first depositing the HTL onto the glass at 0.25 wt% in chlorobenzene. Next, 0.05 wt% PFN in MeOH was spin-coated at 4000 rpm (45s) to provide a thin interlayer that ensures decent wetting of the MAPbI\textsubscript{3} layer. ETL solutions were prepared in chlorobenzene at 23 mg/mL, stirred at 40 °C for 1 hour and filtered with a 200 nm PTFE filter before use. They were then spin-coated on top of the MAPbI\textsubscript{3} film at 2000 rpm (30 s).

\textbf{5. 3. 2. Fabrication of \textit{nip} perovskite solar cells}

\textit{nip} perovskite solar cells were fabricated on indium-doped tin oxide (ITO) coated glass substrates that were sequentially cleaned in acetone, detergent, deionized water (x2), acetone, and isopropanol (using ultrasonics) for 10 minutes. The substrates were then dried with nitrogen and treated by oxygen plasma for 10 minutes.

Tin(IV) oxide (15 wt % in H\textsubscript{2}O colloidal dispersion, Alfa Aesar) was diluted with deionized water to 2.5 wt % and spin-coated onto ITO at 3000 rpm for 40 s. The films were immediately annealed at 150 °C for 30 minutes in ambient conditions forming a 25 nm SnO\textsubscript{2} nanoparticle film. The SnO\textsubscript{2} films were then cooled and further treated by oxygen plasma for 10 minutes to enable sufficient wetting for the next steps. The films were then transferred to a nitrogen filled glovebox for perovskite deposition. For the hole transport materials, a 10 mg/mL solution of PTAA (M\textsubscript{w} = 14,000) and P3HT (M\textsubscript{w} = 24,480) in toluene were prepared by stirring in a nitrogen filled glovebox for 1 h at 65 °C. In the case of our reference \textit{nip} cell, PTAA was doped following our previous report.\textsuperscript{27} Briefly, additives of 8 µL bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) in acetonitrile (170 mg mL\textsuperscript{-1}, TCI) and 4 µL of 4-tert-butylpyridine (tBP, TCI) were added to the 10 mg/mL PTAA solution. The solution was then spin-coated onto the perovskite films at 3000 rpm for 20 s. Finally, 100 nm of Au was thermally evaporated (0.2 Å/s) at a base pressure of 5×10\textsuperscript{-6} mbar.
5.3.3. Spectroscopy

Transient absorption spectroscopy of MAPbI$_3$ films was done with a 510 nm excitation at an initial fluence of 10 µJ cm$^{-2}$, which was then damped with neutral density filters to achieve the operating range of 0.1 - 10 µJ cm$^{-2}$. A probe wavelength characteristic of the hole or electron polaron in the CTL was used to monitor charge injection. Details of our TAS set-up are given in Section 2.3. Steady-state photoluminescence was carried out with an excitation wavelength of 510 nm and samples were probed at 760 nm. TCSPC was carried out with the same probe wavelength at an excitation of 635 nm (0.11 nJ cm$^{-2}$). Details of our ss-PL and TCSPC set-up are given in Section 2.4 and 2.5. The XPS measurements were obtained in MultiLab 2000 with the X-ray source provided by monochromated Al Kα X-ray photons (hv = 14.9 keV). The core level spectra were performed with a pass energy of 20 eV and step size of 0.05 eV.

5.4. Results & Discussion

5.4.1. Passivation-Mediated Charge Transfer in the nip Architecture

5.4.1.1. Sample Design

![Fig 5-1](image)

Fig 5-1: (a) Chemical structures of PTAA, PTPD and P3HT hole transport layers. (b) corresponding energetics at the MAPbI$_3$ hole transport layer interface. The highest occupied molecular orbital (HOMO) energies for the HTLs were extracted from cyclic voltammetry reports in the literature and the value for the valence band maximum of MAPbI$_3$ were taken from photoelectron spectroscopy reports in the literature. More details in Chapter 3: Table 3-1, 28–37

We interfaced MAPbI$_3$ with three well-known polymeric hole transport layers (HTLs): poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), poly[N,N’-bis(4-butylphenyl)-N,N’-bisphenylbenzidine] (PTPD) and poly(3-hexylthiophene) (P3HT). The corresponding structures in Fig 5-1a show that all three HTLs contain Lewis base passivating moieties, with PTAA and PTPD containing tertiary amine groups and P3HT containing a thiophene group. These functional groups have been shown to passivate iodide vacancies in MAPbI$_3$, which in turn are known to provide sites for non-radiative recombination and superoxide formation. When interfaced with MAPbI$_3$, all three HTLs are expected to drive efficient
hole transfer on account of the spontaneous interfacial energy offset, \( \Delta E \geq 0.2 \text{ eV} \) between the HTL highest occupied molecular orbital (HOMO) and the MAPb\(_3\) valence band (VB), as shown in Fig 5-1b.\(^{49}\) We note that the values for the HOMO and VB levels were obtained from literature reports using consistent characterisation methods as described in more detail in Section 3.4.1. Samples were prepared via a one-step deposition of MAPb\(_3\) as reported elsewhere,\(^{26}\) and HTLs were spin-coated on top of MAPb\(_3\) in order to form a 30 nm ± 5 nm thick layer. Further details of sample processing can be found in the Section 5.3.2.

5.4.1.2. Evidence for Passivation

![Fig 5-2](image)

**Fig 5-2:** Evidence for passivation. a) normalised steady-state photoluminescence spectra for MAPb\(_3\)|HTL (HTL = PTAA, PTPD, P3HT) films. Inset: schematic illustrating the origin of blue-shift in passivated MAPb\(_3\) films. (b-e) Normalised steady-state photoluminescence spectra for MAPb\(_3\)|HTL films where the excitation (510 nm) was applied from the substrate|MAPb\(_3\) (black) and MAPb\(_3\)|HTL (coloured) interface respectively. (f) Fluorescence decay, as measured by time-correlated single photon counting (TCSPC) after excitation with a 635 nm laser (fluence: 0.11 nJ cm\(^{-2}\)), of MAPb\(_3\), MAPb\(_3\)|thiophene (T) and MAPb\(_3\)|triallylamine (TAA); (inset) steady-state emission of the same samples excited at 510 nm. (g) Structures of T and TAA.

To confirm passivation of MAPb\(_3\) by the HTLs, we looked to photoluminescence (PL) spectroscopy. Fig 5-2a shows the PL spectra of MAPb\(_3\) and MAPb\(_3\)|HTL (HTL = PTAA, PTPD, P3HT) samples. In the case of MAPb\(_3\), peak emission was observed at \( \lambda_{\text{peak}} = 764 \) nm due to radiative recombination of electrons and holes across the 1.6 eV band gap. In all cases where MAPb\(_3\) was interfaced with an HTL, a blue-shift was observed. Such blue-shift in the MAPb\(_3\) emission has been attributed to passivation of emissive trap-states at the
band edges. The rationale for this is that in highly trapped films, emission occurs on average from states closer together in energy due to the occupancy of emissive trap states. If some of these states are passivated they cannot be occupied and so emission occurs from states slightly further apart in energy. We found the resulting blueshift to be HTL-dependent, with much larger shifts observed for PTAA- and PTPD-based films relative to those capped with P3HT. This gives some qualitative indication that the passivation from the triarylamine HTLs is stronger than with P3HT.

Fig 5-2b, Fig 5-2c and Fig 5-2d contain further proof of passivation from the HTLs. Here, we excited the MAPbI₃ films at the substrate|MAPbI₃ (‘substrate’) and MAPbI₃|HTL (‘film’) interfaces respectively. Using an excitation wavelength of 510 nm meant that we could obtain interface specific information, as the penetration depth, zₑ is just 50 nm at this wavelength. We find that in the case of MAPbI₃, the ‘substrate’ and ‘film’ PL spectra are perfectly overlaid, suggesting that the trap-state density at either location is similar. This behaviour is mirrored in the case of MAPbI₃|P3HT, suggesting the P3HT layer has little impact on the trap-state density. On the other hand, in the case of MAPbI₃|PTAA and MAPbI₃|PTPD, the ‘film’ PL is significantly blue-shifted compared to the ‘substrate’, indicating that some passivation is occurring at the MAPbI₃|HTL interface.

