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CHEMICAL AND MORPHOLOGICAL STABILITY OF
PEROVSKITE AND ORGANIC SOLAR CELLS

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Abstract

The stability of perovskite and organic solar cells remains a major challenge to realise their potential. To overcome the numerous degradation mechanisms, it is important to understand the underlying causes. This thesis will present device and material characterisation on two areas: firstly, elucidating perovskite environmental stability and, secondly, the effects of PCBM dimerisation in organic solar cells.

The first results chapter investigates the environmental stability of methylammonium lead iodide. In this thesis, degradation under light and oxygen is found to be more detrimental than humidity. Injected charge (not photogenerated) also induce the degradation with oxygen; thus, all optoelectronic applications are vulnerable. Efficient electron extraction minimises superoxide generation and subsequent degradation. These results determine the dominant environmental instability and present pathways to curtail it.

The second results chapter explores halide tuning of methylammonium lead iodide-bromide (MAPI-Br) to optimise environmental stability. The stability of thin films and solar cells for all halide ratios is investigated under light and oxygen stress and humid nitrogen stress. Partial bromide substitution does not improve stability. However, for MAPBr, the crystal structure and optical properties are unchanged after 120 h of light and oxygen stress. It is concluded that iodide limits mixed halide stability and MAPBr has excellent environmental stability for high voltage solar cell applications.

The third results chapter investigates the morphological stability of polystyrene:PCBM blends under simultaneous light and thermal stress. Neutron reflectivity and atomic force microscopy are used to probe the vertical stratification and topography, respectively. It is found that PCBM dimerisation inhibits both surface relaxation and PCBM enrichment to the bottom PEDOT:PSS interface. Modelling the diffusion shows PCBM dimers to be effectively immobile over the timescales investigated. These results present a framework to understand polymer:fullerene morphological stability under operating conditions.

The final results chapter develops a complete model to describe PCBM dimerisation. Predicting the photo-dimerisation and thermal decomposition within any polymer matrix, under any light and temperature profile. During operating conditions, the PCBM dimer will dominate the reaction equilibrium; therefore, clarifying the role of dimers is critical. Evidence of distinct dimer populations is observed with differing chemical and electronic properties. DFT simulations conclude this is due to PCBM dimer conformations. These results can rationalise the double-edged effects of PCBM dimerisation previously reported.

Declaration

I hereby declare that the contents of this thesis are of my own work, except where specific reference is made to contribution of work by others. This thesis has not been submitted in whole or in part for consideration for any other degree or qualification at this, or any other university.

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Sebastian Andrew Victor Pont
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Nomenclature

Roman Symbols

D	Diffusion coefficient
E_a	Activation energy
E_e	Irradiance
F	PCBM flux
H_e	Radiant exposure
I_F	Superoxide probe fluorescence
J_{dark}	Current density in the dark
J_{light}	Current density in the light
J_{max}	Current density at MPP
J_{SC}	Current density at short circuit
k	Rate constant
PCDTBT	Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]
P_{max}	Power at MPP
Q	Momentum transfer vector
q_m	Peak wavenumber of radially averaged AFM Fourier transform
Rq	Root mean square roughness
T	Temperature
t	Time
T_g	Glass transition temperature

V_{max}	Voltage at MPP
V_{OC}	Voltage at open circuit

Greek Symbols

α	Correction factor between MAP(I _{1-x} Br _x) ₃ absorbance and tungsten-halogen lamp
β	Attractive potential depth
γ	Attractive potential range
ϕ	Mass fraction

Acronyms / Abbreviations

AFM	Atomic force microscopy
c-TiO ₂	Compact titanium dioxide blocking layer
FA	Formamidinium, CH(NH ₂) ₂ ⁺
FF	Fill factor
FFT	Fast Fourier transform
FTO	Fluorine-doped tin oxide glass
HTM	Hole transporting material
JV	Current-voltage measurement
LiTFSI	Bis(trifluoromethane)sulfonimide lithium salt
m-Al ₂ O ₃	Mesoporous aluminium oxide layer
MAPBr	Methylammonium lead bromide, CH ₃ NH ₃ PbBr ₃
MAPI	Methylammonium lead iodide, CH ₃ NH ₃ PbI ₃
MPP	Maximum power point
m-TiO ₂	Mesoporous titanium dioxide layer
NMR	Nuclear magnetic resonance
NR	Neutron reflectivity
OSC	Organic solar cell
PCBM	PhenylC61-butyrac acid methyl ester

PCE	Power conversion efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PSC	Perovskite solar cell
PS	Polystyrene
PV	Photovoltaics
RGB	Red-green-blue CCD output
SLD	Scattering length density
Spiro-OMeTAD	2,20,7,70-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,90-spirobiuorene
TAS	Transient absorption spectroscopy
tBP	4-tert-butylpyridine
XRD	X-ray diffraction

Chapter 1

Introduction

To minimise the adverse effects of climate change, a transition from fossil fuels to sustainable energy is urgently required. Converting sunlight into electricity is abundant in supply and potentially low cost using photovoltaic technologies. It is one of the most promising options to meet global demand with feasible economics. This chapter will introduce the fundamentals and stability of two emerging technologies: perovskite and organic solar cells. The inexpensive raw materials, rapid processability, and favourable optoelectronic properties of these technologies provide great potential as a low-cost solar energy source. Over the last 10 to 20 years much work has been done to improve the efficiency of these technologies and they are increasingly competitive with established silicon solar cells. However, to enable commercial viability, a solar cell must have sufficient stability alongside the low cost and high efficiency. During the lifetime of a solar cell, it will be exposed to a number of stress factors such as light, heat, oxygen, and humidity. Currently, the stability of perovskite and organic solar cells to these factors are a long way from the required metrics for 25-year lifetimes. Herein, the understanding, measuring, and improving of perovskite and organic solar cell stability will be detailed.

1.1 Motivation

Over the last two centuries, there has been a boom in global energy consumption.^{1,2} This is due to a soaring global population and the requirements from a dramatic improvement in living standards. For millennia, energy has been generated from sustainable sources such as wood or watermills. As illustrated in Figure 1.1, there has been an intense expansion in the consumption of fossil fuels since the 1850's. The advantage of this source has been its low cost and ease of access, resulting in its adoption by all countries during their development to a modern, energy intense society. Evidently, over the last 150 years, fossil fuels have played a major role in improving the health and living standards across the world.

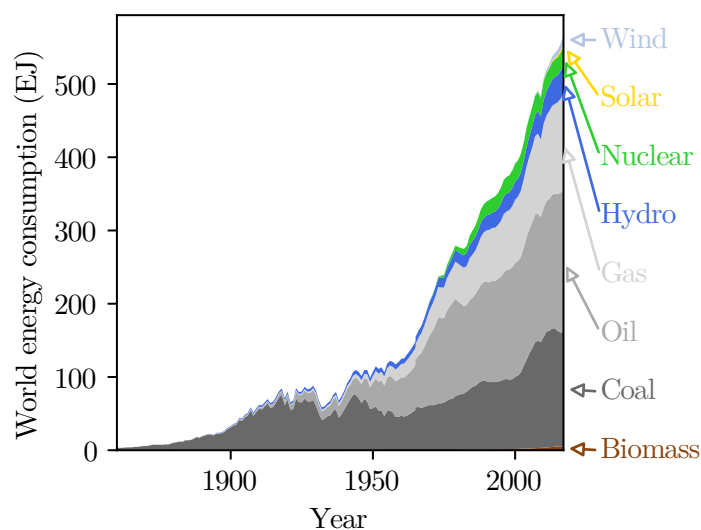


Figure 1.1 World primary energy consumption by fuel type, 1850–2017. A rapid increase in population and living standards has surged fossil fuel consumption. Data pre-1965 from A. Grubler, “Technology and Global Change: Data Appendix,” (1998) and post-1966 from BP, Statistical Review of World Energy (annual).^{1,2}

The advantages of fossil fuels have enabled modernisation in society but there are also major drawbacks. Fossil fuels are generated through a process that takes millions of years but will be mostly consumed in significantly less time, making it inherently unsustainable. As a result, there is a finite supply available which may be consumed in the next hundred years, depending on the path society takes. The second and much more urgent disadvantage is the side effect of releasing greenhouse gases when burning fossil fuels. There is a scientific consensus that the release of carbon dioxide into the atmosphere is resulting in warming of the average global temperature. There is a stark correlation in Figure 1.2 between the dramatic increase in temperature and carbon dioxide levels in recent times. For perspective, over the last 400,000 years the carbon dioxide level has fluctuated between 200 ppm and 300 ppm, whereas over the last 200 years it has increased from below 300 ppm to over 400 ppm.³ Additionally, to the average global temperature rises, there will likely be other drastic climate changes; increased

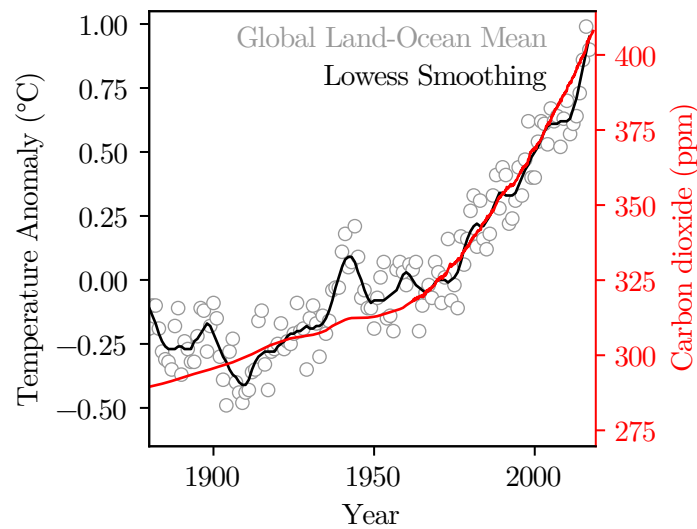


Figure 1.2 Change in global surface temperature (grey circle), and LOWESS regression (black line), with a strong correlation to atmospheric carbon dioxide levels (red). Temperatures relative to 1951-1980 average.³

occurrences of extreme weather conditions, flooding, drought, and storms, are some examples. Thus, it is paramount that sustainable and clean energy sources are quickly developed.

Alternative energy sources are currently available that are both sustainable and do not have major harmful side-effects such as wind, solar, biomass, geothermal and hydropower. In Figure 1.1 it is apparent these are starting to be utilised but are still a very small fraction. Until recently most investment has been towards fossil fuels and as such other sources of energy have been underdeveloped and therefore overpriced. With an international understanding of the requirement for clean energy, such as the Paris Climate Agreement, these technologies are getting increased investment and are starting to become commercially competitive. Two of the most promising technologies are wind and solar.

Solar energy is an abundant renewable energy source with enough supply to meet global demand comfortably. Unlike large fossil fuel power plants, solar energy can be generated at the point of use and does not emit any harmful side effects when generating power. The inherent intermittency of the Sun over diurnal and seasonal variations is a limitation. However, storage technologies, such as pumped hydro or batteries, are being developed to adapt to a changing energy generation landscape. There are two main technologies that can harness solar energy: solar thermal and photovoltaics (PV). Solar thermal converts the radiative heat energy into useful energy that can be used to heat homes or drive steam turbines; whilst photovoltaics, also known as solar cells, converts light directly into electricity. This thesis will report on exciting new technologies of the latter.

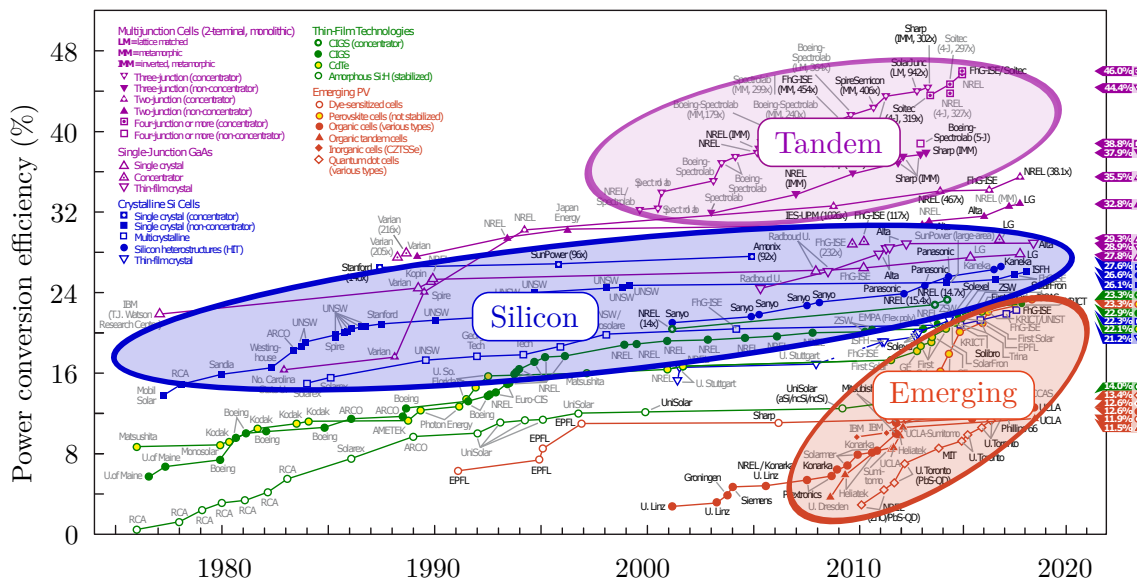


Figure 1.3 Record efficiency for various photovoltaic technologies. Three trends are highlighted: the steady development of silicon since 1970 (blue), the high-cost high-efficiency multi-junction devices (purple), and the rapid development of emerging technologies (orange).⁴

1.2 Photovoltaics: technologies and principles

1.2.1 Comparing photovoltaic technologies

Photovoltaics is a branch of technology whereby electromagnetic radiation is converted into electrical potential energy utilising the photoelectric effect. Many materials have been found to exhibit promising photovoltaic properties and record efficiencies are compared in Figure 1.3.⁴ Annotations added to the plot highlight three technological trends: firstly, high-efficiency tandem and gallium arsenide (GaAs) solar cells (purple), secondly, silicon-based technologies (blue), and lastly, emerging materials (orange). There have been numerous additional points (records broken) over the previous eight years, highlighting the huge growth and potential in photovoltaic technologies as a renewable energy source.

Tandem solar cells and GaAs technologies were developed for niche markets such as space applications and concentrated solar cells. These applications require specifications such as lightweight or high efficiency per unit area and, as such, have a relatively high cost per watt. Generally, these technologies are not well suited for large-scale power generation.

Silicon was the first major photovoltaic technology and was developed at Bell Laboratories in the 1960's. It has progressed as a photovoltaic technology alongside the rapid expansion of the silicon-based electronics industry. Since the discovery of silicon PV, several other efficient materials have been discovered, such as cadmium telluride (CdTe) and copper-zinc-tin-sulphide (CZTS). Currently, silicon dominates the global market share; cadmium telluride has a smaller share. Today the cost of silicon has become incredibly inexpensive compared to even a decade ago. It has gone from over 70 \$/Wp in the 1970's, to 4 \$/Wp in 2008 to <0.3 \$/Wp today. This is

predominately due to a huge increase in production, mostly in China, resulting in savings from economies of scale, which have resulted in a 20 % drop in price for each doubling in capacity, as described by Swanson's law. The dramatic price drop of silicon over the last ten years has made direct price competition of other technologies increasingly challenging. However, there are a number of other limitations of silicon photovoltaics. Firstly, silicon processing requires high-energy to produce single crystal or multi-crystalline wafers that are manufactured into solar modules. Secondly, silicon has a fixed bandgap at 1.1 eV which constricts the optoelectronic properties of a solar cell, (explained later), and effects the colour of the module. For many customers, the blue shine of standard PV modules is visually unappealing and a barrier to the adoption of silicon. Lastly, due to the low absorption coefficient, silicon solar cells must be thick to enable sufficient absorption of solar irradiance. As such the modules are heavy and brittle, complicating the fabrication, transportation and installation of the panels. Other technologies are able to overcome these drawbacks.

The final category highlighted in Figure 1.3 is the emerging technologies; these include organic solar cells (OSC), perovskites solar cells (PSC), quantum dots, and dye-sensitised solar cells. These technologies have a range of properties that can complement and compete with established silicon technologies. Efficiencies are increasing at rates greater than silicon and perovskites are likely to equal and surpass silicon in the coming years. Whilst silicon has an energy and cost-intensive fabrication process, the emerging technologies can be made from a continuous solution-based manufacturing process. Solution processing has the potential for high-throughput and low-cost printing, akin to the newspaper production process. Conversely to silicon, many emerging technologies have tunability of the bandgap. This allows for optimising the aesthetic appearance and enables the possibility of semi-transparent photovoltaic-windows where some visible light passes through and UV or infrared light is converted into electricity.⁵ Building-integrated photovoltaics (BIPV) will enable the implementation of solar cells to be cost-effective and visually attractive. For example, a solar cell that only absorbs a fraction of the light can be used as semi-transparent windows or for building facades. Silicon modules are brittle and heavy which make it hard to develop BIPV systems with this technology. Finally, emerging photovoltaic technologies can be processed into flexible modules whereas silicon cannot. This expands the market application of solar cells to wearable PV or portable solar power, for example. This thesis will report on research of two emerging technologies; organic and perovskite solar cells.

1.2.2 The photovoltaic mechanism

Photovoltaics is the principle of converting electromagnetic radiation into electrical energy. This occurs in three main steps. Firstly, the active material absorbs light to create a photoexcited state. Secondly, the photoexcited state is separated into free charge carriers. Finally, the charge carriers are extracted from the material to drive electrical work in an external circuit.

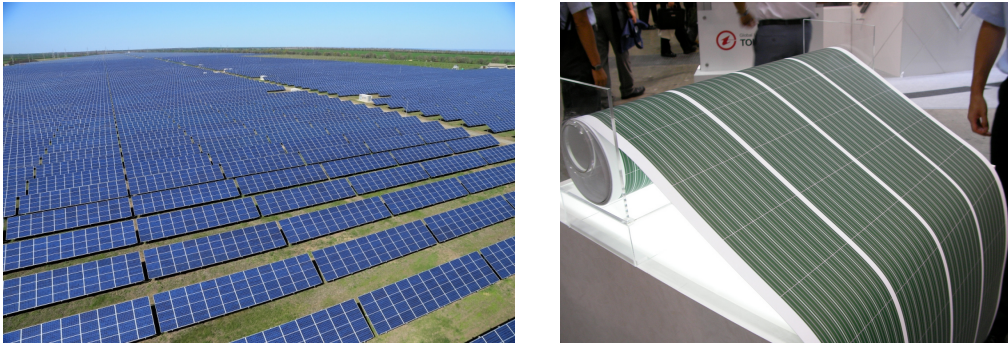


Figure 1.4 (left) Large-scale energy generation with 185,952 multi-crystalline silicon solar modules at the Starokazache Solar Station, Ukraine,⁶ and (right) a flexible light-weight organic photovoltaic module at PV Japan.⁷

When a material absorbs a photon with energy greater than its bandgap an electron is excited from the valence band (E_{VB}) to a free state in the conduction band (E_{CB}). This process results in an excited electron and an empty state, known as a hole, as shown in Figure 1.5(a). For photovoltaic applications, the energy between the valence and conduction bands, known as the bandgap (E_g), is within the range of energy of the Sun's solar spectrum.

For inorganic semiconductors such as silicon, the relative permittivity is such that it screens the interaction between the electron and hole. Thus, after photoexcitation, free charges are generated within the active layer. To extract the charge, the electron and hole must be separated to selective conducting contacts in the device. This process requires an energetic driving force. In silicon solar cells it is done with a junction between oppositely doped layers known as a p - n junction. The difference in Fermi level between the n -doped and p -doped layers results in band bending and an electric field being generated within the material, as shown in Figure 1.5(a). The charges are then collected at contacts with the surplus electrical potential energy provided for useful work.

The three processes of light absorbance, charge generation, and charge extraction should be maximised to ensure optimal power conversion efficiency of light into electricity. The yield of absorbed photons is a combination of the extinction coefficient and the thickness of the active layer according to the Beer-Lambert law. After photoexcitation, an electron may recombine with a hole reducing the yield of charges extracted from a device. This recombination can occur through several mechanisms, such as exciton recombination, bi-molecular charge recombination, trap-assisted recombination, surface recombination, or Auger recombination. These processes may be either radiative or non-radiative. If the recombination is radiative the potential energy of the excited electron is emitted as electromagnetic radiation. However, if it is non-radiative the energy is generally converted to phonons and lost as heat. Recombination is generally a loss mechanism—especially if the decay pathway is non-radiative. Radiative recombination may not result in a loss if the emitted photon can be reabsorbed. However, radiative recombination inhibits the splitting of the quasi-Fermi level to that of the bandgap. This means the maximum obtainable voltage can never reach the bandgap of the material. The voltage

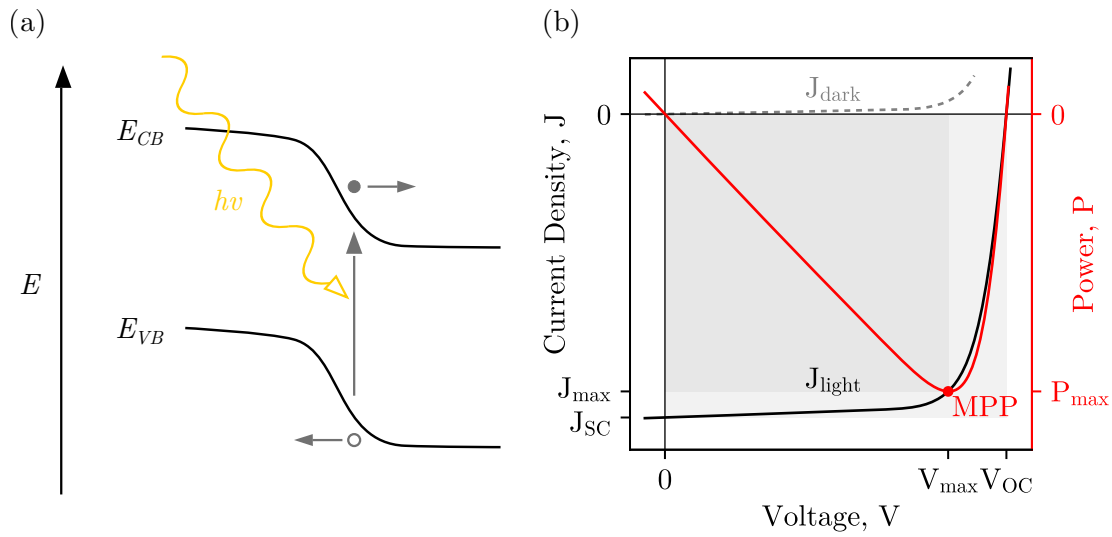


Figure 1.5 (a) Principles of photovoltaics where light ($h\nu$) excitation generates an electron and hole, which are then extracted with electrical potential energy. (b) A current-voltage scan of a solar cell in the dark (J_{dark}) and light (J_{light}). The corresponding power output under light (red).

loss due to radiative recombination is an unavoidable loss mechanism in photovoltaics. Finally, charges require an energetic driving force to be extracted from a device. The energetic driving force must be sufficient to extract charges quickly before recombination occurs but minimised to reduce the loss of electric potential energy.

The characteristics of a solar cell are determined from a current-voltage measurement of the device. Figure 1.5(b) presents an example of the current output of a solar cell as its voltage is varied from negative to positive voltages; several important parameters of a solar cell are highlighted. In the dark, a solar cell acts as a diode (J_{dark}) but upon illumination photoexcited charges result in a photocurrent (J_{light}). Key parameters are the short-circuit current density J_{SC} , the open-circuit voltage V_{OC} , the maximum power point MPP, and the fill factor FF. Under short circuit conditions, there is no voltage applied across the device. Photogenerated charges are extracted by selective contacts resulting in current flowing through the device. Under open circuit conditions, there is no current flowing through the device and charge accumulates in the active material resulting in the splitting of the Fermi level into the quasi-Fermi level. The power output of a device is a product of the photocurrent, J , and the voltage, V , as shown on the right axis of Figure 1.5(b). The bias with the greatest power output, (P_{max}), is known as the maximum power point (MPP) with current J_{max} and voltage V_{max} . The power conversion efficiency (PCE) of a device is the ratio of the power in against the power out, P_{max}/P_{in} . The fill factor (FF) of a device is given by $(J_{max} \times V_{max})/(J_{SC} \times V_{OC})$ and provides a metric related to the quality of the electronic properties of the solar cell. For the greatest power conversion efficiency, the parameters discussed here must be maximised.

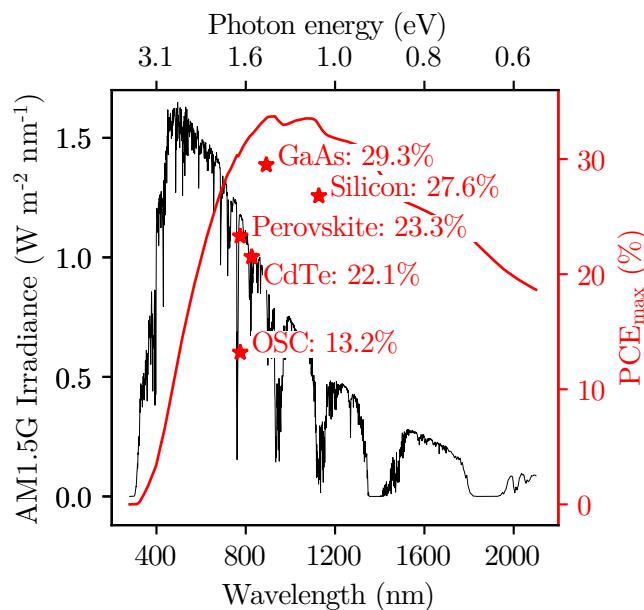


Figure 1.6 Spectral irradiance of the AM1.5G solar spectrum (black, right) and the corresponding maximum theoretical efficiency as calculated from the Shockley–Queisser limit versus absorber bandgap in eV (top) or nm (bottom).

The characteristics of a solar cell are strongly dependent on the bandgap of the photoactive material compared to the Sun's AM1.5G solar spectrum (Figure 1.6). The AM1.5G spectrum is defined as the spectrum of solar irradiance at an angle of 41° above the horizon such it passes through 1.5 air masses—AM1.5—and it includes the surrounding hemispherical sky and ground reflections—G. Under ideal conditions, the short-circuit current is proportional to the flux of photons with energy greater than the bandgap and the open-circuit voltage is proportional to the magnitude of the bandgap and the light intensity. Therefore, increasing the bandgap increases the voltage but decreases the current. The Shockley–Queisser limit for a single junction device presented in Figure 1.6 is calculated from optimising these competing factors. The resulting maximum gives the ideal bandgap for a photovoltaic material absorbing the solar spectrum AM1.5G as ≈ 1.5 eV.⁸ The record efficiency of a few select technologies are compared in Figure 1.6. Silicon has a fixed bandgap of 1.1 eV with a maximum efficiency of $\approx 32\%$ exposed to the AM1.5G solar spectrum.

The fixed bandgap of silicon photovoltaics is well suited to the solar spectrum, but it can be limiting for certain applications; specifically, for indoor applications and for tandem-junction solar cells. The spectrum of incident light greatly affects the ideal bandgap and maximum theoretical efficiency. For example, a white LED light at 800 W cm^{-2} with emission between 400 nm to 800 nm has a maximum theoretical efficiency of 47% at a bandgap of 1.75 eV, as calculated from the Shockley–Queisser analysis. Under this LED light, silicon with a bandgap of 1.1 eV has a maximum theoretical efficiency of only 27%. Perovskite and organic solar cells have tuneable bandgaps and it is possible to match the bandgap to the required solar spectrum.

Therefore, under white LED light a perovskite or organic solar cell with a bandgap of 1.75 eV has a maximum efficiency nearly double that of silicon (47 % vs 27 %). Solar cells can be incorporated into devices for the ‘internet of things’ for indoor applications where the spectrum of light differs greatly compared to AM1.5G. Here, the bandgap tunability of perovskite and organic photovoltaics is greatly advantageous.

A system that can overcome the Shockley-Queisser limit of a single-junction solar cell is a tandem-junction solar cell. In a tandem solar cell, two light absorbing materials are stacked on top of each other to absorb complementary parts of the solar spectrum. The lower energy photons will pass through the top cell to be absorbed by the bottom cell. With this architecture the theoretical maximum efficiency under AM1.5G increases to 42 %. As with the single-junction, the control of the bandgap of the materials in a tandem-junction is critical to reaching this maximum efficiency. The tunability of the bandgap in perovskite and organic materials can enable this optimisation. The tandem solar cell provides an opportunity for these technologies to compete on a \$/W basis with a single-junction silicon solar cell.

1.2.3 Organic solar cell principles

Although the photovoltaic behaviour of organic materials was first reported in the 1960's,^{9,10} the first solar cell utilising a bi-layer architecture was presented in 1983 by Tang et al.¹¹ The bi-layer structure consists of a light absorbing organic material (the donor) deposited on a second organic layer (the acceptor) which assists charge separation and extraction. The mechanism of an organic solar cell can be split into three stages as depicted in Figure 1.7. Firstly, an electron in the highest occupied molecular orbital (HOMO) of the acceptor material absorbs the energy from a photon (stage *i*). The electron is excited into the lowest unoccupied molecular orbital (LUMO) leaving a hole in the HOMO. Generally, organic materials have low dielectric constants such that the electrostatic Coulomb force between the electron and hole result in a bound state known as an exciton. Next, the exciton is separated into free charge carriers at the interface of the donor and acceptor (stage *ii*). Finally, the free charges are extracted to selective contacts in the device often through charge transport layers to assist (stage *iii*).

Exciton lifetime and diffusivity generally give a diffusion length of 4 nm to 20 nm before it will recombine.^{12,13} In a bi-layer architecture excitons are generally formed too far from a donor:acceptor interface yielding a low charge generation yield. The limitations of the bi-layer architecture were overcome by introducing a mixed donor and acceptor layer, as shown in Figure 1.7(b).^{14,15} The system is created with spontaneous phase separation forming domains of donor and acceptor materials, known as a bulk heterojunction (BHJ). An intricate balance of mixing is required for optimal performance: a well-mixed system ensures a high exciton separation yield however a well-separated system with percolation pathways in the donor and acceptor materials for charge extraction ensures a high charge extraction yield. The ideal configuration is system dependent and still a topic of debate in the literature,^{16,17} but it is clear this optimal structure must be stable.

The most commonly used molecular system for organic solar cells consists of a polymer donor and a small molecule acceptor.^{18,19} Frequently, fullerene derivatives such as PCBM are used for the small molecule accepting layer due to its good solubilising properties and a deep LUMO level, which enables charge transfer from the polymer. The absorbance of PCBM is very weak above 400 nm and therefore does not contribute strongly to the photocurrent of the device. New non-fullerene acceptors (NFA) are being developed to overcome this, and other, limitations.^{20–22} However, fullerene-based organic solar cells are continuing to increase in efficiency and are still an active area of interest. The current highest efficiency tandem OSC at 17.3 % contains both NFAs and fullerenes.²³ There is a large range of polymers used for example poly(3-hexylthiophene) (P3HT) or more recently PffBT4T-C9C13 (PCE12). The stability of these systems remains a key challenge to realise the potential of OSCs.

As discussed previously, the morphology of the donor:acceptor in the bulk heterojunction is of critical importance for the device efficiency.¹⁷ Therefore, sufficient donor-acceptor miscibility, percolating charge transport networks, grain size and purity, crystallinity, and vertical stratification are important factors. The driving forces to determine this nanostructure involve multiple thermodynamic interactions within the solvent-polymer-fullerene system.^{16,24} Thus predicting the formation, and subsequent stability, of the bulk heterojunction morphology is complex. Solution processing of the donor:acceptor thin film requires the spontaneous organisation energy to form the microstructure. This is a rapid processing technique resulting in the polymer and fullerene *frozen* in mixed phases generally out of thermodynamic equilibrium. Therefore, the system is intrinsically unstable and morphological changes, such as crystallisation, demixing, and coarsening, of the donor/acceptor blend may be energetically favourable.

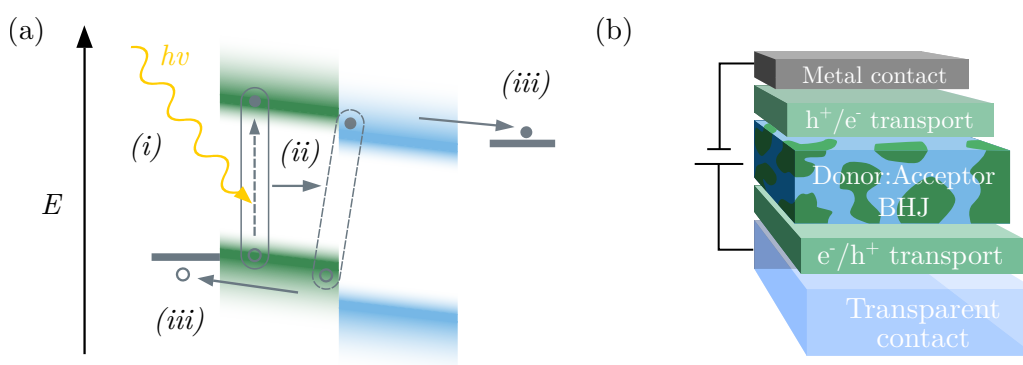


Figure 1.7 (a) A band diagram of a donor:acceptor architecture organic solar cell. The schematic shows the three processes in energy conversion from light to electricity in an OSC: (i) light absorption, (ii) charge generation, and (iii) charge extraction. (b) Organic solar cell device structure with a donor and acceptor bulk heterojunction, charge extraction layers and conducting contacts.

1.2.4 Perovskite solar cell principles

The ABX_3 perovskite crystal structure shown in Figure 1.8(a) was first reported for use in photovoltaic applications in 2009 within a dye-sensitised solar cell architecture.^{25,26} Methylammonium lead iodide (MAPI) was the first combination of ions that worked well as a photoactive layer. However, this material rapidly degraded in the presence of the liquid electrolyte (used as a hole transporting layer in the dye-sensitised solar cell architecture) resulting in the device efficiency dropping within minutes. When the liquid electrolyte was replaced with a solid-state hole transporting material, the stability was greatly improved with an unencapsulated shelf life of over 500 h reported in 2012.^{27,28} This material has been discovered to have remarkable optoelectronic properties; these include high absorbance, low exciton binding energy (< 30 meV), high charge carrier mobilities and long diffusion lengths.²⁹ Even when processing the material from facile, uncontrolled solution deposition methods high-efficiency solar cells can be fabricated.^{30,31} This has enabled the unprecedented increase in efficiency from $< 3\%$ in 2009 to over 23% at the time of writing in 2018.^{4,26}

State-of-the-art perovskite devices generally contain a perovskite layer 300 nm to 600 nm sandwiched between charge extraction layers and selective contacts as shown in Figure 1.8(b). Additional layers are often included to improve the extraction efficiency and minimise recombination losses. In perovskite solar cells, photoexcitation results in the free charge carriers in the perovskite layer which then diffuse to the electron and hole transport layers.²⁹

The perovskite crystal structure can accommodate various ions into the ABX_3 structure with partial or full substitution enabling tunability of properties. The relative size of ions can be used as an indicator for the stability and the most likely crystal structure by calculating the Goldschmidt tolerance factor³²

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.1)$$

where r_A , r_B , and r_X are the radii of the A-cation, B-cation, and X-anion, respectively. For use in photovoltaic applications, the commonly used A-cations with appropriate dimensions are

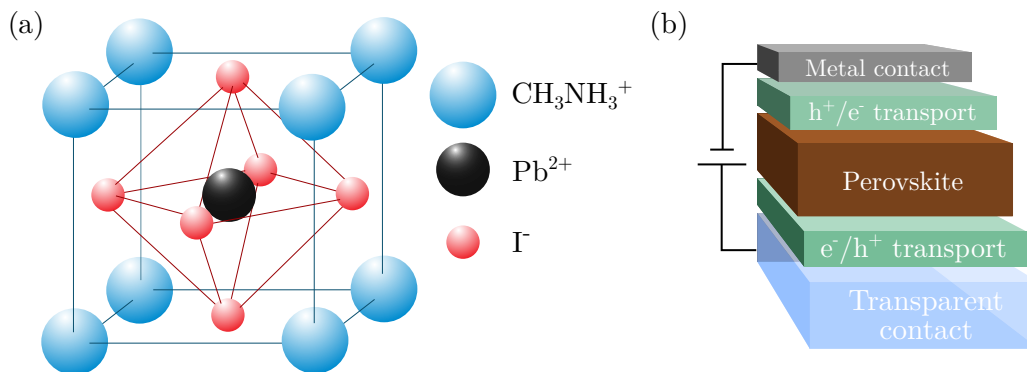


Figure 1.8 (a) The ABX_3 perovskite crystal structure most commonly used for photovoltaic applications; A – methylammonium, B – lead, and X – iodide. (b) A schematic of a perovskite solar cell.

caesium, methylammonium, and formamidinium, whilst at the X site iodide and bromide are commonly used.³¹ Substitution of the B-cation from lead to tin have been reported but the efficiencies are currently not comparable with the lead analogues.³² Halide tuning of $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ results in a bandgap shift from 1.6 eV to 2.3 eV. A bandgap between these values at 1.7 eV is optimal for perovskite/silicon tandem solar cells. However, halide segregation in the crystal structure has so far inhibited a stable device at this bandgap.³¹ The bandgap of formamidinium lead iodide is more favourable than its methylammonium counterpart in a single junction architecture. However, the formamidinium perovskite does not easily form the photoactive ‘black’ perovskite phase and spontaneously converts to the inactive ‘yellow’ phase.^{33,34} Cation tuning has enabled the stability of the ‘black’ phase, improving device performance.^{35,36} State-of-the-art perovskite solar cells now contain mixed cation mixed halide perovskites to enable optimal optical properties whilst maintaining the intrinsic stability of the crystal structure.

1.3 Stability of photovoltaics

1.3.1 Factors of stability

The stability of a solar cell is a measure of the rate of degradation in power conversion efficiency over time. Section 1.2.1 has described the low-cost potential for emerging organic and perovskite technologies with the use of inexpensive raw materials and high throughput processing. Section 1.2.2 has described the high-efficiency potential such as tandem devices and bandgap tuning. However, alongside low cost and high efficiency, long-term stability is required for commercial viability. The lifetime power output of a solar cell is the product of the initial efficiency and the degradation rate of the device. As such, both the efficiency and stability of emerging photovoltaics will significantly affect the commercial viability. Alongside studies on understanding the efficiency of solar cells, research to improve the stability is gaining considerable attention in the literature. More recently, analysis by Li, McCulloch, and Brabec established an industrial figure of merit, $i - FoM$, for comparison of photovoltaic devices on not only power conversion efficiency, but also cost and stability such that³⁷

$$i - FoM = \frac{PCE \times \text{photo-stability}}{\text{Synthetic complexity}} \quad (1.2)$$

Stability stress factors can broadly be put into two categories: intrinsic and extrinsic (Figure 1.9). Intrinsic factors include light, heat, innate instabilities of materials and reactions between layers. This includes interactions between the photoactive material, metal contacts, dopants, and charge transport layers. These factors cannot be protected against by encapsulation and are determined by the operating conditions of a solar cell. Extrinsic factors include stability to humidity and oxygen, which can be minimised with encapsulation, and mechanical stress for flexible modules. However, the degree of protection is application dependent; for example, for flexible solar modules perfect encapsulation is unrealistic. Degradation mechanisms may also be influenced by applied bias within the device. Therefore, the bias during stability testing



Figure 1.9 Intrinsic and extrinsic stability factors of a solar cell.

(open circuit, short circuit, MPP) must be considered. To improve the stability of a solar cell, the limiting stress factor and/or material must be identified and overcome. Therefore, to analyse and optimise the stability of photovoltaic devices it is important to consider all of these factors and critically analyse which are affecting performance.

The state-of-the-art in stability of organic and perovskite photovoltaics has greatly improved over the past decade. There are various standards to compare stability metrics between devices, for example the industrial scale IEC reliability tests³⁸ and the laboratory scale ISOS organic solar cell stability testing protocols.³⁹ These protocols state the required conditions of the environmental factors which include the light exposure, humidity, temperature, and electrical load (e.g. maximum power point or open circuit) and the profile of these factors (e.g. cyclic or continuous). Alongside the environmental factors, there are also device specific factors such as the photoactive layer (e.g. different polymers or crystal ions), the interlayers (e.g. silver, gold, or aluminium contact), or encapsulation method. The combination of the environmental factors and the device specific factors result in a very large number of permutations for comparing stability metrics of solar cells. Despite this complexity there are notable impressive stability results reported in literature. For perovskites 1000 h operational stability of unencapsulated devices has been reported⁴⁰ and for organics stability over thousands of hours has been reported⁴¹. Although these results are impressive there is potential to further improve and understand the limitations of stability of organic and perovskite solar cells.

1.3.2 Organic solar cell stability

Degradation of an organic solar cell may result from a number of factors, often occurring simultaneously making identification of the limiting factor complex.^{41,42} For example, in the presence of oxygen the polymer donor and fullerene acceptor undergo photo-oxidation and metal contacts can also oxidise.^{43,44} Interactions between metal contacts (e.g. aluminium), transparent contacts (e.g. indium doped tin oxide), and charge transport layers (e.g. PEDOT:PSS) have all been associated with degradation of organic solar cells.⁴⁵ In these examples, encapsulation and

selecting correct inter-layers can mitigate the effects; however, the intrinsic stress factors light and temperature affect device stability and must be overcome to develop stable organic solar cells. A commonly observed phenomenon is the loss of performance after a solar cell is stressed under illumination. This is labelled the 'burn-in'. It has been shown to occur in a number of OSC systems and correlated with many factors.^{46–49}

For morphological changes to occur in the bulk heterojunction, the system must be above the glass transition temperature of the film.⁵⁰ This temperature in a blend is a system property of the polymer and fullerene to give a single glass transition temperature. In some systems annealing above the glass transition temperature is beneficial, such as optimising P3HT:PCBM blends, but often it has detrimental effects on device performance. Upon reaching the glass transition temperature, the crystallinity of the polymer greatly affects the degree of separation as it controls the diffusion of fullerenes through the polymer matrix. The rate of diffusion of the fullerene is also strongly temperature dependent. To ensure this morphological instability is not present during operating temperatures (up to 85 °C) the glass transition temperature of the blend matrix can be designed to be above this. However, a polymer with a high glass transition temperature will reduce the ductility of the film and solar cell. If ductility is too low, it will be prone to mechanical failure in roll-to-roll processing or with flexible applications.⁵¹

The majority of polymer:fullerene solar cells are processed such that the thin film is out of thermodynamic equilibrium. However, there have been recent successful attempts to engineer donor:acceptor organisation with molecular design and deposition techniques.⁵² By controlling the polymer solubility, the final morphology is not dependent on the spontaneous self-assembly enabling use with a wide range of acceptor materials. This strategy can enable optimal morphologies by simply annealing the thin film above the glass transition temperature to create a thermodynamically favourable material system.^{53–55} Control of the bulk heterojunction morphological stability for optimal optoelectrical performance remains a challenge.

Photo-dimerisation of fullerene was first reported by Rao et al in 1993. Upon illumination, C₆₀ buckminsterfullerene units were found to undergo a 2 + 2 cycloaddition reaction (Figure 1.10(a)) to form dimers (Figure 1.10(b)) and oligomers with over 20 units.⁵⁶ The well-known mechanism has topological requirements—the alignment between double bonds on hexagonal carbon rings of two monomer units at a distance of < 4.2 Å. In solid films of C₆₀ the distance between molecules can get < 3.5 Å.⁵⁷ Time-dependent Raman spectroscopy was used to probe the reaction mechanism of the oligomerisation. A bi-molecular process involving a monomer in the excited triplet state reacting with a monomer in the ground state was proposed as the photochemical pathway.⁵⁸ At room temperature fullerenes are found to have significant rotational movement about the centre of mass of the unit. As a result, there is a high probability of a reaction at one of the 30 × 30 = 900 fullerene:fullerene reaction site combinations between C₆₀ fullerene units. At elevated temperatures the reaction is found to be reversible with the oligomers decomposing.⁵⁹ Steady-state Raman spectroscopy was used to probe the temperature dependence of the reaction and an activation energy of ≈ 1.25 eV was found for the thermal decomposition.⁵⁹

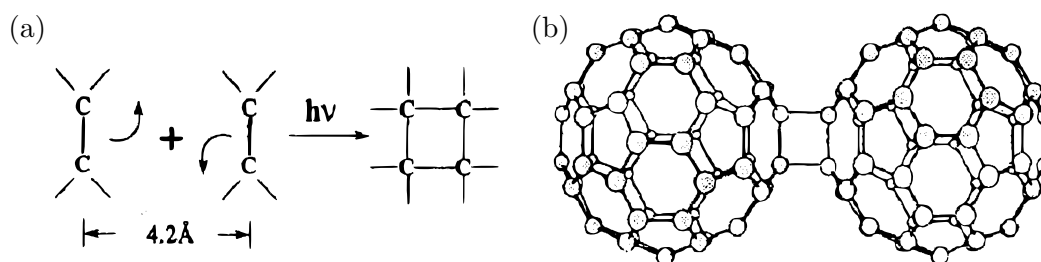


Figure 1.10 (a) Schematic of 2 + 2 cycloaddition reaction between parallel carbon double bonds on adjacent C_{60} fullerene molecules and, (b), the resulting dimer. Adapted with permission from Ref⁵⁷ with permission from Elsevier.

The photo-dimerisation and thermal de-dimerisation are shown to occur in a range of systems, including C_{70} and PCBM.^{60,61} Within a polymer:fullerene solar cell, PCBM dimerisation is reported to have both detrimental and beneficial effects.^{62–65} First, the undesirable effects are discussed. The detrimental effects of PCBM dimerisation were reported by Distler et al in 2014.⁶² Dimerisation was monitored with high performance liquid chromatography and correlated with a drop in device performance. Upon substituting PCBM with an analogue that is unable to undergo dimerisation due to steric hindrance (bis-PCBM), the device degradation was not observed. Simulations suggested the instability was associated with reduced charge carrier mobility. Heumueller went on to investigate the effect of dimerisation on a series of seven polymer:fullerene systems.⁶³ The dimerisation was correlated with a drop in short circuit current. Increased PCBM crystallinity was found to inhibit dimerisation whilst changing the device bias from short circuit to open circuit increased dimerisation. PCBM photoluminescence was directly correlated with PCBM dimerisation, suggesting the reaction mechanism occurs via excitons.

Although there are detrimental effects from dimerisation, it is also reported to have beneficial effects. The beneficial effects of PCBM dimerisation were reported by Li et al in 2013.⁶⁴ Light processing of an OSC resulted in improved stability at elevated temperatures. PCBM dimers were found to inhibit morphological instabilities of the bulk heterojunction whilst device lifetimes increased 10-fold. At temperatures above the glass transition temperature of the polymer:PCBM system, light processing was found to inhibit crystallisation. Further work found dimers to frustrate the nucleation rate, but not the growth rate, of PCBM crystallisation in range of polymer:PCBM systems.⁶⁵ The stability of chemically (rather than photo-) synthesised PCBM dumbbells were also found to improve the thermal stability of polymer:PCBM solar cells.⁶⁶ This work corroborates the hypothesis of PCBM dimers being beneficial for the stability of OSC bulk heterojunctions.

1.3.3 Perovskite solar cell stability

Perovskite solar cell stability has been a heavily discussed topic; this covers a range of mechanisms, stress factors, and timescales.⁶⁷ At shorter timescales, mobile ions and defects in the perovskite layer result in a hysteric phenomenon in the current-voltage output.⁶⁸ This phenomenon results in a higher power conversion efficiency if scanning from forward to reverse bias compared to reverse to forward. As a result of this, there is instability of the maximum power output over short timescales of seconds to minutes. Improved device processing and architecture engineering have predominately eliminated this effect of short-term instability. Despite this, the long-term operational stability of a perovskite solar cell remains an important research challenge.

Increasingly, work is being focused on encapsulated device stability as this is thought to be a key limitation for commercialisation. The perovskite material MAPI is stable as a crystal under illumination and within operating temperatures.⁶⁹ Ion reorientation⁷⁰, ion migration,^{71,72} and crystal phase transition^{73,74} have been reported at operating conditions of a solar cell, however, they are thought not to significantly affect long-term material or device stability.^{75,76} Device degradation with illumination in inert conditions has been found to result from interactions with inter-layers in many different processes: the metal top contact can diffuse into the perovskite at the upper limit of operational temperatures,⁷⁷ and both the hole and electron transporting layers⁷⁸ have been shown to limit operational stability. The biasing condition during stability testing significantly affects the rate of degradation in operational conditions, which is partially reversible when the device is placed in the dark.⁷⁹ Encapsulation may benefit device performance by inhibiting volatile materials escaping the device—an effect that would not be observed in an un-encapsulated device in an inert atmosphere. Evidently, there are a large number of stability factors which are often material, device architecture, and condition dependent. To enable quantitative analysis between different laboratories and systems there is an impetus to standardise the testing procedure.⁸⁰

The loss of stability due to environmental factors has been a popular topic in perovskite photovoltaics. Initially, there was great sensitivity to water in the dye-sensitised solar cell liquid electrolyte. This was transferred to great concern over humidity for all solid-state devices and often quoted as the primary instability of earlier perovskite photovoltaics.^{81–84} Afterwards, there were reports of several other factors, including oxygen. To improve stability, novel device architectures incorporating barrier layers have been developed,^{85–88} and tuning the mixed ion at the A (e.g. formamidinium, caesium) and X (iodide, bromide) site of the perovskite crystal are reported to significantly improve environmental stability.^{89–92}

The impact of humidity on perovskite solar cells is clearly significant; however, it is also non-trivial. Processing of the perovskite layer in a humid atmosphere has been correlated with improved device efficiency and greater photoluminescence quantum efficiency.⁹³ This was associated with controlling the perovskite crystallisation process.⁹⁴ Although some reports show beneficial effects of humidity, the majority of work highlights the degradation of perovskite and

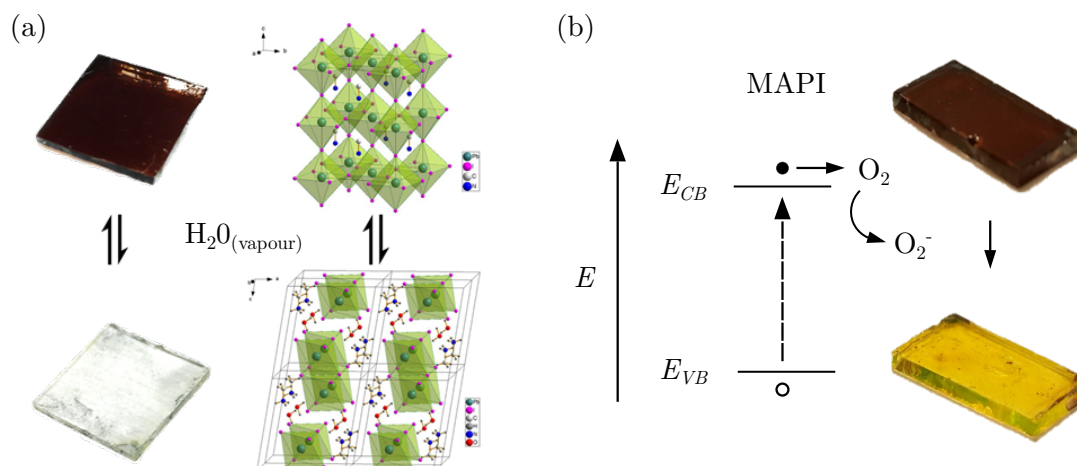


Figure 1.11 (a) Reversible MAPI crystal phase transition to mono-hydrated MAPI in the presence of water vapour. Adapted with permission from Ref⁸³. Copyright 2015 American Chemical Society. (b) MAPI degradation pathway in light and oxygen proposed by Aristidou et al.⁹⁵ Formation of superoxide results in MAPI degrading to reactants including lead iodide, observed with a colour change to yellow.

subsequent device degradation under these conditions. Leguy et al reported on the crystal phase transitions under humid conditions of perovskite thin films and devices.⁸³ In the presence of water vapour, MAPI can undergo a phase transition to a mono-hydrated crystal structure, as shown in Figure 1.11(a). This causes a dramatic shift in the bandgap, observed as the film going from brown to colourless, and degradation of the photovoltaic properties. The degradation mechanism under water vapour can be fully reversed,⁸³ contrary to MAPI degradation from the liquid electrolyte previously mentioned.

The impact of oxygen in the dark is reported to not result in device degradation for over 500 h.²⁷ However, oxygen in combination with light was first reported by O'Mahony et al to result in dramatic degradation of MAPI perovskite crystal.⁹⁶ A thin film stressed in light and nitrogen or dark and ambient air conditions does not show a change in the charge transfer processes, however in light and oxygen degradation was observed.⁹⁶ Aristidou et al eluded superoxide to be a critical pathway of the degradation reaction mechanism.⁹⁵ Increasing the MAPI electron extraction efficiency by changing the supporting scaffold from aluminium dioxide to titanium dioxide reduced the yield of superoxide and increased photo-stability. Upon MAPI photoexcitation in the presence of oxygen, free charge carriers may be transferred to oxygen to form superoxide which then degrades the perovskite crystal structure, as shown in Figure 1.11(b). In summary, light with oxygen, and humidity are the two major stress conditions limiting the environmental stability of perovskite solar cells.

1.4 In this thesis

This chapter has introduced the complex mechanisms that affect the stability of perovskite and organic solar cells. It is dependent on both the photovoltaic materials and the stress conditions used during stability testing. To overcome an instability the underlying cause must be understood such that improvements can be designed. The work in this thesis will investigate several instability mechanisms and provide frameworks to minimise or inhibit them. The objectives of this thesis can be broken down as follows:

1. **Determining the limiting environmental factor in perovskite photovoltaics.** The stability of methylammonium lead iodide (MAPI) thin films and solar cells under several environmental stress factors is investigated. Specifically, comparing the stability under light and oxygen to the stability under humid nitrogen. From this, the limiting stress factor of MAPI solar cells under operating conditions can be elucidated.
2. **Investigating the tunability of perovskite stability.** Tuning of ions in the ABX_3 perovskite is commonplace for optimising the power conversion efficiency of solar cells. Whether this principle is transferable to optimising light and oxygen stability of solar cells is unclear. The effects of halide tuning and the underlying mechanism of the changes to stability will be scrutinised.
3. **Comparing the competitive effects of illumination and annealing in PCBM morphological stability.** PCBM dimers inhibit coarsening and spinodal decomposition of the bulk heterojunction in organic solar cells. However, during *in-operando* conditions both illumination and thermal stress are experienced. The aim of this study is to determine which of these effects dominates under operating conditions and how that affects the morphological stability of a model polymer:fullerene system.
4. **Developing a framework of PCBM dimerisation considering illumination, heat, and the polymer matrix.** The photo-dimerisation of PCBM is dependent on the illumination and rigorous topo-chemical requirements of the 2 + 2 cycloaddition reaction controlled partly by the blend matrix. The PCBM dimer is reversible to monomers at elevated temperature. This work will combine previous work on dimerisation related to illumination and the polymer matrix, together with novel temperature dependence results. With this complete work, PCBM dimerisation, and subsequent solar cell stability, may be predicted within any polymer:fullerene blend being used under any diurnal temperature and light fluctuations.
5. **Presenting a framework to rationalise double-edged effects of PCBM dimerisation in OSC stability.** The photochemical reaction is reported as having both beneficial and detrimental effects on solar cell stability. The energetic variation between conformations of PCBM dimers and the irradiance dependence of formation will be investigated as a possible cause of these discrepancies.

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Chapter 2

Experimental details

This chapter will detail the experimental techniques used throughout the thesis. Firstly, the fabrication procedure of perovskite and organic thin films and solar cells. Secondly, the characterisation of the materials and devices.

2.1 Thin film and device fabrication

Perovskite thin film fabrication

Methylammonium lead iodide was fabricated with a previously reported anti-solvent dripping method.¹ Glass substrates were cleaned sequentially with soap, acetone, and isopropanol, followed by a 10 min oxygen plasma treatment. For methylammonium lead iodide (MAPI), the perovskite precursor solution was made by mixing a stoichiometric ratio of lead iodide and methylammonium iodide dissolved in a mix of DMSO and GBL (7:3) and stirred for 10 min. For methylammonium lead iodide-bromide (MAPIBr), stock solutions of MAPI and MAPBr were prepared by dissolving stoichiometric ratios of PbX_2 and $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X} = \text{I}, \text{Br}$) in a DMSO and GBL solution (7:3) at 1.25 M and stirred for 60 min at 50 °C and 20 °C, respectively. To obtain the range in $\text{MAP}(\text{I}_{1-x}\text{Br}_x)$, the stock solutions were combined in volumetric ratios. The perovskite solution was spin-coated with a two-step procedure in a glovebox; toluene was dripped onto the glass substrate during the second step followed by annealing at 100 °C post-deposition. The times for each step were optimised to ensure a glassy film.

Perovskite solar cell fabrication

Methylammonium lead iodide solar cells were fabricated with the same anti-solvent dripping method used for the thin film samples. An FTO glass substrate was coated with compact titanium dioxide (c- TiO_2) by spray pyrolysis, of a 20 mM titanium diisopropoxide bis(acetylacetonate) solution (Aldrich) at 475 °C. In instances where a mesoporous titanium dioxide (m- TiO_2) layer was used, a commercially available paste (18-nrt, dyesol) was first diluted 1:9 wt with ethanol before spin coating deposition at 4500 rpm for 45 s and sintering at 500 °C. In instances where a mesoporous aluminium oxide (m- Al_2O_3) layer was used, a 4%wt. suspension of Al_2O_3 nanoparticles in 2-propanol (Aldrich) was spin coated at 4500 rpm and dried at 150 °C. The perovskite precursor solution was made by mixing a stoichiometric ratio of lead iodide and methylammonium iodide dissolved in a mix of DMSO and GBL (7:3) and stirred for 10 min. The perovskite solution was deposited with the same procedure as the thin films: the solution was spin-coated with a two-step procedure where toluene was dripped onto the surface during the second step followed by annealing at 100 °C post-deposition. A solution of 8 % wt. 2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD, Borun Chemical) in chlorobenzene was then spin-coated onto the perovskite films. The spiro-OMeTAD solution contained additives including 19 mM bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI), 7 mM 4-tert-butylpyridine (tBP). V_2O_5 powder (99.99 %, Aldrich) was added to the spiro-OMeTAD solution in the quantity of 2.5 %wt with respect to the spiro-OMeTAD powder to aid oxidation. Finally, a 50 nm gold contact was evaporated onto the cell under vacuum leaving an active area of 0.045 cm^2 . Device data present in Figure 3.2 was obtained by the author and statistical analysis of this trend presented in Table 3.1 was obtained by Danial Bryant.

For MAPIBr solar cells, the fabrication procedure described above for MAPI was used but with solutions of MAPIBr. In instances where P3HT was used as a hole transporting material, a 12 mg mL^{-1} solution of high molecular weight poly(3-hexylthiophene) (P3HT) ($M_w = 135 \text{ kDa}$, $D = 1.5$, regio-regularity = 99 %) ² in chlorobenzene was spin-coated onto perovskite films at 2000 rpm for 30 s.

Polymer:PCBM sample preparation

For polystyrene:PCBM samples, solutions of phenyl-C61-butyric acid methyl ester, PCBM, (supplied by Nano-c) and polystyrene, PS, with $M_w = 100 \text{ kg mol}^{-1}$ (supplied by BDH Chemicals LTD) were prepared at a combined concentration of 25 mg mL^{-1} in chlorobenzene. Neutron reflectivity samples were prepared on silicon wafer substrates with a diameter of 50 mm and UV-visible absorption samples were prepared on glass to allow for transmission measurements. Substrates were plasma treated in an oxygen atmosphere with an Emitech K1050X before PEDOT:PSS (Al 4083) was spin coated at 1000 rpm for 40 s. Solutions of PS:PCBM were made up at volumetric ratios of 20:80, 35:65, 50:50, 65:35, and 80:20 and spin coated at 1500 rpm for 30 s. The resulting film thicknesses ranged from 90 nm to 120 nm, measured by stylus profilometry (Dektak XT) and confirmed by neutron reflectivity.

For PCDTBT:PCBM samples, solutions of phenyl-C61-butyric acid methyl ester, PCBM, supplied by Nano-c and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)], PCDTBT, supplied by 1-materials (structures in Figure 2.1) were prepared at a combined concentration of 25 mg mL^{-1} in chlorobenzene. Glass substrates were plasma treated in an oxygen atmosphere with an Emitech K1050X before solutions of 1:2 PCDTBT:PCBM were spin coated at 1500 rpm for 30 s. The resulting film thicknesses were $\approx 100 \text{ nm}$, measured by stylus profilometry (Dektak XT). For the GPC measurements, the samples were re-dissolved in chlorobenzene.

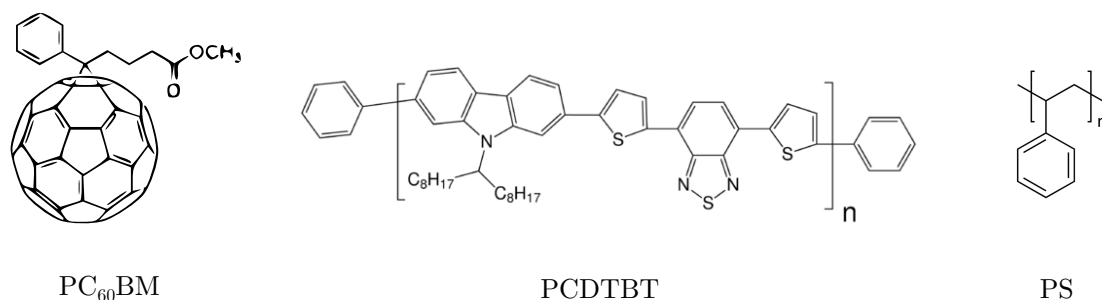


Figure 2.1 Molecular structures of phenyl-C61-butyric acid methyl ester (PCBM), poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), and polystyrene (PS).

Polymer:PCBM sample illumination and thermal annealing

Illumination and annealing were carried out in a nitrogen-filled glovebox with oxygen and humidity levels kept below 15 ppm. A Bridgelux 4000 K white LED light source was used with the spectrum shown in Figure 5.2(a). The intensity was matched to give an equivalent photocurrent response from a silicon photodiode at AM1.5G. Thermal annealing was carried out on a hotplate and calibrated with an infrared thermometer in-situ with and without illumination.

2.2 Characterisation and stability measurements**2.2.1 Optical characterisation****UV-visible absorbance spectroscopy**

UV-visible absorbance spectroscopy was carried out with a Shimadzu UV-1601 spectrophotometer.

Photoluminescence spectroscopy

Photoluminescence spectra were measured on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer. The bias-dependent photoluminescence measurements were taken with the assistance of Daniel Bryant.

Time-resolved photoluminescence spectroscopy

The excitation source for time-resolved photoluminescence measurement was a pulsed laser diode (PicoQuant) emitting at 485 nm with a repetition rate of 10 MHz. Photoluminescence is collected using a 0.5 m focal length spectrometer and a GaAs photodetector (PMC-100-20, Becker & Hickl). For continuous-wave measurements a mechanical light modulator and a lock-in amplifier were used, whereas for time-resolved measurements, the signal of the detector is sent to a correlation card (Becker & Hickl), giving a time resolution of 0.3 ns. Measurements were taken with the assistance of Diego Alonso Alvarez.

Transient absorption spectroscopy

Sub-microsecond timescales transient absorption spectroscopy (μ s-TAS) decays were acquired on a custom-built system. Samples were excited at 420 nm ($40 \mu\text{J cm}^{-2}$) by using an Opolette 355 laser (OPOTEK), white probe light generated by a tungsten halogen lamp, and detected by a silicon photodiode detector. A probe wavelength of 530 nm was selected by a monochromator and long pass optical filters were used to limit light exposure to the sample and reduce the effect of laser scatter. Samples were measured in a nitrogen or dry air atmosphere, as specified. Measurements were taken with the assistance of Ching-Hong Tan.

2.2.2 Perovskite characterisation

Current-voltage (JV) measurements

JV characteristics were measured using a Xenon lamp AM1.5G solar illumination (Oriel Instruments) and a Keithley 2,400 source meter. Calibration of the irradiance was performed with a silicon photodiode. For MAPI devices, scans were performed at a slow rate of 0.005 V s^{-1} to negate hysteric effects encountered during the JV scan. For MAPIBr devices, cyclic scans were performed from 0 V to 1.5 V forward bias and back to 0.5 V reverse bias at a rate of 0.125 V s^{-1} . Cells were unmasked during measurements using the area created by the overlap of the metallic contact and the FTO substrate as the defined active area of 0.15 cm^2 .

JV measurements as a function of ageing

Samples were enclosed in chambers with a quartz window, initially held under nitrogen to allow measurements of 'pristine' devices. Devices were exposed to varying environmental conditions via a valve system on the chamber using bottled clean dry air or nitrogen with and without moisture. Clean dry air and nitrogen were provided in cylinders from BOC UK. The air contains less than or equal to 21 % oxygen and greater than or equal to 79 % nitrogen, both are quoted as containing ($< 2 \text{ vpm}$ water) however the gases were still passed over silica desiccant before the devices were exposed to them. Light exposure was performed at equivalent 1 Sun white light illumination provided by an array of white LEDs, calibrated to the device short circuit current as measured under AM1.5G and a Keithley 2,400 source meter. The spectrum of the LED light used throughout the measurements and AM1.5G solar spectrum are presented in Figure 5.2. The PCE was first allowed to stabilise under initial exposure to illumination and once stabilised this point is defined as time 0 s. JV measurements were performed periodically with a dwell time of 200 ms per 1 mV step to try and negate hysteresis effects using the same LED light array described previously. Devices in 'dark' conditions were exposed to light only during JV scans. Ten devices per data set were used to give an accurate representation of performance. The same Keithley 2,400 sourcemeter was used to vary the conditions from open circuit to short circuit by applying a voltage bias to the devices. A fan was used to keep the sample chambers (and the devices inside) at a constant 30°C (as measured with an IR gun) during measurements. The stability software was designed by Dr Scot Wheeler.

Thin film environmental stability characterisation

Stability analysis of thin film materials was done in a glovebox with a Bridgelux 4000 K LED light, humidity control, and atmospheric control between nitrogen and dry air, as shown in Figure 2.2. For perovskite stability, the LED light source was calibrated to current match a MAPI device under an AM1.5G solar spectrum to obtain a 1 Sun equivalent intensity. Dry air conditions were obtained from bottled gas of a nitrogen and oxygen mix, at 21% oxygen concentration; the same used for device stability measurements. The humidity level was controlled using two circuits;

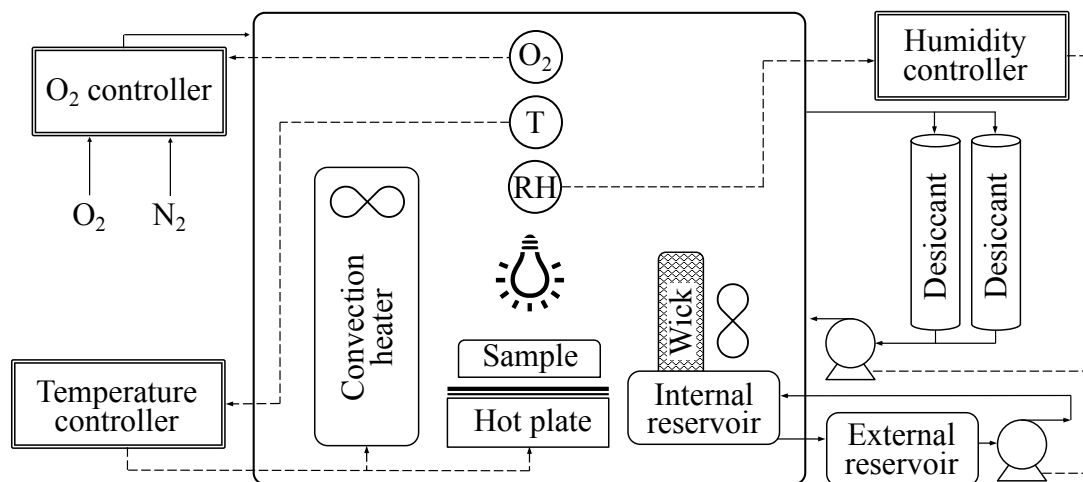


Figure 2.2 Schematic of the environmental chamber used to control the atmosphere (nitrogen, oxygen, and humidity), temperature, and illumination.

firstly, desiccant columns were used to dry the atmosphere and, secondly, a humidifying circuit was used to wet the atmosphere. A setpoint controller would then adjust the flow to obtain the desired humidity level. For samples tested in nitrogen, a chamber was used to transfer samples from the fabrication glove box to the stability glovebox to ensure no exposure to air.

Optical degradation of samples was monitored with a CCD camera, and the change in the average red-green-blue output was monitored against background values according to

$$\text{Optical degradation} = \frac{RGB_t - RGB_{final}}{RGB_{initial} - RGB_{final}} \quad (2.1)$$

where RGB is the average red-green-blue value from the CCD of the pristine film, $RGB_{initial}$, the fully degraded film, RGB_{final} , and at time t , RGB_t .

Superoxide generation characterisation

The rate of superoxide generation in the perovskite films was quantified with a fluorescing probe. A film was placed in a solution of toluene containing the probe and dry air bubbled through the solution to ensure an oxygen environment. Superoxide generated in the film upon light exposure reacts with the probe (hydroethidine) increasing its photoluminescence quantum efficiency. By monitoring the photoluminescence over time during exposure to light and oxygen it is possible to quantitatively compare the rates of superoxide generation between different perovskite films.

These studies were conducted following a previously published method with the assistance of Nicholas Aristidou.³ A stock solution (31.7 μM) of the hydroethidine probe was prepared by dissolving 10 mg hydroethidine in 10 mL of dry toluene; sonication was used to facilitate miscibility. Films were then added to 10 mL of 0.317 μM solution created from the stock solution.

Photoluminescence spectra were recorded using an excitation wavelength of 520 nm and a slit width of 10 nm on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorometer. In the experiments involving oxygen, dry oxygen was bubbled through the toluene.

For the $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ samples there is a shift in the bandgap resulting in inconsistent absorption between films. To determine the superoxide yield per photon absorbed a spectral mismatch correction factor was used, as described below:

$$\frac{I_F(t)}{I_F(t_0)}(\text{corrected for absorbance}) = 1 + \frac{I_F(t) - I_F(t_0)}{\alpha \times I_F(t_0)} \quad (2.2)$$

where $I_F(t)$ is the average fluorescence intensity from 605 nm to 615 nm at time t , $I_F(t_0)$ is I_F at $t = 0$ min and α is the spectral mismatch factor relative to MAPI as given in Table 2.1. Superoxide measurements were taken with the assistance of Nicholas Aristidou.

Table 2.1 Absorbance correction factor, α , for $\text{MAP}(\text{I}_{1-x}\text{Br}_x)$ thin films calculated from the spectral overlap of the perovskite absorbance and the spectrum of the tungsten-halogen lamp, normalised to MAPI.

MAP($\text{I}_{1-x}\text{Br}_x$), where x:						
	0.00	0.10	0.20	0.50	0.75	1.00
α	1.00	0.85	0.84	0.52	0.44	0.35

NMR characterisation

Potassium superoxide and methylammonium bromide were dissolved in a 1:1 molar ratio in dry ethanol. The reaction was monitored by ^1H nuclear magnetic resonance (NMR) using a 400 MHz Bruker spectrometer. Measurements were taken with the assistance of Irene Sanchez-Molina.

X-ray diffraction

X-ray diffraction (XRD) measurements on perovskite thin film samples with glass substrates were performed using a Bruker D8 Discover X-ray diffractometer equipped with Ni-filtered Cu K α radiation ($\mu = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. XRD patterns were acquired in the Bragg-Brentano geometry with a standard 2θ step size of 0.01671° from 10° to 40° at $26 \text{ s} / ^\circ$.

2.2.3 Polymer:PCBM characterisation

Gel permeation chromatography

Gel permeation chromatography with in-situ optical measurements was performed using an Agilent Technologies 1260 Infinity GPC System with 1260 RID and DAD VL attachments. Measurements were performed at 80°C , using analytical grade chlorobenzene as eluent with two PLgel $10 \mu\text{m}$ MIXED B columns in series. Samples were prepared using analytical grade chlorobenzene

in concentrations of 1 mg mL^{-1} to 2 mg mL^{-1} and filtered with VWR PES membrane $0.45 \mu\text{m}$ syringe filters before submission. An injection volume of $50 \mu\text{L}$ and GPC flow rate of 1.00 mL min^{-1} was used. The absorbance at 300 nm, 320 nm, and 335 nm was used to monitor the elution and found to give equivalent results. Measurements were taken with the assistance of Adam Marsh.

Dimer concentration quantification from absorbance spectroscopy

The absorbance spectra of PCBM monomer and dimer differ with an exaggerated trough at $\approx 320 \text{ nm}$ for the former. Therefore, monitoring of the absorbance of a film allows for the quantification of the ratio of dimerised PCBM to pristine PCBM. To allow for small spatial variation in the film the absorbance spectra were normalised to the peak at $\approx 340 \text{ nm}$. The change in the absorbance trough at $\approx 320 \text{ nm}$ in films of dimerised PCBM is correlated to known ratios of PCBM to dimer PCBM from GPC measurements. This method allows for the correlation of the change in absorbance at $\approx 320 \text{ nm}$ with PCBM dimerisation.

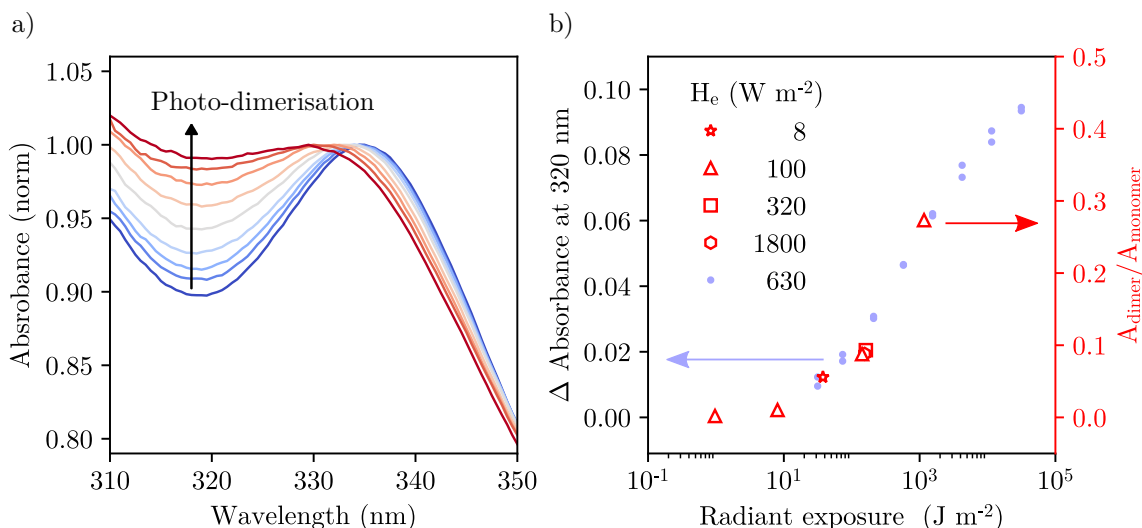


Figure 2.3 (a) Normalised absorbance spectra of a PCDTBT:PCBM film during light exposure in a nitrogen atmosphere. The photo-dimerisation results in a shift in the absorbance trough at $\approx 320 \text{ nm}$. (b) Correlating the change in absorbance at 320 nm to the dimer/monomer ratio ($A_{\text{dimer}}/A_{\text{monomer}}$), as determined from GPC, for varying radiant exposure (light dose) and irradiance, H_e (light intensity).

Atomic Force Microscopy

Atomic force microscopy was carried out with a Bruker Innova microscope in tapping mode at 0.2 Hz with Si tips (MPP-11100-W, Bruker). Data analysis of the topography data extracted the height frequency distribution (from the 'numpy histogram' function), Fourier transform (from with 'scipy fftpack fft2' function), and surface roughness, Rq , using custom code written in Python 3.0.

Neutron reflectivity

Neutron reflectivity is a specular reflection technique used to measure the vertical stratification of thin films, as shown in Figure 2.4. Fitting of the momentum transfer of the neutrons gives information about the nuclear contrast referred to as the scattering length density. Calibrating this with known values gives the composition profile of the film perpendicular to the substrate.

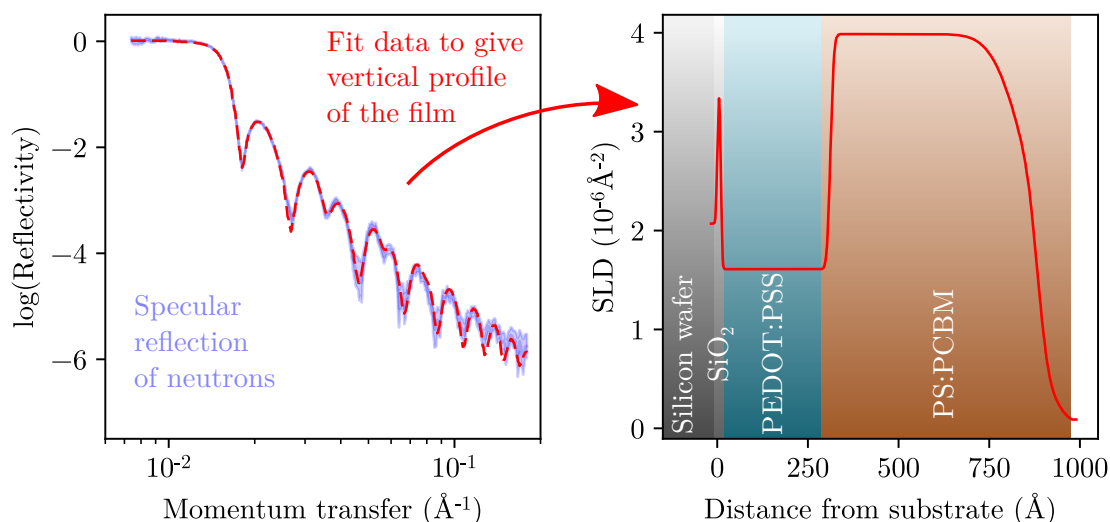


Figure 2.4 Exemplar neutron reflectivity measurement of a polystyrene:PCBM thin film supported on a Si-wafer/PEDOT:PSS substrate.