Encouraged by this finding, we decided to isolate the passivation effect from the electron-donating moieties present on the HTLs by treating MAPbI₃ with their “pseudo-monomers”. We selected triallylamine (TAA) to simulate the tertiary amine groups on both PTAA and PTPD, and thiophene (T) to simulate the thiophene group on P3HT. Their structures are indicated in Fig 5-2g. Steady-state PL (Fig 5-2f, inset) shows that TAA passivation roughly doubles the PL intensity, while T passivation has a more incremental effect. Interestingly, TAA passivation also results in a significant blue-shift of the MAPbI₃ emission, in agreement with that obtained for PTAA and PTPD in Fig 5-2a.

These findings are backed up by time-resolved PL (TRPL) studies, presented in Fig 5-2f. Unpassivated MAPbI₃ exhibits a rapid PL decay typical of non-radiative recombination, which dominates at the low excitation fluence used (0.11 nJ cm⁻²). Addition of both TAA and T results in an enhanced PL lifetime consistent with the passivation of trap-states. Again, we find that TAA has a more considerable passivation effect than T in agreement with the steady-state PL findings.
Fig 5-3: Comparison of the PL decay dynamics for MAPbI$_3$ (black) and MAPbI$_3$:3HT (red) films, measured via time-correlated single photon counting (TCSPC). Structure of 3HT is given in the inset.

The ss-PL and TCSPC studies of T and TAA provide strong evidence for the superiority of tertiary amine functional groups in passivating iodide vacancies relative to thiophene groups. This is in line with the work of Noel et al, who also found that amine groups (pyradine) are more capable than thiophene groups at passivating the MAPbI$_3$ surface. Moreover, we also measured the PL dynamics of MAPbI$_3$ films treated with 3-hexylthiophene (3HT), the exact monomer of P3HT, with details in Fig 5-3. In this case, we observe no enhancement in the PL decay lifetime, suggesting that trap-state passivation is minimal. We suggest that while pure T is capable of passivating the MAPbI$_3$ surface, albeit less than TAA, 3HT is incapable of doing so, potentially due to steric hindrance associated with the bulky hexylthiophene chain. A similar mechanism was put forward by Noel et al to explain the lack of passivation in the case of tert-butylpyradine, even when pure pyradine was highly effective.

We further probed the extent of passivation with X-ray photoelectron spectroscopy (XPS). Fig 5-4a-c shows the C 1s spectra for 30 nm thick PTAA, PTPD and P3HT deposited on top of MAPbI$_3$. The spectra agree well with those in the literature for pure HTL films, suggesting that the HTL layer is well formed and free from contaminants or degradation products.

Next, we investigated the core-level spectra of the N 1s (PTAA and PTPD) or S 2p (P3HT) orbitals, as these atomic positions within the polymers were suspected of being responsible for the passivating interactions observed in the PL study. We therefore expected an increase in binding energy, $E_b$, of the passivating element upon moving from the HTL|air interface to the MAPbI$_3$|HTL interface. In order to investigate this, we prepared MAPbI$_3$ films with ‘thick’ (30 nm) and ‘thin’ (<10 nm) HTL overlayers to probe the HTL|air and MAPbI$_3$|HTL interfaces respectively, manipulating the strong surface sensitivity of XPS (1-10 nm). The resulting core-level spectra are summarised in Fig 5-4d-f.
Fig 5-4: X-Ray Photoelectron spectra of MAPbI₃|HTL (HTL = PTAA, PTPD, P3HT) films. (a-c) C 1s spectra for 30 nm thick PTAA (a), PTPD (b) and P3HT (c) on MAPbI₃. (d-f) N 1s core level spectra for (d) MAPbI₃|PTAA and (e) MAPbI₃|PTPD films. (f) S 2p core level spectra for MAPbI₃|P3HT films. The deconvoluted peaks are colour coded and coordinated to the corresponding bonding environments in the polymer or MAPbI₃ structures, inset. In each panel (d-f), the upper and lower spectra correspond to thick (30 nm) and thin (< 10 nm) HTL films.

Table 5-1: Parameters from XPS spectra. Binding energies ($E_b$) are for N 1s (PTAA and PTPD) and S 2p₃/₂ (P3HT). $\Delta E_b$ is the difference between $E_b$ measured for the 30 nm and < 10 nm films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HTL thickness (nm)</th>
<th>$E_b$ (eV)</th>
<th>$\Delta E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI₃</td>
<td>PTAA</td>
<td>30</td>
<td>398.90 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>&lt; 10</td>
<td>399.10 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>PTPD</td>
<td>30</td>
<td>399.05 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>&lt; 10</td>
<td>399.25 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>MAPbI₃</td>
<td>P3HT</td>
<td>30</td>
<td>163.20 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>&lt; 10</td>
<td>163.20 ± 0.05</td>
<td></td>
</tr>
</tbody>
</table>
The N 1s core-level spectra of MAPbI₃|PTAA in Fig 5-4d show two important features. The high binding energy peak at 401.05 eV is assigned to N in MAPbI₃ and the low binding energy peak at 398.90 eV is assigned to N in PTAA. We observe a similar spectrum for MAPbI₃|PTPD samples (Fig 5-3e) with the N 1s (MAPbI₃) and N 1s (PTPD) peaks centred at 401.25 eV and 399.05 eV respectively. Interestingly, the N 1s peaks associated with PTAA and PTPD were found at higher binding energies (399.10 and 299.25 eV respectively) in the thinner samples i.e. when the MAPbI₃|HTL interface was targeted. This suggests an interaction between the N atoms of the triarylamine HTLs and the MAPbI₃ surface.

The S 2p core-level spectra for MAPbI₃|P3HT samples are given in Fig 5-4f. The spectra are readily fitted to a 2p₁/₂/2p₃/₂ doublet from the S-atoms in the thiophene unit, with the two components centred at 164.40 and 163.20 eV respectively. We also observed a weaker contribution centred at 166.0 eV, which has been attributed previously to slight oxidation of the polymer surface. For the purpose of measuring the relative binding energy of the thick and thin films, we monitored the change in the 2p₃/₂ peak. In contrast to the PTAA- and PTPD-capped MAPbI₃ films, no increase in binding energy was observed upon moving from the P3HT surface to the MAPbI₃|P3HT interface.

The interaction between the different HTLs and the MAPbI₃ surface is summarised in Table 5-1, which shows the change in binding energy, ∆Eₖ for the three HTLs upon moving from the HTL|air to the MAPbI₃|HTL interfaces. PTAA and PTPD show evidence of strong interfacial interactions with a ∆Eₖ of 0.20 ± 0.1 eV in both cases. On the other hand, P3HT demonstrates negligible interaction with ∆Eₖ = 0 ± 0.1 eV. We therefore assert that the weak passivation effect displayed by P3HT is due to the weaker interaction between its thiophene moiety and the MAPbI₃ surface. On the other hand, the more significant passivation effect from PTAA and PTPD is underpinned by the relatively strong interfacial interactions between the tertiary amine group and the MAPbI₃ surface, potentially at iodide vacancy (Vᵢ) sites. This supports the suggestion originally made by Heo et al that triarylamine-based HTLs (e.g. PTAA) should be more capable of binding to the perovskite surface than those involving thiophene functionalities (e.g. P3HT).

5. 4. 1. 3. Passivation-Mediated Charge Transfer

We next looked at how passivating interactions at the MAPbI₃|HTL interface impact charge transfer through intensity-dependent transient absorption spectroscopy (TAS). An overview of the TAS technique is given in Section 2. 3 and details specific to this chapter in Section 5. 3. 4. Furthermore, samples were excited at 510 nm via the glass substrate, such that the direct excitation density in the HTL layer was small (> 1%) compared to that in the MAPbI₃ layer (See Section 2. 2. 2).
Fig 5-5: An example set of TAS traces for a TiO$_2$|MAPbI$_3$|PTPD sample where the excitation fluence was varied from 0.1 to 12.5 µJ cm$^{-2}$. Stretched exponential fits - $\Delta\text{OD} \propto \exp\left[-\left(\frac{t}{\tau_0}\right)^\alpha\right]$ - to the data are also shown. $\Delta OD_{max}$ and $\tau_{\text{rec,h}}$ can be extracted from the fit as the $\Delta\text{OD}$ at $10^{-6}$ s and the time taken for this value to reach 50% respectively.

We characterised the spectra of PTAA, PTPD and P3HT in earlier in this thesis, in Section 3.4.2, where we found that intense features centred at 1500, 1600 and 950 nm respectively were produced after hole injection from MAPbI$_3$. Given this assignation, we looked to investigate how the yield and recombination rate of injected holes varies with the initial carrier density, $n_0$ in the MAPbI$_3$ layer.