Neutron reflectivity measurements were carried out at the D17 reflectometer at the Institut Laue Langevin (Grenoble, France). Both static and time-resolved measurements were employed to determine the cross-sectional structure of PS:PCBM films exposed to various environmental conditions. Static measurements were performed at angles 0.9 and 3.4, covering a momentum transfer normal to the surface ($Q = (4\pi/\lambda) \sin \theta$) ranging from 0.006 Å^{-1} to 0.3 Å^{-1} . Kinetic measurements were acquired at a single angle of 2.6, yielding Q from 0.01 Å^{-1} to 0.09 Å^{-1} , with 30 s time resolution, employing an enclosed hot stage with a steady N_2 gas purge, and a Bridgelux 4000 K white LED light source; the temperature was controlled directly at the measured sample and any offset accounted for. Specular reflectivity profiles were analysed using Motofit⁴, both in single and batch fit mode for the static and kinetic measurements, respectively, enabling simultaneous, self-consistent data fitting.

Batch fitting of the *in-situ* measurements was done using the batch fit function in Motofit. This was used to fit the kinetic data with a number of constraints that were found to improve the robustness of the data fit. The initial fit at $t = 0$ min was obtained from the full- q measurements. Subsequently, the roughness and thickness were fixed, as well as the SLD values, except for two: that of a 30 Å layer at the bottom interface, and that of an adjacent layer of 150 Å towards the bulk of the film. A genetic + Levenberg-Marquardt algorithm was used to optimise the fit to the data. The uncertainty from the algorithmic fit is shown in the error bars.

Neutron reflectivity measurements were taken at the Institut Laue Langevin (ILL, Grenoble) with the technical assistance from Philipp Gutfreund. The assistance of the measurement and analysis of the results was given by Fabrizia Foglia, Anthony Higgins, and João Cabral.

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Chapter 3

The limiting environmental factor of perovskite stability

This chapter is based on the work published by Bryant et al. in Energy and Environmental Science, 2016.¹

Within this chapter light and oxygen-induced degradation is shown to be the primary factor for the low operational stability of methylammonium lead triiodide (MAPI) perovskite solar cells exposed to ambient conditions. When exposed to both light and dry air, unencapsulated MAPI solar cells can rapidly degrade on timescales of minutes to a few hours. This degradation mechanism is also initiated with injected charge, instead of photo-generated, in the presence of oxygen, without illumination. Significantly slower degradation is observed when the MAPI devices are exposed to moisture alone (e.g. 85% relative humidity in nitrogen). Light and oxygen induced degradation can be slowed down by the use of interlayers that are able to remove electrons from the perovskite film before they can react with oxygen to form superoxide. These observations demonstrate that the operational stability of electronic and optoelectronic devices that exploit the electron transporting properties of MAPI will be critically dependent upon the use of suitable barrier layers and device configurations to mitigate the oxygen sensitivity of this remarkable material.

3.1 Introduction

Methylammonium lead trihalide perovskites (MAPI) are currently generating extensive interest with respect to their use in a range of devices such as light emitting diodes, solar cells, transistors and lasers.^{2–8} The excellent optoelectronic properties of this material, along with the solution processable nature and low cost of the precursor materials provide great potential, as discussed in Section 1.2.4. Over the last few years, remarkable progress in perovskite solar cells has been made and solar light to electrical power conversion efficiencies of such devices have quickly risen from approximately 10% in 2012 to over 23% at present.^{5,9,10} As such, it is increasingly recognised that stability is a key challenge for this technology.^{11–13}

At the time of this study, promising operational stability has been reported for MAPI solar cells encapsulated under an inert atmosphere using glass as a barrier layer.^{14,15} Whilst it is commonplace to encapsulate similar optoelectronic devices (such as OSCs and OLEDs), sensitivity to environmental exposure, and specifically to water and/or oxygen ingress, is likely to be a key concern for many practical technology applications where flexibility is needed and glass barrier layers are not viable. Some progress has been made in this regard, with promising shelf life (dark) stability reported for unencapsulated MAPI employing a metal-oxide top contact.¹⁶ Under operation devices employing enhanced electron extraction and optimised extraction layers have improved stability.^{16–18} However, the relative importance of different factors limiting material and device stability is unclear. While several external agents (e.g. temperature, phase behaviour, pressure, ultraviolet light, moisture and crystallinity) have been reported to influence the stability of perovskite solar cells.^{19–24} At the time of the study (2016), it was assumed moisture-induced degradation was the dominant issue affecting MAPI device stability under ambient conditions. As such, most stability studies were focused on the role of moisture in the deterioration of MAPI solar cell performance.^{22,25,26}

Several reports have shown MAPI to have intrinsic stability. Storage lifetimes of over 500 h were reported in the seminal work on solid-state perovskites by Kim et al. in 2012.^{4,5} Regarding the extrinsic stability, there have been several studies on the severe sensitivity of MAPI to humid atmospheres.^{27,28} MAPI has been shown to have significant sensitivity to humidity, resulting in either detrimental or beneficial effects depending on the system.²⁹ The humidity affects the perovskite crystallisation which can, in certain systems, result in improved performance.^{30–32} Leguy et al. studied the perovskite degradation mechanism in MAPI thin films and solar cells to a humid atmosphere at >80 % relative humidity (RH). Upon exposure to humid air it was shown the crystal structure converted from perovskite to a mono-hydrate phase, consisting of one-dimensional isolated double-chains of $[\text{PbI}_3]^-$.²² This was shown to form at the grain boundaries of the perovskite crystal and cause a dramatic decrease in the power conversion efficiency of a solar cell. This mechanism was shown to result in the degradation of device PCE, which was found to be partially reversible when exposed to dry air. Furthermore, much work on the humid sensitivity of MAPI is done in non-inert conditions (e.g. air, light) where

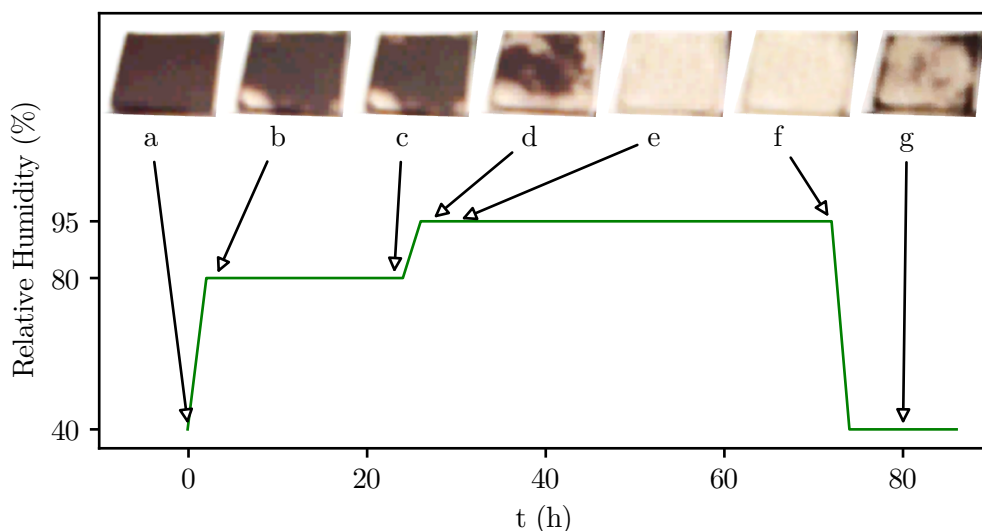


Figure 3.1 Images of a glass/MAPI thin film exposed to varying humidity conditions in a nitrogen atmosphere. The pristine film (a) only shows modest discolouration at 80 % RH (b, c) whereas at 95 % rapid degradation of the film is observed to the transparent mono-hydrated state (d, e). It is stable in this state for 40 h (f) and shows semi-reversibility when returned to 40 % RH (g).

alternative degradation pathways may be present. Thus, uncertainty remains on the exact influence humidity has on the stability without other environmental factors.

Previous to the study described in this chapter, it has been demonstrated that exposure of MAPI films to both light and molecular oxygen can cause rapid degradation.^{33,34} Specifically, it is shown this reaction is initiated by the deprotonation of the methylammonium cation of the perovskite by a photogenerated reactive oxygen species (superoxide, O_2^-) where the superoxide is generated by the reaction of photo-generated electrons in the perovskite and molecular oxygen.³³ These observations raise two important questions, namely does oxygen induced degradation affect the stability of fully-functioning perovskite solar cells and secondly whether the degradation can also be induced by the reaction of electrically injected electrons in the perovskite and oxygen. The ability of oxygen induced degradation to be facilitated by electrical bias would be expected to have a profound impact on the stability of a wide range of devices such as light emitting diodes and transistors as well as solar cells. This chapter will address these two issues.

3.2 Results and discussion

To selectively address the effect of humidity on perovskite stability, thin films of MAPI were stressed in a nitrogen atmosphere with controlled humidity levels. The levels of humidity required to initiate the phase transition to the transparent mono-hydrate phase are found to be relatively high at greater than 80 % RH as shown in Figure 3.1. Conversely, after 60 h at 60 % RH the perovskite film was found to remain in the dark perovskite crystal phase. At 80 % RH

partial conversion to the mono-hydrate is observed at the film edge within the first hour, shown in Figure 3.1, image b. This is likely due to a slight overshoot of the humidity as it remains stable for the following 24 h (Figure 3.1, image b and c). At 95 % RH there is rapid conversion to the transparent mono-hydrate (Figure 3.1, image d and e) which is unchanged for 60 h (Figure 3.1, image f).²² Upon dehydration in a nitrogen atmosphere the mono-hydrate shows partial reversibility to perovskite (note, full reversibility was observed during alternative conditions but here oxygen ingress prevented full reversibility). Although MAPI thin films show severe sensitivity to humidity, the results presented here highlight this is only at relatively high levels and it is therefore unclear how significant a factor it will be in the operating conditions of a solar cell.

3.2.1 Light and oxygen stability

When exposed to both light and oxygen, MAPI thin films rapidly degrade from the dark brown perovskite to a yellow film. Figure 3.2(a) presents the absorbance characteristics of MAPI films prepared on non-conducting glass before and after ageing for 48 h in controlled environments. Four conditions were compared: light and nitrogen, dark and clean dry air, light and clean dry air, and light and ambient air (RH $\approx$ 48 %). The as-prepared MAPI films all exhibit the reported absorption onset at approximately 780 nm.⁵ It is apparent that degradation of the MAPI film takes place in dry air with light and ambient air with light. However, no degradation is observed in control samples aged in nitrogen with light and dry air in the dark (Figure 3.2). Moreover, exposure to light and oxygen for just 48 h results in a dramatic blue shift in the absorption onset from 780 nm to 520 nm and a profound change in colour of the sample from dark brown to yellow; both these observations being consistent with the breakdown of the perovskite crystal and the subsequent presence of lead iodide in the final degraded films.³⁴ The data presented herein confirm the presence of a degradation pathway that is light activated, independent of moisture and requires molecular oxygen.³³

Thin films of MAPI films are shown to have a profound sensitivity to light and oxygen which raises a key question, namely whether this degradation pathway contributes to the low stability of MAPI based solar cells. To investigate whether light and oxygen induced degradation occurs in complete photovoltaic applications, device stability studies were undertaken. The relevant experimental details of device fabrication are given in Section 2.1. Briefly, solar cells of type: FTO/compact-TiO₂/mesoporous-TiO₂/MAPI/spiro-OMeTAD/Au were fabricated in a dry, oxygen-free glove-box. The subsequent devices, without further encapsulation, were then placed in an environmental chamber for stability measurements. Ageing illumination was provided by a 1 Sun equivalent white LED array. Power conversion efficiencies (PCE) of the solar cells were determined from current-voltage measurements at regular time intervals (0.02 V s⁻¹ scan speed, using same LED light source) over the course of 12 h with the solar cells being subjected to different environmental conditions. Figure 3.2 shows the PCE versus time with the solar cell devices aged in controlled conditions, namely light with nitrogen, dark with

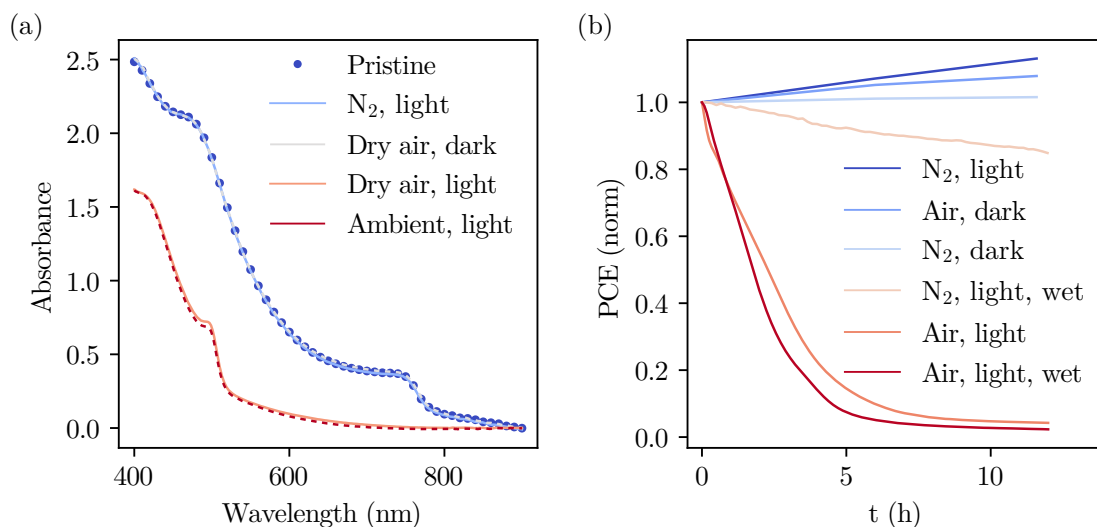


Figure 3.2 (a) Absorbance spectra for MAPI films with ageing in different conditions. Only films exposed to the combination of light and oxygen show photo-bleaching of MAPI. After degradation, the absorbance onset at 780 nm of MAPI shifts 520 nm, associated to lead iodide. Measurements were taken with the assistance of Nicholas Aristidou. (b) Normalised power conversion efficiencies (PCE) of MAPI solar cells measured following exposure to different environmental conditions. Air was supplied from a gas cylinder with 20.95 % O₂, 78.09 % N₂, and 0 % RH. Wet samples were tested in an atmosphere with a relative humidity of 85 %. Solar cells with the following architecture were used for this study: FTO/c-TiO₂/m-TiO₂/MAPI/spiro-OMeTAD/Au. Light exposure was provided by a 1 Sun equivalent white LED array.

dry air, dark with nitrogen, light with nitrogen at 85 % RH, light with dry air, and light with dry air at 85 % RH. Raw data (device parameters obtained from current-voltage scans under these different environmental conditions as a function of time) are presented in Table 3.1.

It is evident from the data presented in Figure 3.2 that the performance of control devices (light with nitrogen, dark with dry air, dark with nitrogen) remain relatively constant (i.e. no drop in PCE) over 12 h. In contrast, the device exposed to light and dry air shows a dramatic and large drop in PCE with ageing time with, for example, this device exhibiting a 50 % drop in PCE from its original value within 2 h. This observation clearly demonstrates that the performance and stability of MAPI based solar cells is critically affected when exposed to both light and oxygen. In contrast, the PCE of the device exposed to light, 85 % relative humidity (RH) in nitrogen (with no oxygen present) remains relatively constant with this device showing a comparatively small 10 % drop in PCE over the 12 h ageing period. To ensure severe humidity testing the air temperature was held at 30 °C meaning that the absolute humidity was very large at 26 g per kilogram dry air (for reference at 85 % RH, 20 °C the absolute humidity is 12 g per kilogram dry air). Furthermore, it can be seen from the data presented in Figure 3.2 that the rate of decrease in PCE is similar in devices exposed to light in dry air and light, dry air in 85 % RH. These results show that light and oxygen induced degradation, and not moisture induced degradation, is the dominant factor that determines the stability of MAPI based solar cells under ambient operating conditions.

Table 3.1 Solar cell JV characteristics at 0.01 V s^{-1} under AM1.5G in a nitrogen atmosphere before and after 12 h at various conditions, using the average of ten devices. The device structure was FTO/c-TiO₂/m-TiO₂/MAPI/spiro-OMeTAD/Au. 'Light' samples were exposed to 1 Sun equivalent LED white light. 'Dark' samples were exposed to light for initial and final JV measurements only. 'Dry air' was supplied from bottle gas to ensure no humidity.

	Dark Nitrogen 0% RH	Light Nitrogen 0% RH	Dark Dry air 0% RH	Light Nitrogen 85% RH	Light Dry air 0% RH	Light Air 85% RH
0 h: Jsc (mA cm^{-2})	19.76 ± 1.68	19.86 ± 1.19	19.11 ± 1.18	19.27 ± 0.73	19.76 ± 1.68	19.16 ± 0.70
Voc (V)	1.00 ± 0.01	0.98 ± 0.03	0.99 ± 0.02	1.00 ± 0.03	1.00 ± 0.01	1.00 ± 0.03
FF	0.47 ± 0.03	0.48 ± 0.06	0.45 ± 0.02	0.45 ± 0.04	0.47 ± 0.03	0.45 ± 0.04
PCE (%)	9.30 ± 1.25	9.42 ± 1.04	8.48 ± 0.59	8.70 ± 1.06	9.30 ± 1.25	8.54 ± 1.00
12 h: Jsc (mA cm^{-2})	20.51 ± 0.45	20.52 ± 0.35	20.36 ± 0.49	18.51 ± 0.58	1.35 ± 0.47	1.17 ± 0.52
Voc (V)	1.02 ± 0.01	1.00 ± 0.03	0.98 ± 0.02	0.84 ± 0.04	0.71 ± 0.19	0.58 ± 0.14
FF	0.47 ± 0.03	0.49 ± 0.03	0.43 ± 0.06	0.48 ± 0.04	0.36 ± 0.10	0.29 ± 0.07
PCE (%)	9.81 ± 0.71	10.12 ± 0.43	8.62 ± 1.28	7.37 ± 0.53	0.36 ± 0.18	0.19 ± 0.14

3.2.2 Electron extraction effects on stability

Next, a mechanism to minimise the impact of light and oxygen induced degradation on MAPI device stability is considered. It has been reported that superoxide, O_2^- , (the reagent that initiates the degradation of MAPI) is generated through an electron transfer from the photo-excited state of the perovskite to molecular oxygen.³⁴ Moreover, it was demonstrated that the yield of superoxide generation can be decreased by the use of suitable electron acceptor layers within the MAPI film.³³ In this context, the electron acceptor layer functions to extract photo-generated electrons from the MAPI layer before they react with oxygen thereby reducing the yield of superoxide. As such, it is reasonable to expect that perovskite solar cell structures comprising of layers that are able to efficiently extract electrons would exhibit better stability, consistent with reports of promising stability for perovskite solar cells employing inorganic charge extraction layers.¹⁷ To test this hypothesis, the relative stability of three types of MAPI perovskite solar cell structures comprising different electron extractor layers were investigated. This includes (1) c-TiO₂/m-TiO₂/MAPI film; (2) c-TiO₂/MAPI film; and (3) c-TiO₂/m-Al₂O₃/MAPI film, as shown in Figure 3.3(a), where c- is a compact layer and m- is a mesoporous layer. All three devices employed doped spiro-OMeTAD and gold as the hole-transporting material and top metal contact respectively. Figure 3.3(b) shows the PCE versus time profile for devices aged in dry air and light. The time taken for the performance of these devices to drop by 50 % is 2.2 h, 0.6 h and 0.17 h, respectively. The relatively better stability of the c-TiO₂/m-TiO₂ structure is attributed to the superior electron extraction capability from the perovskite, as compared to c-TiO₂ and c-TiO₂/m-Al₂O₃ electrodes.

A further factor that can affect the rate of perovskite light and oxygen induced degradation is the crystal morphology and grain size.³⁵ The crystallisation of the perovskite precursor during film fabrication is controlled by a number of factors, including the substrate. As such, the four architectures presented in Figure 3.3(a) may cause variation in the perovskite crystal morphology. In this experiment the films were made from the same precursor solution and in the same environment to minimise differences of the perovskite layer between samples. It is therefore expected in this scenario the perovskite crystal is similar between samples and is not the reason for the different device stability.

MAPI photoluminescence (PL) quenching and superoxide yield experiments were employed to investigate the origin of the trend in device stability. Figure 3.3(c) presents the steady-state PL data for c-TiO₂/m-TiO₂/MAPI, c-TiO₂/MAPI, c-TiO₂/m-Al₂O₃/MAPI and glass/MAPI films. It is clear that all three electrode systems show reduced emission intensity relative to the glass/MAPI sample. By evaluation of the integrated areas of the respective spectra in Figure 3.3(c), it is found the yield of MAPI PL quenching is 85 % 78 % and 56 % for the c-TiO₂/m-TiO₂, c-TiO₂, c-TiO₂/m-Al₂O₃ films respectively. This trend in the efficiency of electron extraction between these three device architectures is expected due to the difference in surface area of mesoscopic architectures and due to the non-conducting properties of alumina.³⁶ The same trend in PL quenching efficiency was obtained from time-resolved PL measurement, as illustrated in Figure

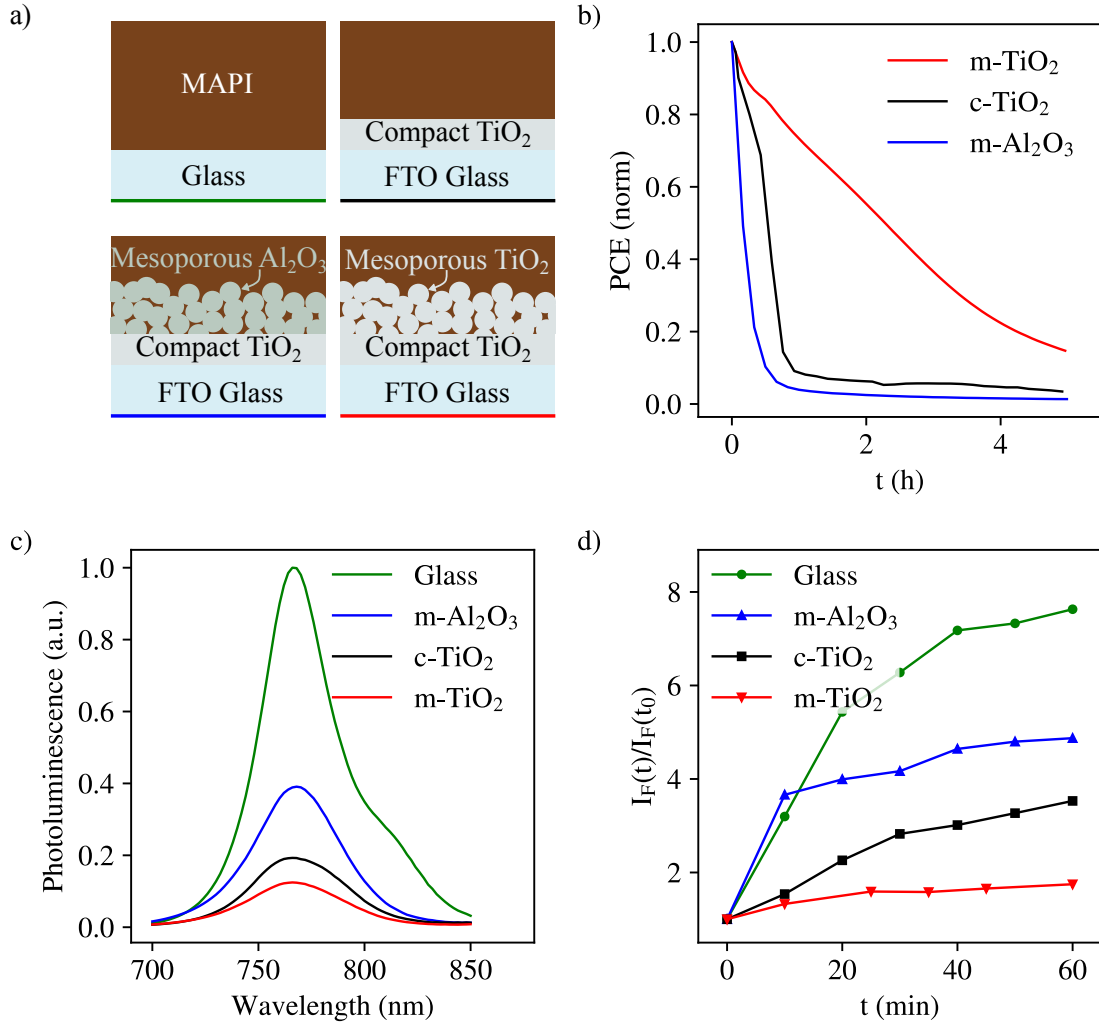


Figure 3.3 (a) Schematic of the four architectures used to investigate the effect of electron extraction efficiency on device stability. (b) Normalised power conversion efficiency, over time of three different MAPI solar cells aged in dry air and light with varying bottom interlayers: FTO/[extraction layer]/MAPI/spiro-OMeTAD/Au, where the extraction layer was c-TiO₂/m-TiO₂, c-TiO₂, and c-TiO₂/m-Al₂O₃. (c) MAPI photoluminescence spectra for three architectures relative to a MAPI control film (measured in the absence of spiro-OMeTAD/Au) using 485 nm excitation. The PL has been corrected for absorbance between the films. (d) Normalised fluorescence intensity at 610 nm (following 520 nm excitation) of the O₂⁻ probe solution. $I_F(t)$ is the probe fluorescence intensity maximum at time t , whilst $I_F(t_0)$ is the background fluorescence intensity of the probe at $t = 0$. The ratio $I_F(t)/I_F(t_0)$ is a measure of the yield of superoxide generation.

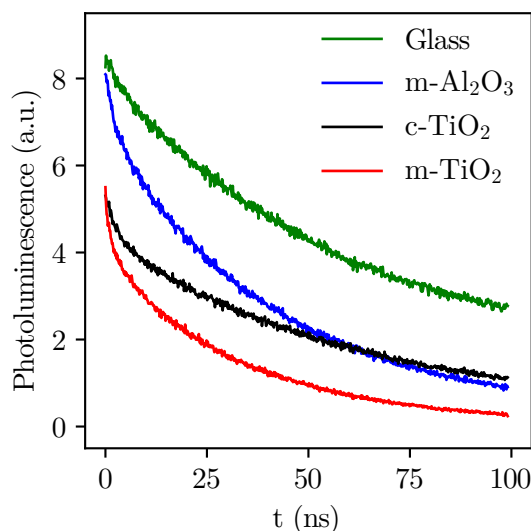


Figure 3.4 Time-resolved PL measurements taken at the peak emission wavelength of the MAPI perovskite devices incorporating varying architectures: FTO/[extraction layer]/MAPI/spiro-OMeTAD/Au, where the extraction layer was c-TiO₂/m-TiO₂, c-TiO₂, and c-TiO₂/m-Al₂O₃. A reference sample of glass/MAPI without a hole transport layer is also shown. Excitation at 485 nm of a 3 nJ cm⁻² pulse onto the MAPI film side with an instrument response time of 0.3 ns. Measurements were taken with the assistance of Diego Alonso Alvarez.

3.4. Next, the correlation between the yields of MAPI PL quenching and superoxide generation in the three films is considered. The presence of superoxide was detected, as previously, by using a fluorescent molecular probe, hydroethidine.³³ Figure 3.3(d) shows the rate of increase in probe emission ($I_F(t)/I_F(t_0)$ versus ageing time) as an assay of superoxide generation yield. As expected, a good correlation can be seen between the MAPI PL quenching efficiency and superoxide generation yield. Interestingly, it is apparent that the c-TiO₂/m-Al₂O₃/MAPI film exhibits a lower PL quenching efficiency and a higher superoxide yield as compared to the c-TiO₂/MAPI film. This is most likely due to: (i) the presence of the m-Al₂O₃ film reducing the effective electron extraction area of the c-TiO₂ layer and (ii) reduced crystal size of MAPI in c-TiO₂/m-Al₂O₃/MAPI relative to that in the ‘planar-type’ c-TiO₂/MAPI film. It is reasonable to suppose that both these factors would lead to poorer electron extraction and therefore an increased probability of electron transfer to oxygen. Taken together, the data presented in Figure 3.3 indicates that better electron extraction leads to better device stability. This improved stability derives from a reduction in the yield of superoxide generation as a consequence of better electron extraction from the MAPI film.

3.2.3 Electrically injected charge induced degradation

Further evidence for the importance of electron extraction for the stability of MAPI solar cells was obtained from device performance measurements as a function of externally applied bias in the presence of oxygen. Figure 3.5(a) shows the PCE versus time profile for solar cells biased

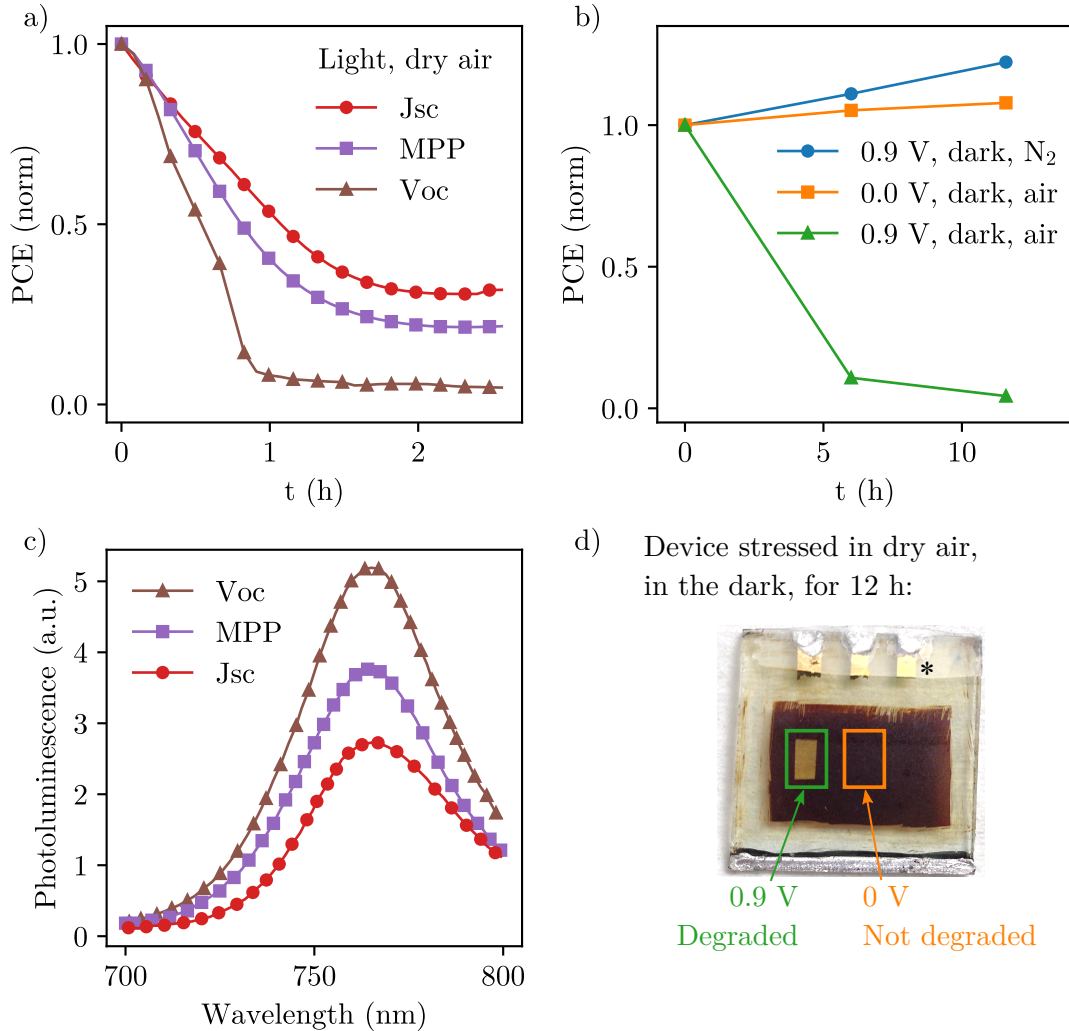


Figure 3.5 (a) PCE stability of FTO/c-TiO₂/MAPI/spiro-OMeTAD/Au solar cells under light and dry air. Data was collected with the solar cells biased at open circuit ($V_{bias} = 0.9$ V), short circuit ($V_{bias} = 0$ V) and maximum power point ($V_{bias} = 0.66$ V). (b) The relative PCE of solar cells aged in the dark in the presence of either dry air or nitrogen and under varying electrical bias of 0.9 V (giving an initial current density 20 mA cm⁻² or at 0 V). The ageing was performed in the dark but the PCE measurements were performed under 1 sun equivalent illumination using a white LED array. (c) Photoluminescence data measured at open circuit ($V_{bias} = 0.9$ V), short circuit ($V_{bias} = 0$ V) and maximum power point ($V_{bias} = 0.66$ V) employing 485 nm excitation. (d) A picture of the device degraded in the dark under bias, used in (c). The pixel held under bias can be seen to photo-bleach to a degraded yellow film, suggesting the formation of lead iodide. *Note the gold top contact has been removed to photograph the pixels.

at short-circuit ($V_{applied} = 0\text{ V}$, $J = 19\text{ mA cm}^{-2}$) and open-circuit ($V_{applied} = V_{oc} = 0.9\text{ V}$, $J = 0\text{ mA cm}^{-2}$). As expected, more rapid degradation is observed when the device is biased at open-circuit rather than short-circuit, consistent with better electron extraction under short circuit conditions. This enhanced electron extraction was confirmed by enhanced MAPI PL quenching at short-circuit compared to open-circuit (Figure 3.5(c)). These observations further highlight the importance to device stability of removing electrons from the photoactive layer before they can react with oxygen to form superoxide. Now the wider relevance of these observations to other electronic and optoelectronic devices that exploit the semiconducting properties of MAPI is considered. Thus far, it is shown that the degradation of MAPI solar cells can be triggered by the reaction of photo-generated electrons and oxygen. The next question that arises relates to whether degradation can also be induced by the reaction of electrically injected electrons and oxygen. In order to address this, the degradation of the MAPI solar cells in the dark (no illumination) under forward bias ($V_{applied} = 0.9\text{ V}$, $J = 20\text{ mA cm}^{-2}$) in a nitrogen or dry air environment is investigated. Device degradation in the dark was monitored by brief measurements of device photovoltaic PCE under light irradiation (Figure 3.5(b)), as well as by monitoring MAPI decolouration using a camera (Figure 3.5(d)). Remarkably, these results show MAPI devices degrade even in the dark when operating in the forward bias regime when oxygen is present. However, no such degradation was observed when the device was in a nitrogen atmosphere or in the absence of forward bias. The observation of device degradation under negative forward bias in the dark suggests that in the presence of oxygen, MAPI is fundamentally unstable when transporting electrons. This finding indicates that oxygen induced degradation of MAPI is likely to be important in limiting the operational stability of not only MAPI based solar cells, but also that of other electronic and optoelectronic devices employing MAPI as an electron transport material, such as LEDs and transistors.

Here it is shown MAPI thin films and solar cells degrade remarkably quickly, on timescales of minutes to a few hours when exposed to both light and oxygen. In organic solar cells, the presence of a metal top contact has been observed to substantially improve device stability under light / oxygen exposure, attributed to slow lateral oxygen diffusion kinetics through the organic layer.³⁷ It is apparent that for MAPI devices studied herein, the presence of a metal top contact does not appear to substantially enhance stability. Here it is unclear if the rapid oxygen diffusion is associated with the perovskite layer or with the hole transporting material and further work should be done to better understand this mechanism.

3.3 Conclusions

In summary, this work elucidates a major cause of the relatively low stability of MAPI solar cells when operating in ambient conditions and provides a pathway to address the problem. Specifically, it is demonstrated that light and oxygen induced degradation can be the dominant factor that determines the operational stability of MAPI solar cells in ambient conditions. Under these technologically important conditions, light and oxygen induced degradation is more rapid

than the more widely studied moisture induced degradation. This degradation can be slowed down by the integration of an efficient electron extraction layer within the device architecture. Specifically, better electron extraction leads to a reduction of the superoxide yield and an improvement in device stability. Further improvements in device stability can be expected through optimisation of the electron extraction efficiency within the device architecture (e.g. via the use of organic / molecular based electron extractor layers, surface modifiers and alternative inorganic materials). Finally, it is shown MAPI devices also degrade in the dark under negative forward bias when exposed to oxygen. The present findings suggest that oxygen induced degradation can influence the operational stability of not only solar cells but also other devices that utilise MAPI as an electron transporting material.

The work discussed in this chapter is based on state-of-the-art devices and topics of interest in 2016. Comments on how this relates to the field in 2018 are presented in Section 4.3.2.

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Chapter 4

Halide tuning for perovskite environmental stability

This chapter is based on the work published by Pont et al. in Journal Material Chemistry A, 2017.¹

The tunability of ions in the perovskite structure for maximising power conversion efficiency is well established. However, analogous studies on improving stability are not as rigorous. In this chapter, the stability of $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ varied from $x = 0$ to 1 is investigated in thin films and solar cells under controlled humidity, light, and oxygen conditions. It is demonstrated that higher bromide ratios increase tolerance to moisture, with MAPBr thin films being stable to 120 h stress under humidity, light and oxygen. Under light and dry air, partial bromide ($x < 1$) substitution does not enhance film stability significantly, with the corresponding solar cells degrading within two hours. In contrast, MAPBr films have improved stability, with device stability being limited by the organic hole transport layer. Photo-generated charge carriers in MAPBr thin films are quenched in the presence of oxygen and all halide ratios form superoxide, including the stable perovskite MAPBr. However, in contrast to perovskites containing iodide, superoxide does not degrade the MAPBr perovskite crystal. The chapter concludes that iodide limits the oxygen and light stability of $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ perovskites, but that MAPBr provides an opportunity to develop inherently stable high voltage photovoltaic devices and 4-terminal tandem solar cells.

4.1 Introduction

One property of the ABX_3 perovskite crystal structure is their ability to partially or fully substitute ions into the lattice, as discussed in Section 1.2.4. Certain criteria are required for the substitution, such as an equivalent charge of the ion and the relative size of the A, B, and X ions must meet the specifications given by the Goldschmidt tolerance factor.² For solar cell applications, common variations to MAPI include: B site replacement of tin for lead; X site replacement of bromide for iodide; and A site replacement of caesium or formamidinium for methylammonium.^{3–6} The change in crystal structure affects the optoelectronic performances and can be used to optimise the performance factors of solar cells.⁷ Although much work has been done to explore the potential tuning the optoelectronic properties of perovskite, little work has looked at the effect of stability. Herein, the halide tuning of methylammonium lead iodide-bromide ($MAP(I_{1-x}Br_x)_3$) perovskite stability is investigated under humidity, oxygen and/or light exposure. It is concluded the promising potential of methylammonium lead bromide to be stable under these stress conditions.

PSCs employing a mixture of halide anions (iodide and bromide) have been gaining much attention due not only to their high efficiency but also to their improved resistance to moisture degradation.³ Tuning the environmental stability of perovskites has been shown by Noh et al in 2013.³ The stability of the $MAP(I_{1-x}Br_x)_3$ with $x = 0, 0.06, 0.20$, and 0.29 was investigated at 50 % humidity in the dark and in air. For devices with $x \leq 0.06$ a rapid degradation was observed but the devices with $x \geq 0.20$ remained stable. This was associated with the different size of the halide ions resulting in smaller bromide ions initiating the transition to the cubic crystal structure. However, this work only looked at lower concentrations of bromide and modest humidity levels. It was also not undertaken at the operating conditions of a solar cell, i.e., it was without light exposure, which is a common trend of stability results stated in the literature to date. In the previous chapter, it was concluded a combination of light and oxygen is the dominant degradation mechanism in MAPI devices, with severe degradation occurring in less than two hours in some architectures.^{8,9} Here, the effect of methylammonium lead iodide/bromide mixed perovskites on stability is investigated, when exposed to humidity or light and oxygen. This work aims to provide insights into the ability of ‘ion tuning’ to enhance the thin film and device stability and compliment the impressive results on ion tuning in enhancing PSC efficiency.^{5,7} Furthermore, the effect of iodide inclusion in a mixed perovskite structure results in significant instability under light and oxygen conditions, whereas MAPBr films and PSCs have promising stability, with device stability being limited by the organic hole collection interlayer and not the perovskite layer.

4.2 Results and discussion

The mixed methylammonium iodide-bromide perovskite results in a shifting of the band gap with absorption onset at 760 nm for MAPI and 560 nm for MAPBr (Figure 4.1). One of the effects

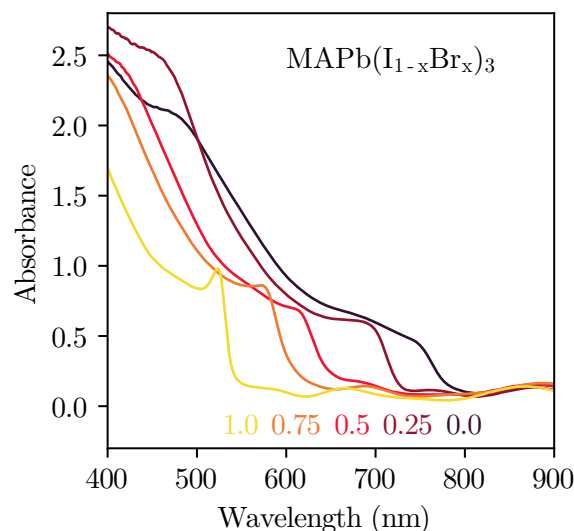


Figure 4.1 Absorbance spectra of mixed halide, $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$, perovskite thin film samples on glass. Increasing the bromide ratio results in absorbance onset shift from 760 nm to 560 nm.

is a change in colour from dark brown for MAPI to orange for MAPBr. The tunability of colour of solar cells is of interest for building-integrated photovoltaics due to the aesthetic control. From a physics perspective, the shift in the band gap has a dramatic effect on the maximum potential efficiency of a single junction solar cell due to the Shockley-Queisser limit.¹⁰ For MAPI with a band gap of 1.6 eV the maximum efficiency is 30 % whereas for MAPBr with a band gap of 2.3 eV the maximum efficiency is only 15 %. However, for tandem solar cell applications a range of bandgaps may be required, dependent on the sub-cells used. Thus, the bandgap tunability of the $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ series is potentially very beneficial for optimising the performance of tandem solar cells.

4.2.1 MAPIBr thin film environmental stability

To assess the stability of mixed halide perovskites, the material properties of neat films deposited on glass were first investigated, expanding on recent results reported on thin film samples.¹¹ A range of six concentrations of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$, from $x = 0$ to $x = 1$, were exposed to controlled environmental conditions to analyse the effect of mixed halide films to high humidity conditions and to light and dry air conditions. To investigate the hydration, the films were held at a controlled relative humidity (RH) within a nitrogen atmosphere in low light and the optical changes were monitored with a CCD camera. An inert atmosphere and low light levels ensured the degradation was isolated to effects from humidity only. This degradation mechanism causes the dark perovskite phase to form a visibly transparent mono-hydrated perovskite phase and therefore it is possible to monitor this degradation process via optical changes.¹² The humidity was incrementally adjusted from 80 % to 97 % over a series of days. Exemplar camera images from 13 h to 18 h of Figure 4.2(a) are presented in Table 4.1. To quantify the rate of degradation,

Table 4.1 Exemplar image analysis of $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ thin film hydration, with a step increase from 85 % to 90 % RH. At 85 % RH MAPI is already hydrated. At 90 % RH $\text{MAP}(\text{I}_{0.9}\text{Br}_{0.1})_3$ converts from the perovskite crystal structure to the mono-hydrated crystal structure, seen by the characteristic colour change from dark brown to colourless. Films with $x \geq 0.5$ remain stable at this humidity level.

t (h)	RH	MAP($\text{I}_{1-x}\text{Br}_x$) ₃ , x:				
		0.00	0.10	0.50	0.75	1.00
13.0	85%					
14.7	90%					
16.3	90%					
18.0	90%					

an assay of the optical degradation was calculated from the output of the CCD and normalised to pristine and fully degraded samples, explained in more detail in Section 2.2.2. The optical degradation of the $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ series under humid conditions are presented in Figure 4.2(a). It is apparent from this figure that films with increased bromide ratio have a higher tolerance to hydration degradation and are stable at higher levels of RH. Rapid degradation of MAPI to the mono-hydrate phase occurs at 85 % RH whereas $\text{MAP}(\text{I}_{0.5}\text{Br}_{0.5})_3$ does not significantly change below 95 % RH. Interestingly, for all halide ratios full reversibility of the films from the monohydrate phase to the perovskite phase was observed if films were kept in a nitrogen atmosphere and below the dew point (100 % RH); the dehydrate phase previously report in experiments in humid air was not observed.¹²

Next, the stability of the mixed halide perovskite photoactive films in the presence of oxygen and light is investigated; films were exposed to conditions of 1 Sun equivalent visible LED intensity and dry air. On exposure to these conditions, an optical change in the methylammonium lead iodide perovskite is observed with the absorption onset shifting from 780 nm to lead iodide at 520 nm.⁸ Therefore, it is possible to monitor the degradation via a change in the optical absorption of the $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ pristine films in Figure 4.1. Optical degradation in light and dry air for the series of mixed halide perovskites are presented in Figure 4.2(b). Control data in light and nitrogen do not significantly degrade, consistent with previous studies.⁹ Upon exposure to light and oxygen, for films containing iodide (i.e. $x < 1$) degradation is initiated after approximately equal time. In contrast, MAPBr thin films have remarkable stability under these conditions. After 130 h exposure to light and dry air, only a very small change in optical characteristics are observed. A time to 50 % optical change for the MAPBr is extrapolated to over 5500 h compared to 9.8 h for MAPI, more than two orders of magnitude improvement in stability.

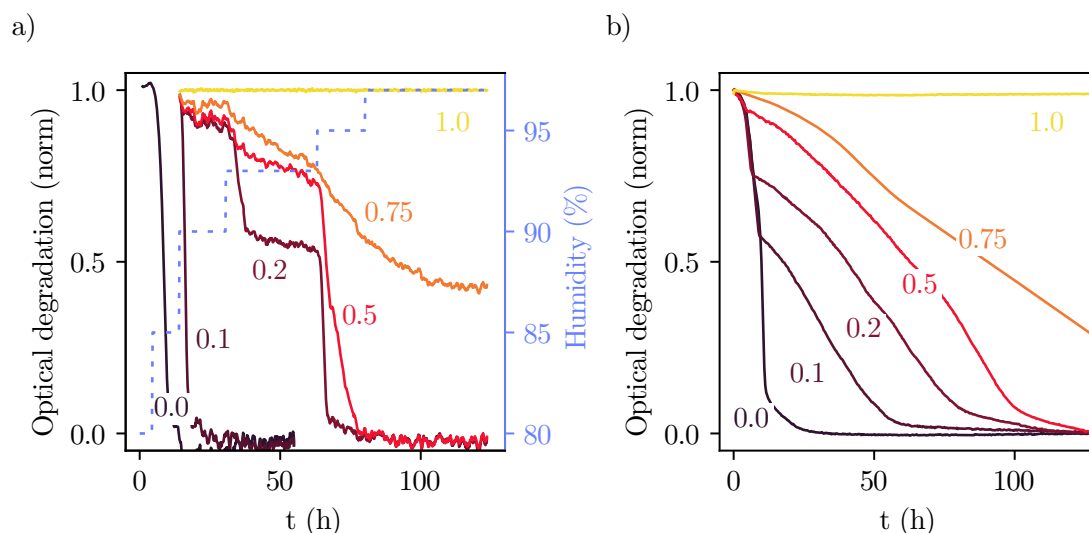


Figure 4.2 (a) Optical analysis of MAP(I_{1-x}Br_x)₃ films exposed to humid conditions in a nitrogen atmosphere. The humidity was incrementally increased over the course of 120 h from 80 % to 97 %. Increasing bromide ratio improved the stability but only when $x = 1$ did it not degrade. (b) Optical analysis of MAP(I_{1-x}Br_x)₃ films exposed to 1 Sun equivalent LED light in dry air. For $x < 1$, films start to degrade within the first three hours but increasing bromide ratio slows the rate of degradation. However, only when $x = 1$ does the perovskite is stable after 120 h.

Therefore, it is clear that in this system the bromide containing perovskite has far greater stability to both humidity and photo-oxidation stress compared to the iodide perovskite.

For the mixed halide films, increasing bromide concentration results in an increased time for complete degradation. Whereas the $x = 0$ film fully degrades after 10 h, the $x = 0.5$ film took over 100 h to fully degrade. In the optical property investigations of $x = 0.1$, 0.2, and 0.5 two clear stages of degradation are seen, with a faster phase during the first 10 h followed by a slower phase of degradation. Increased bromine content reduces the ratio of the fast to slow phase, but it does not significantly affect the kinetics. This fast degradation phase can be assigned most obviously to degradation of iodide clusters of the mixed structure, as it is consistent with the degradation rate of neat MAPI. Therefore, it appears bromide provides little screening against the degradation of iodide regions within mixed halide perovskite films. Previous studies in literature demonstrated the importance of iodide in perovskite stability, which is likely the reason mixed halide degradation is observed but $x = 1$ perovskite maintains impressive stability.^{13,14} In mixed halide films up to 75 % bromide, the bromide does not prolong the initiation of degradation in light and oxygen but rather only extends the time of complete degradation. This contrasts to the effect of bromide substitution on hydration induced degradation, where the onset of degradation is seen to shift to higher levels of RH with increased bromide ratio. In summary, under oxygen and light stress, MAPBr films are over two orders of magnitude more stable than MAPI, but that in mixed halide systems, the presence of ≥ 75 % iodide results in a rapid initial optical absorption degradation.

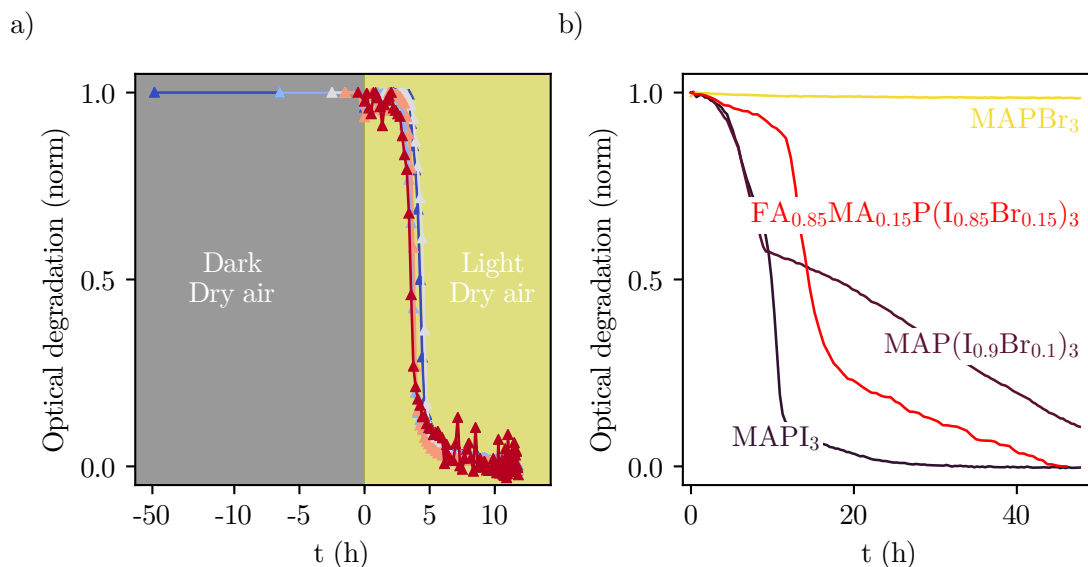


Figure 4.3 a) Optical tracking of thin film MAPI samples after exposure to 1 Sun equivalent LED light and dry air. Before exposure to light and dry air, films were kept in the dark in ambient air for varying lengths of time. Note the scale is linear between -2 and 2 and logarithmic outside of this range. b) Optical tracking of $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$, $\text{MAP}(\text{I}_{0.9}\text{Br}_{0.1})_3$, MAPI_3 , and MAPBr_3 thin films exposed to 1 Sun equivalent LED light in dry air. $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ with little improvement in stability compared to MAPBr_3 under these environmental conditions.

It is apparent from Figure 4.2(b) that even for the least stable MAPI films, there is a time delay of ≈ 4 h from initiating the light soaking before the onset of significant optical degradation. In order to identify if this time delay is associated with the kinetics of oxygen diffusion into the films, the effect of dry air exposure time prior to light turn on is investigated. Films fabricated in a nitrogen-filled glovebox were exposed to the air for times varying from 0.5 h to 48 h before being placed under illumination. From the resulting optical degradation results (Figure 4.3(a)) it is seen that all films degraded at the same rate independent of the air soaking time. Even for a film with only 0.5 h exposure to air there is a delayed onset of 4 h before a dramatic change is observed. This suggests that prior oxygen diffusion into the film does not limit the degradation process observed in these conditions. Rather it appears more likely that this time delay in the onset of light and oxygen induced degradation is due to degradation products resulting in an autocatalytic reaction sequence.

High performing perovskite devices often contain mixed organic cations in the perovskite structure, typically both formamidinium, $\text{CH}_2(\text{NH}_2)_2$ (FA), and methylammonium, CH_3NH_3 (MA), cations.^{5,15,16} To address the effect of such organic cation substitution, optical degradation data was also collected for a thin film of $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ in dry air and under one Sun illumination, as this has been reported as an optimal formulation for high-efficiency devices. Figure 4.3(b) demonstrates similar overall degradation kinetics to the equivalent $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ films, apart from a longer time delay before the onset of degradation. This result suggests the

oxygen and light degradation mechanism is not significantly affected by the organic cation in this system and that the oxygen and light reaction may also limit the stability of mixed organic cation perovskite materials.

4.2.2 MAPIBr device environmental stability

Thus far the stability studies have concluded $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ thin films have non-trivial effects from halide tuning. Next, the effect of oxygen and light degradation on device performance is investigated. Preliminary investigations were done with the following device architecture: $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3/\text{spiro-OMeTAD}/\text{Au}$, where spiro-OMeTAD was doped with Li-TFSI, tBP and V_2O_5 . The initial device current-voltage characteristics are presented in Figure 4.4(a) and stability in dry air and light in Figure 4.4(b). Under these conditions, it is found that this architecture is particularly sensitive to light and oxygen, which is attributed to the sensitivity of the HTM.^{17,18} Therefore doped spiro-OMeTAD will unlikely be a good candidate for the development of environmentally stable perovskite solar cells.

Due to the instability of spiro-OMeTAD, stability studies were done with an alternative HTM material, to enable selective investigations of the perovskite layer. P3HT was selected and it was used undoped to mitigate additional instabilities resulting from dopants.¹⁸ Full details of device fabrication are given in Section 2.1. In short, mesoporous titania perovskite devices with P3HT as a hole transporting material (HTM) were fabricated in a $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/\text{perovskite}/\text{P3HT}/\text{Au}$ architecture.

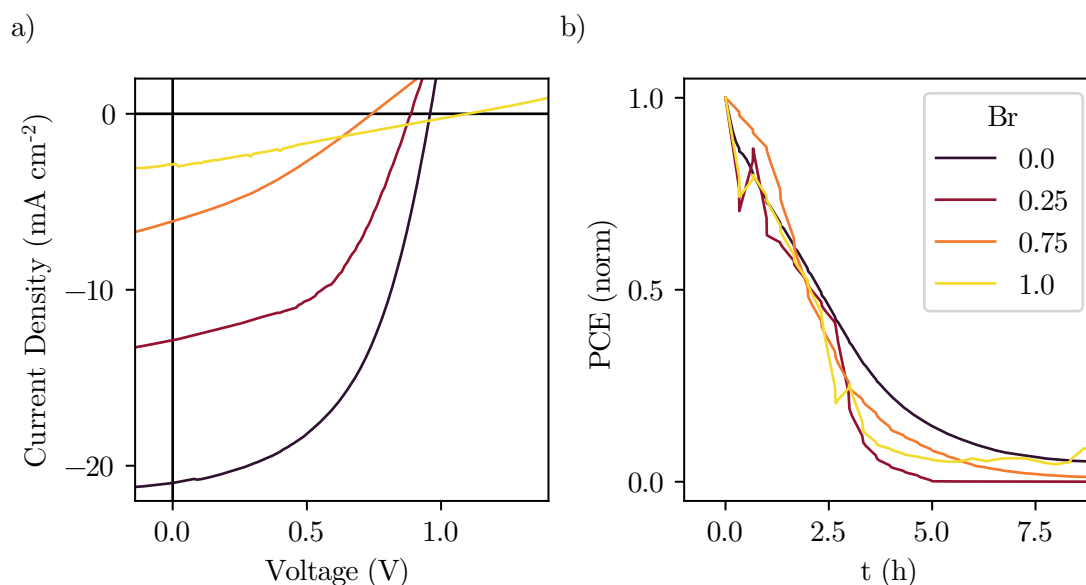


Figure 4.4 (a) Current-voltage measurements under AM1.5G solar simulator of $\text{FTO}/\text{c-TiO}_2/\text{m-TiO}_2/\text{perovskite}/\text{spiro-OMeTAD}/\text{Au}$ devices, where the perovskite was $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ ($x=0, 0.25, 0.75, 1$). A drop in the current is seen due to lower absorbance. (b) Normalised power conversion data of these devices exposed to 1 sun equivalent LED light and dry air, held at open circuit between measurements. No difference in stability between I:Br ratios is observed suggesting it is not the limiting factor but instead it is the HTM spiro-OMeTAD.

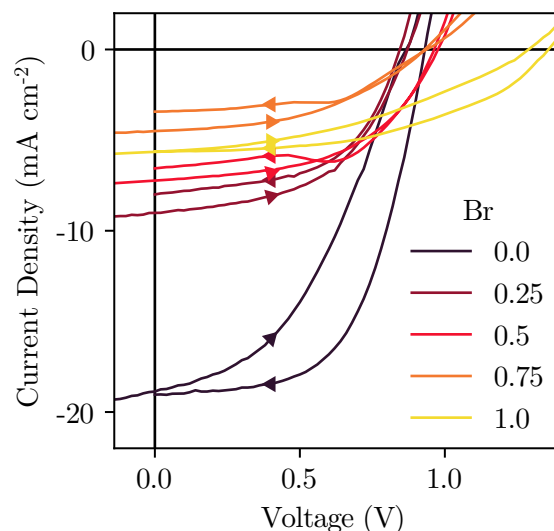


Figure 4.5 Current-voltage scan of pristine FTO/c-TiO₂/m-TiO₂/MAP(I_{1-x}Br_x)₃/ undoped-P3HT/Au devices measured with xenon lamp AM1.5G simulated solar spectrum at a scan rate of 0.125 V s⁻¹. A sweep scan was performed to measure the hysteresis of the device. Initially the device is held at open circuit conditions for 15 s to stabilise followed by scanning from -0.5 V to 1.5 V and back to 0 V.

TiO₂/MAP(I_{1-x}Br_x)₃/P3HT/Au architecture where c-TiO₂ is a titanium dioxide compact layer and m-TiO₂ is a mesoporous titanium dioxide layer. Current-voltage characteristics of devices in Figure 4.5(a) and Table 4.2 illustrate two trends: firstly a drop in short-circuit current due to decreased absorption of AM1.5G with a higher band gap and secondly, an increase in open circuit voltage due to the larger bandgap. The pristine devices were then exposed to light and dry air in the environmental chamber and their photovoltaic performance monitored as a function of time under the same 1 Sun equivalent LED light exposure as that employed for the thin film studies.

The MAP(I_{1-x}Br_x)₃ solar cell device stability data are presented in Figure 4.6(a). This figure demonstrates $x < 1$ perovskite PCE degradation is approximately equal, with a 50 % drop in PCE after 1 h to 1.5 h. In contrast, MAPBr demonstrates relatively good stability, with a fivefold increase in device lifetime relative to the iodine-containing devices. In all cases, the loss of PCE was primarily caused by a loss of photocurrent. As for the film optical degradation data, the $x = 0.75$ device is substantially less stable than the $x = 1$ device; these two devices differ in optical band gap by only 50 nm (Figure 4.1), clearly indicating that the increase in stability for the all bromine device does not primarily derive from a difference in light absorption. It is also apparent that the device PCE degradation data that devices exhibit much faster degradation than the film optical degradation under the same conditions. This indicates that even small amounts of degradation in the perovskite photoactive layer can dramatically reduce the performance of a device. This conclusion is supported by observations in Figure 4.2(b); here, the optical degradation data has an initial fast decay for all ratios of x , due to degradation of iodide-rich

Table 4.2 Current-voltage characteristics for pristine mixed halide devices measured under AM1.5G solar simulation as presented in Figure 4.5(a), with architecture FTO/c-TiO₂/m-TiO₂/MAP(I_{1-x}Br_x)₃/undoped-P3HT/Au. Un-doped P3HT results in non-optimised device parameters.

	MAP(I _{1-x} Br _x), x:				
	0.00	0.25	0.50	0.75	1.00
J _{sc} (mA cm ⁻²)	19.04	9.01	7.23	4.50	5.65
V _{oc} (V)	0.87	0.85	0.97	0.94	1.33
FF	0.63	0.54	0.57	0.45	0.49
PCE (%)	10.36	4.11	4.02	1.89	3.72

perovskite clusters within the mixed halide crystal. This appears to result in a catastrophic drop of device PCE. In summary, MAPBr solar cells are significantly more resistant to light and oxygen induced degradation compared to MAPI solar cells, however, the inclusion of bromide in a mixed halide photovoltaic device does not increase the stability under this stress condition.

Although MAPBr solar cell exhibits a five-fold increase in device efficiency lifetime under light and oxygen compared to MAPI devices (Figure 4.6(a)), this is still substantially less than the approximately 500-fold increase in optical degradation time observed in the film data (Figure 4.2(b)). Previous studies in the literature have reported reactions between device interlayers

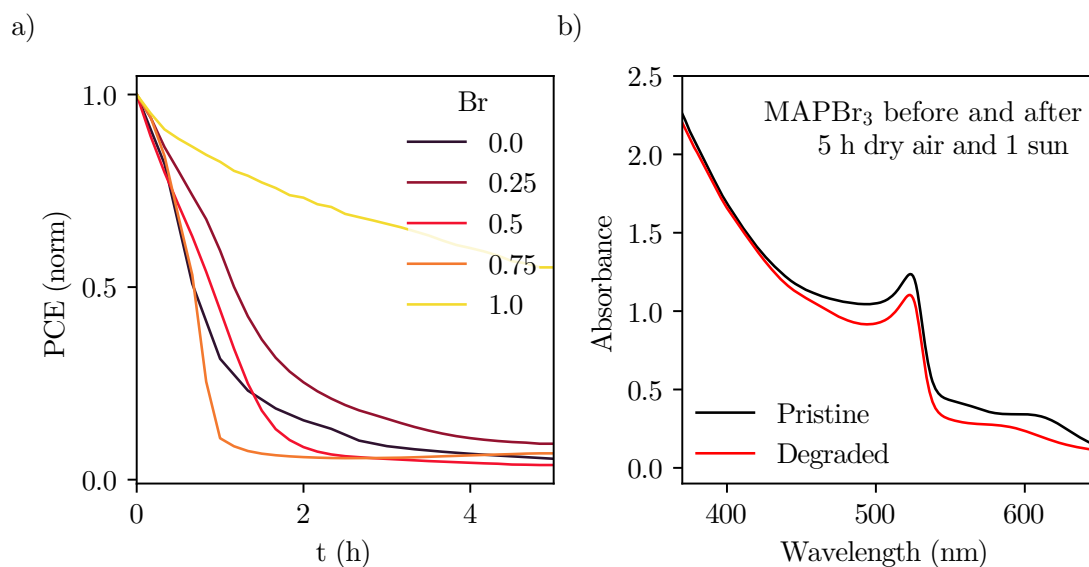


Figure 4.6 (a) Power conversion data of MAP(I_{1-x}Br_x)₃ solar cell devices exposed to 1 Sun equivalent LED light and dry air. The device structure is FTO/c-TiO₂/m-TiO₂/MAP(I_{1-x}Br_x)₃/P3HT/Au. Devices were held at open circuit between measurements. Rapid device degradation after 2 h is shown for devices with $x < 1$ but $x = 1$ shows stability up 5 h. (b) Absorbance data of a MAPBr device before and after degradation in 5 h in light and dry air (note: a point next to the Au contact was measured to allow for transmission measurements). Photobleaching is observed above 520 nm, where only P3HT absorbs, and not MAPBr.

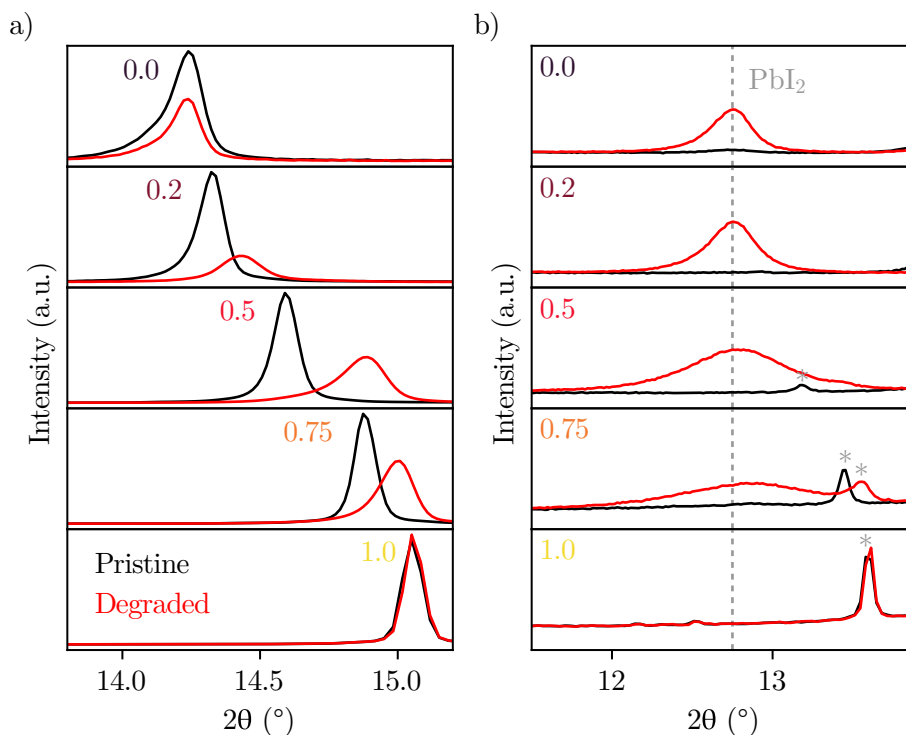


Figure 4.7 (a) XRD analysis of MAP(I_{1-x}Br_x)₃ thin films before and after exposure to light and dry air for 6 h. Increasing bromide ratio results in a shift from the tetragonal (220) to the cubic (200) peaks. Degraded films shift to the higher angles, indicating an increased bromide fraction in the perovskite phase. Only MAPBr remains stable. (b) XRD analysis of lead iodide formation at all halide ratios except MAPBr. At lower iodide ratios, the full width at half maximum (FWHM) greatly increases due to an increased amorphous structure. (* indicates peaks from perovskite.)

can limit stability, such as the gold top electrode diffusing to the perovskite active layer.¹⁹ Therefore, the instability of MAPBr devices may be due to an interaction between the perovskite layer and gold. However, at the operating conditions used here (1 Sun equivalent LED light) the temperature was found to be 35 °C; as such, it is expected that insignificant metallic diffusion will occur over the timescales measured.¹⁹ Upon further investigation, it was found that the organic P3HT HTM layer in these devices exhibited significant photo-bleaching upon this exposure to light and oxygen. This is apparent as a loss of absorbance between 450 nm to 650 nm, a wavelength range corresponding to P3HT absorption and distinct from MAPBr absorbance (with an onset at $\approx$ 525 nm, see Figure 4.6(b)). Therefore, it appears the decrease in performance of the MAPBr devices is primarily due to degradation of the organic P3HT HTM layer, and subsequent loss of charge transport properties from the perovskite to the electrode indicating that the perovskite layer is not limiting stability in this instance.

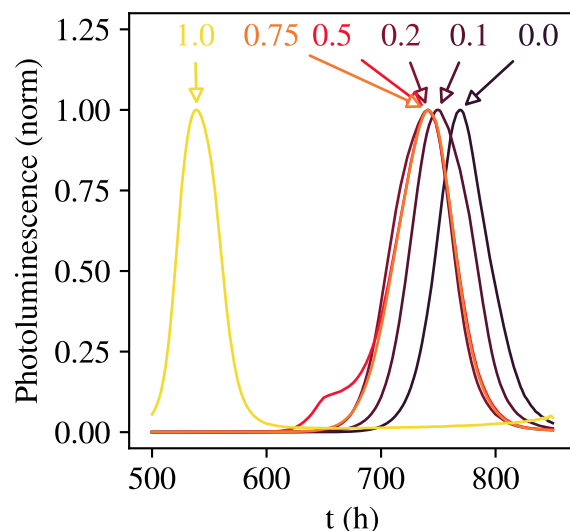


Figure 4.8 Normalised photoluminescence spectra of mixed halide, $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$, perovskite films showing the emission from the lower-energy iodide-rich domains.

4.2.3 Determining the origin of the improved stability of MAPBr

To understand in more detail the mechanism(s) causing the oxygen and light induced degradation in thin film absorbance and device PCE, further characterisation measurements were performed on mixed halide perovskite thin films. Figure 4.7 presents XRD spectral analysis of the crystal lattice before and after 6 h light and oxygen exposure. In Figure 4.7(a), the data indicate a continuous shift from the tetragonal MAPI peak at 14.2° to the cubic MAPBr peak at 15.05° with increasing bromide concentrations, indicating that these films form an intermixed structure on the length scale of X-ray diffraction (XRD). Following exposure to light and dry air for 6 h, the crystal lattice peak of the mixed halide films ($x = 0.25, 0.5$ and 0.75) can be seen to shift towards higher angles, indicating a reduction in iodide content in the perovskite regions of the film. Furthermore, the XRD peak of lead iodide can be seen to form in all iodide containing perovskites (Figure 4.7(b)) but no lead bromide peak is observed. Note the peak at 13.6° is the perovskite crystal, hence the shift seen in the $x = 0.75$ after degradation. At lower iodide concentrations a larger full width at half maximum (FWHM) of the lead iodide peak is observed indicating a more amorphous structure. These data are indicative that for the mixed halide films, light and oxygen degradation results in a reduction of iodide content in the perovskite phase of the film (and therefore increased bromide content of this phase), and the concomitant formation of lead iodide.

Photoluminescence (PL) measurements were taken of $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ thin films to probe the radiative recombination processes in the mixed halide crystals. Figure 4.8 presents the emission maxima close to the lower energy MAPI emission peak independent of bromide content, consistent with previously reported results.²⁰ This emission data indicates the presence of small MAPI clusters in all mixed halide films, with photoluminescence from the mixed films primarily

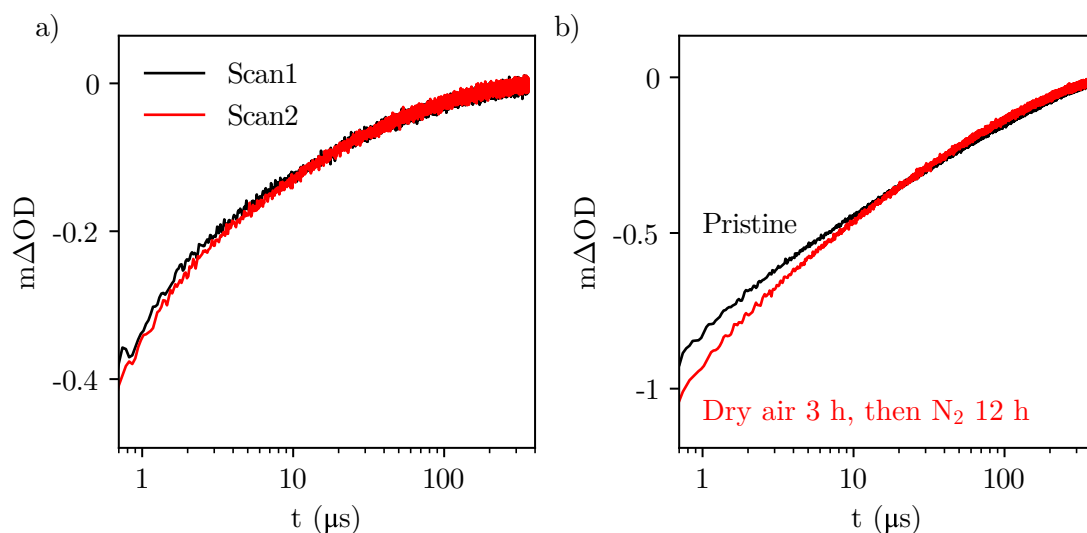


Figure 4.9 Transient absorption measurements of MAPBr films at 520 nm and exciting at 420 nm probing the ground state bleaching signal. (a) A repeated TAS measurement does not change the signal. (b) A trace of a sample before and after being exposed to 3 h dry air followed by 12 h nitrogen purging also not significantly changing the signal.

deriving from these clusters. This observation contrasts the XRD data in Figure 4.7(a) where an even shift is observed from the MAPI to MAPBr crystal structure. The difference between PL and XRD data is due to these measurements probing different lengths; XRD diffraction has a probing length-scale larger than that of PL. In mixed halide films, the iodide and bromide are sufficiently mixed such that the XRD observes the crystal size and orientation of an average of the pristine iodide and bromide (tetragonal and cubic perovskite structures). However, within the mixed crystal there are areas of unbalanced iodide-bromide ratio which are too small to affect XRD results but significant enough to permit PL. The PL is emitted from the lower energy level iodide-rich areas. A crystal landscape of deviating iodide:bromide ratio helps explain the non-linear trend of stability improvement with bromide addition to MAPI; for example, although $\text{MAP}(\text{I}_{0.25}\text{Br}_{0.725})_3$ is predominately bromide there are likely regions of high iodide concentration that may result in an initiation of the degradation. From these results, it is apparent ion diffusion is a factor in the environmental stability of mixed halide perovskites.

To monitor the presence of long-lived charges in MAPBr, transient absorption spectroscopy (TAS) measurements were performed. Following pulsed laser excitation, the ground state bleach signal at 530 nm was monitored as an assay of the lifetime of these charges (following previous literature reports). To confirm the validity of the measurements two calibration experiments were done; firstly, repeated TAS measurements on a sample shows there is perovskite stability to the high-intensity laser (Figure 4.9(a)). Secondly, exposure to the presence of oxygen without light does not affect the charge dynamics of the perovskite and therefore oxygen in the dark does not affect perovskite stability (Figure 4.9(b)). However, in Figure 4.10 exposure to oxygen results

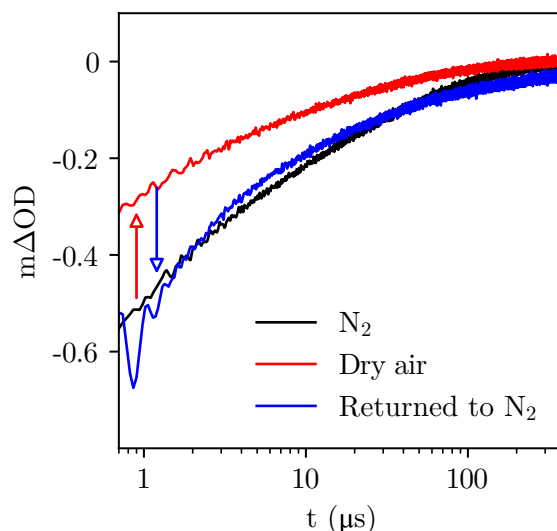


Figure 4.10 Transient absorption measurements of MAPBr thin films excited at 400 nm and probing the photobleaching signal at 520 nm. On exposure to air, quenching of the charge carrier population can be seen by a reduction in the photo-bleaching signal and returns with re-exposure to nitrogen.

in significant reversible quenching in the amplitude of the ground state bleach signal, indicating that oxygen can indeed react with photo-generated MAPBr charge carriers.

Previously the degradation mechanism for MAPI thin films and devices under light and oxygen stress has been correlated with a reaction series involving the transfer of photo-generated electrons in MAPI to molecular oxygen, resulting in the formation of superoxide (O_2^-). The previous TAS measurements conclude MAPBr charge carriers are quenched in oxygen but it is not clear if superoxide is still formed. To assess the role of superoxide in the degradation of mixed halide perovskite films under exposure to light and oxygen, $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ films were monitored using a previously reported method.⁸ The assay uses a fluorescence probe (hydroethidine) where the signal is increased upon exposure to superoxide; Figure 4.11(a) presents exemplary results of hydroethidine fluorescence when in a toluene solution with a perovskite film illuminated with light and bubbled with dry air. Monitoring the superoxide generation over a 60 min period demonstrates all halide ratios produce superoxide (Figure 4.11(b)). When these data are normalised for differences in film light absorption (detailed in Section 2.2.2) it is apparent that the rate of superoxide generation is independent of the iodide / bromide content of the film. From these results, it is concluded the increased stability of MAPBr thin films does not result from an inability to generate superoxide.