Fig 5-5 shows an example set of TAS traces for a TiO$_2$|MAPbI$_3$|PTPD sample probed at 1600 nm - i.e. at the maximum of the PTPD* polaron - over a range of fluences. Given the Beer-Lambert law, $\Delta\text{OD}$ is directly related to the concentration of injected holes in the HTL and so the initial intensity and subsequent decay are indicative of the hole injection yield and recombination time respectively. Each TAS trace decays nonexponentially and can be modelled with a stretched exponential function: $\Delta\text{OD} \propto \exp\left[-\left(\frac{t}{\tau_0}\right)^\alpha\right]$. This type of decay is consistent with recombination in systems that contain a significant amount of disorder.$^{65}$ Therefore, the initial intensity $\Delta OD_{max}$ of the TAS trace, normalised to photons absorbed, reflects the relative hole transfer yield. Given the non-exponential decay dynamics, we assign an approximate lifetime, $\tau_{\text{rec,h}}$ as the time taken for the signal to reach $\Delta OD_{max}/2$. $^{65}$ We could then find these values as a function of $n_0$ by analysing TAS traces at different fluences, under the assumption that each absorbed photon produces one electron/hole pair.
Fig 5-6: Characterisation of hole injection in TiO$_2$|MAPbI$_3$|HTL (HTL = P3HT, PTAA, PTPD) films: (a) Relative hole injection yield, $\Delta O_D_{\text{max}}$ normalised to photons absorbed, versus the initial carrier density, $n_0$ in the MAPbI$_3$ layer. Inset: schematic illustrating the competing charge transfer processes at the MAPbI$_3$|HTL interface. Samples were excited via the glass substrate at 510 nm and probed at the maximum of the HTL polaron absorption: 950, 1500 and 1600 nm for PTAA, PTPD & P3HT.

Fig 5-6 shows the relative hole yield, $\Delta O_D_{\text{max}}$, normalised for photons absorbed, as a function of $n_0$ for the TiO$_2$|MAPbI$_3$|HTL (HTL = PTAA, PTPD, P3HT) samples. The $\Delta O_D_{\text{max}}$ shown is a three-sample average and the error bars indicate the standard deviation between the three repeats. The general shape of the individual curves presented therein can be explained in terms of the competing rates of recombination in the MAPbI$_3$ layer ($k_{\text{rec,M}}$) and injection into the HTL ($k_{\text{inj}}$) (Fig 5-6, inset).$^{56}$ At high carrier density ($n_0 \geq 10^{18}$ cm$^{-3}$), recombination in MAPbI$_3$ is governed by fast, three-body Auger recombination where $k_{\text{rec,M}} > k_{\text{inj}}$, resulting in low hole injection yields. As the carrier density is lowered ($10^{16}$-$10^{18}$ cm$^{-3}$), recombination in MAPbI$_3$ becomes dominated by bimolecular recombination, which is slower, typically on the order of 10-100 ns.$^{66}$ In this case, $k_{\text{rec,M}} < k_{\text{inj}}$ and so the hole injection yield increases. As we approach the low carrier-density limit of our TAS setup ($n_0 \leq$...
the recombination kinetics in the MAPbI₃ layer begin to be dictated by trap-mediated monomolecular recombination. Here, the hole injection yield starts to plateau. This range of behaviour has been observed previously for MAPbI₃|spiro-OMeTAD interfaces. However, the more intriguing aspect of Fig 5-6 is the divergence between MAPbI₃|P3HT and MAPbI₃|PTAA, PTPD samples in the trap-limited regime. At high carrier-density when trap-states are filled, the $\Delta OD_{\text{max}}$ of the HTLs is similar, as predicted by the favourable interfacial energetics given in Fig 5-1b. However, $\Delta OD_{\text{max}}$ is three times higher for PTAA and PTPD relative to P3HT at $n_0 \sim 10^{16}$ cm$^{-3}$ when trap-states are not filled by photoexcited carriers and the effects of passivation become apparent. Additionally, the order of improvement goes P3HT < PTAA ~ PTPD, which agrees with the extent of passivation deduced from $\Delta E_b$ in Table 5-1. We therefore propose that PTAA and PTPD are not only capable of passivating defects at the MAPbI₃ surface, but that this interaction is integral to the hole injection process. This supports the hypothesis of Heo et al, who suggested that the higher efficiency of MAPbI₃ devices based on triarylamine- rather than thiophene-based HTLs was due to the enhanced interfacial interaction in the former case. This idea links with the later work of Brauer et al, who suggested that poor contact between MAPbI₃ and P3HT could lower the hole injection yield across the MAPbI₃|P3HT interface.

![Graph showing hole injection yield vs initial carrier density](image)

**Fig 5-7**: Relative hole injection yield, $\Delta OD_{\text{max}}$, normalised to photons absorbed, as a function of the initial carrier density, $n_0$, in the MAPbI₃ layer for Al₂O₃|MAPbI₃|HTL (HTL = PTAA, PTPD, P3HT) films. Samples were excited via the glass substrate at 510 nm and probed at the maximum of the HTL polaron absorption: 950, 1500 and 1600 nm for PTAA, PTPD & P3HT.

We also measured $\Delta OD_{\text{max}}$ versus $n_0$ for Al₂O₃|MAPbI₃|HTL films to rule out the overlapping TA contribution from free electrons in TiO₂ (TiO₂) at 1600 nm as the reason for the enhanced hole injection yields in PTAA- and PTPD-capped films (Fig 5-7). In this system, the insulating character of Al₂O₃ means that hole injection to the HTL is the only
energetically favourable means of interfacial charge injection. Therefore, given the striking resemblance between Fig 5-7 and Fig 5-6 - with PTPD and PTAA exhibiting much greater hole injection yields than P3HT as the carrier density is lowered – we can confidently discard the impact of the TiO$_2$ contribution.

**Fig 5-8:** Kinetics of recombination at the MAPbI$_3$|HTL (HTL = PTAA, PTPD, P3HT) interface. (a) Recombination time, $\tau_{\text{rec,h}}$ - established as the time taken for the injection yield to drop to 50% of its initial value – as a function of the initial carrier-density, $n_0$ in the MAPbI$_3$ layer. (b) Interfacial recombination rate constant, $k_{\text{rec,h}}$ taken as $1/\tau_{\text{rec,h}}$ across the same range. (c) Normalised transient absorption decays for the MAPbI$_3$|HTL films at $n_0 \sim 2 \times 10^{16}$ cm$^{-3}$. Samples were excited via the glass substrate at 510 nm and probed at the maximum of the HTL polaron absorption: 950, 1500 and 1600 nm for PTAA, PTPD & P3HT.

Next, we measured $\tau_{\text{rec,h}}$ as a function of $n_0$ (Fig 5-8a) for the same TiO$_2$|MAPbI$_3$|HTL (HTL = PTAA, PTPD, P3HT) samples. Crucially, $\tau_{\text{rec,h}}$ denotes the recombination time of injected holes in the HTL either with electrons in the MAPbI$_3$ layer or via interfacial traps ($k_{\text{rec,h}}$, Fig 5-8a inset). Therefore, any differences in the extent of passivation from the HTLs should be evident in an increase in $\tau_{\text{rec,h}}$ upon lowering the carrier density into the trap-limited regime. It is therefore interesting that $\tau_{\text{rec,h}}$ at the MAPbI$_3$|P3HT interface is unchanged over the carrier density interval studied. In contrast, $\tau_{\text{rec,h}}$ in the case of MAPbI$_3$|PTAA and MAPbI$_3$|PTPD slows by more than a factor of three across the same range.

The intensity dependence of the interfacial recombination rate constant, $k_{\text{rec,h}}$ calculated as $1/\tau_{\text{rec,h}}$, for the three MAPbI$_3$|HTL combinations is given in Fig 5-8b. We observe that $k_{\text{rec,h}}$ for injected holes in P3HT is independent of light intensity in the range covered, consistent with monomolecular i.e. trap-mediated recombination kinetics. On the contrary, the
dependence of $k_{\text{rec}}$ on $n_0$ in the case of PTAA and PTPD is non-trivial with a transition from 1st ($k_{\text{rec}}$ is intensity independent) to 2nd ($k_{\text{rec}}$ is intensity dependent) order kinetics occurring at $n_{1/2}$. For MAPbI$_3$|PTAA samples, $n_{1/2} \sim 10^{17}$ cm$^{-3}$ and a similar transition occurs for MAPbI$_3$|PTPD films with $n_{1/2} \sim 10^{16}$ cm$^{-3}$. Given that non-radiative recombination processes are 1st order and the bimolecular recombination processes associated with well-passivated films are 2nd order, this suggests that the trap density in MAPbI$_3$|HTL (HTL = PTPD, PTAA) films is considerably lower than in MAPbI$_3$|P3HT films.