Superoxide can act as a proton scavenging free radical which has been suggested to break down the MAPI perovskite structure via a deprotonation reaction of the methylammonium group.⁸ The Pauling electronegativity of bromine is 0.03 higher compared to iodine and therefore will increase the stabilisation to the methylammonium group due to the increased inter-molecular interaction. To test if exchanging iodide for bromide leads to a change in the reactivity

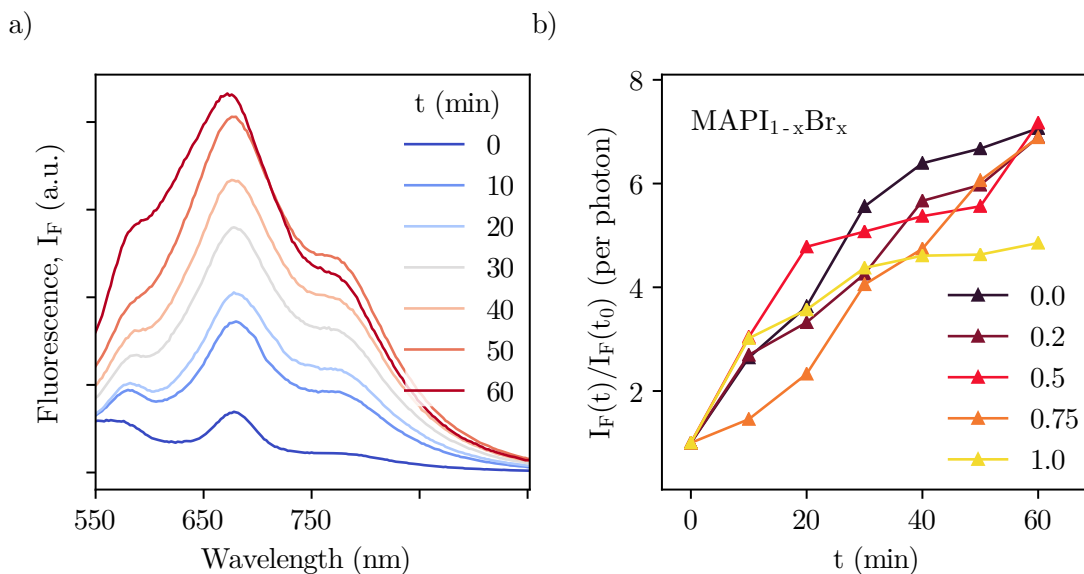


Figure 4.11 (a) Photoluminescence of the superoxide probe solution in toluene solution with a MAPI film exposed to light and bubbled with dry air. Superoxide generation results in an increase in the amplitude of the probe PL. (b) Photoluminescence intensity of the superoxide probe at 610 nm, with excitation at 520 nm, where $I_F(t)$ is the photoluminescence intensity at time t and $I_F(t_0)$ is the initial photoluminescence of the probe. A spectral mismatch correction between the thin film absorption and tungsten–halogen light source gives the superoxide generation all halide ratios relative to MAPI as detailed in Section 2.2.2. Measurements were taken with the assistance of Nicholas Aristidou.

between methylammonium cations and the superoxide species, a solution study of the reaction of $\text{CH}_3\text{NH}_3\text{Br}$ and $\text{CH}_3\text{NH}_3\text{I}$ with potassium superoxide was done, following previous literature procedures.⁸ Proton NMR spectra of the reaction products in Figure 4.12 presents the signal for the NH_3^+ and the methyl group protons shift up-field upon addition of potassium superoxide, which is consistent with the deprotonation of the ammonium group to form methylamine (CH_3NH_2) suggesting there is no difference in reactivity of the cation owed to the changing anion species. It is suggested that the reason superoxide does not degrade the MAPBr structure is due to the increased thermodynamic stability of the crystal structure, compared to MAPI. A report of first-principle calculations demonstrates MAPI is thermodynamically unstable at room temperature with respect to a phase segregation to $\text{CH}_3\text{NH}_3\text{I}_3$ and PbI_2 with a negative energy cost of -0.060 eV/f.u. to -0.063 eV/f.u..²¹ In contrast, MAPBr is thermodynamically stable compared to the corresponding phase segregation to $\text{CH}_3\text{NH}_3\text{Br}_3$ and PbBr_3 with a positive energy cost of 0.077 eV/f.u. to 0.065 eV/f.u..²¹ This result indicates that the crystal structure of MAPBr is thermodynamically more stable than MAPI, which appears to be the most likely reason superoxide degrades the MAPBr perovskite structure at a dramatically slower rate and the reason why in the mixed halide films, the iodide component of the film is preferentially degraded to lead iodide.

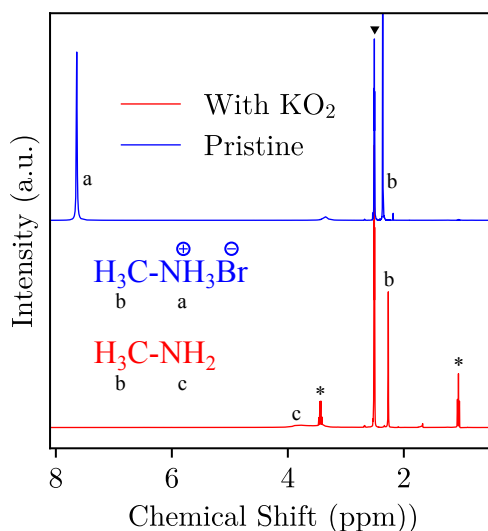


Figure 4.12 NMR spectra of a reference methylammonium bromide sample before (top) and after (after) the addition of potassium superoxide demonstrating the reactivity of MAPBr to superoxide.

4.3 Conclusions

4.3.1 Summary

In summary, this work indicates the major instability of MAPI devices to light and oxygen is also seen in mixed iodide/bromide $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ devices; however, in MAPBr both films and devices show significantly improved stability in these conditions. XRD measurements illustrate the iodide perovskite degrading separately to the bromide phase in mixed films. The improved stability of MAPBr films and devices is not derived from lower yields of superoxide formation but rather is attributed to the increased thermodynamic stability of the MAPBr crystal structure. Promisingly, the stability of bromide perovskite devices under light and oxygen stress was found to be limited by the organic HTM interlayer and not by the perovskite photoactive layer. With the development of stable interlayers unsealed MAPBr devices can be produced with excellent stability in ambient air under irradiation, with potential application in high voltage or 4-terminal tandem solar cells.

4.3.2 Recent literature on perovskite stability

The field of perovskite photovoltaic research is rapidly changing. Since this study in 2016, there have been significant developments in state-of-the-art device performance and stability. The environmental stability of MAPI devices continues to be limited by light and oxygen, and only small improvements in the lifetime have been made.²² However, alternative strategies have resulted in operational stability of thousands of hours. For example, the use of amino acids and small molecules as partial substitution of the MA organic cation.²³ The larger cations

are thought to replace crystal termination of the A site, inhibiting the oxygen degradation process. Another strategy has been tuning of the perovskite ions and optimising of the interlayers. Although halide tuning and cation tuning does not work to dramatically increase environmental stability as described here, the addition of inorganic caesium into the perovskite A site can improve stability.⁵ The triple cation (methylammonium, formamidinium, and caesium) is not as sensitive to transport layers and diffusion of metal contacts. Tailoring of both the interlayers and perovskite ions has led to >1000 h unencapsulated stability under operating conditions.²⁴ Due to the current impressive stability reported for perovskites, this issue is no longer thought to be the major limitation it once was. A large effort of work is now focused on encapsulated stability as this is thought to be the most relevant for practical applications.

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Chapter 5

Morphological stability of PS:PCBM thin films under illumination and thermal stress

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The intricate acceptor-donor morphology in the bulk heterojunction of a solar cell significantly affects device performance. While illumination is known to cause fullerene dimerisation and thermal stress de-dimerisation, the operation of solar cells involves exposure to both combined effects and so it is not well understood. This will be addressed in the following chapter by examining the combination of illumination and temperature on blends of PCBM and polystyrene, supported on PEDOT:PSS. UV-vis spectroscopy is used to quantify PCBM dimerisation, time-resolved neutron reflectivity to resolve the vertical composition stratification and atomic force microscopy for demixing and coarsening of the thin film topography. Under thermal stress at the blend glass transition temperature PCBM diffuses to the PEDOT:PSS interface. By modelling this enrichment, it is shown that PCBM dimers are effectively immobile over the timescales investigated.

5.1 Introduction

To fulfil the potential of organic solar cells both efficiency and long-term stability require improvement, as discussed in Section 1.2.3.² While efficient encapsulation can mitigate some extrinsic factors, exposure to light and heat are intrinsic to solar cell operation and thus remain the focus of considerable research.^{3–5} Morphological changes within the active layer of a bulk heterojunction, for instance via crystallisation, or demixing and coarsening of the donor/acceptor blend, can evidently result in performance loss (as well as an improvement).^{6–8} However, the initial light exposure of organic solar cells often results in ‘burn-in’, manifested by an initial exponential loss of device efficiency.^{9,10} The exact mechanism has remained elusive however correlations with a number of factors including polymer crystallinity,^{11,12} spinodal demixing,¹³ fullerene and polymer cross-linking,¹⁴ reactions with device contacts,¹⁵ and fullerene dimerisation^{16,17} have been proposed. While many studies have shown the beneficial effects of PCBM dimerisation on device stability,^{18,19} there are other reports that suggest detrimental^{16,17} or neutral²⁰ effects to PCE upon illumination. Evidently, a range of failure processes are likely responsible for the diverse ‘burn-in’ and ‘stabilisation’ observations, and further work in this area is needed.

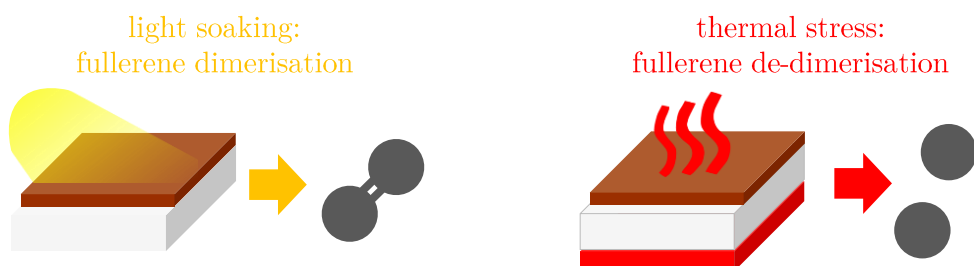


Figure 5.1 Under illumination fullerenes can undergo a 2+2 cycloaddition reaction to form dimers (left), whilst under elevated temperatures this reaction can be reversed (right). This chapter will attempt to investigate the interplay of illumination and thermal stress during solar cell *in-operando* conditions on the morphological stability.

The practical utilisation of solar cells involves the *simultaneous* exposure to varying temperature and light intensity over time, with diurnal and seasonal fluctuations, and these effects are adversarial and competitive, at least in what concerns fullerene photo-transformations. With these ideas in mind, the interplay between PCBM photo-induced dimerisation and thermally-induced decomposition is examined to assess their overall impact in the morphological stability of a polymer:fullerene blend. This is the first *in-operando* investigation coupling thermal and light stresses on polymer:PCBM thin films.

To monitor the PCBM dimerisation within thin films, a UV-visible absorbance feature was employed as an assay, which has previously been shown to correlate to PCBM dimerisation.¹¹ The complete experimental details are given in the experimental section. In short, five PS:PCBM blend ratios were studied ranging from 20% to 80%. In Figure 5.2(a) the absorbance of the films

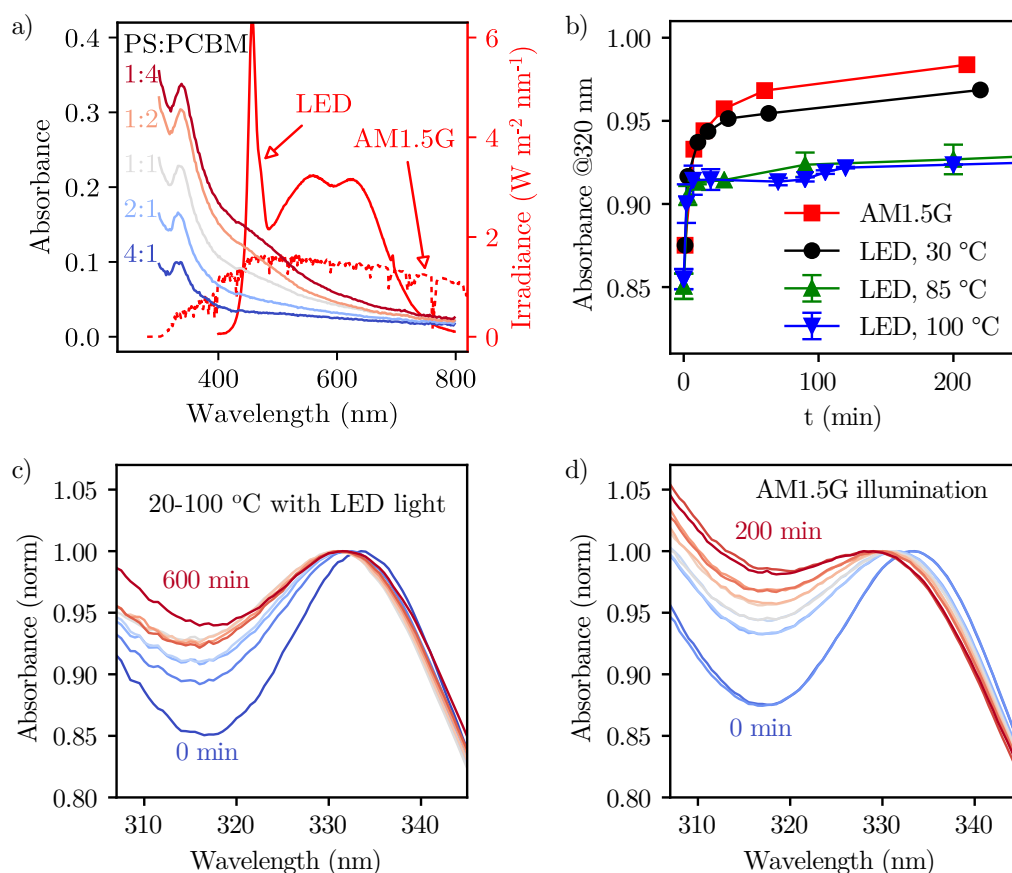


Figure 5.2 (a) Absorbance spectra of PS:PCBM films and the LED spectrum used for light soaking within this study. AM1.5G is included as a comparison. (b) Absorbance at 320 nm under variation illumination conditions of a glass/PEDOT:PSS/PS:PCBM (35:65) film, used as an assay of dimerisation. Normalised UV absorbance spectra of a representative 35:65 PS:PCBM film, (c), annealed from 20 °C to 100 °C over 120 min and then at 100 °C for a further 480 min all under LED white light at 1 Sun equivalent (following the procedure Figures 5.4(a)) and (d) under AM1.5G illumination. The peak minima at 320 nm for (c) and (d) are plotted in (b), in blue and red respectively.

are compared with the LED irradiance and the AM1.5G solar irradiance. Polymer blend films of ≈ 100 nm were spun cast on glass/PEDOT:PSS substrates and illuminated (1 Sun equivalent) in a nitrogen atmosphere for prescribed time intervals. A white LED (spectrum shown in Figure 5.2(a)) was used and the intensity calibrated to ensure similar absorbance compared to illumination under an AM1.5G solar simulator. To determine the dimerisation a change in the absorbance spectrum is used. The absorbance spectra are normalised to the peak intensity between the 330 nm to 340 nm band, to account for minor measurement variability, where example spectra are shown for LED illumination while annealing from 20 °C to 100 °C and under an AM1.5G solar simulator presented in Figures 5.2(c) and 5.2(d), respectively. Polystyrene is featureless in this range and does not show any changes. The value of the peak minimum between 310 nm to 320 nm is taken as an assay of dimerisation (in relative terms), which is

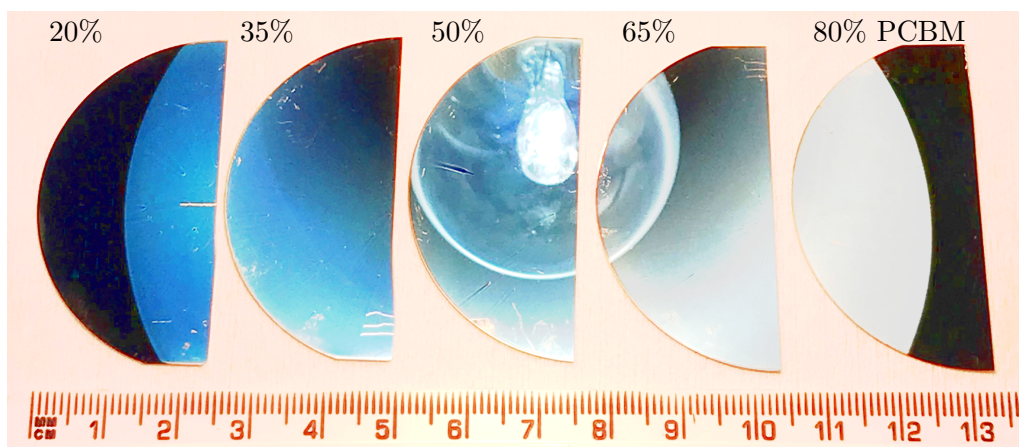


Figure 5.3 Representative Si/PEDOT:PSS/PS:PCBM samples of various compositions, exhibiting high uniformity, over a large area. These were used for neutron reflectivity measurements. (N.B. the samples were split in half and intentionally scratched after NR measurements for subsequent topographical analysis.)

shown in Figure 5.2(b). In Figure 5.2(b) dimerisation is found to be similar under AM1.5G solar simulator compared to the LED irradiance used. At elevated temperatures the steady state dimer concentration lowers as the dimer decomposition starts to dominate.

Samples for neutron reflectivity measurements used silicon wafers as a substrate. This enabled a distinct interface to resolve for fitting the neutron specular reflections. Solutions of PS:PCBM at varying blend ratios were spun onto the substrates giving uniform thin films. Examples of the consistency of the film quality for all the blend ratios are shown in Figure 5.3. As neutron reflectivity measurements average over an area of several square centimetres it is very important to ensure homogeneous film morphology. It should be noted the samples were split in half and intentionally scratched for subsequent analysis. Measurements of the film height at the centre and edge of the sample are found to be consistent. The homogeneity of the film gives confidence to the neutron reflectivity analysis discussed later in this chapter.

5.2 Results and discussion

Given the complexities regarding the system-dependence of stability, a model system of PCBM and an amorphous non-conjugated polymer, polystyrene (PS), is selected. This makes it possible to resolve the physical-chemical changes of PCBM alone. The active layer is deposited on PEDOT:PSS to ensure representative bottom interface properties of standard devices. The sample architecture is thus Si/PEDOT:PSS/PS:PCBM where the PCBM concentration was varied from 20 % to 80 %. Figure 5.4 illustrates the experimental plan, which investigates the separate and combined effects of light exposure and thermal exposure.

Two thermal profiles were examined: (i) ‘isothermal’ conditions at 85 °C, corresponding to usual thermal stress tests, for 10 h, followed by annealing at 120 °C in the dark, and (ii) a ‘thermal ramp’ from 20 °C to 100 °C, approaching the glass transition temperature, T_g , of the

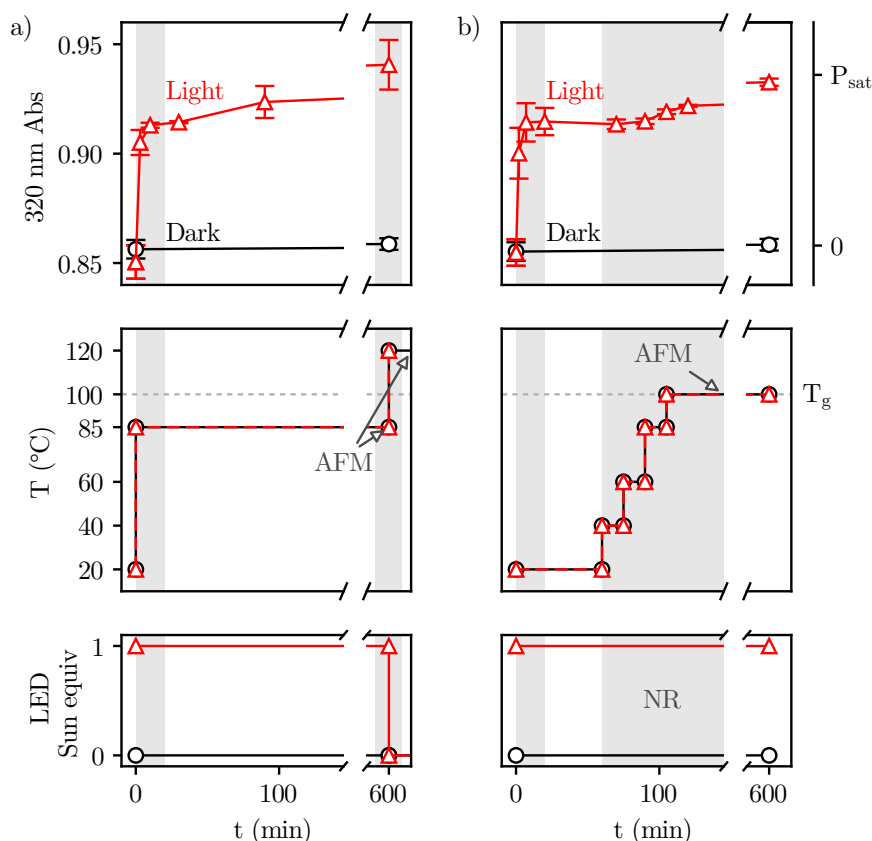


Figure 5.4 Conditions of (a) isothermal stress and (b) thermal ramping, with (red) and without (black) illumination investigated in this chapter. The top panels show PCBM dimer concentration estimated by UV-vis spectroscopy (as discussed in Figure 5.2). The middle and bottom panels show the temperature and illumination profiles. Shaded areas correspond to neutron reflectivity (NR) measurements and arrows highlight atomic force microscopy (AFM) measurements. Samples used in this study have the architecture Si/PEDOT:PSS/PS:PCBM and varying blend ratios, with $\phi(PCBM)=0.2, 0.35, 0.5, 0.65, 0.8$ mass fraction.

PS matrix. These are illustrated in the middle panels of Figures 5.4. Each profile was examined both under ‘dark’ and ‘light’ conditions (1 Sun equivalent, white light), depicted in the bottom panels. UV-vis spectroscopy was employed to estimate the PCBM dimer:monomer population, using a previously-reported absorbance feature at 320 nm discussed earlier.²¹ Populations for the four conditions studied are given in the top panel of Figure 5.4, shown here for a 0.65:0.35 PS:PCBM blend. Under these conditions, the PCBM dimer concentration was found to approach saturation within 30 min of illumination, while under dark (control) conditions PCBM remains in the monomer form. Representative UV-vis absorbance data are shown in Figure 5.2.

5.2.1 Isothermal annealing at 85 °C

The morphological stability of polymer:PCBM films was monitored by AFM following an isothermal profile at 85 °C, with and without illumination. Figures 5.5(a) and (b) shows the AFM

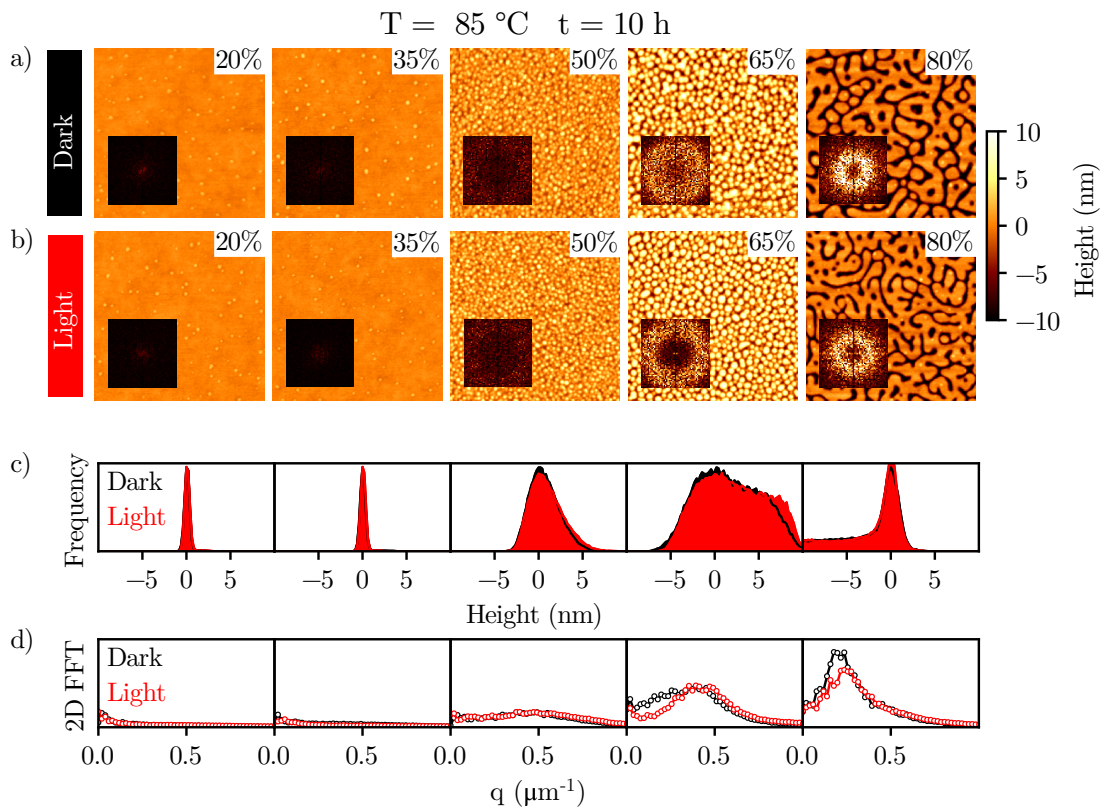


Figure 5.5 AFM topography of PS:PCBM samples annealed at $85\text{ }^{\circ}\text{C}$ for 10 h in the dark, (a), and upon illumination (1 Sun equivalent), (b), for 600 min at various PCBM concentrations (20 to 80% PCBM), following the profile in Figure 5.4(a). The AFM image is a $5\text{ }\mu\text{m}$ square representative sample. The inset shows the 2D Fourier transforms of the AFM topography. (c) The AFM height histogram. (d) The radial average of the 2D Fourier transform shown in (a) and (b).

topographical analysis of PS:PCBM blends of various composition, after 10 h of thermal stress at $85\text{ }^{\circ}\text{C}$, in both dark and light conditions respectively. From 20 % to 80 % PCBM loading there is a large variation in blend morphology, which is reminiscent of nucleation at low PCBM loading to spinodal decomposition at 80 % PCBM, accompanied by an increase of pattern amplitude. The inset in the images is the corresponding 2D Fourier transform, showing the clear ring shape for the spinodal structure at 80 % PCBM. Various experimental observables were employed to compare topographical differences upon light and thermal stress. A height histogram is shown in Figure 5.5(c) and the radially-averaged Fourier transform of the AFM height data in Figure 5.5(d). For all compositions, similar profiles are found for samples annealed in the light or dark, within measurement uncertainty (sample to sample variability).

Neutron reflectivity measurements of the PS:PCBM samples with varying blend ratios were acquired to probe the PCBM stratification within PS:PCBM films. The bulk scattering length densities (SLD) of the blends, and of neat reference films of PS and PCBM, are compared with the corresponding PCBM compositions, as shown in Figure 5.6. The trend of SLD in the bulk of

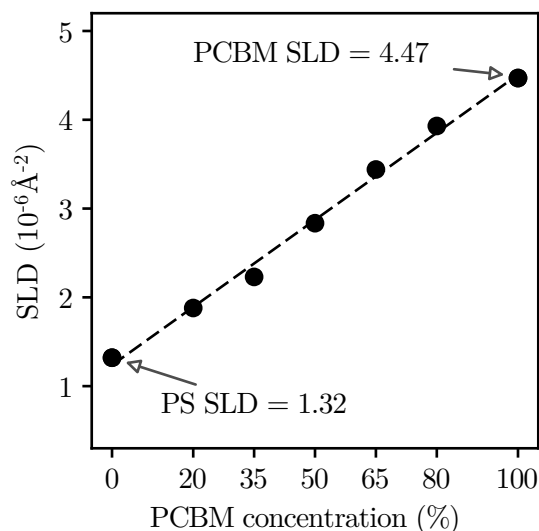


Figure 5.6 Scattering length density within the bulk of PS:PCBM thin films as extracted from the fit to the neutron reflectivity data of pristine samples presented in Figure 5.7. The dashed line shows the linear correlation, as expected.

the film against PCBM concentration is linear, as expected. Therefore, the SLD of the thin film can be used as an assay of the PCBM concentration perpendicular to the film substrate.

Figure 5.7 shows NR data for pristine and annealed samples (10 h at 85 °C), in both dark and light conditions, at all compositions investigated. The solid lines are fits to the data with corresponding scattering length density (SLD) profiles shown in Figure 5.7(b). On top of the 12 Å silicon oxide layer, the PEDOT:PSS layer thickness ranged from 295 Å to 305 Å, with an SLD of $1.61 \times 10^{-6} \text{Å}^{-2}$. The bulk SLD reflected the concentration ratios of the PS:PCBM mixtures, considering $\text{SLD}(\text{PS}) \approx 1.32 \times 10^{-6} \text{Å}^{-2}$ and $\text{SLD}(\text{PCBM}) \approx 4.47 \times 10^{-6} \text{Å}^{-2}$ determined from NR measurements of neat samples. The composition is broadly uniform throughout the film, especially for high and low PCBM loading (while the intermediate compositions are likely affected by surface roughness, as shown in Figure 5.7). For 50 % and 65 % PCBM loading there is a slight depletion of PCBM at the PEDOT:PSS interface, as previously reported.^{22,23} The pristine samples with low PCBM loading show a modest PCBM enrichment at the top surface.

Under these conditions significant morphological change is not expected as 85 °C is below the glass transition temperature of the polymer matrix ($T_g(\text{PS}) \approx 100 \text{°C}$), which is not expected to be significantly affected by the addition of fullerenes.^{24,25} While photoexcitation with energy greater than the bandgap can relax to the band edge, potentially releasing excess energy as a phonon, and in turn cause local temperature hot spots, such photo-induced local heating effects, if present, are modest and do not result in morphological instability, even in the vicinity of $T_g(\text{PS})$. Even though photochemical changes are evidently taking place under illumination, as shown in Figure 5.4(a), these do not impact morphology, either in terms of topography or vertical stratification, since the glassy polymer matrix restricts fullerene mobility at this relatively modest, but standard thermal stress condition.

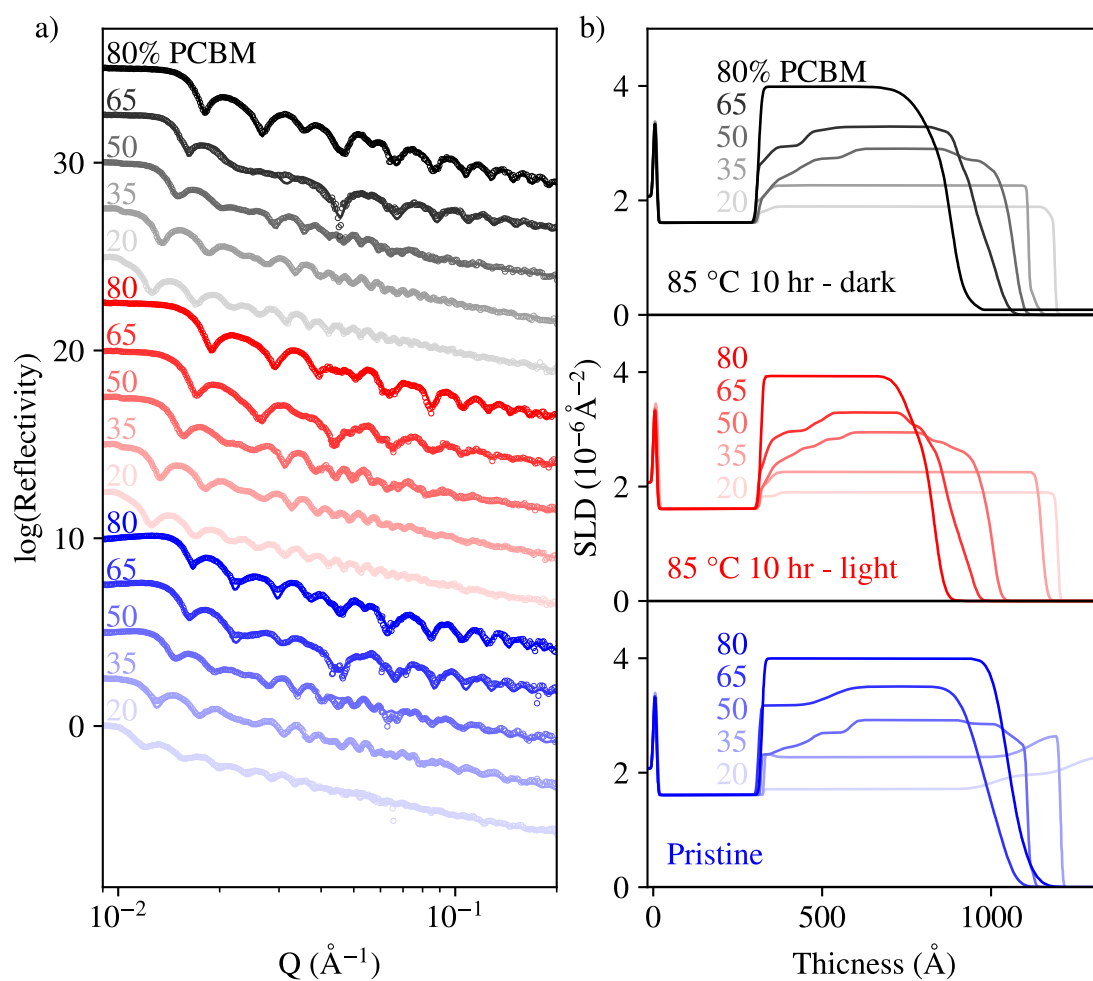


Figure 5.7 (a) Neutron reflectivity data and fits (solid line) and (b) fitted SLD profiles of PS:PCBM (20% to 80% PCBM) samples for three conditions: 'as-cast' (pristine, blue); after 10 h isothermal 85 °C annealing under light exposure (red) and in the dark (black). After annealing under light stress, or in the dark, little change is seen the stratification of the films, corroborating the AFM results. At lower PCBM concentrations a slight relaxation of PCBM from the top interface is observed.

5.2.2 Thermal stress above the glass transition temperature

Next, the effect of thermal stress above the T_g of the polymer matrix is considered, namely at 120 °C in the dark, following *prior* light exposure (10 h, 1 Sun equivalent) or a dark control. AFM measurements of the 20:80 PS:PCBM blends were acquired at various time intervals, as shown in Figures 5.8(a) and 5.8(b) for dark and light conditions, respectively. Insets show the 2D Fourier transforms of the AFM images, from which a characteristic spinodal length scale q_m can be extracted from the position of the maximum intensity of the spinodal ring (as shown in Figure 5.8(d)). Films not previously illuminated exhibit rapid coarsening of the spinodal structure and their topography relaxes, manifested by a decrease in image contrast. By comparison, morphology coarsening of pre-light-soaked films is effectively delayed (by ≈ 60 min). For the pre-illuminated sample, the AFM height histogram after 300 min (Figure 5.8(c)) is approximately equivalent to that of the dark sample after only 25 min annealing at 120 °C. The AFM root mean square (RMS) roughness are compared in Figure 5.8(e) and show that the pre-illuminated film relaxes over much longer timescales than the dark sample. From a morphological perspective, coarsening appears to take place via a hydrodynamic relaxation process. The radially-averaged 2D Fourier transforms of the AFM height data, Figure 5.8(f), shows that pre-illuminated samples exhibit a time-invariant plateau before coarsening commences. The corresponding peak wavenumber q_m follows a power law time-dependence, as expected; however, the power is much less than one which is expected under thin-film confinement.²⁶ This lag time is interpreted as due to the time required for thermal decomposition (or “de-dimerisation”) of PCBM to occur, thus enabling sufficient mobility that is required for the coarsening of the spinodal structure. The timescale agrees with previous data that show after 60 min annealing at 120 °C the dimer concentration reduces by ≈ 50 %.¹⁹ These results show that, at temperatures greater than the matrix T_g , the presence of dimers inhibits the relaxation of the spinodal morphology, and significant decomposition must occur before the mechanism can initiate. Dimerisation has thus a stabilisation effect of the morphology which is visible at these thermal stresses.

5.2.3 Annealing from 20 to 100 °C with *in-situ* time-resolved NR

Following the thermal ramp from room temperature to 100 °C, AFM data compare the topographical stability of all blend compositions exposed to thermal stress without and with illumination, in Figures 5.9(a) and 5.9(b), respectively. Qualitatively, a lower contrast can be seen in the dark samples, further quantified in narrowing of the height histogram for illuminated samples, Figure 5.9(c), which show narrower height distributions compared to the illuminated films. Films annealed at 100 °C with simultaneous illumination (Figure 5.5(b)) are equal to samples annealed below T_g at 85 °C (Figure 5.9(a,b)) suggesting morphological stability has been imparted by the light. The 2D Fourier transform data, shown in Figure 5.9(d), indicate that the periodicity of the structure is not significantly affected by these parameters at these timescales, except for a modest peak shift toward lower q for dark samples of intermediate compositions, which is expected upon coarsening.

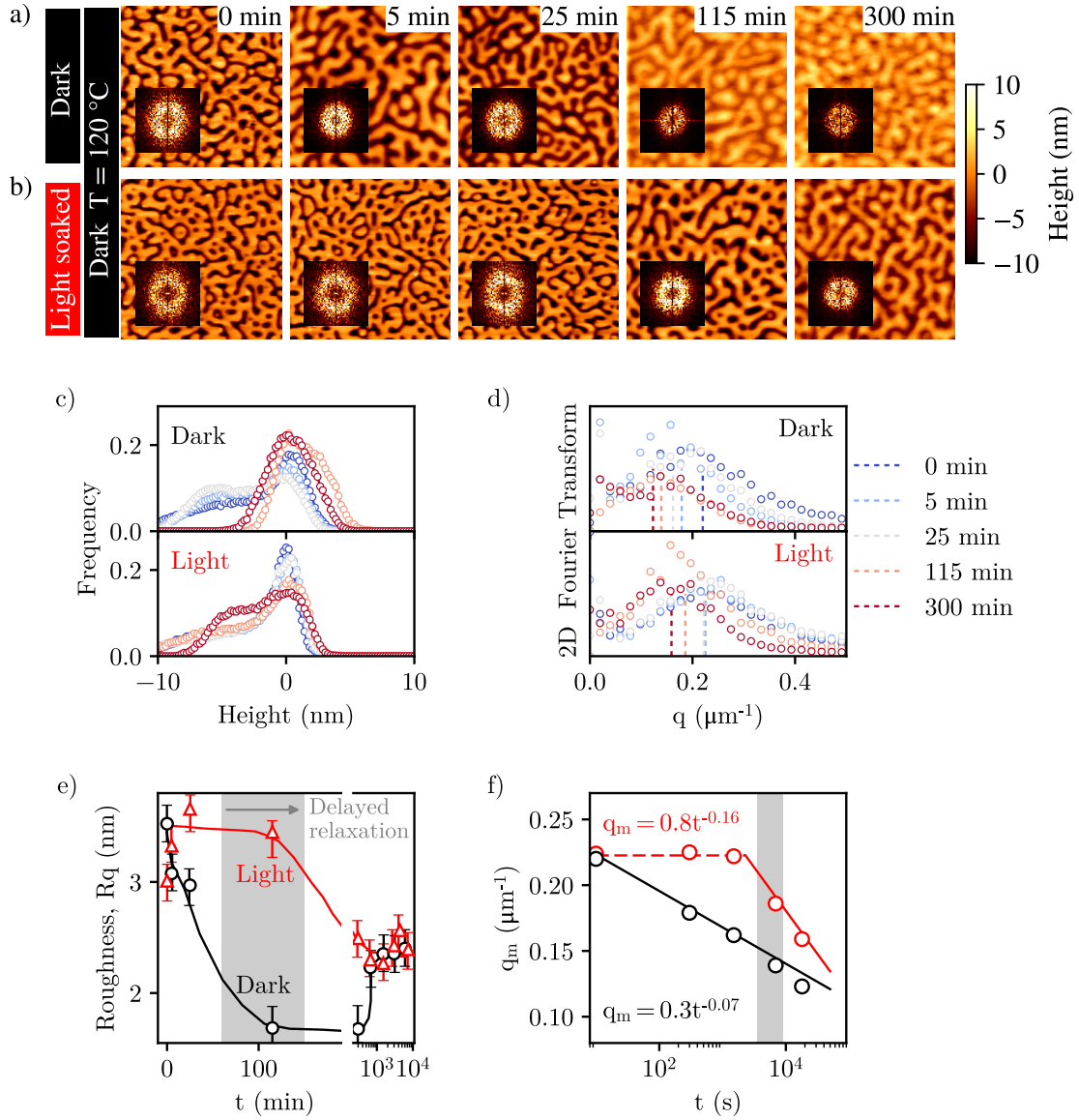


Figure 5.8 (a) AFM images of 20:80 PS:PCBM blends annealed at 120 °C (> T_g of PS), in the dark, following 85 °C stress for 10 h, without (a) and with (b) light soaking. The AFM image is a 5 μm square representative sample. Insets are 2D Fourier transforms. (c) Corresponding AFM height histogram. (d) The radial average of the 2D Fourier transform. (e) AFM root mean squared (RMS) roughness. (f) The peak position of the 2D Fourier transform, q_m , showing a delayed structural relaxation of the blend with prior light exposure. The shaded areas in (e) and (f) indicate the relaxation onset, interpreted as the time required for sufficient dimer decomposition to enable morphological coarsening.

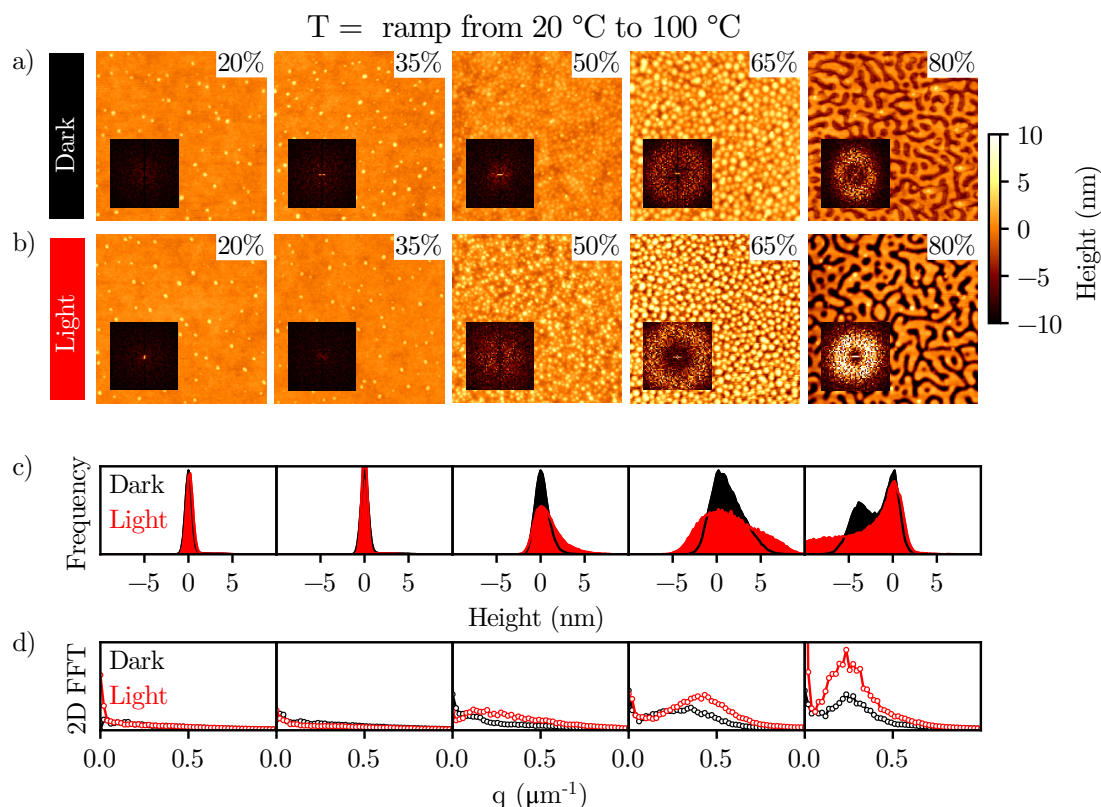


Figure 5.9 AFM images following thermal ramping from room temperature to 100 °C in the dark, (a), and light, (b), (depicted in Figure 5.4(b)) for PS:PCBM blends of all compositions investigated, showing characteristic nucleation and spinodal morphologies. The AFM image is a 5 μm square representative sample. A significant relaxation of the topography is observed for the blends annealed in the dark, shown by a reduction in contrast of the AFM images and narrowing of the height histograms, (b). (c) A radial average of the 2D Fourier transforms (shown in the insets of (a) and (b)).

Root mean squared (RMS) roughness in Figure 5.10 provide arguably the clearest observation of the enhanced stability: data for samples initially illuminated and thermally stressed at 100 °C (for 30 min) superpose with low-temperature data, with or without illumination, and are morphologically ‘stable’ (up to this time and temperature), while dark samples thermally stressed at 100 °C are unstable. The relaxation of the topography corroborates the observations of *in-situ* NR data (Figure 5.12) which will be discussed later.

To complement the analysis of the topographical stability from the AFM data, NR with *in-situ* thermal stress from room temperature to 100 °C ($\approx T_g$) is used to probe the stratification of the cross-sectional composition in PS:PCBM blends. This was done for all PS:PCBM blend ratios with and without light stress. Figure 5.11 presents exemplar NR data of a 50:50 PS:PCBM blend annealed from room temperature to 100 °C (in the dark), corresponding to the temperature profile shown in Figure 5.4(a). The data show no significant changes occur in the PCBM cross-sectional distribution until 100 °C, when the T_g of the PS matrix is reached. However, after

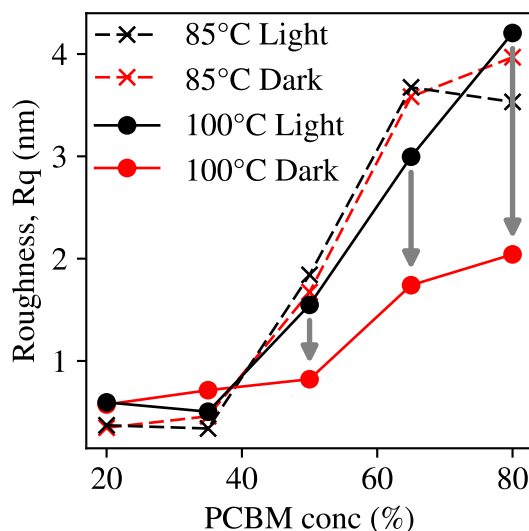


Figure 5.10 Root mean square (RMS) roughness of the AFM images for PS:PCBM samples annealed at 85 °C for 10 h and 100 °C ($\approx T_g$) for 0.5 h, with and without light. Only samples annealed at 100 °C without light exposure show a relaxation in roughness, whereas samples annealed with light do not relax due to dimerisation suppressing morphological changes.

30 min annealing at 100 °C a rapid enrichment of PCBM is observed at the PEDOT:PSS interface, quantified later. The enrichment observed here in PCDTBT:PCBM films agrees with reported results of annealed P3HT:PCBM films.²⁷

Figure 5.12 shows NR data for all PS:PCBM compositions studied before and after the temperature ramp to 100 °C, with and without light. For all samples an enrichment of PCBM at the PEDOT:PSS interface is observed, except the 80 % PCBM samples. The enrichment layer is approximately 20 Å to 30 Å thick, corresponding to 1-3 fullerene units²⁸ coating the PEDOT:PSS surface and the maximum SLD of this layer approaches that of neat PCBM. There is a slight relaxation seen in the surface roughness shown in Figure 5.12, corroborating the AFM data in Figure 5.10. It can also be seen that the PEDOT:PSS layer contracts slightly upon annealing, likely due to dehydration of this hydrophilic layer, which is expected.

In order to quantify the interplay between dimer formation and morphological instability under light and thermal stress, time-resolved neutron reflectivity measurements of PS:PCBM films were carried out during thermal annealing at 100 °C ($\approx T_g(\text{PS})$) with and without simultaneous illumination (1 Sun equivalent). Representative NR data (and SLD fit profiles) for 50:50 PS:PCBM without (a, c) and with (b, d) light exposure are shown in Figure 5.13. The solids lines are batch fits to the data. The scattering length density (SLD) profiles quantify the kinetics of PCBM enrichment at the PEDOT:PSS (bottom) interface, which is much greater for ‘dark’ than ‘light’ conditions. The enrichment of PCBM is calculated from the time-resolved NR data to determine the rate of enrichment at the interface over time, as shown in Figure 5.13. In fact, for the dark samples, the PCBM concentration at the PEDOT:PSS interface saturates at the SLD value of neat PCBM. In solar cell operation, the aggregation of electron-accepting PCBM towards

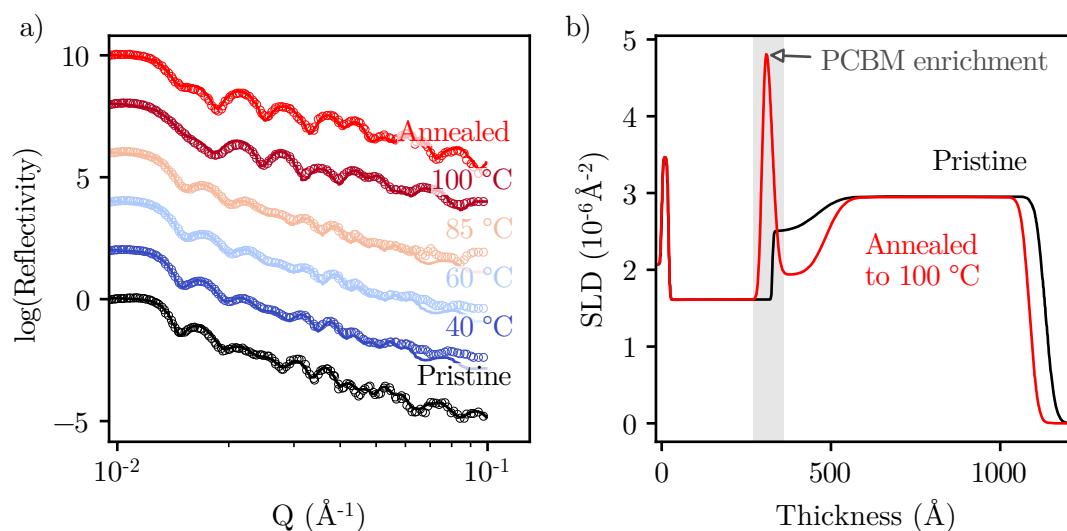


Figure 5.11 (a) Neutron reflectivity data and fits (solid line) and (b) fitted SLD profiles of 50:50 PS:PCBM blends, supported by PEDOT:PSS/SiO₂ in the dark, heated from room temperature to 100 °C. Enrichment of PCBM at the PEDOT:PSS interface is observed at $T \geq T_g$, while remaining largely unchanged at lower temperatures. Curves in (a) shifted vertically for clarity. Data indicated as annealed corresponds to a 30 min isothermal hold upon reaching 100 °C.

the hole-transporting interface is generally detrimental to device performance, hampering the required extraction of electrons to the top contact and increasing recombination at the hole extracting interface. The symmetry and magnitude of component segregation is, however, known to be both interface- and polymer-dependent.

The batch fit function in Motofit was used to fit the kinetic data with a number of constraints that were found to improve the robustness of the data fit. The initial fit at $t = 0$ min was obtained from the full- q measurements shown in Figure 5.12. Subsequently, the roughness and thickness were fixed, as well as the SLD values, except for two: that of a 30 $\text{\AA}$ layer at the bottom interface, and that of an adjacent layer of 150 $\text{\AA}$ towards the bulk of the film. A genetic + Levenberg-Marquardt algorithm was used to optimise the fit to the data. The uncertainty from the algorithmic fit is shown in the error bars of Figure 5.13(e). A detailed example of the fitting procedure, sensitivity of the fit to SLD changes, and uncertainty estimation is shown in Figure 5.14. Although the differences of the time-resolved data in Figures 5.13 (a) and 5.13(b) are not directly obvious, it is evident from Figure 5.14 that there is great sensitivity of the enrichment peak intensity to the goodness of fit of the NR data. Therefore, the differences presented for the enrichment between light and dark samples in Figure 5.13(e) are well within error.

Time-resolved NR measurements were also performed on samples with a PS:PCBM blend ratio of 35:65 and 65:35. Batch fits to the NR data were done for samples annealed without light, Figures 5.15(a) and 5.15(b), and with light, Figures 5.15(c) and 5.15(d). In both instances, enrichment of PCBM occurs on the PEDOT:PSS interface and it is inhibited in light conditions, as shown in Figures 5.15(e) and 5.15(f).

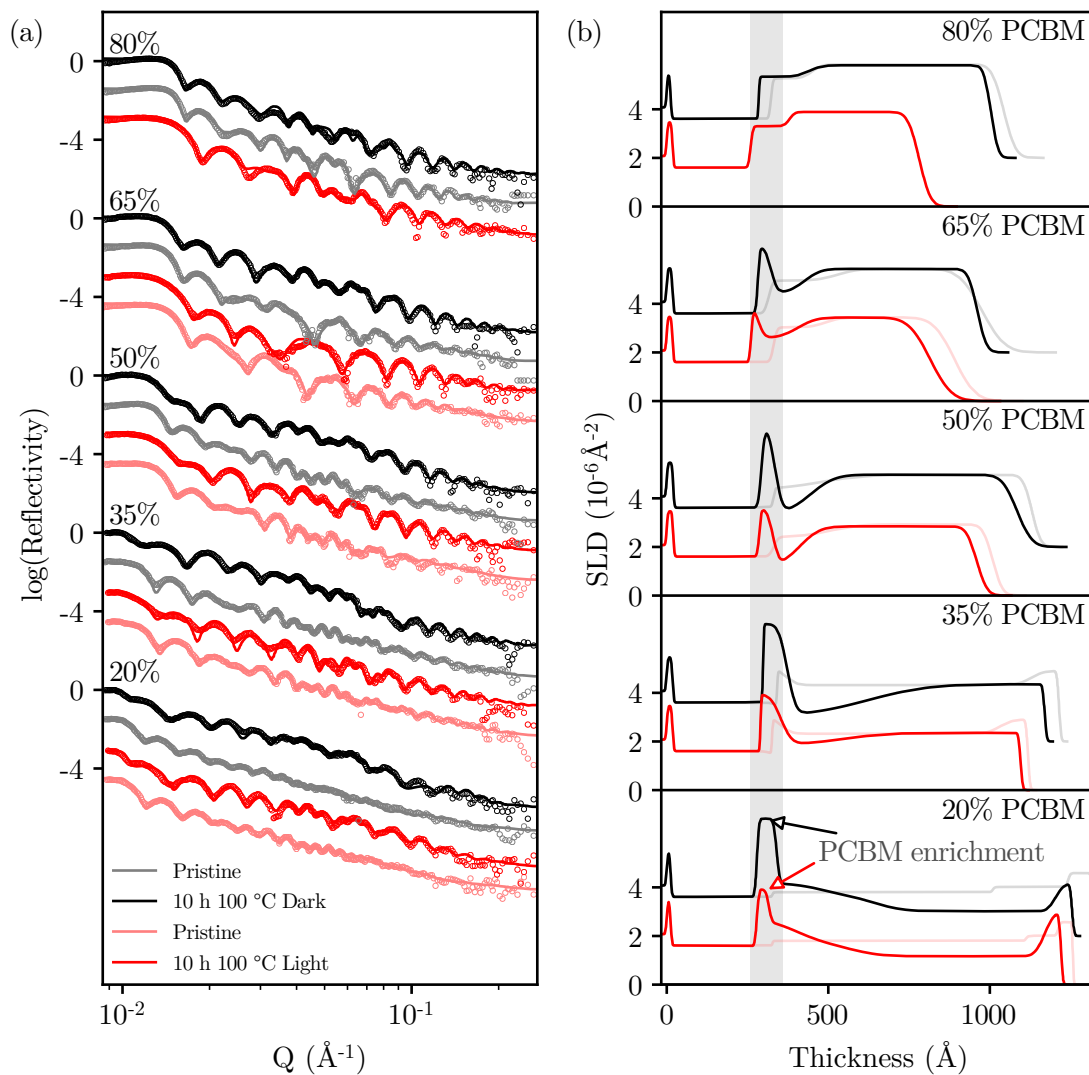


Figure 5.12 Neutron reflectivity data before (lighter shaded trace) and after (darker shaded trace) annealing with light (red) and without light (black). The temperature ramp from room temperature to 100 °C of PS:PCBM blends of various compositions follows the profile shown in Figure 5.4b. Accumulation of PCBM at the bottom interface can be seen for all samples, except for 80 % PCBM loading.

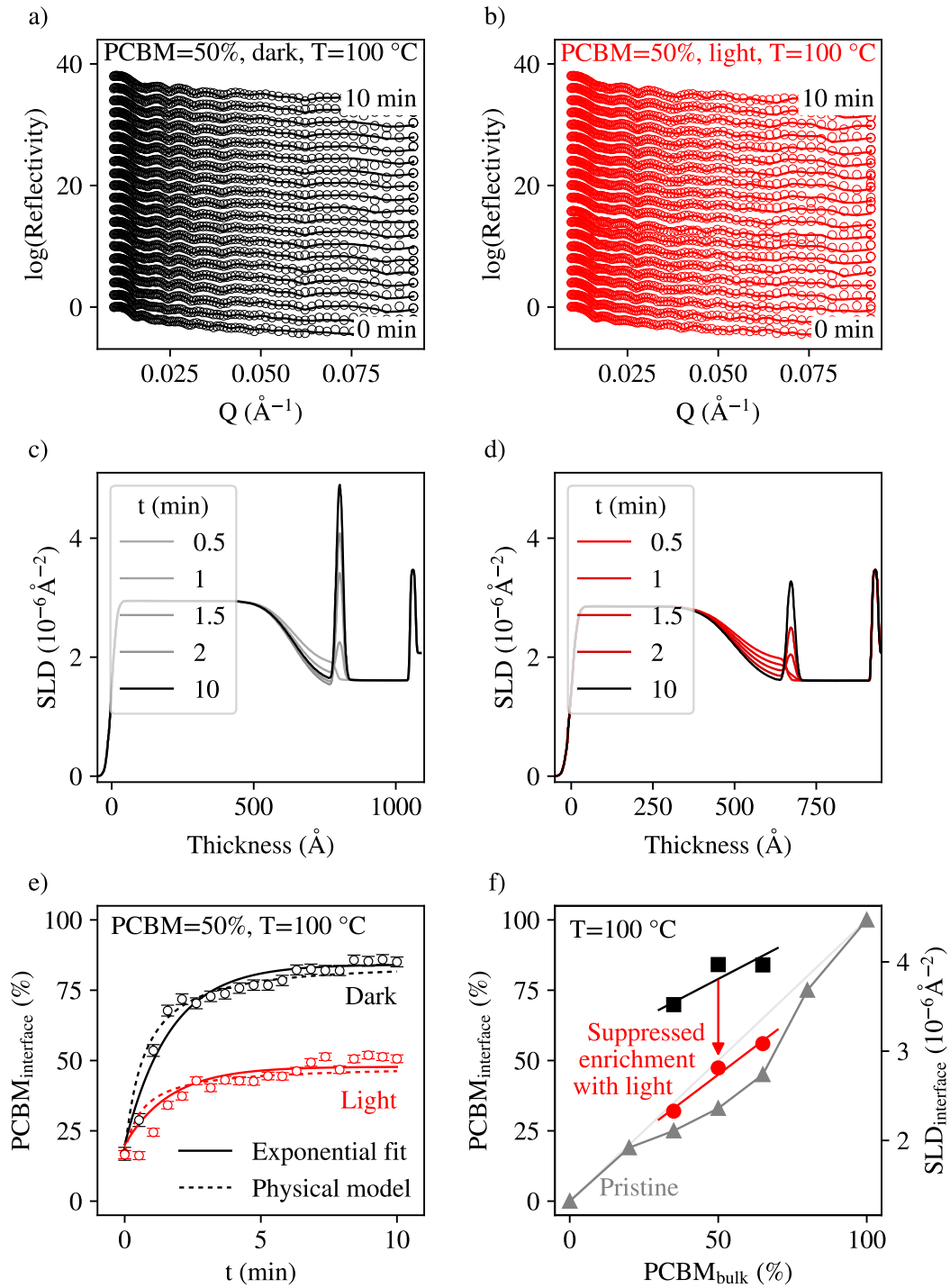


Figure 5.13 Time-resolved neutron reflectivity of 50:50 PS:PCBM blends annealed at 100 °C for 10 min without (a) and with (b) illumination where solid lines are fits with corresponding SLD profiles (c) and (d). e) Evolution of PCBM concentration (computed from SLD, shown on the right axis) at the bottom interface in both dark and light cases, with data fits (detailed in the text). f) Initial and final (asymptotic) PCBM concentration at the bottom interface, with and without light exposure; the diagonal grey line indicates the average PCBM composition in the film.

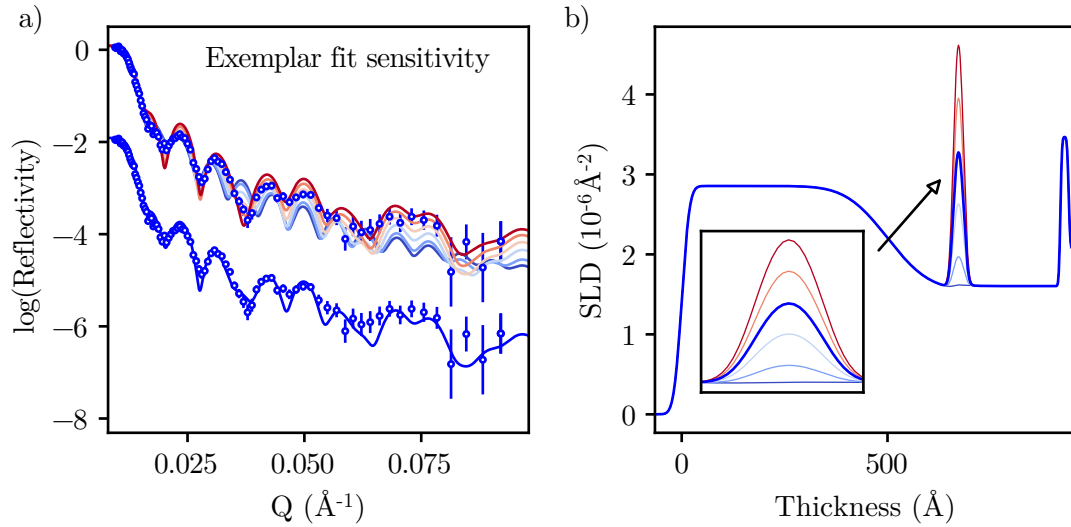


Figure 5.14 Illustration of the sensitivity of the data fit and uncertainty estimation for the kinetic scattering data of a 1:1 PS:PCBM film annealed at 100 °C for 10 min with light, shown in Figure 5.13(b). (a) A band of curves with varying SLD of the enriched layer is superposed onto the NR data; the best fit is shown below (shifted for clarity). (b) Corresponding SLD profiles showing the 'optimal' SLD value (in dark blue) and values above and below. The sensitivity of the fit quality to the change in SLD of the enriched layer is employed to estimate its uncertainty.

PCBM segregation kinetics were quantified by fitting the SLD over time at a fixed distance of 25 Å from the PEDOT:PSS interface, from which the PCBM concentration was estimated. Other criteria (e.g. peak integration) yielded similar results, and this procedure was repeated for all test conditions. Experimental results for 50:50 PS:PCBM are shown in Figure 5.13: the PCBM concentration increases asymptotically over time, and can be empirically described by an (inverse) exponential relationship

$$\phi_{interface} = \phi_{t_0} + (\phi_{t_\infty} - \phi_{t_0})(1 - e^{-kt}) \quad (5.1)$$

where ϕ is the interface concentration of PCBM at, ϕ_{t_0} , 0 min and, ϕ_{t_∞} , at saturation, while k is a constant describing the rate of enrichment to the interface. With and without light the enrichment can be well described with a constant k , and for all concentrations of PCBM. Instead, ϕ_{t_∞} is the main constant that changes between conditions of thermal stress in the light and dark. This suggests that it is not that PCBM dimers slowing the diffusion of PCBM but that the dimers are unable to diffuse to the interface and are effectively immobile over the timescales investigated and within the system studied here.

Diffusive modelling of PCBM interface enrichment was performed to determine the characteristic properties that can be compared between different PCBM concentrations and dimerisation effects. A simple coarse-grained model, combining diffusion and surface attraction, can describe the full cross-sectional composition profile of PCBM, including the enrichment of PCBM at the PEDOT:PSS interface. The PCBM flux, F , at point x perpendicular to the substrate

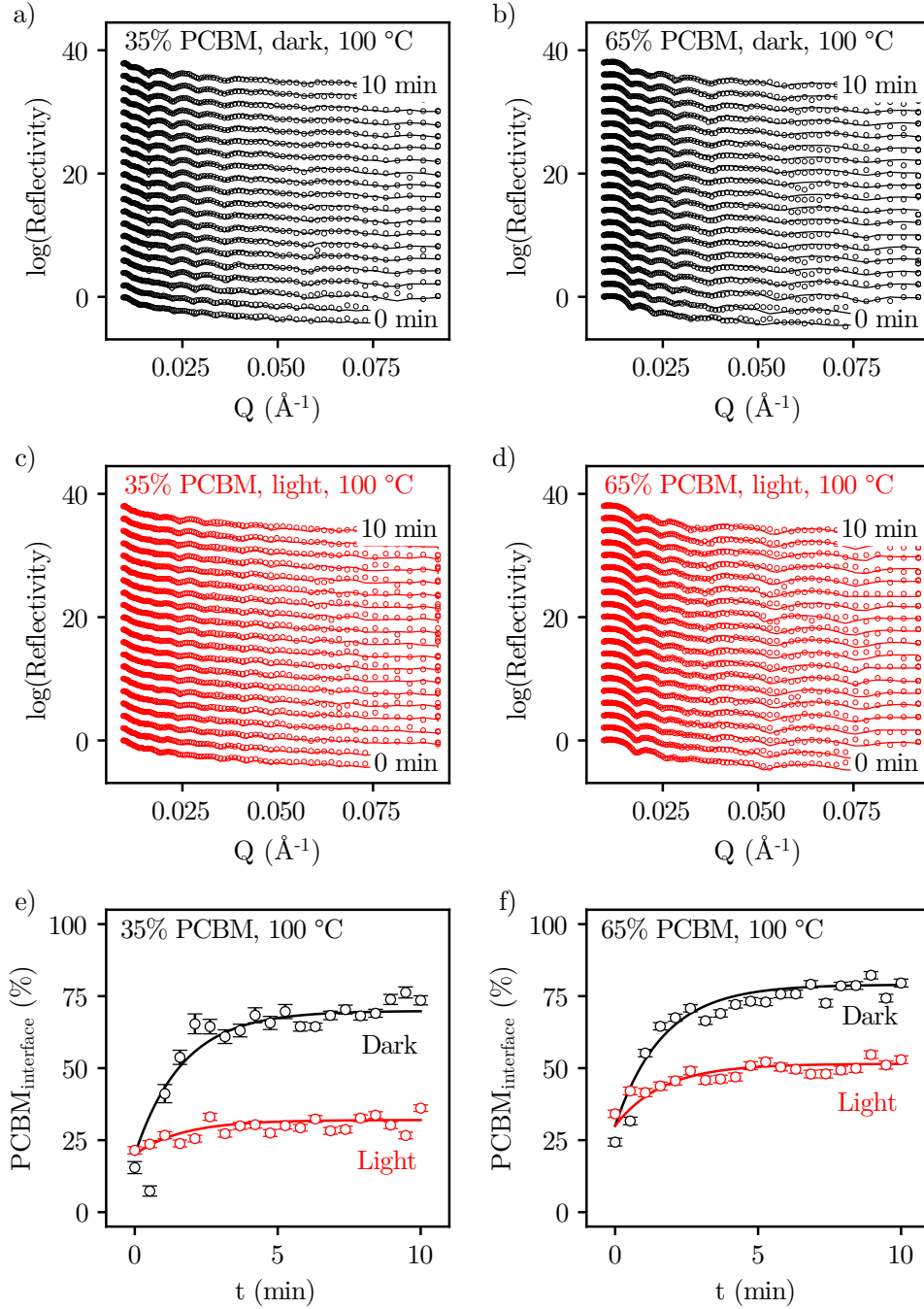


Figure 5.15 Batch fitting of NR with samples annealed at 100 °C with 35 % PCBM (a, c) and 65 % PCBM (b, d), where each trace corresponds to 30 s. (e) and (f) show the PCBM concentration at 25 Å of the PEDOT:PSS interface determined from the batch fits for 35 % and 65 % PCBM.

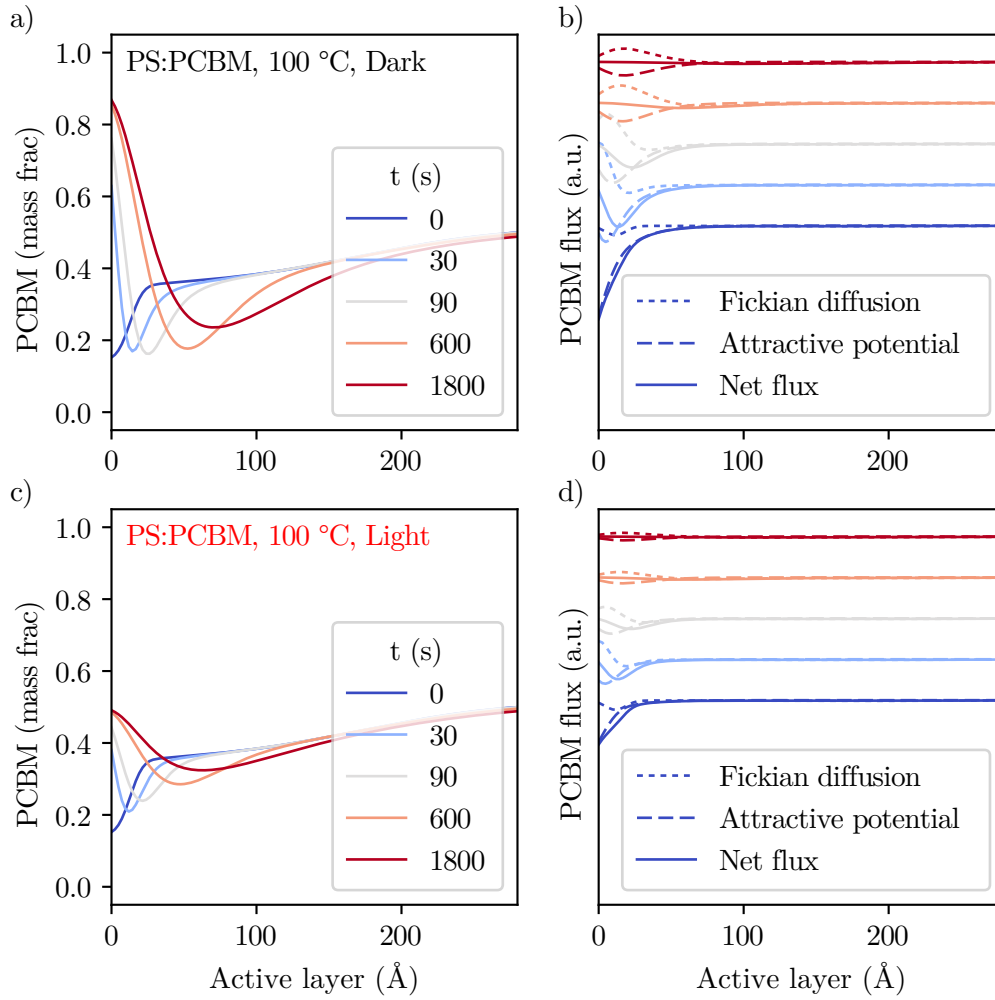


Figure 5.16 Modelling PCBM diffusion with Fickian diffusion and an attractive potential surface at the PEDOT:PSS interface (0 Å). Note curves in (b) and (d) are offset for clarity.

and at time t is written as a sum of two components; a Fickian diffusion term and an additional flux driven by the attractive surface field, taken as an attractive exponential (although a high power law yields similar agreement with data). This is parameterised as

$$F(x, t) = -D \frac{\partial \phi(x, t)}{\partial x} + \beta(\phi_{t_\infty} - \phi(x, t)) \exp\left(\frac{-x}{\gamma}\right) \quad (5.2)$$

where $\phi(x, t)$ is the PCBM concentration, x is the distance from the PEDOT:PSS interface, t is time, D is an effective diffusion coefficient of PCBM within the matrix; β and γ are the depth and range of the attractive potential well; as before ϕ_{t_∞} is the saturation concentration of PCBM at the interface. From the initially measured composition profile $\phi(x, t = 0)$, this solution was iteratively evolved over time until a steady state solution was reached. It is found that a single diffusion coefficient $D \approx 5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ satisfactorily describes all data, in line with the single k parameter found with the descriptive fit in Equation 5.1. This D value is of the same

order of magnitude, albeit larger, than previously reported values for PCBM within various polymer matrices ($0.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ to $1.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) at these temperatures.^{29,30} Similarly, it is found that a single $\beta \approx 0.09 \text{ cm s}^{-1}$ and $\gamma \approx 18 \text{ \AA}$ accounts for the attractive surface potential (from PEDOT:PSS), which seems sensible since the interface remains the same for all blend compositions and light exposure conditions. The asymptotic PCBM surface composition differs in every case, as expected, giving $\phi_{t_\infty} = 0.50$ and 0.85 , respectively, for the 50:50 PS:PCBM films annealed at 100°C with and without illumination. The agreement with the spatio-temporal PCBM composition data is very good, as shown in Figure 5.16, despite the simplicity of the model. The agreement with the interfacial PCBM composition, shown as dashed lines in Figure 5.13(e) is equally very good.

While it is clear that the presence of PCBM dimers improves the morphological stability of polymer:PCBM blends, the dimer population is governed by a subtle competition between light exposure and thermally-induced decomposition. The latter can be described by an activated process with $E_A \approx 1 \text{ eV}$ ¹⁹ (similar to that of neat C_{60} ³¹) and becomes significant above 100°C . This means that at lower temperatures ($<100^\circ\text{C}$), the forward (dimerisation) reaction prevails under illumination conditions. The dimerisation reaction (since it is a photochemical process) is likely to have a weak temperature dependence, associated with network diffusion and the statistics of topo-chemical requirements, although this must still be quantitatively examined. If so, at sufficiently high temperatures and competitive illumination, thermal decomposition can be expected to dominate. In the time-resolved NR measurements, fullerene diffusion is shown to take place even at *simultaneous* illumination and annealing at 100°C , although the mobile (monomer) population is considerably reduced.

5.3 Conclusions

The morphological stability of polymer/fullerene solar cells to thermal stress and light exposure was investigated with model PS:PCBM thin films. This work builds upon numerous reports of C_{60} and PCBM photo-transformations, dimerisation and burn-in effects in organic solar cell stability.^{16–19,32–34} This study is the first time that the coupling of illumination, known to induce fullerene dimerisation, and thermal stress, known to induce decomposition (or de-dimerisation), were simultaneously investigated. Examination of this coupling is essential for the understanding of morphological (and performance) stability of organic solar cells, which are exposed to modulated light and heat profiles with diurnal and seasonal variations during operation. The use of PS as a polymer matrix instead of a conjugated polymer (e.g. P3HT, PCDTBT) enabled us to clearly isolate the photo-transformations in PCBM.

Significant morphological changes are not observed within this system upon annealing up to 100°C (above the usual 85°C thermal stress condition), regardless of light exposure, both in terms of topography (measured by AFM) or component stratification (measured by NR). Above T_g , in the absence of light, a gradual relaxation of the thin film topography and structural coarsening is observed, which are significantly hindered for the light-exposed samples. Structural relaxation

is effectively delayed in samples that have been previously exposed to light, compatible with the requirement of thermal de-dimerisation occurring prior to relaxation. Employing NR, it is observed that no stratification up to 100 °C (i.e. up to T_g of the polymer matrix), beyond which PCBM rapidly enriches at the PEDOT:PSS interface. While thermally driven de-dimerisation has been established to occur above 80 °C (in the absence of light³⁵), there is a significant dimer population under conditions of *simultaneous* light exposure and heat, up to 85–100 °C, even at long times. These results show that dimerisation prevails under these competitive conditions, while the mobile monomer fraction remains able to diffuse.

A temperature ramp is employed to emulate the effect of temperature fluctuations in operation conditions and find that simultaneous light exposure effectively suppresses structural relaxation at the top film interface, while film stratification is diminished. The kinetics of PCBM attraction to the bottom (PEDOT) interface were quantified by time-resolved NR and described by a simple model. Interestingly, the rate constant is found to be unchanged between illuminated and non-illuminated films; by contrast, the mobile PCBM population is significantly reduced upon illumination. These results are compatible with an interpretation of the dimer population being effectively immobile within these timescales and responsible for the hindered structural rearrangement processed observed. These findings are relevant to the understanding of stability in polymer:fullerene solar cells under operating conditions, that involve simultaneous (and varying) light and thermal stress exposure, and provide a fundamental and quantitative framework for morphological control.

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Chapter 6

PCBM dimerisation: a comprehensive reaction model and distinct populations

This chapter is based on work presented in two manuscripts currently submitted by Pont et al.

Photo-induced dimerisation of phenyl-C61-butyric acid methyl ester (PCBM) has a significant impact on the stability of polymer:PCBM organic solar cells (OSC). This reaction is reversible, as dimers can be thermally decomposed, at sufficiently high temperatures, and both photo-dimerisation and decomposition are temperature dependent. This chapter will examine and quantify the kinetics of dimer formation and decomposition as a function of temperature, light intensity, blend composition and time. The activation energy for photo-dimerisation is estimated to be (22 ± 3) meV, considerably smaller than 960 meV for decomposition. The findings are compared with a variety of conjugated polymer matrices to propose a descriptive dynamic model of PCBM:dimer population in OSCs. The model enables prediction of the dynamic and long-term PCBM:dimer populations of *in-operando* conditions. Furthermore, the presence of ‘weakly’ and ‘strongly’ bound dimers are revealed, with higher light intensities preferentially generating the latter. DFT simulations corroborate our experimental findings and suggest a distribution of dimer binding energies, correlated with the orientation of the fullerene tail with respect to the dimer bond on the cage. These results provide a framework to rationalise the double-edged effects of PCBM dimerisation on the stability of organic solar cells.

6.1 Introduction

The dimerisation of PCBM is a significant factor in controlling OSC stability. It is therefore important to be able to accurately model the likely concentration of PCBM dimer under operating conditions and subsequently predict long-term stability. Additionally, the effect of dimerisation has been correlated with beneficial, neutral, and detrimental effects, depending on the conditions and material system investigated, as discussed in Chapter 1.3.2.¹⁻⁶ Therefore further work is required to understand the varied effects from the photophysical process.

Whilst dimerisation is known to be affected by light, temperature and the polymer matrix, a comprehensive model of the large parameter space and interactions between these parameters has not been established. In this chapter, the rates and associated activation energy of photo-dimerisation are computed from simultaneous illumination and annealing experiments. Further, the relationships between morphology and charge dynamics on dimerisation are examined. Alongside thermal decomposition kinetics, these results are used as building blocks to construct a model for the evolution of PCBM:dimer populations, under prescribed illumination and thermal conditions and, specifically under diurnal and seasonal fluctuations associated with *in-operando* conditions. A minimal model is then presented that subsumes the reaction mechanisms and parameterised kinetics and allows dynamic predictions of dimerisation, and subsequent stability, of material systems subjected to a temporally varying environment.