We stress here that the $n_{1/2}$ discussed here is purely a relative measure of trap-density at the MAPbI$_3$|HTL interface and not the absolute trap-state density in the MAPbI$_3$ film. This method could be used to obtain a more quantitative estimate of the trap-state density at the MAPbI$_3$|HTL interface, but for this the hole density in the HTL, $n_+$ rather than the initial carrier density in MAPbI$_3$ ($n_0$) would need to be calculated. This could be done via the Beer-Lambert law ($n_+ = \Delta OD \cdot N_p / \varepsilon_+$) but would require a reliable measurement for the polaron extinction coefficient, $\varepsilon_+$. We note that given $n_0 > n_+$, it is likely that the trap-state density in MAPbI$_3$ is significantly lower than $n_{1/2}$ found in Fig 5-8b.

The better passivation performance of PTAA and PTPD versus P3HT is further underlined by the kinetic traces at $n_0 \sim 2 \times 10^{16}$ cm$^{-3}$ shown in Fig 5-8c. It is clear to see that recombination across the MAPbI$_3$|P3HT interface is an order of magnitude faster than in the case of MAPbI$_3$|PTAA or MAPbI$_3$|PTPD. This provides further supporting evidence that PTAA and PTPD are capable of passivating defects at the MAPbI$_3$ surface thus increasing $\tau_{\text{rec,h}}$.

**Fig 5-9:** Recombination time, $\tau_{\text{rec,h}}$ versus relative hole injection yield normalised to photons absorbed, $\Delta OD_{\text{max}}$ for all MAPbI$_3$|HTL (HTL = P3HT, PTAA, PTPD) films studied herein.
Throughout Section 5.4.1.3 we have set out the case for passivation-mediated charge injection by showing that the HTLs (PTAA, PTPD) that are capable of passivating the MAPbI$_3$ surface produce much larger hole injection yields than those that do not (P3HT). In Fig 5-9, we offer an alternative representation of this idea by plotting $\Delta OD_{\text{max}}$ against $\tau_{\text{rec},h}$ for all of the MAPbI$_3$|HTL combinations studies herein. In this representation, the extents of passivation and hole injection increase towards the right and top sides of Fig 5-9. Therefore, the strong correlation between $\Delta OD_{\text{max}}$ and $\tau_{\text{rec},h}$ is striking evidence of the importance of passivation in determining the hole injection yield.

![Graph showing $\Delta OD_{\text{max}}$ vs $\tau_{\text{rec},h}$]

**Fig 5-10:** Steady-state photoluminescence spectra for MAPbI$_3$ (dashed line) and BA$_{0.09}$MA$_{0.91}$PbI$_3$ (solid line). Films were illuminated at 510 nm.

We next designed an experiment to further probe passivation-mediated hole transfer at the MAPbI$_3$|HTL interface by altering the extent to which the HTL could interact with defects at the MAPbI$_3$ surface. We measured the hole injection yield in the case of both MAPbI$_3$ and its highly pristine BA$_{0.09}$MA$_{0.91}$PbI$_3$ (BA = butylammonium) counterpart. The lower trap-density in BA$_{0.09}$MA$_{0.91}$PbI$_3$ is demonstrated by the PL spectra in Fig 5-10, in which BA$_{0.09}$MA$_{0.91}$PbI$_3$ yields 39-times more intensity compared to MAPbI$_3$. This has previously been attributed to the passivation of MAPbI$_3$ grain boundaries by microscopic 2D domains.\(^{68}\) Therefore, the highly pristine nature of the perovskite in this case should limit the extent to which the HTLs can interact with defects at the surface. We also note that despite the 3D-2D character of BA$_{0.09}$MA$_{0.91}$PbI$_3$, the valence band remains unchanged for small amounts of BA.\(^{68,69}\) Therefore, any changes in the rate of hole transfer are likely to be due to passivation alone.
Fig 5-11: Effect of perovskite trap density on hole injection. (a-c) Relative hole injection yield, $\Delta OD_{max}$, normalised per photon absorbed, as a function of the initial carrier density, $n_0$, in the MAPbI$_3$ layer for $\text{TiO}_2$|$\text{MAPbI}_3$|HTL (coloured symbols) and $\text{TiO}_2$|$\text{BA}_{0.09}\text{MA}_{0.91}\text{PbI}_3$|HTL (white symbols) where the HTL was PTAA, PTPD or P3HT. Samples were excited via the glass substrate at 510 nm and probed at the maximum of the HTL polaron absorption: 950, 1500 and 1600 nm for PTAA, PTPD & P3HT.

Fig 5-11a-c shows the intensity dependent hole injection yield for perovskite|HTL samples (perovskite = MAPbI$_3$, BA$_{0.09}$MA$_{0.91}$PbI$_3$; HTL = PTAA, PTPD, P3HT). For PTAA-capped films, the hole injection yield is four times higher for MAPbI$_3$ than for BA$_{0.09}$MA$_{0.91}$PbI$_3$. This trend is reflected in the perovskite|PTPD samples, which also demonstrate much higher yields in the case of MAPbI$_3$ than with BA$_{0.09}$MA$_{0.91}$PbI$_3$. This suggests that the lower defect
density at the BA$_{0.09}$MA$_{0.91}$PbI$_3$ surface limits the injection yield by forbidding the binding interaction. We again see very little dependence on trap-state density in the case of P3HT regardless of the perovskite layer used, adding further weight to the argument that passivation does not play a significant role in the charge transfer process at the perovskite|P3HT interface. Furthermore, little distinction can be made between the effectiveness of the three HTLs on BA$_{0.09}$MA$_{0.91}$PbI$_3$, suggesting that it is the passivating interactions that give PTAA and PTPD the advantage over P3HT in MAPbI$_3$ films.

\[ k_{rec,h}(S^{-1}) \]

\[ n_0 (cm^{-3}) \]

**Fig 5-12:** Interfacial recombination rate constant, $k_{rec,h}$ taken as $1/\tau_{rec,h}$ as a function of initial carrier density in the perovskite layer, $n_0$ for perovskite|P3HT [perovskite = MAPbI$_3$ (coloured circles) and BA$_{0.09}$MA$_{0.91}$PbI$_3$ (empty circles)] films.

Finally, our earlier TAS measurements on MAPbI$_3$|P3HT films showed that this interface is prone to fast recombination and a large density of traps, as evidenced by the relatively large values of $k_{rec,h}$ and $n_{1/2}$. Therefore, we finally wanted to investigate whether the significantly reduced trap density in BA$_{0.09}$MA$_{0.91}$PbI$_3$ alters the picture of recombination at the perovskite|P3HT interface. Fig 5-12 shows $k_{rec,h}$ as a function of $n_0$ for MAPbI$_3$|P3HT (coloured circles) and BA$_{0.09}$MA$_{0.91}$PbI$_3$|P3HT (empty circles). Upon switching the perovskite layer from MAPbI$_3$ to BAMAPbI$_3$, the value for $n_{1/2}$ is markedly reduced from $n_{1/2} > 10^{18}$ cm$^{-3}$ to $n_{1/2} < 5 \times 10^{15}$ cm$^{-3}$, as evidenced by the intensity dependence of $k_{rec,h}$ over the entire range studied. The implied lower trap density ($n_t < 5 \times 10^{15}$ cm$^{-3}$) in BA$_{0.09}$MA$_{0.91}$PbI$_3$ is manifest in an order of magnitude lower $k_{rec,h}$ at $n_0 \sim 10^{16}$ cm$^{-3}$ compared to the MAPbI$_3$-based film.
These observations are further proof that interfacial recombination of injected holes occurs via trap-states in the MAPbI$_3$ layer. Moreover, effective management of these traps, in our case by alloying MA with BA, puts $k_{\text{rec,hi}}$ in the BA$_{0.09}$MA$_{0.91}$PbI$_3$|P3HT system (900 s$^{-1}$) in line with the MAPbI$_3$|PTAA, PTPD systems (1800 and 1600 s$^{-1}$ respectively). This ties in with our measurements in Section 3.4.5 on the Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$PbI$_3$|HTL system, where we showed that HTLs exhibit much longer lifetimes when interfaced with this relatively defect-free perovskite. As such, despite being an inherently poor passivator, efficient devices should still be possible with P3HT, provided the perovskite layer is modified to reduce recombination at the perovskite|P3HT interface. This is perhaps less necessary in the MAPbI$_3$|PTAA or MAPbI$_3$|Spiro-OMeTAD system because these HTLs have an inherent capacity to passivate. Indeed, Jung et al recently showed that highly efficient (>22%) PSCs could be made using P3HT by modifying the perovskite surface to mitigate trap-state formation.\textsuperscript{24}

5.4.1.4. Device Characteristics

![Image of device characteristics](image)

**Fig 5-13:** Characterisation of ITO|SnO$_2$|MAPbI$_3$|HTL|Au (HTL = PTAA, P3HT) devices: (a) current-voltage (J-V) characteristics of a PTAA-based device, in which the PTAA is doped with 4 µL of 170 mg mL$^{-1}$ LiTFSI. (b) J-V characteristics of undoped devices containing PTAA, PTPD and P3HT. (c & d) Intensity dependence of (c) the short-circuit current ($J_{SC}$) and (d) the open-circuit voltage ($V_{OC}$). The gradients $\alpha$ (c) and $n_{1D}, k_{B}T/q$ (d) are stated. Devices were fabricated by Dr Thomas MacDonald.
Table 5-2: J-V parameters for the ITO|SnO$_2$|MAPbI$_3$|HTL|Au (HTL = P3HT, PTAA) cells in Fig 5-13.