To study the kinetics of PCBM dimerisation an absorbance assay was used to probe the fraction of dimers to monomers.^{2,4} This non-destructive assay enables time-resolved monitoring of the PCBM dimerisation and de-dimerisation. Herein, representative polymer:fullerene thin films were exposed to varying duration and intensity of light exposure followed by dark thermal annealing. By analysing the kinetics of the thermal de-dimerisation the resulting PCBM

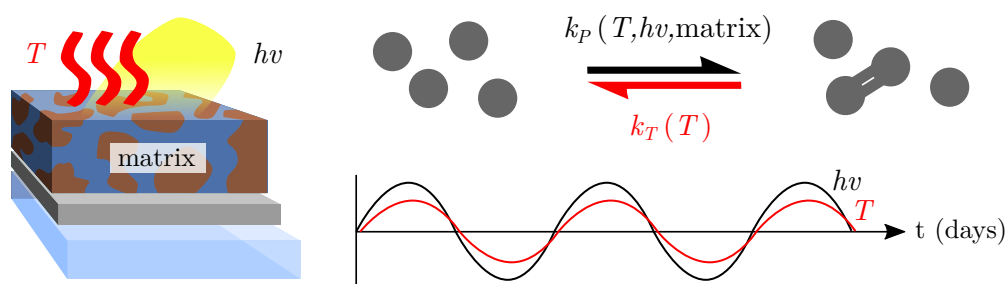


Figure 6.1 PC₆₀BM dimerisation within the bulk heterojunction of a polymer:fullerene organic solar cell is known to be affected by factors including temperature, light intensity, and the blend matrix. For each individual polymer, and the specific solar cell operating location, there will be a set of kinetic parameters to determine the dynamic fullerene dimerisation, and decomposition. In this chapter each factor is explored to enable situation-specific predictions of the monomer:dimer population balance over time. The kinetics of de-dimerisation will be used to uncover an energetic distribution of bond energies resulting from dimerisation.

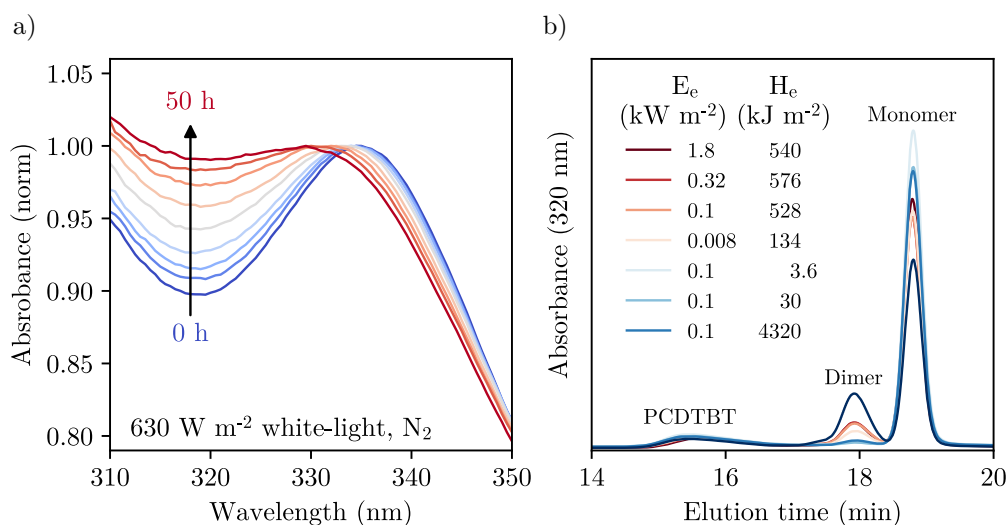


Figure 6.2 (a) Normalised absorbance spectra of a PCDTBT:PCBM film over 50 h illumination at 630 W m^{-2} from a white LED in a nitrogen atmosphere. A feature change is observed at 320 nm due to the PCBM dimerisation. (b) Gel permeation chromatography (GPC) of a PCDTBT:PCBM film after illumination at varying irradiance (E_e) and radiant exposure (H_e) from a white LED source. After illumination the monomer peak at 18.8 min decreases while the dimer peak at 17.9 min increases.

dimer bond energies are correlated with light intensity and duration. This work will present a framework to understand the conflicting effects of PCBM dimerisation in OSC and strategies to maximise both performance and stability.

6.2 Modelling PCBM dimerisation

Upon illumination in an inert (N_2) atmosphere, PCBM dimerisation results in a spectral absorbance feature, that has been previously discussed in Chapter 5.² Figure 6.2(a) presents the absorbance of a PCDTBT:PCBM 1:2 thin film during 50 h illumination at 630 W m^{-2} from a white LED. Other methods used to quantify PCBM dimerisation have several disadvantages: in Raman spectroscopy (vis, UV and even near IR), for instance, the illumination itself causes dimerisation and thus is convoluted in the measurement outcome;⁷ high performance liquid chromatography (HPLC) requires re-dissolution of the thin film (often with sonication) which can potentially cause both agglomeration and de-dimerisation;⁴ is it also comparatively time intensive and, crucially, destructive of the sample. By contrast, the UV-visible absorbance assay used here allows rapid quantification of PCBM dimerisation. This allows investigations of a much wider parameter space, range of systems and environmental factors. Although the dimerisation absorbance feature has been previously reported, here a quantification to absolute dimer concentration by calibration to ancillary measurements is reported.

Gel permeation chromatography (GPC) was thus employed as a size exclusion measurement to determine PCBM monomer:dimer ratio. Figure 6.2(b) presents GPC elution absorbance

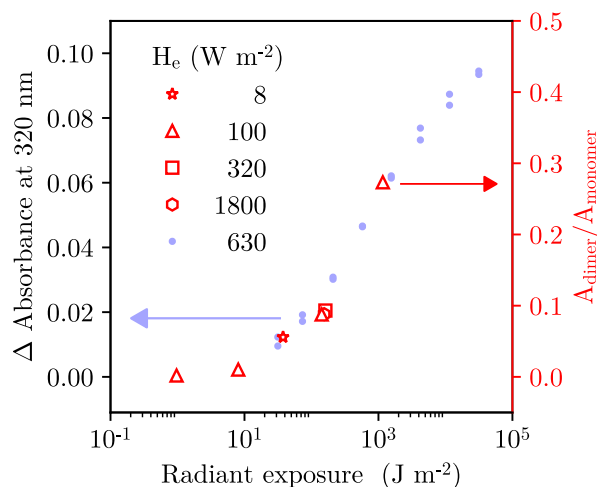


Figure 6.3 Correlated absorbance feature change at 320 nm, Figure 6.2(a), to the PCBM dimer:monomer ratio from the GPC measurement, Figure 6.2(b).

with peaks at 15.5 min, 18 min, and 19 min corresponding to PCDTBT, PCBM dimer, and PCBM monomer, respectively. By comparing the integrated intensity of the dimer and monomer peak, the absolute ratio of dimer to monomer can be determined. To calibrate the absorbance assay to dimer concentration, a series of PCDTBT:PCBM films were illuminated at varying irradiance (E_e) and radiant exposures (H_e). Figure 6.3 compares absorbance change at 320 nm to the dimer:monomer ratio from the GPC measurements for films soaked with varying radiant exposures. Over the small absorbance range, it is assumed the Beer-Lambert law can be simplified to a linear dependence on concentration. A clear correlation between the absorbance and the dimer ratio from GPC analysis is found, suggesting this assumption is valid. Illumination of constant radiant exposure with *varying* irradiance (the first three red traces in Figure 6.2(b)) results in a constant dimer concentration after similar radiant exposure (540, 576 and 528 kJ m⁻²) with varying irradiance (1.8, 0.32 and 0.1 kW m⁻²). Thus, it is concluded that dimerisation is independent of irradiance, in line with previous findings.⁸ From the direct correlation between GPC and absorbance measurements at 320 nm, the latter is employed as a quantitative (and facile) assay for dimerisation.

6.2.1 Dependence of polymer:fullerene matrix, irradiance and temperature on k_p

The polymer:fullerene blend morphology, at the molecular and mesoscopic scales, is expected to control both the topo-chemical requirements and the photophysical mechanism of the dimerisation reaction. A topological requirement of the 2+2 cycloaddition reaction is that the distance between adjacent fullerene molecules must be less than 4.2 Å. To investigate the role of concentration on dimerisation, model polystyrene (PS):PCBM blends with ratios of 1:4, 1:2, 1:1, 2:1, 4:1 were studied. Since films with lower PCBM loading have reduced absorbance, a spectral mismatch factor was applied to the radiant exposure. This factor was calculated by

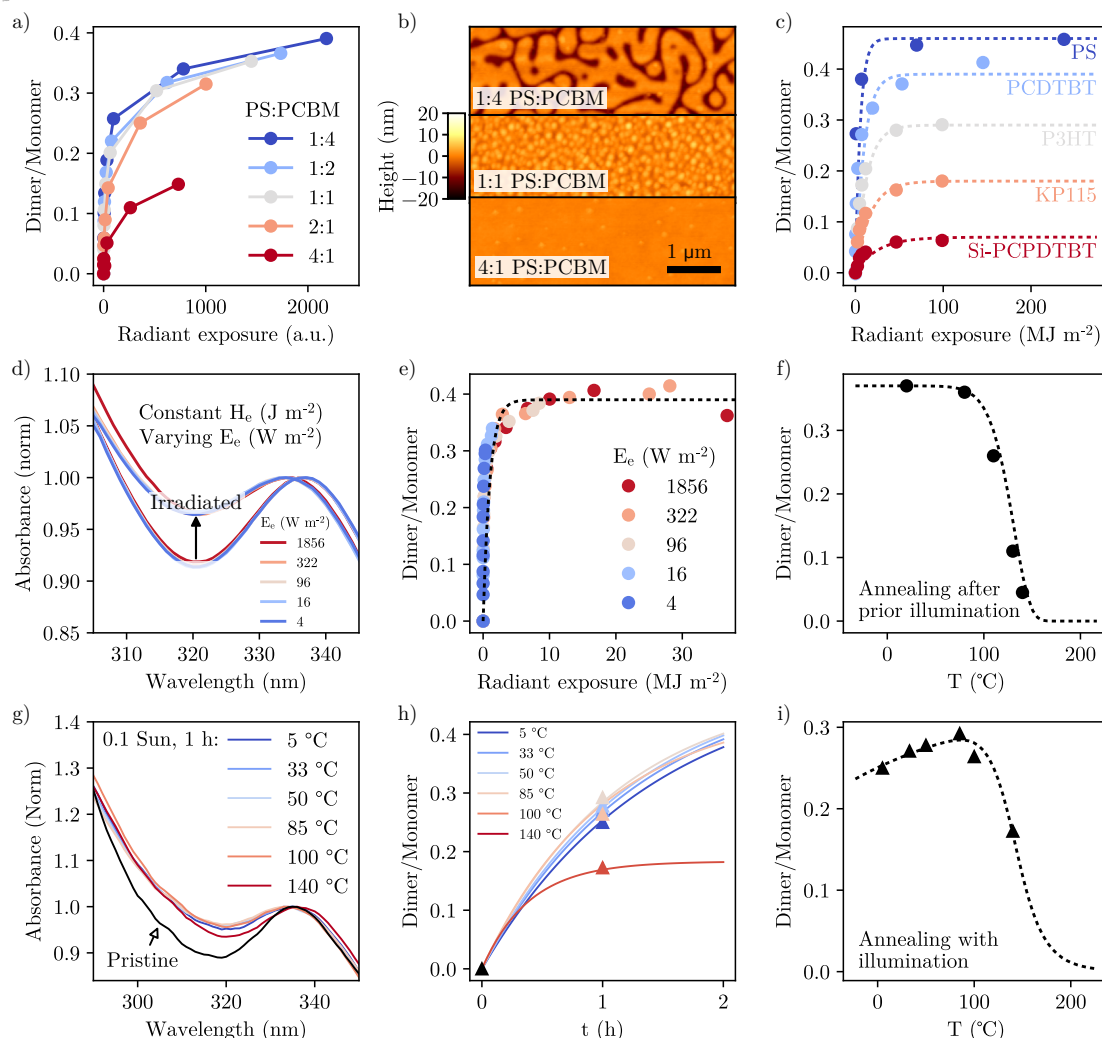


Figure 6.4 (a) PCBM dimer:monomer ratio of PS:PCBM at varying blend ratios with 96 W m^{-2} white LED light for 4 h. The radiant exposure for is corrected for absorbance variation. (b) AFM of PS:PCBM blend films with a blend ratio of 1:4 (spinodal characteristics), 1:1 (nucleation-like) and 4:1 (isolated clusters). Ratios of 1:4 to 2:1 yield similar rates of dimerisation, (a), despite a dramatic difference in morphology. (c) The dependence of the polymer matrix on dimerisation for five polymer:PCBM (1:2) blend systems. Data for P3HT, KP115, Si-PCDTBT was adapted from Ref⁴. (d) Absorbance of a PS:PCBM (1:2) film before and after $\approx 500 \text{ J m}^{-2}$ radiant exposure (H_e) with irradiance (E_e) from 4 W m^{-2} to 1856 W m^{-2} (H_e , E_e , and t are detailed in Table 6.2). (e) Dimerisation of a PS:PCBM (1:2) films with varying radiance. Irradiance independence corroborates a first-order triplet mechanism, suggested previously.^{8,9} (f) PCDTBT:PCBM films with prior photo-dimerisation to 0.36 dimer:monomer (100 W m^{-2} for 4 h) annealed in the dark for 1 h, from previous work.³ The dashed line presents a fit using Equation 6.1. (g) Normalised absorbance spectra of PS:PCBM films before (pristine) and after 4 h illumination at 100 W m^{-2} LED at 5°C to 140°C . (h) With the de-dimerisation rate, k_T , known³ the reaction model Equation 6.3 is fitted at temperature T and illumination 100 W m^{-2} to the data points of $D(t=0)$ and $D(t=4 \text{ h})$ determined in (g). The solution gives temperature dependence of the dimerisation rate, k_P . (i) The dimer concentration after 4 h illumination at 100 W m^{-2} for experimental results (triangles) and the solution of the reaction model (dashed line).

the integral between the white LED spectrum and the absorbance of the film. Over this series, blend morphology changes significantly from spinodal characteristics at 1:4 PS:PCBM loading (Figure 6.4(b) top), to clustering at 1:1 PS:PCBM (Figure 6.4(b) middle), and well-dispersed PCBM at 4:1 PS:PCBM (Figure 6.4(b) bottom). From the dimerisation dependence on PCBM concentration, shown in Figure 6.4(a), it emerges that neither the rate nor conversion are significantly affected, with the exception of very low (4:1) PCBM loading, which is considerably lower than the remainder. It is hypothesised that, up to this concentration, sufficient PCBM is aggregated such that the topological requirements are not inhibited. At the lowest PCBM loading (PS:PCBM 4:1), PCBM is likely excessively dispersed and the reaction limited by the distance between fullerenes. In summary, for this model miscible system with an amorphous polymer, it is found that concentration only affects dimerisation at low PCBM concentrations that are rarely used in OSCs.

The photophysical properties of polymer:fullerene blends are expected to affect the rate of dimerisation. PCBM triplet lifetimes are impacted by blend morphology: while in dispersed PCBM films, singlet exciton generation rapidly undergoes intersystem crossing to form triplets,¹⁰ triplet yield is greatly inhibited in neat PCBM films. In PS:PCBM blends, the yield has been reported not to be significantly affected until very low loading of PCBM,¹¹ which is corroborated by the independence of PCBM dimerisation with concentration presented in Figure 6.4(a). Alongside the photophysics, the amorphous or crystalline nature of the polymer matrix can be expected to impact the dimerisation process, and dimerisation has been reported to correlate favourably with increasing crystallinity.⁴ The physical picture is that polymer crystallinity induces PCBM segregation and that, in turn, this increases the chance of meeting the topochemical requirements for dimerisation. These results, for P3HT, KP115, Si-PCPDTBT, in decreasing degree of polymer aggregation⁴, are compared alongside amorphous polymers PS and PCDTBT measured in this study in Figure 6.4(c), where all systems have a composition ratio of polymer:PCBM of 1:2. The first observation is that the two amorphous polymer matrices actually exhibit the largest dimer conversion of this polymer series. Secondly, analysis of the fit parameters given in Table 6.1 shows the rate of dimerisation correlates with the saturation concentration, such that for PS:PCBM it shows the fast rate of photo-dimerisation and also the greatest conversion. Evidently, the degree of crystallinity of the polymer matrix alone cannot be used as a predictor for the ability of PCBM to undergo photo-dimerisation. In the case of PS, for instance, since it is not a photoactive polymer, the excited triplet state is not quenched, thus likely resulting in higher dimerisation conversion. The interplay between blend morphology (including crystallinity) and specific blend photophysics must therefore be considered.

The dimer saturation concentration and pre-exponential factor reaction constant are both affected by the polymer matrix. From Figure 6.4(c) the steady-state concentration is found to vary from 0.46 in the PS:PCBM blend to below 0.08 for the Si-PCPDTBT:PCBM blend. The fraction of fullerenes available for dimerisation is clearly dependent on the polymer matrix. For the photoactive polymer systems compared in Figure 6.4(c), namely PCDTBT, P3HT, KP115, and Si-PCPDTBT, the rate of is 0.84, 0.63, 0.39, and 0.15 relative to the rate with PS. The rate of

Table 6.1 The parameters of fittings to dimerisation kinetics in a range of polymer:PCBM photo-dimerisation, presented in Figure 6.4(c). The data is fitted to $[D : M](t) = A(1 - \exp - k_p t)$.

	A	k_p	$k_p/k_p(PS)$
PS	0.46	0.18	1
PCDTBT	0.39	0.1	0.6
P3HT	0.29	0.08	0.4
KP115	0.18	0.06	0.3
Si-PCDTBT	0.07	0.04	0.2

dimerisation is likely dependent on the quenching of the triplet states minimising the chance of photo-dimerisation and hence the reduced rate of dimerisation.

The intensity dependence of dimerisation is a result of the photophysical mechanism. Reports on the dimerisation of fullerenes have suggested a mechanism that is either a mono-molecular (triplet-ground state) or bi-molecular (triplet-triplet state), as discussed in the introduction. To clarify this, PS:PCBM films were illuminated with irradiances over nearly three orders of magnitude, from 4 W m^{-2} to 1856 W m^{-2} (detail of the irradiance, radiant exposure, and time for each sample are given in Table 6.2). Analysis of the absorbance before (pristine) and after approximately equal radiant exposure is presented in Figure 6.4(d). This result demonstrates the absorbance feature change upon dimerisation is independent of irradiance and therefore suggesting an equivalent process is occurring across all irradiances studied. The change in dimer concentration over time for five PS:PCBM films irradiated with varying irradiance are presented Figure 6.4(e). This further demonstrates the dimerisation is independent of irradiance. Therefore, it is concluded PCBM dimerisation proceeds via a mono-molecular process involving a triplet state and a ground state. This triplet driven cycloaddition reaction mechanism is well known in photochemistry. For example, within the DeMayo reaction mechanism or during the formation of mutagenic DNA in pyrimidine dimers which are the primary cause of melanomas in humans.^{12,13} These reactions are thought to proceed via one triplet state forming bi-radicals that initiate the electrocyclic reactions.^{14,15} It is therefore logical to follow that the fullerene photo-dimerisation cycloaddition also follows a one triplet-state reaction mechanism.

Table 6.2 The irradiances (E_e), times (t), and subsequent radiant exposure (H_e) of PS:PCBM films illuminated with a white LED light. The resulting dimerisation is present in Figure 6.4(d).

Irradiance, E_e (W m^{-2})	Time, t (min)	Radiant exposure, H_e (J m^{-2})
1856	5	557
323	31	600
97	90	523
16	330	319
4	672	163

The temperature dependence of the rates of reaction are required to simulate diurnal fluctuations of OSC *in-operando* conditions. The de-dimerisation activation energy of both C₆₀

and PCBM have previously been found with similar values at 1.25 eV and 0.96 eV, respectively. The temperature dependence of a de-dimerisation in PCDTBT:PCBM films is demonstrated in Figure 6.4(f) with results previously reported.³ Films with prior illumination are annealed at varying temperatures to monitor the rate of de-dimerisation temperature dependence. The data fits well to simple model whereby the dimer concentration, D , at time t is given by $D(t) = D(t_0) \exp(-k_T t)$.¹⁶ Arrhenius analysis of the rate constant k_T versus temperature gives the relationship presented in Figure 6.5.

The temperature dependence of the dimerisation is required to model systems under illumination and thermal stress. As the de-dimerisation k_T is known, during simultaneous irradiance and annealing it is possible to determine the rate of dimerisation, k_P . The dimerisation of PCBM was monitored after a constant radiant exposure at temperatures varying from 5 °C to 140 °C. The absorbance spectrum was then taken and compared to a pristine sample, as shown in Figure 6.4(g). This was converted to dimer concentration using the calibration described earlier, and fitted with the previously reported¹⁶ reaction material balance as described in

$$\frac{dD}{dt} = 0.5k_P M(t) - k_T D(t) \quad (6.1)$$

where D is the dimer concentration, M is the monomer concentration, t is time, k_P is the rate of photo-dimerisation, and k_T is the thermal de-dimerisation. By substituting the molar balance in Equation 6.2 into Equation 6.1, it is possible to solve for the dimer concentration, D , at time t as described in Equation 6.3, given the initial conditions of $D(t_0) = 0$.

$$M(t) = M(t_0) - 2D(t) \quad (6.2)$$

$$D(t) = \frac{k_P}{2(k_T + k_P)} (1 - \exp(-(k_T + k_P)t)) \quad (6.3)$$

With k_T known for all temperatures it is possible to solve Equation 6.3 to calculate k_P for each temperature in Figure 6.4(g). The solution to each equation is presented in Figure 6.4(h) and the dimer:monomer ratio after equal radiant exposure at different temperatures is presented in Figure 6.4(i). Qualitatively it is observed at lower temperatures the rate of photo-induced dimerisation is slower and hence the decrease from 100 °C to 5 °C; while at temperatures above 120 °C the thermally driven de-dimerisation starts to dominate. By analysing the temperature dependence of k_P using an Arrhenius analysis the activation energy of dimerisation can be calculated as (22 ± 3) meV. It is expected that the dimerisation has low temperature dependence as it is primarily driven by a photochemical mechanism. The temperature dependence is likely related to greater rotational freedom increasing the rate of bond alignment between fullerenes.

The interplay between dimer and monomer concentration at specific conditions of temperature and light intensity is dependent on the rate of the forward and backward reactions. To analyse the temperature dependence of the rates of reaction, an Arrhenius analysis is used: $k = A \exp(-E_a/k_B T)$ where A is the pre-exponential factor, E_a is the activation energy for the

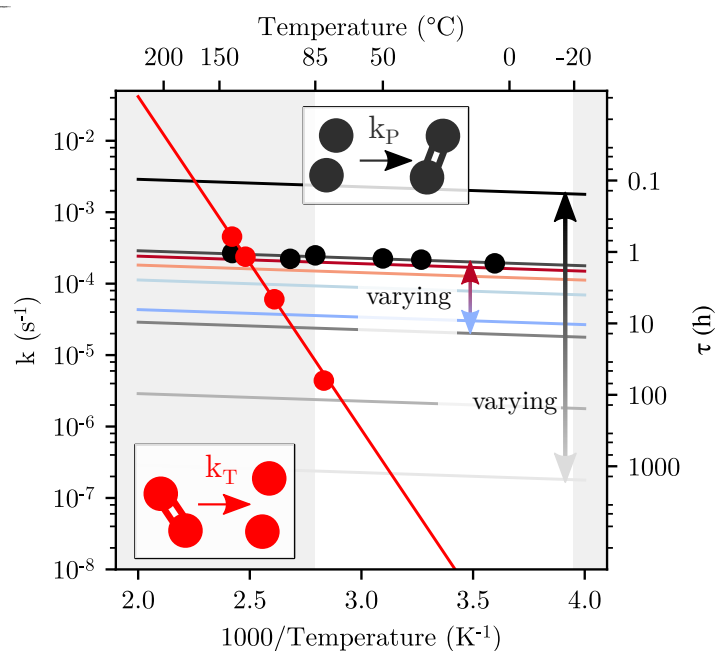


Figure 6.5 Thermal decomposition (or de-dimerisation rate), k_T , dependence on temperature (experimental data shown by red circles, reproduced from Figure 6.4(f)) and the corresponding Arrhenius fit (red line). Photo-dimerisation rate, k_P , at 0.1 Sun in a PS:PCBM film (experimental results (black circles, Figure 6.4(i)) and an Arrhenius fit (black line). The series of grey-scale lines present the effects of irradiances with the quickest rate at approximately 1 Sun equivalent, reducing in orders of magnitude. The series of red to blue lines present the effects of the polymer:fullerene matrix, adapted from Figure 6.4(c).

reaction, k_B is the Boltzmann constant, and T is the temperature. The rate constants calculated at various temperatures for k_T (Figure 6.4(f)) and k_P (Figure 6.4(i)) result in a good fit to the Arrhenius relationship, as presented in Figure 6.5. The photo-dimerisation k_P has an activation energy of (22 ± 3) meV and a pre-exponential factor of $4.69 \times 10^{-4} \text{ s}^{-1}$. The de-dimerisation has a much greater temperature dependence compared to the photo-dimerisation. This is expected as the reactions occur via thermally-driven and photo-driven mechanisms, respectively. The activation energy of the photo-dimerisation is not expected to have a significant dependence on light intensity. In Figure 6.4(d, c) the rate is determined to be proportional to irradiance. Therefore, the irradiance will result in a vertical translation of k_P in Figure 6.5. Light intensities were calculated for 1 Sun equivalent in a PS:PCBM film (topmost black line), decreasing in orders of magnitude. In the previous section, the polymer matrix was shown to affect the dimerisation rate (Figure 6.4(c)). The magnitude of varying blend matrix is depicted in Figure 6.5 where the colours of red to blue correspond to the polymer:fullerene blends in Figure 6.4(c). Clearly the reaction dynamics can occupy a large parameter space and the population equilibrium is very dependent on the environmental conditions.

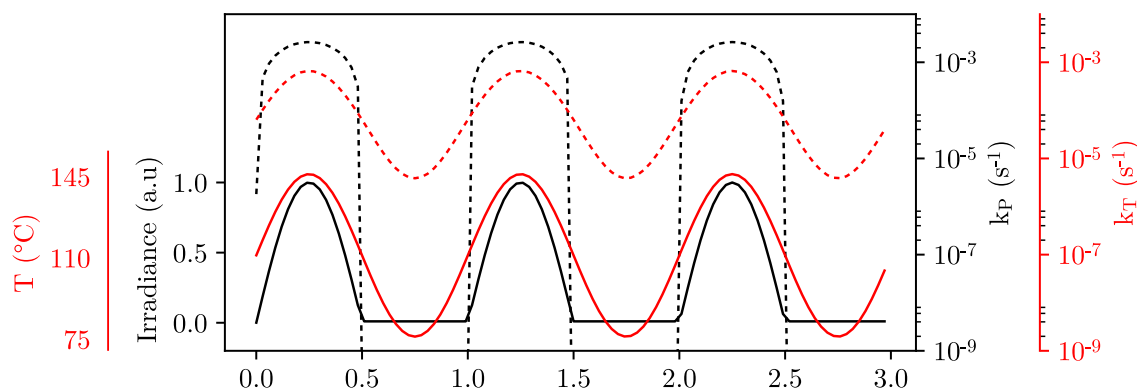


Figure 6.6 Diurnal fluctuations of temperature and light used for the *in-operando* modelling, and the resulting photo-dimerisation (k_P) and de-dimerisation (k_T) rate constants for an average temperature of 110 °C, as used in (II) in Figure 6.7.

6.2.2 Modelling the long-term stability of PCBM dimers

To simulate OSC *in-operando* conditions, the interplay of k_P and k_T with fluctuating light and temperature is considered. With the activation energy of dimerisation and de-dimerisation known it is possible to solve the differential reaction balance in Equation 6.1. The simulation can include diurnal variations of the conditions to calculate the changing rate constants (Figure 6.6). To represent the *in-operando* temperature a sinusoidal profile around the average temperature, $T_{average}$, is used. It has a period of 24 h and an amplitude of ± 35 °C, as this is a diurnal fluctuation occurring within a solar module under operating conditions.¹⁷ The light irradiance was modelled on a truncated sinusoidal with a period of 24 h, in phase with the temperature. Half the 24 h period is equal to zero to simulate night conditions. These models and subsequent rate constants are presented in Figure 6.6. The maximum and minimum population of PCBM monomer is based on analysis of PCDTBT but will be specific to the polymer:fullerene matrix, as shown in Figure 6.4(c). The effect of changing the average temperature is then investigated on the dimer:monomer population by solving Equation 6.1 (Figure 6.7(c)). The solutions to three temperatures are highlighted in Figure 6.7: (I) Firstly, at lower temperatures the rate of dimerisation is much greater than the rate of de-dimerisation, such that the dimer dominates; (II) secondly, k_P and k_T are similar such that there are dynamic fluctuations during the diurnal light and temperature variations; (III) lastly, at higher temperatures the rate of de-dimerisation dominates and the PCBM is mostly in the monomer form, but still continues to fluctuate during the 'day'. At an average temperature below 50 °C k_P dominates whereas for temperatures above 150 °C k_T dominates. Modelling of the PCDTBT:PCBM thin film suggests under operating conditions the PCBM dimer is likely to dominate over long time periods.

Within this model there are a number of variables that will affect the resulting dimer stability. These include the maximum daily irradiance, the diurnal temperature swing, and the initial PCBM dimer concentration. The maximum daily irradiance was varied from 0.01 to 10 Sun

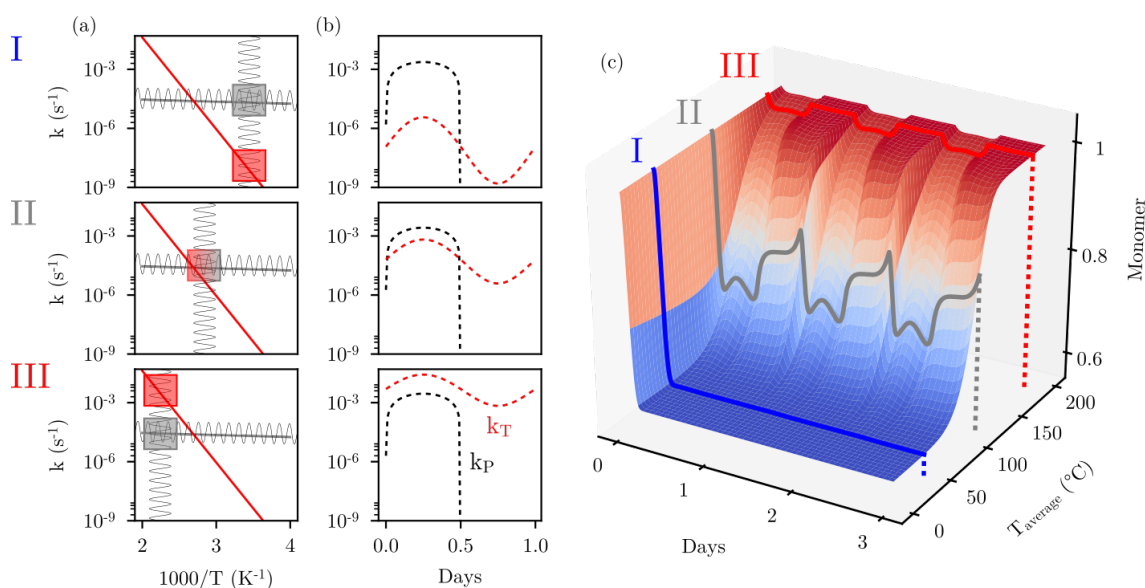


Figure 6.7 Representative simulated scenarios for dimerisation with varying light and temperature obtained by solving Equation 6.1 with temporally varying environmental conditions (light and temperature exposure). The temperature profile is modelled as a sinusoidal function with $T_{\text{average}} \pm 35^\circ\text{C}$, while the illumination profile is modelled with a 12 h truncated sinusoidal function for the day and a 12 h zero rate for the night. These are shown in Figure 6.6. Three scenarios are illustrated for the relative magnitude of k_P and k_T (a,b) and the effect on the dimer population (c): (I) At 40°C the photo-dimerisation dominates and the PCBM dimer concentration is saturated. (II) At 110°C $k_P \approx k_T$ resulting in large fluctuations in monomer:dimer ratio. (III) At 180°C $k_P \ll k_T$, de-dimerisation dominates and PCBM remains predominately in monomer form.

equivalent irradiance, as shown in Figure 6.8(top). At higher light irradiance there is considerably greater fluctuations in the diurnal whilst at lower irradiance it takes considerably longer to reach steady-state conditions. Next, the effect of the initial PCBM dimer concentration was investigated, as shown in Figure 6.8(middle). Under the conditions modelled here the quasi-steady-state is reached relatively quickly such that the initial concentration does not affect the system greatly. Finally, the diurnal temperature swing was varied from $\pm 35^\circ\text{C}$ to $\pm 0^\circ\text{C}$, as shown in Figure 6.8(bottom). Two effects are observed when the average temperature swing is reduced from $\pm 35^\circ\text{C}$ to $\pm 0^\circ\text{C}$: Firstly, the diurnal fluctuations increase and secondly the average monomer concentration decreases. The examples presented here highlight the power of this simple model to implement a range of temperatures, irradiances, and polymer matrix conditions to simulate the PCBM dimer to monomer populations over time.

6.3 Strong and weak PCBM dimer populations

Next, the kinetics of thermally induced PCBM de-dimerisation are probed in polymer:fullerene blends in order to investigate the energetic distribution of dimer bond strengths. Previous studies have probed the yields of de-dimerisation using gel permeation chromatography (GPC)

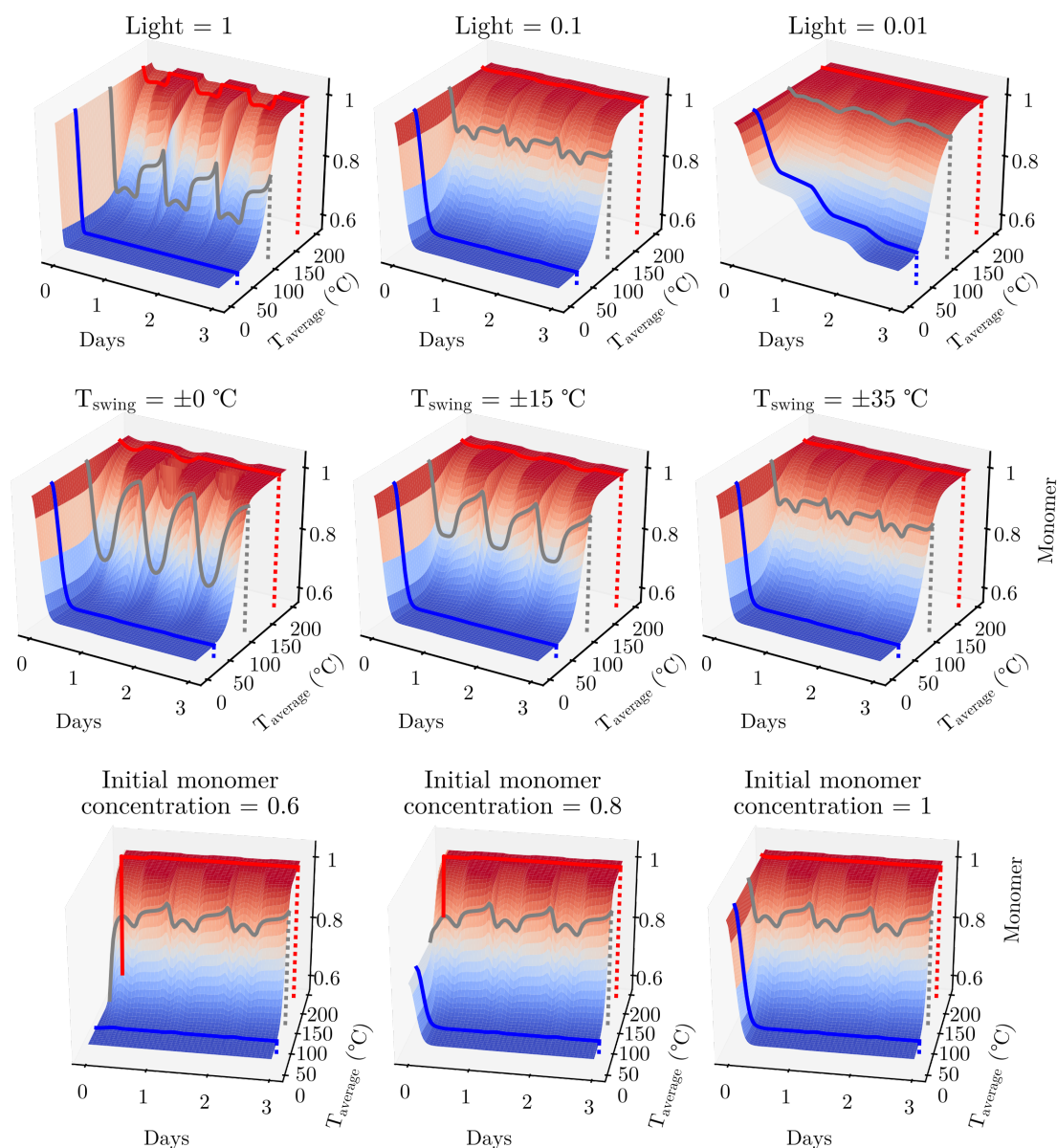


Figure 6.8 Modelling the PCBM monomer concentration over time with the average temperature from 0°C to 200°C using the sinusoidal profile given in Figure 6.6. Changing the light intensity, degree of temperature fluctuation, and initial PCBM concentration is investigated. (Top) Varying light intensity. The temperature swing kept at $\pm 35^{\circ}\text{C}$ and the initial PCBM concentration 1. (Middle) Varying diurnal temperature swing. Light irradiance was kept at 0.1 and the initial PCBM concentration 1. (Bottom) Varying the initial PCBM monomer concentration on the dimerisation dynamics. Light irradiance was kept at 0.1 Sun equivalent and the temperature swing at $\pm 35^{\circ}\text{C}$.

or high-performance liquid chromatography (HPLC).^{2–4} As these techniques require destruction of the sample, time-resolved measurements are not feasible. Within this chapter, it has been shown that the relative proportions of PCBM monomer and dimer states can be readily assayed from UV-visible absorption spectroscopy.^{2,6} This absorbance assay facilitates collecting time-resolved dimer concentrations. For the first time, this enables monitoring of the kinetics of PCBM dimerisation and de-dimerisation without the detection method affecting the reaction.

6.3.1 PCBM de-dimerisation kinetics

To investigate the de-dimerisation kinetics, PCDTBT:PCBM films were initially irradiated with the white light LED to induce partial PCBM dimerisation, and then annealed at 100 °C in the dark to induce de-dimerisation. Absorbance spectra were taken periodically while annealing to monitor the kinetics of de-dimerisation. Specifically, the change in an absorbance feature at 320 nm was converted to a dimer:monomer ratio using a previously reported calibration in this chapter. Figure 6.9 presents dimer population decay over time following prior irradiation at 186 W m⁻² for 82 h. Complete reversibility of the photo-dimerisation has previously been shown to occur in this system and therefore expected to occur here at very long timescales.^{3,16} It was expected that the decay would follow the reaction model described by Eklund and co-workers and used in previous analyses of the de-dimerisation kinetics.³ This model states the dimer concentration, D , should exhibit a (mono-exponential) decay over time upon isothermal annealing, following where $D(t) = D(t_0) \exp(-kt)$ at time t and decay rate k . However, a mono-exponential decay does not fit the data in Figure 6.9. Empirically, it is found that a bi-exponential

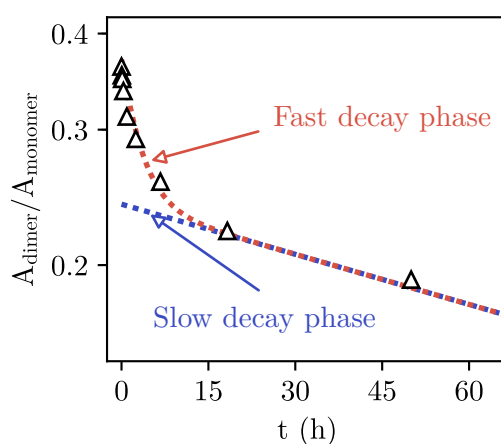


Figure 6.9 The PCBM dimer:monomer ratio of a PCDTBT:PCBM 1:2 thin film whilst annealing at 100 °C in the dark. The film had prior illumination at 186 W m⁻² for 82 h which resulted in the PCBM dimer concentration at $t = 0$ min. Two phases of de-dimerisation are observed: firstly, a fast-phase with rate of $\approx 181 \text{ min}^{-1}$ upon which the ‘weakly’ bound dimers separate and, secondly, a slow-phase with a rate of $\approx 12.6 \times 10^3 \text{ min}^{-1}$ where ‘strongly’ bound dimers separate.

decay describes all data in full:

$$D(t) = D_{slow} \exp(-k_{slow}t) + D_{fast} \exp(-k_{fast}t) \quad (6.4)$$

where D is dimer concentration at time t , D_{slow} and D_{fast} are termed the slow- and fast-phase, respectively, and k_{slow} and k_{fast} are the associated decay rate constants, respectively. Several possible interpretations can be considered for this behaviour. Fullerenes have been shown to oligomerise¹⁸ and the formation of PCBM trimers was reported by several groups³; these could contribute to an additional time decay profile. Alternatively, the dimerisation process itself could be non-exponential (e.g. described by a stretched exponential) potentially associated with matrix rearrangements required for thermal decomposition to occur; however, a bi-exponential description is found to provide better agreement with experiment. Given that the light spectrum has a broad frequency range, one could conceivably access different reactions, and thus dimer pathways, depending on incident photon energy; however, no wavelength-dependence in dimerisation was reported in PCBM films.⁹ Finally, it is hypothesised that the intrinsic distribution of relative spatial configurations of PCBM molecules with a film might result in the formation of distinct photo-dimers, which could then be expected to exhibit different de-dimerisation energetic requirements and thus kinetics. Some evidence for dimer complexity is suggested by structured HPLC traces upon light exposure and re-dissolution.⁴ Next, the role of light intensity and time (and thus radiant exposure, or dose) on the de-dimerisation time profile is experimentally investigated to examine this bi-exponential behaviour, and then report on a theoretical examination of dimer topology.

The factors determining the ratio of fast- to slow-phase were investigated by controlling the dimerisation illumination conditions prior to annealing. Specifically, three parameters are investigated: the radiant exposure (total energy dose), the irradiance (light intensity), and duration of the light exposure. Firstly, to probe the effect of radiant exposure, PCDTBT:PCBM films were exposed to a constant 15 kJ m^{-2} from a white light LED array whilst the irradiance was varied from 63 W m^{-2} to 2155 W m^{-2} . Secondly, to probe the effect of irradiance, films were illuminated for 50 h with irradiances of 63 W m^{-2} to 2155 W m^{-2} . Lastly, to probe the time dependence, films were exposed to 630 W m^{-2} with a duration of 18 min to 14 400 min. After light soaking, the films were annealed at 100°C in the dark and absorbance measurements taken intermittently to monitor the de-dimerisation. The results of these three conditions are presented in Figure 6.10(a-c). The decay of the dimer population was fitted with Equation 6.4. After fitting with the least-squares error, $k_{slow} = (0.135 \pm 0.023) \times 10^{-5} \text{ s}^{-1}$ and $k_{fast} = (9.31 \pm 0.99) \times 10^{-5} \text{ s}^{-1}$ to one standard deviation for all the decays in Figure 6.10(a-c). As such, it can be concluded that the dissociation kinetics of the two separate dimer populations are independent of light irradiation conditions, with differences in overall decay kinetics as a function of light irradiation conditions resulting only from variations in the relative magnitudes of the fast and slow de-dimerisation phases.

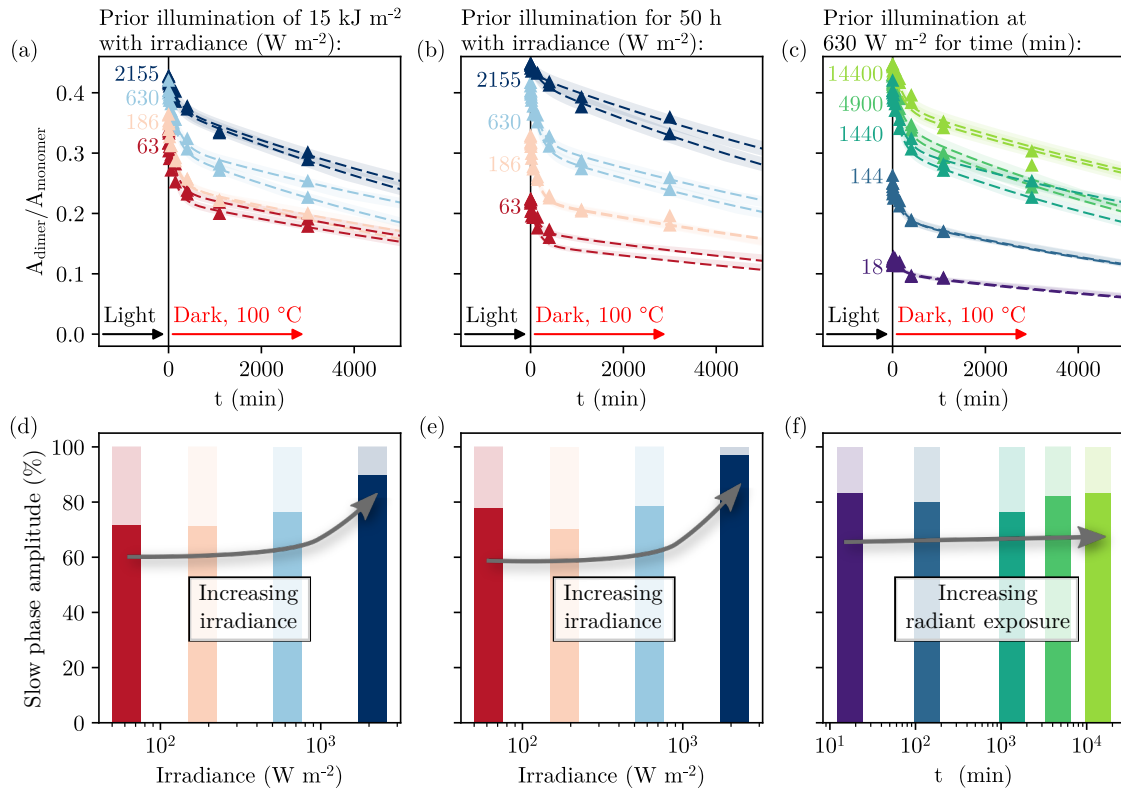


Figure 6.10 (a–c) PCBM dimer:monomer ratio in PCDTBT:PCBM thin films whilst annealing at 100 °C in the dark with prior illumination with three scenarios: (a) equal radiant exposure, (b) equal illumination time, and (c) equal irradiance. For each measurement repeats are presented as separate markers. Fitting of the two-phase decay gives the amplitude of the fast-phase and the slow-phase after the illumination. (d–f) The percentage of the slow-phase formed for the various conditions. These results show the amount of slow-phase is dependent on irradiance, and not radiant exposure or illumination time.

The previously reported rate of de-dimerisation in PCDTBT:PCBM was $2.28 \times 10^{-5} \text{ s}^{-1}$ which is between the values of the slow and fast kinetics observed here.³ The percentage of slow-phase to total dimer ($D_{\text{slow}}/[D_{\text{slow}} + D_{\text{fast}}]$) is plotted in Figure 6.10(d–f). Figures 6.10(d) and 6.10(e) show that illumination at a higher irradiance causes a greater fraction of slow-phase, independent of the radiant exposure or duration of light soaking. In Figure 6.10(f), the fraction of slow-phase is independent of illumination duration. The fraction of fast- to slow-phase is therefore dependent on the irradiance of illumination, and not the duration of illumination or the radiant exposure. From these measurements, it can be concluded that a key factor controlling the distinct populations is the irradiance. Its underlying mechanism was investigated by analysing the absolute yield of the slow- and fast-phase. The amplitude of each decay phase (as calculated from Figure 6.10) was compared with the light duration and with the radiant exposure. Figure 6.11(a) shows the slow-phase correlates with the radiant exposure. This follows the expected trend whereby increasing the illumination duration increases the yield of dimers, independent of intensity. However, the fast-phase correlates with the duration of light exposure,

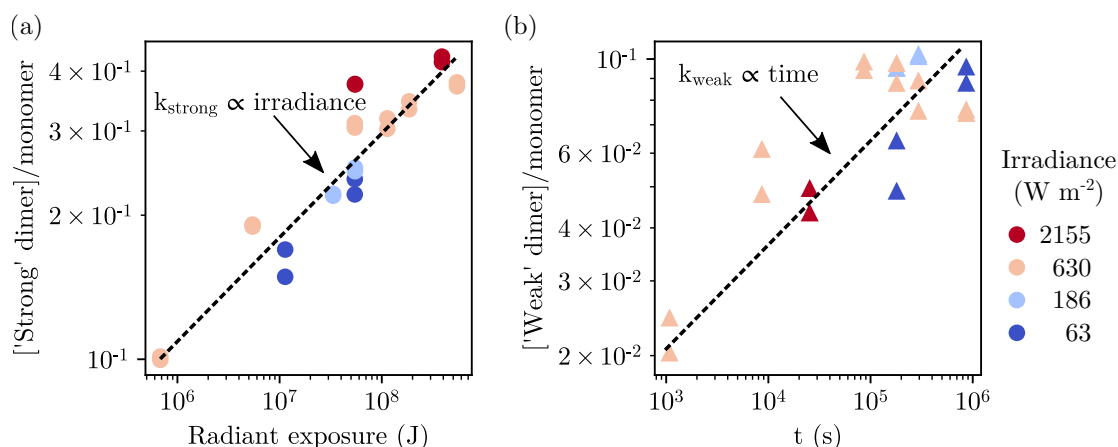


Figure 6.11 (a) The fraction of the slow decay to total dimerisation correlated against prior radiant exposure. This suggests the reaction follows the expected triplet mechanism previously reported for PCBM dimerisation. (b) The fraction of the fast decay to total dimerisation correlated against prior illumination exposure time. This suggests that even at the lowest irradiance used (63 W m^{-2}) the rate of formation is not limited by the illumination.

and not with the radiant exposure (Figure 6.11(b)). This is understood as even at the lowest irradiance investigated (63 W m^{-2}) the illumination is not limiting the formation of the fast-phase. Therefore, increasing the irradiance does not increase the rate of formation, contrary to the slow-phase amplitude. Instead, for the fast-phase amplitude, there is time dependence limiting the reaction.

6.3.2 PCBM trimers

PCBM trimers are examined as the potential cause of one of the fast and slow phases, alongside dimers, observed in the thermal decomposition process. GPC measurements were used to probe the kinetics of PCBM trimer formation. Fullerene light exposure can result in high order units such as trimers and oligomers which will affect the bond energy. In C_{60} , the oligomerisation can result in molecules with 21 units.¹⁸ To determine if this mechanism is responsible for the two-phase kinetics of thermal decomposition observed, the illumination dependence on oligomerisation of PCBM is investigated. Gel permeation chromatography (GPC) eludes the trimer unit faster than the smaller dimer unit (Figure 6.12). As with the previous absorbance experiments, a select range of radiant exposures and irradiances were used to determine the reaction kinetics of trimerisation. In Figure 6.12, the trimer signal correlates with radiant exposure (H_e) and is independent of irradiance. This does not follow the trends observed for the formation of the two-phase kinetics where a dependence on irradiance is observed. Furthermore, the fraction of trimer:dimer is determined from the amplitude of each signal in the GPC. The fraction of PCBM trimer to dimer (1:12) does not correlate with the fraction of fast to slow phase (1:4), accounting for reaction stoichiometry. From these observations, it is concluded that PCBM trimerisation does not account for the bi-phase kinetics of decomposition.

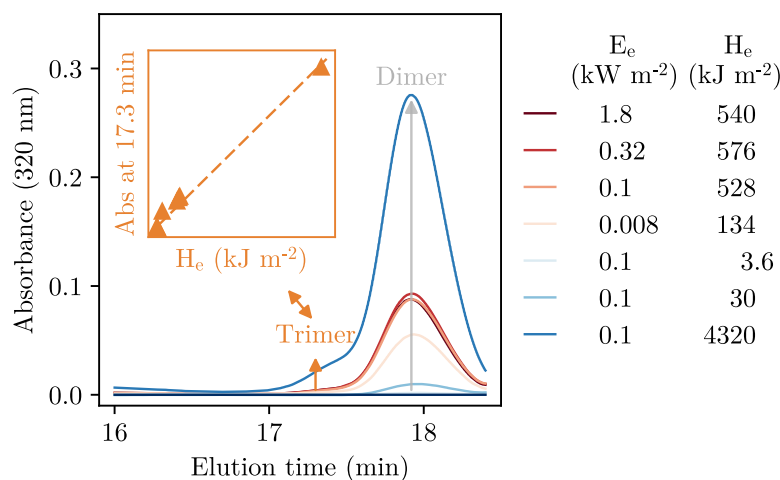


Figure 6.12 PCBM trimers are observed in PCDTBT:PCBM films which are identified by a shoulder at 17.3 min in the GPC measurements. The inset shows the linear correlation of trimerisation with radiant exposure, H_e . The red traces have similar radiant exposure ($\approx 550 \text{ kJ m}^{-2}$) with irradiances from 0.1 kW m^{-2} to 1.8 kW m^{-2} and all form approximately the same concentration of dimer; therefore, the trimer formation is independent of the irradiance, E_e . This is different to the trend observed between the strong and weak dimer (E_e dependence) thus the different dimers are not dimer and trimer formation.

6.3.3 PCBM dimer configurations

Another potential mechanism resulting in the formation of populations of dimers with different bond energies is the configuration of the PCBM dimer bond. The position of the PCBM tail on each of the fullerene units relative to the dimer bond location will affect the bond strength. There are 30 double bonds on a C_{60} cage located at the edge of hexagonal faces of a truncated icosahedron and as such called [6,6] double bonds.¹⁸ Aside from the [6,6] double bonds, there are bonds located between a hexagon and pentagon known as [6,5] bonds. These bonds can undergo the 2+2 cycloaddition reaction to form fullerene dimers. In C_{60} , a dimer between [6,6]/[6,6] bonds is more stable than the [6,6]/[6,5] bonds or [6,5]/[6,5] bonds by 83 kJ mol^{-1} and 163 kJ mol^{-1} , respectively.¹⁹ Herein, the [6,6] bonds are assumed to be the location of the [2+2] cycloaddition in PCBM. The symmetry of C_{60} means there is no effect of the dimer bond location on the bond energy. However, due to the asymmetry of PCBM, the location of the dimer bond relative to the PCBM tail will likely affect the associated bond energy. To investigate how significant this effect is density functional theory (DFT) calculations were done on a selection of dimer configurations. On PCBM there are 29 dimer bond locations, excluding the bond with the PCBM tail, resulting in $29 \times 29 = 841$ possible dimer orientations. The asymmetry of the side group means bonds on each configuration will result in different properties.

To effectively investigate the energetic landscape of the possible 841 PCBM dimer configurations a two-step methodology was used. Firstly, the possible bonding sites were split into 8 classes relating to the distance to the PCBM tail, termed β , as depicted in Figure 6.13(a). Pre-

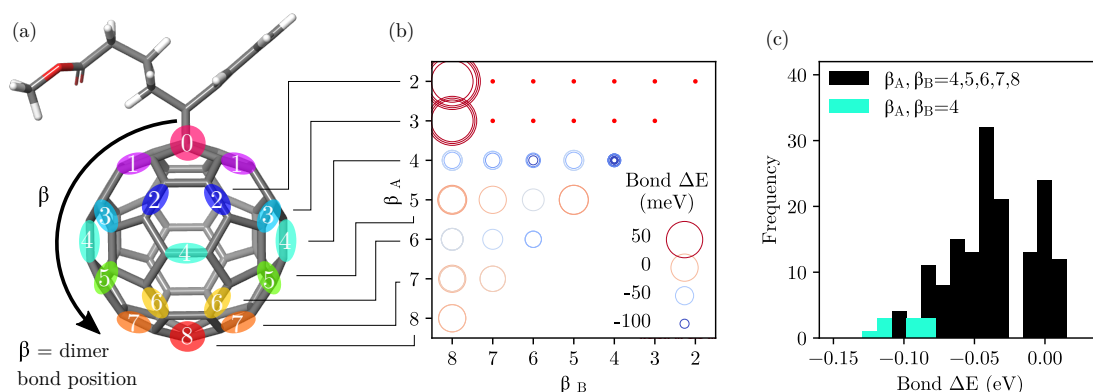


Figure 6.13 DFT calculations of the possible PCBM dimer configurations. (a) Dimerisation sites occur at double bonds between hexagonal faces. There are eight classes of equivalent distance from the PCBM tail unit. (b) The PCBM dimer bond energy dependence on the class on each fullerene; namely β_A and β_B . Each ring represents a different DFT calculation noting that for each $\beta_A : \beta_B$ point there are 16 orientations due to the asymmetry of the side group (examples are in Figure 6.14). Both the size and colour of each ring represent the bond energy relative the $\beta_A : \beta_B = 8$ configuration. (c) A histogram of the bond energies of all possible dimer configurations. The $\beta_A : \beta_B = 4$ dimers are the most stable and the spread is not as significant compared to the class, β . Thus, the class (β) is a greater factor than the orientation of the PCBM tail of each fullerene.

screening eliminated the class closest to the PCBM tail ($\beta = 1$). For the first step of calculations, the lone bond at class eight was fixed for fullerene-b ($\beta_b = 8$) and this was connected with all 25 bond locations on fullerene-a. All DFT simulations are presented in Figure 6.13(b) as an individual ring where the size and colour relate to the energy of the bond. From these results, $\beta = 2$ and $\beta = 3$ dimer bond energies are approximately 100 meV higher than the $\beta \geq 4$ configurations, giving a total distribution of 200 meV for $2 \leq \beta \leq 8$. The variation in bond energy should result in a change of reaction constant as defined by an Arrhenius relationship. In the instance of an energy difference of $\Delta E_{a-b} = 0.2$ eV between reactions a and b , and assuming the equivalent pre-exponential factor, then the ratio of rate of reactions is $k_a:k_b = 504:1$ at 100 °C. Under these conditions, the reaction would be either too slow or too quick and therefore $\beta = 2$ and $\beta = 3$ is assumed to be too unstable and unfeasible. In the instance where $\Delta E_{a-b} = 0.13$ eV as with $\beta \geq 4$ then $k_a:k_b = 57.1$ at 100 °C. This is remarkably close to the ratio found when modelling the results in Figure 6.10, where $k_{slow}:k_{fast} = 68.6$ at 100 °C. Therefore, the configurations of PCBM dimers with $\beta = 2$ and $\beta = 3$ are energetically unfavourable and thus expected not to form under these conditions. However, energy distribution for dimer configurations at $\beta \geq 4$ are consistent with energies observed experimentally.

For the second step of DFT calculations the remaining configurations with the class of $\beta \geq 4$ are considered. For each class (except $\beta = 8$) there are four bonds on the fullerene. As such a dimer between monomers a and b has $4 \times 4 = 16$ possible orientations (i.e. for a bond between class 7 on monomer a and class 6 on monomer b the possible orientations are $\beta_a:\beta_b = 7_1:6_1, 7_1:6_2, 7_2:6_1$ etc.). In each case only one was considered, except for the most stable

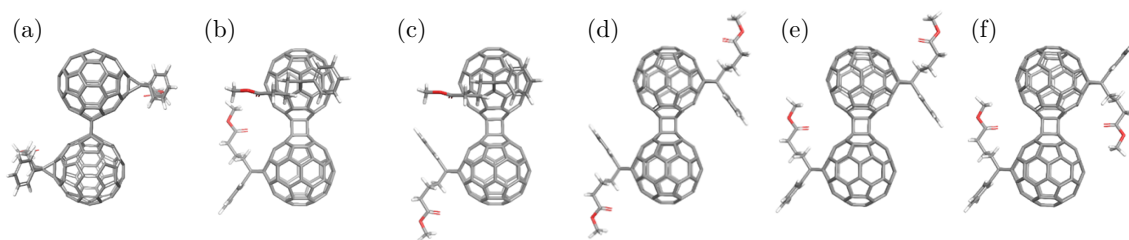


Figure 6.14 Possible $\beta_A : \beta_B = 4 : 4$ bond orientations calculated with DFT simulations. Note the $\beta = 4$ bond position has two orientations; either vertical or horizontal with respect the PCBM tail, as shown in Figure 6.13. Therefore, the range of configurations is diverse.

configuration, $\beta_a : \beta_b = 4 : 4$, where six orientations were calculated. Bonds not calculated with DFT calculations were extrapolated from the dimers with equivalent classes. A histogram of all configurations where $\beta \geq 4$ is presented in Figure 6.13(c). The range of energies is >0.1 eV and therefore significant within the range of temperatures used in this studied.

The correlation between the class (β) and bond energy is considered as a possible origin of the fast and slow bond energies observed in Figure 6.9. In Figure 6.13(c), bonds at $\beta = 4$ and $\beta = 6$ are the more stable, and specifically $\beta_B : \beta_A = 4 : 4$ is the most stable. Surprisingly, class eight is not as stable. When a bond is formed with the fullerene cage it distorts the sphere.^{20,21} This results in increased strain across the cage. If bonds on the fullerene are at opposite sides the distortion will be increased and the strain on the cage will be exaggerated. However, if the bonds are adjacent the distortion and strain are minimised. At bond positions where $\beta = 4$ both the steric hindrance of the side chain is minimised and the distortion of the fullerene cage is minimised.

Inspection of the energy landscape for dimer formation suggests that configurations at class $\beta=4$ and 6 yield the lowest energies, and that substitutions near the fullerene tail are energetically unfavourable and thus unlikely to occur. The bi-exponential behaviour observed experimentally is tentatively assigned to two configuration classes, combining DFT estimates and relative topological dimerisation requirements between PCBM molecules. Excluding sites (1-3) adjacent to the tail, it is hypothesised that two populations comprise sites around the equatorial plane (most favourable energetically) those near the antipode of the tail. It is thus likely that the activation energy associated to PCBM thermal decomposition, previously estimated as 0.96 eV^3 , is thus a weighted average $\langle E_a \rangle$ of the site distribution revealed in the present work. Given the DFT energy range computed as approximately $\Delta E_a \approx 0.10 \text{ eV}$ and the experimental decay rates calculated here, it is estimated that the two populations exhibit $E_{a,slow} \approx 0.9 \text{ eV}$ and $E_{a,fast} \approx 1 \text{ eV}$, compatible with the observations here.

To determine the dominating factor of bond stability the variation of bond energies between classes (i.e. $\beta_a : \beta_b = 4:4, 4:5, 4:6$ etc.) are compared to the variation of bond energies between the same class, but at different orientations (i.e. $\beta_a:\beta_b = 4_1:4_1, 4_1:4_2, 4_1:4_3$ etc.). The most stable class, $\beta = 4$, has greater variability still as two bonds are perpendicular and two parallel, with respect to the PCBM tail. Six configurations of $\beta_A : \beta_B = 4 : 4$ dimers are simulated in Figure

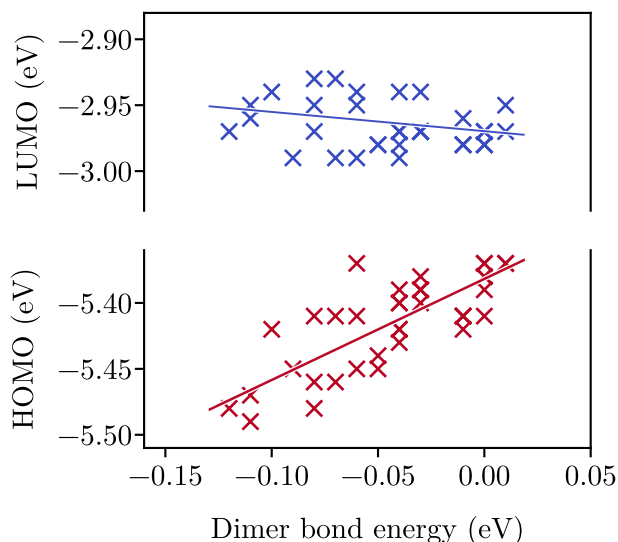


Figure 6.15 The effect of PCBM dimerisation on the frontier molecular orbital levels as calculated by DFT simulations. The stabilization of the dimer bond energy results in the widening on the band gap. Dimerisation results in the increased disorder of both the HOMO and LUMO level. The solid lines present fits with the least-squares error.

6.14. The bond energies of these are highlighted in the histogram in Figure 6.13(c) and given in Table 6.3. Although the dimers are topologically very different the effect on bond energy is less significant. This is not unexpected as changing the bond orientation might have little effect on the strain experienced by the cage. From these results the dimer bond position relative to the PCBM tail, β , is the dominant factor in determining the bond energy of the dimer. In addition, the formation energy of dimer 8:8 was calculated to be +28 meV, which is less stable than the dimer formation set to a reference value of zero. This can be explained considering that on the one hand, two new bonds are created, but on the other hand, some of the fullerene aromaticity is lost, and since these are antagonist effects, it explains the positive energy of formation required. To gain insight into this apparent anomaly, aromaticity analysis was performed. The NICS(0) indexes of the rings involved in the bond creations became strongly antiaromatic. In detail, from values of -2.90 and -2.97 for a single PCBM to values of +3.77 and 5.96 for position 8 (negative values mean aromaticity, positive antiaromaticity). This aromaticity lost sheds light into the positive formation energy obtained for position 8:8.

Table 6.3 Calculated bond energies for simulated dimers with a $\beta_A : \beta_B = 4 : 4$ configuration, as modelled in Figure 6.14.

DFT simulation in Figure 6.14	(a)	(b)	(c)	(d)	(e)	(f)
Bond ΔE (eV)	-0.09	-0.11	-0.08	-0.12	-0.11	-0.08

Finally, to understand the effect of PCBM dimer configuration on device performance the variations on frontier molecular orbitals (FMO) are considered. Figure 6.15 reports the HOMO and LUMO energy values compared to the dimer bond energy of formation. The HOMO and LUMO energies of the PCBM molecule calculated with these simulation conditions, at -5.57 eV and -3.00 eV, respectively, are considered as a reference. The lines are least-squares error fits to the data. As for the previous analysis, a strong correlation is obtained between the bond formation energy and the FMO energy. A stabilisation of the HOMO and LUMO with greater dimer bond energy was found. This is directly related to the fact that the higher the stability of a molecule, the deeper the electronic levels of the HOMO, which corresponds to a gain in electronic energy. From these results, it is concluded the dimer bond energy will affect the electronic properties of PCBM.

6.4 Discussion

At the majority of relevant OSC operating conditions, our modelling results suggest that only moderate perturbations of PCBM dimer concentration will occur (Figure 6.7(c)). Given that the expected operating lifetime of solar panels is over 20 years, the numerous (10^3 - 10^4 diurnal cycles) light and temperature fluctuations are likely to impact OSC device performance.

The location of an OSC will have specific meteorological conditions of temperature and irradiance. The model presented in Figure 6.7 uses a sinusoidal trend of environmental conditions. However, it is possible to input historical sensor readings of light and temperature of the point of application. This enables predictions of the long-term dimer population in a specific location, and potentially the PCE stability. Therefore, this tool allows for a powerful way to predict the stability of PCBM dimer populations for any application in any location.

Evidently, the parameterisation of the dimerisation model presented here allows for predictions of the monomer:dimer equilibrium over time in a range of blend matrix and environmental conditions. Alongside the factors described here, the temporal evolution of the polymer matrix will likely affect the dimerisation kinetics. These subtle morphological changes over time are controlled by a number of factors and present theoretically complex and convoluted problems. Therefore, for a holistic model, this factor should be considered to enable the prediction of the topo-chemical requirements from temporal morphological adjustments over long timescales.

Previous studies have shown PCBM dimerisation to correlate with both beneficial and detrimental effects on stability. Typically, studies presenting the preferential effect of PCBM dimerisation are performed at low light irradiance (≈ 0.1 Sun). However, studies demonstrating the degradation induced by dimerisation are performed at higher light irradiance (≈ 1 Sun). Here it is shown that the irradiance affects the formation of the dimer configuration and, subsequently, the molecular orbital levels. At high light intensities, a larger proportion of strongly-bound dimers are formed. These dimers are calculated to have a LUMO level 2-3 kT greater than that of PCBM and as such effect the mobility of polarons through PCBM. At lower light intensities greater weakly-bound dimers are formed which have a LUMO approximately equal the PCBM

monomer. With this understanding, it is possible to comprehend the double-edged effects of dimerisation.

The formation of the fast- and slow-phase of the de-dimerisation has different photophysical mechanisms. The fast phase of weakly-bound dimers was time-dependent whilst the slow phase of strongly-bound dimers was irradiance dependent. This is likely due to the matrix constraining the orientation of the weak dimers such that the correct alignment occurs infrequently. Interpreting the formation of strong and weak dimers with these mechanisms allows for the comprehension of the irradiance dependence of dimerisation. At higher irradiance, dimers are saturated in the strong configuration before weak dimers are formed. Whilst at lower irradiance, dimers are able to form in both weak and strong configuration. The different factors limiting the weak and strong dimerisation results in an irradiance dependence of formation.

The dominant PCBM dimerisation mechanism during the operation of a solar cell will be greatly affected by the location. To predict the overall beneficial or detrimental effects of dimerisation it is important to consider the diurnal and annual irradiance variation. A solar cell is likely to exhibit the greatest thermal stress whilst at high light intensities. The beneficial effects of morphological stability under thermal stress will only be experienced under high light intensity resulting in strongly-bound dimers. Additionally, the cyclic conditions will result in the equilibrium tending towards the most stable strongly-bound dimer. Therefore, under operating conditions of a solar cell, it may be unavoidable not to form the detrimental strongly-bound dimers that have been associated with 'burn-in'.

6.5 Conclusions

In summary, a minimal model is presented capable of describing the dynamic nature of PCBM fullerene photo-dimerisation and decomposition, under varying environmental conditions of temperature and illumination. Model parameters are obtained by a systematic experimental study of the (coupled) effects of light exposure time and irradiance, as well as polymer matrix and composition, and temperature. Experimental approaches are comparatively examined to quantify dimerisation and calibrate the simple UV-vis (320 nm) absorbance method by ancillary GPC measurements. The reaction rates and activation rates are established for both the forward and reverse reactions, and for the first time the activation energy of dimerisation is obtained as (22 ± 3) meV. The results show that dimerisation is *independent* of irradiance across three orders of magnitude encompassing the range relevant for practical applications, and that radiant exposure (the product of irradiance and time) is the relevant control variable. The nature of the polymer matrix, in terms of its impact in blend morphology and PCBM segregation, as well as photophysics, impacts primarily the prefactor of the dimerisation reaction rate. A significant decrease of the PCBM dimer population is observed with temperature, in particular above $\approx 100^\circ\text{C}$, where thermal decomposition becomes important. Under environmentally relevant operating conditions, however, PCBM dimerisation is found to generally dominate. This means that a steady-state asymptotic dimer population is rapidly attained, and is not

significantly affected by temperature fluctuations (which could reverse it). This is caused by the near concurrence of exposure to high irradiance and elevated temperature and the fact that the forward reaction dominates in those circumstances, which have now been quantified. The minimal model provides a predictive tool for PCBM dimerisation in any polymer:fullerene blend matrix comprising the active layer of a solar cell, under any environmental condition (set by a time-varying temperature and light intensity profile), with a few and simple calibration steps. Such knowledge enables predictions for solar cell morphological stability over both the short- and long-term. Furthermore, this work rationalises a potential reason for the double-edged effects of PCBM dimerisation previously reported in the literature. By investigating the de-dimerisation kinetics upon thermal annealing two populations of dimers have been found to form. Photo-dimerisation at high irradiance is shown to result in strongly-bound dimers whilst at lower irradiance weakly-bound dimers are also formed. DFT calculations suggest the origin of this energetic distribution in dimer bond energy originates in the location of the PCBM tail with respect to the dimer bond on the fullerene cage. The simulations also show the dimer bond energy is correlated with molecular orbital levels. The ideas presented enable a pathway to comprehend the varied effects of PCBM dimerisation on device stability.

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Chapter 7

Concluding remarks

7.1 Summary

The aim of this thesis has been to determine the degradation mechanisms limiting the stability of perovskite and organic solar cells and develop frameworks to overcome them. By specifically probing individual stability stress factors, the mechanisms limiting the long-term operation of the solar cells have been found. Material characterisation of the photochemistry and morphology has been correlated with light, temperature, and atmospheric conditions and, in some cases, device ageing. By understanding the cause of instability, it has been possible to present a pathway to overcome, or minimise, the rate of degradation of these devices. The findings presented highlight a range of both intrinsic and extrinsic instabilities to enable the future development of perovskite and organic solar cells with long-term stability under operating conditions.

In Chapter 3, the environmental factor resulting in low instability of MAPI solar cells under operating conditions was investigated. A design framework to minimise the photochemical degradation mechanism was presented for these perovskite optoelectronic devices. Specifically, it was demonstrated MAPI thin films undergo rapid hydration only at a relatively high level of humidity whereas photo-bleaching is observed under light and air conditions. MAPI solar cell efficiency in humid nitrogen is relatively stable compared to light and oxygen induced degradation. The dominant factor, which is initiated via the formation of superoxide, can be slowed by the integration of efficient electron extraction from the perovskite layer; using alternative device architectures or different organic/ inorganic materials. Furthermore, this degradation mechanism can be initiated with electrically injected (and not photogenerated) electrons in the presence of oxygen, resulting in rapid degradation of MAPI devices held under bias in the dark. The present findings suggest that oxygen induced degradation can influence the operational stability of not only solar cells but also other devices that utilise MAPI with excited state electrons.

Chapter 4 investigated the effect of halide tuning $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ on the environmental stability of thin films and solar cells. This work indicates the dominant instability of MAPI devices to light and oxygen is observed in mixed iodide/bromide $\text{MAP}(\text{I}_{1-x}\text{Br}_x)_3$ devices, for

$x < 1$. For MAPBr both thin films and solar cells show significantly improved stability in light and oxygen. During degradation of the mixed halide films, XRD analysis illustrates a shift towards increased bromide concentration as the iodide phases degrade. The superoxide generation yield is independent of halide ratio. Instead, it is suggested the increased thermodynamic stability of the MAPBr to degradation products improves stability. The solar cell stability was limited by the hole transporting material, and not the MAPBr perovskite. The band gap of MAPBr is not well suited for single junction solar cells but may be employed for high voltage applications or as a sub-cell in tandem solar cells. The inherent stability of MAPBr to environmental factors, combined with stable interlayers, can enable long-term operation of unencapsulated solar cells.

In Chapter 5, the combined effect of thermal stress with illumination was investigated regarding PCBM dimerisation and the resulting morphological stability in the polymer:fullerene systems. Whilst annealing at 85 °C, no morphological changes are observed in polystyrene:PCBM films throughout the vertical stratification or topography, independent of illumination. However, at the glass transition temperature of the blend, structural relaxation of the film surface is inhibited by PCBM dimerisation. Time-resolved neutron reflectivity measurements with *in-situ* annealing up to 100 °C reveals PCBM enrichment to the bottom interface (PEDOT:PSS). The diffusion kinetics of this enrichment are quantified with both a non-physical and physical model to show that PCBM dimers are effectively immobile in the polymer:fullerene matrix on the timescales probed. These results aid the understanding of morphological stability in polymer:fullerene solar cells under operating conditions of temperature and illumination.

In Chapter 6, the PCBM dimerisation reaction mechanism was intricately investigated using a novel UV-vis absorbance assay. The effect of temperature, light, and polymer matrix on dimerisation reaction rates were investigated and the kinetics of the de-dimerisation. The light intensity dependence of dimerisation is found to be first-order and the temperature dependence of dimerisation reaction gives an activation energy of (22 ± 3) meV. Modelling of *in-operando* conditions shows the dimer is dominate in the reaction equilibrium for the majority of polymer:fullerene systems. Analysis of the kinetics of de-dimerisation during dark thermal annealing shows evidence for two populations of dimers with a ‘slow’ and ‘fast’ phase of de-dimerisation. DFT simulation suggest this is due to different conformations of the dimer bond position with respect to the PCBM tail. To conclude, these results comprehensively probe PCBM dimerisation reaction kinetics and are a pathway to comprehend to varied effects of PCBM dimerisation on device stability.

7.2 Outlook

Stability studies of solar cells are laborious. There are numerous interlinked factors with parallel degradation mechanisms occurring simultaneously. The time required to get a single dataset can be months. This can be orders of magnitude longer compared to device optimisation of active layer thickness, transport materials, annealing temperatures, etc. Therefore, it is important to select the correct samples to study. Detailed characterisation of why an unstable device

was unstable often does not provide useful information. Analogous measurements of why a low-efficiency device is low efficiency would be deemed needless. Screening of device stability is time intensive but potentially very fruitful to develop this problem.

Which stress factors to consider during stability studies is often poorly considered. Generally, this is split between intrinsic and extrinsic. However, before contemplating extrinsic stability it is essential to ensure intrinsic stability for the operating lifetime. If a solar cell is not stable for thousands of hours under operating conditions when encapsulating, the stability to environmental factors is somewhat irrelevant. Within the perovskite community there is now a shift from degradation mechanism described in this work towards intrinsic stability. Although environmental stability research often poses interesting scientific questions it is often not going to assist commercialisation of these technologies.

For perovskites, stability is not the challenge it was once thought to be. Promisingly, there are demonstrable solar cells that show no degradation for thousands of hours under operating conditions. Although the continuation of new interlayers and architectures present ever-changing problems for stability. Undoubtedly there is still work to be done in this area and perovskite stability remains a hot topic of research. For practicality of commercialisation, there has been a transition from environmental to encapsulated stability.

For organics, stability is still a major challenge with intricate complexities. The requirement of the nanoscale morphology, alongside the material and interlayer stability, poses degradation from several factors. Although the stability can be relatively good—1000's of hours—there are still hurdles to overcome. This length of stability has not been demonstrated in the state-of-the-art high-efficiency devices. A problem still to be understood is degradation initiated during exposure to light—labelled 'burn-in'. This is also observed in perovskite solar cells and in silicon solar cells where it is called 'light-induced degradation' or LID. Within organic and perovskite solar cells the 'burn-in' is not associated with any specific mechanism. It remains an elusive problem of these technologies.

For solar cells, the future is bright. 150 years ago it was discovered light from the Sun can be converted into electricity—but only now is the potential being realised. Over the last decade, a surge of interest has boosted the performance in a variety of solar cell technologies. This thesis has presented studies on two of them: perovskite and organic. Both the efficiency and stability has surpassed what was thought possible at the start of this PhD—only four years ago. The bar keeps moving ever higher. There is still great potential for these technologies to either compete against or complement silicon solar cells. For research and industry, exciting times lie ahead.