<table>
<thead>
<tr>
<th>HTL</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>17.10</td>
<td>0.90</td>
<td>0.612</td>
<td>9.45</td>
</tr>
<tr>
<td>PTAA</td>
<td>22.35</td>
<td>1.07</td>
<td>0.674</td>
<td>16.19</td>
</tr>
</tbody>
</table>

We measured the current-voltage (J-V) characteristics of ITO|SnO$_2$|MAPbI$_3$|HTL|Au (HTL = PTAA, P3HT, PTPD) devices in order to understand the effect of passivation under working conditions. For this study, experimental control was valued over device efficiency and so we avoided the use of additives, which complicate the picture of passivation and interfacial charge extraction.$^{57}$ However, we show a reference J-V curve in Fig 5-13a for an ITO|SnO$_2$|MAPbI$_3$|HTL|Au device, where PTAA contained additives bis-(trifluoromethane) sulfonimide lithium salt (Li-TFSI) and 4-tert-Butylpyridine (tBp) to achieve high hole mobility and conductivity.$^{70}$ We achieve an efficiency of 19.2% with this device, which is well in line with other reports in the literature on pure MAPbI$_3$-based solar cells in the nip architecture.$^{71}$

The J-V characteristics for the undoped PTAA-, PTPD- and P3HT-based devices at 1 sun are presented in Fig 5-13b. Firstly it is clear to see that the devices containing PTPD performed poorly, which we attribute to the order of magnitude lower hole mobility in this HTL compared to PTAA in its undoped form.$^{72}$ We suggest that while PTPD is highly capable of extracting holes from MAPbI$_3$ – as evidenced by our TAS studies - the low hole mobility of this HTL could hinder the subsequent hole transport towards the contacts. We therefore focus the following discussion on devices that incorporate PTAA and P3HT, as these are more prevalent in the literature.$^{24,73}$

The cells incorporating PTAA were observed to perform markedly better than those using P3HT, with efficiencies of 16.19% and 9.45% respectively. This difference was driven by improvements in both the short-circuit current ($J_{SC}$; 17.10 to 22.35 mA cm$^{-2}$) and open-circuit voltage ($V_{OC}$; 0.90 V to 1.07 V). As evidenced by our TAS results, charge separation is much enhanced at MAPbI$_3$|PTAA interfaces as compared to those involving P3HT. Therefore, we expect this enhanced charge separation yield, as well as the greater mobility of PTAA$^{72}$ to be factors in the improved $J_{SC}$.

The $V_{OC}$ is defined as the quasi-Fermi level splitting (QFLS) of electrons and holes under illumination and is consequently intertwined with (i) the trap-state density in the MAPbI$_3$ layer and (ii) the energetic alignment at the perovskite|HTL interface. We have shown throughout this work that non-radiative recombination at the MAPbI$_3$|PTAA interface is significantly
supressed relative to MAPbI$_3$|P3HT, most likely due to enhanced passivation from PTAA. This should be manifest in a larger internal quasi-Fermi energy splitting, $\Delta E_F$ in PTAA-based relative to P3HT-based devices. Stolterfoht et al have done extensive work in this regard, finding $\Delta E_F$ values of 1.20 and 1.15 eV for PTAA- and P3HT-based (CsPbI)$_{0.05}$[(FAPbI)$_{0.83}$(MAPBr)$_{0.17}$]$_{0.95}$ perovskite solar cells. Therefore, the improved $V_{OC}$ in our PTAA-based devices can be assigned in part to better control of non-radiative recombination at the MAPbI$_3$|HTL interface. However, this 50 mV difference in $\Delta E_F$ cannot entirely explain the 170 mV difference between the performance of the two HTLs. We therefore attribute the remaining voltage loss in the P3HT-based devices to poor energetic alignment at the MAPbI$_3$|P3HT interface.\textsuperscript{15} We discussed this effect in more detail in Chapter 3.

To further probe the impact of recombination at the MAPbI$_3$|HTL interface in the P3HT- and PTAA-based devices, we measured the J-V characteristics as a function of light intensity. In Fig 5-13c we present a logarithmic plot of $J_{SC}$ against light intensity for the two types of device. The slopes in both plots of $J_{SC}$ vs light intensity are 1, suggesting that minimal bimolecular recombination is occurring in either case.\textsuperscript{74}

Fig 5-13d displays the relationship between $V_{OC}$ and light intensity. In the case of pure bimolecular recombination, the slope of the semi-logarithmic plot should be equal to the thermal voltage, $k_bT/q$.\textsuperscript{75} However, in the presence of trap-mediated recombination, the slope deviates towards steeper values, with a value of $2k_bT/q$ being the fingerprint of pure monomolecular recombination.\textsuperscript{76} Intermediate situations with $n_{ID}k_bT/q$ ($1 < n_{ID} < 2$) can then be assessed by their ideality factor, $n_{ID}$.\textsuperscript{18}

The device incorporating P3HT as the HTL demonstrates an $n_{ID}$ of 2.06, indicating that recombination occurring in the device is dominated by monomolecular trap-mediated recombination. On the other hand, a marked improvement was observed when PTAA was used, with $n_{ID}$ reduced to 1.45. We therefore conclude that PTAA mitigates trap-mediated recombination to a greater extent than P3HT, contributing to the enhanced $V_{OC}$ in PTAA-based devices.

5. 4. 1. 5. Extension to other Hole Transport Layers

So far in this chapter, we have focused our attention on PTAA, PTPD and P3HT for the simplicity of their repeating units, allowing for more experimental control linking passivation to charge transfer. However, once we established the effectiveness of TAS in assessing the extent of passivation and subsequent impact on charge transfer, we sought to probe a wider set of HTLs. Therefore we also investigated PTB1 and spiro-OMeTAD, two well-known
organic p-type conductors. PTB1 has been shown to be an effective HTL in PSCs,\textsuperscript{77} albeit with limited efficiency due to the large overpotential at the MAPbI₃|PTB1 interface and spiro-OMeTAD is widely lauded as the most effective HTL for PSCs.\textsuperscript{78}

**Fig 5-14:** (a) The chemical structures of PTB1 and spiro-OMeTAD, with potential passivating moieties highlighted. (b) dependence of the recombination rate constant, $k_{\text{rec,h}}$ obtained from transient absorption decays as $1/\tau_{\text{rec,h}}$, as a function of the initial carrier density, $n_0$ in the MAPbI₃ layer. Inset: DFT-calculated highest occupied molecular orbital (HOMO) map of spiro-OMeTAD. Taken with permission from \textsuperscript{78}. (c) The hole injection yield normalised to photons absorbed, $\Delta\text{OD}_{\text{max}}$ for TiO₂|MAPbI₃|HTL (HTL = Spiro-OMeTAD, PTB1) samples as a function of $n_0$. Samples were excited at 510 nm and probed at the maximum of the polaronic absorption – 1100 and 1600 nm for PTB1 and Spiro-OMeTAD respectively. The data for PTAA-, PTPD- and P3HT-capped MAPbI₃ films, found earlier in this chapter, are given in the semi-transparent points.

Both of these HTLs have numerous passivating moieties about their structure, as highlighted in Fig 5-14a. PTB1 contains a number of thiophene moieties as well as several lone pair species including carbonyl and ether groups. Spiro-OMeTAD also contains ether (methoxy) groups as well as the tertiary amine groups that we associated with passivation in the triarylamine HTLs. We note that the ether groups common to both spiro-OMeTAD and PTB1 have been shown by Saliba et al to bind to the MAPbI₃ surface.\textsuperscript{78}
Fig 5-14b shows the carrier density dependence of $k_{\text{rec}}$ – calculated as $1/\tau_{\text{rec}}$ – as a function of $n_0$ for MAPbI$_3$|HTL (HTL = PTB1, spiro-OMeTAD, PTAA, PTPD, P3HT) films. As described previously, $n_{1/2}$ - the carrier density at which the recombination kinetics switch from 1st to 2nd order – is a good indicator of the relative trap-state density at the MAPbI$_3$|HTL interface. We also measured $n_{1/2}$ for PTAA-, PTPD- and P3HT-capped MAPbI$_3$ earlier in this chapter obtaining $n_{1/2} \sim 10^{17}$ cm$^{-3}$, $n_{1/2} \sim 10^{16}$ cm$^{-3}$ and $n_{1/2} > 10^{18}$ cm$^{-3}$ respectively. Here, we observe largely bimolecular recombination kinetics for MAPbI$_3$|PTB1 and MAPbI$_3$|spiro-OMeTAD samples throughout the entire measurable range. Therefore, an upper limit of $n_{1/2} < 10^{16}$ cm$^{-3}$ can be set for both HTLs, suggesting that the MAPbI$_3$ film is well passivated relative to e.g. P3HT-capped films. This makes for interesting comparison with the relative hole injection yield, $\Delta$OD presented in Fig 5-14c. Here, we find that $\Delta$OD in the case of MAPbI$_3$|PTB1 and MAPbI$_3$|spiro-OMeTAD is significantly larger than with the other HTLs at $n_0 < 10^{16}$ cm$^{-3}$. This is consistent with the greater extent of passivation driving more efficient hole transfer.

Here, we must exercise caution in drawing conclusions as the picture of hole transfer at MAPbI$_3$|HTL interfaces is a complex one, with structure, energetics and mobility likely to play a role. However, there is a striking correlation here between chemical interaction (i.e. passivation) and charge transfer. In particular, the science behind the success of spiro-OMeTAD has previously been linked to chemical interactions. Most notably, Bi et al found that recombination is significantly slower in spiro-OMeTAD based samples, due to the reduced interfacial coupling that comes about due to its cross-linked spiro centre.$^{25}$ They posit that the resultant physical distancing of the spiro-OMeTAD core and the MAPbI$_3$ layer reduces the interfacial coupling and increases the lifetime of injected holes compared to more planar structures e.g. with P3HT. We can support this assertion with the data in Fig 4-14c, which shows that at $n_0 = 10^{16}$ cm$^{-3}$ carriers, recombination is an order of magnitude slower in the case of MAPbI$_3$ capped with spiro-OMeTAD than with P3HT. More recently, Saliba et al showed that binding between spiro-OMeTAD and MAPbI$_3$ occurs via the -OMe groups on the periphery of the molecule.$^{78}$ In this study, we have added to this limited literature by presenting evidence for a link between passivation and charge transfer at the MAPbI$_3$|spiro-OMeTAD interface.

How can a molecule simultaneously enhance and suppress interfacial coupling? Inspection of the HOMO distribution on spiro-OMeTAD presents a potential explanation to unify these seemingly contradictory ideas. The inset of Fig 4-14b presents the two degenerate HOMO distributions in spiro-OMeTAD delocalised over the symmetric halves of the molecule.$^{78}$ The HOMO is mainly located on the spiro and methoxy-substituted phenylamine moieties,
meaning that injected holes are on average located closer to the core of the molecule rather than on the -OMe groups at the periphery. Therefore, we suggest that the -OMe groups bind to the MAPbI3 surface via passivating interactions and efficiently transport charges towards the spiro-OMeTAD core. Once there, the hole is less likely to recombine because of the increased distance between the spiro core and the MAPbI3 surface. This would compare favourably to the case of PTAA for example, where although strong interfacial coupling enhances the initial charge transfer, the injected hole would be located on the planar PTAA structure, close to the MAPbI3 interface. This could explain the two-fold longer lifetime of injected holes in spiro-OMeTAD compared to e.g. PTAA in Fig 14b.

5.4.2. Passivation-Mediated Charge Transfer in the pin Architecture

Fig. 5-15: (a-b) Relative hole injection yield, $\Delta OD_{max}$, normalised per photon absorbed, as a function of the initial carrier density, $n_0$, in the MAPbI3 layer for nip (TiO2|MAPbI3|HTL) and pin (HTL|MAPbI3|PCBM) films (HTL = PTAA & P3HT). Films were excited at 510 nm via the glass substrate and probed at the maximum of the HTL polaron: 950 & 1500 nm for PTAA & P3HT.
The *pin* architecture is the most widely used in contemporary high-performance PSCs on account of the increased resistance towards hysteresis and UV-light.\textsuperscript{79,80} Moreover, it is the only viable architecture for perovskite-silicon tandems given the inherent \( p \)-type doping of conventional silicon technologies.\textsuperscript{81,82} Nevertheless, the \( V_{OC} \) of *pin* PSCs (1.15 \text{ V})\textsuperscript{83} is significantly lower than their *nip* counterparts (1.26 \text{ V}).\textsuperscript{14} Therefore, we also investigated the impact of passivation on charge injection and recombination in this class of materials. Firstly, we explored the impact on hole transfer at the perovskite|HTL interface upon reversing the architecture. To do this, we prepared *pin* (HTL|\text{MAPbI}_3|PCBM) and *nip* (TiO\textsubscript{2}|\text{MAPbI}_3|HTL) films and compared hole injection in the range, \( 10^{16} < n_0 < 10^{18} \text{ cm}^{-3} \).

Fig 5-15a and Fig 5-15b show the intensity-dependent \( \Delta O D_{\text{max}} \) for \text{MAPbI}_3 interfaced with PTAA and P3HT in the two architectures. For PTAA, a stark contrast between *pin* and *nip* configurations is observed, with the hole injection yield being four times higher in the latter case at \( n_0 = 4 \times 10^{16} \text{ cm}^{-3} \). Conversely, hole injection across the \text{MAPbI}_3|P3HT interface is similar irrespective of the architecture.

We have shown throughout this work that TAS can give unique insight into the chemical interactions at \text{MAPbI}_3|CTL interfaces. It is our view then, that the results in Fig 5-15 can be rationalised in terms of the differing chemical interactions in the two architectures. Precisely, the *pin* architecture consists of a PFN interlayer between the HTL and \text{MAPbI}_3 layers, that allows for better wetting of the latter.\textsuperscript{84} Moreover, while there are some reports of passivation from underlayers,\textsuperscript{85} it is possible that the change in architecture affects the scope of such interactions. Therefore, we expect passivation at the \text{MAPbI}_3|HTL interface in the *pin* architecture to be obstructed to a degree. Conversely, in the *nip* architecture, the HTL is deposited directly on top of the \text{MAPbI}_3 layer, allowing it to interact with the active layer surface.

We therefore postulate that the four-times lower hole transfer yield upon switching from *nip* to *pin* architecture in the case of PTAA is due to the obstruction of passivation and the resulting decrease in interaction between the two layers. On the other hand, the similarity between *pin* and *nip* for P3HT-based films suggests that passivation-mediated hole transfer is negligible in either case. This provides further evidence that passivation plays a critical role in the high charge transfer yields exhibited by some HTLs e.g. PTAA.

We next investigated whether \textit{electron} transfer at the top interface in *pin* films is affected by passivation. To do this, we interfaced \text{MAPbI}_3 with three fullerene-derivatives: [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), indene-C60-propionic acid hexyl ester (IPH) and a fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG). The structures given in Fig 5-16a show that the ETLs contain functional groups capable of Lewis base
passivation. PCBM and IPH contain lone-pair oxygen in the form of C=O and C-O-C bonds, while PTEG has numerous possibilities including an oxygen-rich triethylene glycol chain and a tertiary amine group.

Fig 5-16: Transient optical characterisation of MAPbI₃|ETL (ETL = PTEG, IPH, PCBM) samples. (a) Structures of the ETLs and their associated energetics. (b-d) transient absorption spectra measured at 1µs after excitation at 510 nm.

Fig 5-16b and Fig 5-16c gives the transient spectra of Al₂O₃|MAPbI₃|ETL and PTPD|MAPbI₃|ETL (ETL = PCBM, IPH, PTEG) films taken 1µs after excitation at 510 nm. The samples deposited on PTPD show the characteristic absorption associated with hole polarons on the PTPD (peak at 1600 nm). However, the samples containing the fullerene derivatives contain an additional contribution around 900-1000 nm. Given that (i) this peak is clearly resolved in Al₂O₃|MAPbI₃|ETL films, and that (ii) MAPbI₃ absorption is zero at 1 µs (Fig 5-16, white circles) we categorically assign this peak to the ETL anion. This is in line with the transient spectrum of PCBM measured by Ohkita and Ito.⁸⁶
Fig 5-17: The recombination rate, \(k_{\text{rec,h}}\) calculated as \(1/\tau_{\text{rec,h}}\) of the TAS trace - for injected electrons in the ETLs, as a function of the initial carrier density in the MAPbI\(_3\) layer, \(n_0\). Samples were excited at 510 nm via the glass substrate and probed at 900, 1000 and 1000 nm for PTEG, PCBM and IPH i.e. the TA maxima of the respective fullerene anions.

We have shown throughout this chapter that TAS is capable of giving insight into the extent of passivation from CTLs, via the value \(n_{1/2}\). Fig 5-17 then suggests that PCBM and IPH have \(n_{1/2} > 10^{18} \text{ cm}^{-3}\), while \(n_{1/2}\) for PTEG is roughly \(2 \times 10^{17} \text{ cm}^{-3}\). This suggests that the trap-density in PTEG-capped films is significantly lower than that of those using IPH and PCBM. We attribute this to the more numerous passivating moieties on the PTEG molecule, including ethylene glycol and tertiary amine groups, which could target traps at the MAPbI\(_3\) surface. Indeed, the extra passivating power of PTEG has been shown previously by Shao et al to be a factor in boosting the efficiency of MAPbI\(_3-x\)Cl\(_x\) cells to higher values than could be achieved with PCBM.\(^8\)

Encouraged by evidence of enhanced passivation from PTEG, we turned our focus to how such passivation impacts electron transfer. The raw change in optical density, \(\Delta OD_{\text{max}}\) obtained from TAS measurements for the different MAPbI\(_3\)|ETL combinations can be converted into the electron injection yield, via the Beer-Lambert law:

\[
\text{Yield} = \frac{n_{-}}{n_{0}} = \frac{\Delta OD_{\text{max}} \cdot N_{A}}{1000 \cdot \varepsilon_{-} \cdot n_{0}} \tag{5.1}
\]

where \(n_{-}\), \(n_{0}\), \(\varepsilon_{-}\) and \(N_{A}\) are the area density of fullerene anions in the ETL (\(\text{cm}^2\)), area density of photoexcited electrons in the MAPbI\(_3\) layer (\(\text{cm}^2\)), extinction coefficient of the fullerene anion (6000 \(\text{M}^{-1} \text{ cm}^{-1}\))\(^87\) and Avogadro’s constant respectively. We obtain \(\Delta OD_{\text{max}}\)
as the value of $\Delta OD$ at 1 µs in the raw transient absorption spectra and $n_0$ by assuming that every photon absorbed by the perovskite is converted to an electron/hole pair.

![Fig 5-18: Electron transfer yield (%) as a function of irradiance for MAPbI$_3$|ETL (ETL = PTEG, IPH, PCBM) films gathered via transient absorption spectroscopy (TAS; red) and photoluminescence spectroscopy (PL; blue). PL data was collected via steady-state photoluminescence spectroscopy where the electron transfer yield = $PL - PL_0/PL$, where $PL$ and $PL_0$ are the photoluminescence intensities of the pure MAPbI$_3$ and MAPbI$_3$|ETL films respectively. 1 Sun is indicated by the red line. The electron injection yield as measured by TAS is outlined in the right-hand panel of Fig 5-18 (red highlighting). In the high-irradiance limit, the performance of the ETLs is similar, as one would predict from their identical LUMO levels. However, as the intensity of excitation is decreased, we start to see significant distinctions between the different ETLs. Interestingly, PTEG outperforms the other fullerenes at 200 W cm$^{-2}$, while PCBM and IPH have almost identical responses as the intensity is lowered. Both observations can be explained in terms of the passivating moieties on the individual ETLs. While the structure of IPH and PCBM is different, they contain the same amount of C=O and C-O-C groups capable of binding to the MAPbI$_3$ surface. On the other hand, PTEG has a much stronger propensity to passivate on account of its extra electron-donating functionalities in the form of ethylene glycol and tertiary amine groups. The resultant interactions with the MAPbI$_3$ surface result in enhanced electron injection in a similar way to that observed with the HTLs investigated earlier in this chapter.

5.5. Implications for Device Design

Excitation power is of critical concern when linking pump-probe spectroscopy to device performance. As is clear from this study, the photophysics at the MAPbI$_3$|CTL interface is highly intensity dependant. This means that conclusions about devices drawn from TAS
where typical fluences are > 25 µJ cm\(^{-2}\) \((n_0 \sim 10^{18} \text{cm}^{-3}; \sim 100,000 \text{Suns})\) can often be wildly incorrect even for concentrator applications (< 500 Suns). Consequently, in Fig 5-18 we show the injection yield over 7 orders of magnitude from PL (blue highlighting) and TAS (red highlighting) studies indicating 1 Sun of irradiance at roughly 0.1 W cm\(^{-2}\).

1 Sun lies well within the trap-dominated recombination regime, which has some important implications. Firstly, although the ETLs appear to perform similarly in the high irradiance limit, PTEG clearly outperforms PCBM and IPH as the irradiance is lowered towards 1 sun. We have presented comprehensive evidence herein that passivating interactions are at the heart of such enhancements in charge transfer. This partly explains the greater efficiency of PTEG-based devices (15.7%) over those incorporating PCBM (11.7%).

By the same token, passivation-enhanced charge transfer could also explain the success of HTLs such as PTAA over others e.g P3HT. We have shown in this work (Fig 5-13b) that inclusion of PTAA rather than P3HT as an HTL in nip devices improved the PCE by an additional 7%, which we can break down into two contributions. Firstly, the \(J_{SC}\) is significantly enhanced (+30%), which we attribute to stronger interfacial coupling between MAPbI\(_3\) and PTAA that leads to greater hole transfer yields. Indeed, PSCs incorporating P3HT have recently surpassed 20% but not without extensive modification of the perovskite surface to enhance interfacial interactions. This was achieved by functionalising the perovskite with \(n\)-hexyl trimethyl ammonium bromide (HTAB), which simultaneously passivates the perovskite and improves the P3HT|perovskite contact via alkyl-alkyl Van der Waal interactions, enhancing charge transfer.

Secondly, the \(V_{OC}\) is significantly enhanced (+19%) when P3HT is replaced with PTAA. While some of this improvement will be down to better energetic alignment, we must also discuss the important role of interfacial recombination. We showed in this study (Fig 5-14) that the recombination rate at MAPbI\(_3\)|HTL (HTL = PTAA, PTPD, spiro-OMeTAD) interfaces was an order of magnitude slower than in the case of MAPbI\(_3\)|P3HT. This is in good agreement with Stolterfoht et al who found that the recombination current, \(J_{0,rr}\) at the MAPbI\(_3\) interface with P3HT was around an order of magnitude larger \((J_{0,rr} = 1 \times 10^{-17} \text{A m}^{-2})\) than for PTAA \((J_{0,rr} = 1.3 \times 10^{-18} \text{A m}^{-2})\), PTPD \((J_{0,rr} = 1.1 \times 10^{-18} \text{A m}^{-2})\) and spiro-OMeTAD \((4.6 \times 10^{-18} \text{A m}^{-2})\). But we added to this study by showing that HTL chemical structure, and the resulting passivating interactions with the MAPbI\(_3\) surface are key in determining the rate of interfacial recombination.

Functional Characterisation of Perovskite Films for Solar Cell Applications We note that in addition to direct passivation, other effects such as strain exerted by - and self-assembly of - CTLs on
the MAPbI₃ layer also likely play an important role in determining the extent of interfacial recombination. In particular, it is possible that as-deposited P3HT incorporates additional trap-states at the MAPbI₃ surface either due to disorder in the P3HT layer, or strain exerted on the MAPbI₃ surface by P3HT agglomerates. The improved performance of P3HT-based devices on 3D/2D perovskite as reported here and elsewhere may then be due to better organisation of the P3HT on MAPbI₃.

All of this points to the critical nature of the perovskite| CTL interaction in determining efficiency of interfacial charge transfer processes and ultimately of devices. Careful design of next-generation CTLs with passivating functionalities capable of binding to specific defect sites at the perovskite surface could improve interfacial charge-transfer, supress non-radiative recombination and enhance stability.

Additionally, the impact of this study is not limited to PV applications: such CTLs could also boost the efficiency of emerging perovskite light-emitting diodes (PeLEDs). Passivation has been an important part of the drive forward in external quantum efficiency (EQE) in blue-(10%) and NIR- (21.4%) emitting PeLEDs. However, there is significant room for improvement with optimistic estimates for the EQE limit for PeLEDs at around 75%. We have shown here that careful selection of charge transport layers can simultaneously enhance charge extraction and mitigate recombination in PSCs. It therefore follows that careful design of charge injection layers for PeLEDs could simultaneously passivate defects and enhance injection, leading to a bilateral improvement in the EQE.

5.6. Conclusions & Outlook

In summary, we showed that passivation is an important part of the charge transfer mechanism at the interfaces of PSCs. PL spectroscopy confirmed strong passivation in the case of PTAA and PTPD but little effect from P3HT. By conducting PL studies on TAA and T, we found the most likely mechanism was via Lewis base passivation from the tertiary amine groups on PTAA and PTPD with little effect from thiophene on P3HT. XPS further confirmed this as the binding energy of the N 1s orbital in PTPD and PTAA was significantly increased upon approach to the MAPbI₃|HTL interface, but no such effect was found with S 2p in P3HT.

Crucially, TAS measurements showed that charge separation at the MAPbI₃|HTL interface was much enhanced in those HTLs that underwent strong binding interactions. This partially explains why PTAA outperforms P3HT as an HTL in PSCs. We also showed that passivation-mediated electron transfer occurs at the perovskite|ETL interface in the pin architecture. Specifically, PTEG promoted larger electron injection yields than PCBM and
IPH on account of its numerous passivating moieties. Finally, we underlined the importance of excitation power in relating pump-probe techniques – which can often be as high as 100,000 Suns – to operational conditions of 1 sun. The results reported herein reveal a new aspect to the charge separation mechanism in PSCs, which should be considered in the design of next-generation CTLs for perovskite optoelectronics.
5. 7. References


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Chapter 6

Concluding Remarks & Future Work
6.1. Concluding Remarks

The main aim of this thesis has been to understand the key factors that drive interfacial charge transfer and recombination in perovskite solar cells, with the view to developing design rules to enhance their efficiency and stability. To this end, we focused on how energy offset, passivation and chemical interactions at the perovskite|CTL interface impact the yield and kinetics of charge injection and recombination. We did this using a combination of optical spectroscopic techniques, such as transient absorption (TAS) & time-correlated single photon counting (TCSPC), and device studies.

Chapter 3 focused on the relationship between interfacial energy offset, $\Delta E$ and hole injection at perovskite|HTL interfaces. Most notably, we found that a remarkably small interfacial energy offset of $\Delta E = 0.17 \pm 0.1$ eV is required to drive high hole injection yields (77%) with sub-nanosecond kinetics. We also showed that the kinetics of recombination of the injected hole population are slow for $\Delta E > 0$, typically on the order of milliseconds i.e. around $10^5$ times slower than the initial injection process. This work culminated in our first design rule:

**Design Rule 1:** Hole transport layers for perovskite solar cells should be designed such that their highest occupied molecular orbital (HOMO) satisfies $0 < \Delta E < 0.2$ eV, to maximise $V_{OC}$.

Chapter 4 concentrated on the passivation of MAPbI$_3$ with iodide salts such as phenethylammonium iodide (PhEtNH$_3$I) and methylammonium iodide (MAI). We found that an optimum PhEtNH$_3$I concentration of 10 mM yielded an efficiency of 16.73% compared to just 12.95% in the unpassivated control. Even more remarkably, the stability improved from a few hours in control samples to over 20 days in passivated samples. Crucially, we elucidated the full mechanism behind these performance improvements, namely: (i) I$^-$ anions target $V_I$ sites and suppress $O_2^-$ production, (ii) RNH$_3^+$ cations target $V_{MA}$ sites, forming a (PhEtNH$_3$I)$_2MA_1nPb_{n}I_{3n+1}$ layer at the top surface of the MAPbI$_3$ film. Proper control of this 2D layer is critical to device performance with $n = 1$ yielding significant improvements in efficiency but $n > 1$ degrading efficiency. This work concluded in our second and third design rules:

**Design Rule 2:** MAPbI$_3$ should be treated with I$^-$ ions to fill $V_I$ sites, suppress $O_2^-$ production and enhance stability.
Design Rule 3: Deposition of a phase-pure (PhEtNH$_3$I)$_2$PbI$_4$ layer at the perovskite|hole transport layer interface enhances efficiency.

Finally, in chapter 5 we bought the themes of chapters 3 and 4 together by investigating inherent passivation from the CTL layers. Crucially, we found strong correlation between the extent of binding of a given CTL to the MAPbI$_3$ surface and charge transfer across a number of p-i-n and n-i-p systems. Moreover, in systems which have an inherently large density of interfacial traps e.g. MAPbI$_3$|P3HT, interactions can be enhanced via interfacial modification with a 2D layer. This led to the development of our fourth and final design rule:

**Design Rule 4:** Charge transport layers should be designed with functional groups (e.g. triarylamine, methoxy groups) capable of binding to the perovskite surface.

6.2. Future Work

Despite the main objectives of this thesis being achieved, different questions arose from the work.

In chapter 3, we established that the interfacial energy offset should satisfy $0 < \Delta E < 0.2$ eV to obtain the optimum combination of efficient hole transfer and minimum overpotential. This $\Delta E$ space should be explored further by screening a number of HTLs that satisfy this condition. Additionally, the relationship between hole injection yield and interfacial energy offset, $\Delta E$ was found to be in close agreement for CH$_3$NH$_3$PbI$_3$- and Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$-based films. However, with the advent of 3D-2D Sn-based perovskites at hand and the different conditions in that system - e.g. self p-doping – a detailed study of hole injection in (PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$|HTL systems would be interesting. This could enhance the open-circuit voltage (record: 0.88 V; Noel et al, *Energy Environ. Sci.*, 2014,7, 3061-3068) on two fronts: (i) finding the minimum $\Delta E$ that drives efficient hole transfer and (ii) potentially mitigating some of the self p-doping.

In chapter 4, we found strong evidence that the efficiency enhancements associated with PhEtNH$_3$I passivation are predicated by the formation of (PEA)$_2$PbI$_4$ rather than its higher order (PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$ ($n > 1$) counterparts. In order to properly establish the reason for this, accurate measurement of the energetics (e.g. via ultraviolet photoelectron spectroscopy) at the MAPbI$_3$|(PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$ interface would be required. Moreover, our fs-TAS measurements suggests that hole injection to the (PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$ is slower than 6 ns but the presence of a (PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$ signal in µs-TAS measurements suggests it is faster than 1 µs. Therefore, ns-TAS measurements should reveal for certain the (slow) rate of hole transfer at the MAPbI$_3$|(PEA)$_2$MA$_{1-x}$Pb$_n$I$_{3n+1}$ interface. Moreover, we proposed
that PEA\(^+\) mainly targets methylammonium vacancies \((V_{MA})\) sites given that interaction between the PbI\(_6\) octahedra and PEA\(^+\) must precede formation of \((PEA)_2MA_1-xPb_{n}I_{3n+1}\). However, simulations should be carried out in order to confirm that \(V_{MA}\) is the preferred site for PEA\(^+\) passivation. Finally, while superoxide measurements suggest that MAPbI\(_3\) \(V_I\) sites are targeted by I\(^-\) in PhEtNH\(_3\)I, control experiments with PhEtNH\(_3\)Br could provide further supporting evidence. Here, we would expect a similar 2D layer to be formed by PhEtNH\(_3\)+, but no treatment of \(V_I\) sites. This would help decouple the two elements of the bilateral passivation mechanism and elucidate the extent to which the \((\text{PhEtNH}_3)_2(\text{MA})_1-xPb_nI_{3n+1}\) layer enhances stability.

In chapter 5, we correlated passivation with enhanced interfacial charge injection yields. However, the future direction of this research line will rely on determining the exact nature of the passivating interactions. For example, we put forward that simple Lewis base passivation is likely to occur between e.g. triarylamine units and iodide vacancies \((V_I)\). However, simulations should be carried out to confirm this. For example, adsorption energies of polymer monomer units at perovskite defect and lattice sites could be carried out to determine the exact nature of the interactions. This information would then feed into the design of next-generation passivating charge transport layers. Additionally, it appears that passivation effects are much stronger when the charge transport layer is at the top interface, more work should be done to elucidate the role that architecture plays.