

Hole extracting layers in perovskite solar cells: influence on performance and stability



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A thesis submitted for the degree of
Doctor of Philosophy

Michaelmas, 2017

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Abstract

As one of the most promising technologies for highly efficient and low-cost photovoltaics, hybrid organic-inorganic metal halide perovskites solar cells have received a great deal of attention over the past 5 years. However, the moisture sensitivity of this material hinders commercial deployment, and the next grand challenge is now the long-term, stable operation of such devices. This thesis presents novel hole-extraction layers for perovskite solar cells, and studies their impact on both the performance and the long-term stability of the devices.

Initially, this work focuses on the development of a polymer composite hole transporting material (HTM) based on poly(3-hexylthiophene) nanowires (P3HT-NW) embedded in an inert poly(methyl methacrylate) (PMMA) matrix. This HTM gives superior efficiency when compared to a neat P3HT HTM, and outperforms conventional HTM systems after thermal stressing in air. Next, the commonly employed and unstable lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) *p*-dopant for 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), is successfully replaced by two molybdenum tris(dithiolene)s. These devices show a substantial enhancement of the long-term stability, due to a significant enhancement of the moisture resilience of the HTM layer while maintaining high device power conversion efficiencies. Finally, the interaction of these molybdenum complexes with the perovskite is studied. This study demonstrates that the molybdenum complex modifies the treated interface in two ways; it passivates surface defects and create an interfacial dipole. As a result, the perovskite/HTM interface shows greater hole selectivity resulting in a substantial enhancement of the device performance, underscoring the importance of the charge-selective interfaces for carrier extraction.

To my Parents who forever supported my crazy dreams, even when separated by oceans and continents.

Acknowledgements

I would like to deeply thank my supervisor, Professor Henry Snaithe, for giving me the opportunity to explore academic research in the City of Dreaming Spires. Despite frustrations along the way, your incredible enthusiasm and excitement for science have made the journey a truly special experience. You have offered me the chance of a lifetime with constant challenges, which has helped me to grow both academically and personally. I will always be grateful.

To all past and present Snaitheings, exceptional scientists and wonderful people. Thank you for making those long hours in the lab much more enjoyable and for being the friendliest, the funniest but also the craziest research group I have ever known. I would not be here today without the unwavering support of Nakita Noel. Kita, thanks for your patience, advice, wonderful cakes and for looking after me like a big sister would. You have always believed in me, even at those times when I wasn't. A particular thank you goes to Severin Habisreutinger (aka Mr. Toobs) for his assistance in the lab, precious advices, and valuable comments on this manuscript. I want to thank Grey and David, for making the office a better place at night. Grey, thank you for constantly looking after me and making sure I would never run out of of Babybels. David, your glasses will now remain unbroken, but still you should get new ones. A special thank to Tomas Leijtens for always being excited about my research and for sharing his passion for science. More thanks goes to the long list of Snaithe's colleagues and friends who crossed my path: Bernard, Jong, Giulio, Jay, Jonny, Liv, Marti, Fede, Derek, Florian, Ivan, Matt, James, Giles, Rebecca, and many others.

A very special thanks to Laure for being an amazing friend, for having my back all these years on and off the water, and for making all those 5am much more enjoyable. My Oxford

experience would not have been the same without all the precious friendships and fantastic people I met through rowing, both Blues and Stanners. In particular, my two pair partners in crime, Kirstin and Lucy.

To Heidi. You have been a fantastic friend and flatmate. Thank you for your endless positivity and support. I will miss those mad dancing evenings and our tragic cooking sessions on Sundays.

To all my friends back home, especially Justine, Marie and Sophie for being present, no matter what, for the past 15 years.

Finally, I would like to thank my family with all my heart. Maman and Papa, thanks for never doubting me and letting me follow my dreams. You have always supported me in all my decisions, even when they implied living on the other side of the planet. To my sister and brother, Ines and Miguel, their partner and wife, Olivier and Chloé, for your love and encouragement. Finally, to my nephews and nieces, Timoté, Malo, Antoine, Zélie, Léonie, Prune and Louise, thanks for helping me seeing the world through the eye's of a child and for reminding me that we all have to fight for your future.

Men argue. Nature acts.

Voltaire (1696-1778)

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1 | Introduction

“All across the world, in every kind of environment and region known to man, increasingly dangerous weather patterns and devastating storms are abruptly putting an end to the long-running debate over whether or not climate change is real. Not only is it real, it’s here, and its effects are giving rise to a frighteningly new global phenomenon: the man-made natural disaster.” Barack Obama, April 2006

1.1 The climate change challenge

Throughout history, the Earth’s climate has always experienced changes, alternating between ice ages and warmer periods. Those inevitable climatic cycles are tightly dependent on the composition of the atmosphere and have occurred as a consequence of natural changes. About 7000 years ago, the abrupt end of the last ice age marked the beginning of human civilisation, starting point of modern climate era.

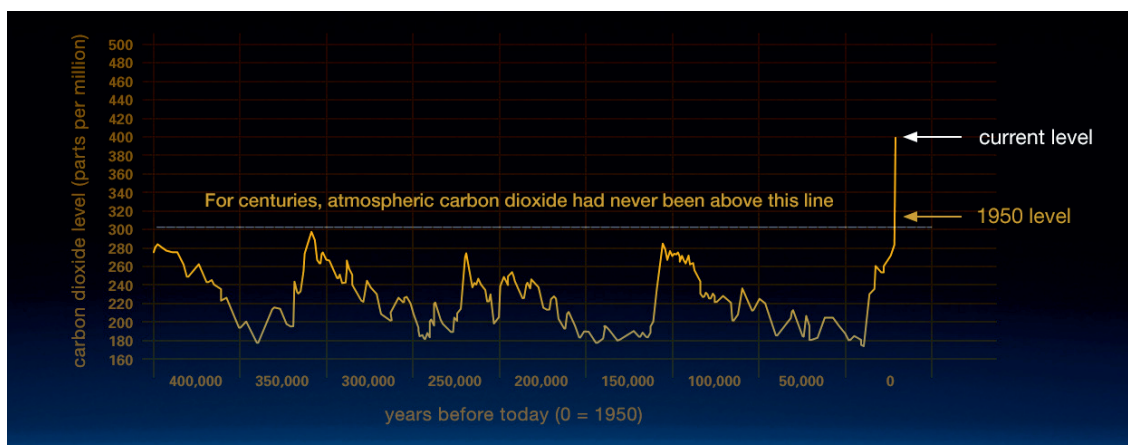


Figure 1.1: Global CO₂ concentration in the atmosphere. (Copyright NASA Goddard Institute for Space Studies [1])

The surge of the global population [2] alongside a rapid increase in industrialisation marked the modern society with the most destructive climate change in Earth's past (Figure 1.1). The world's increasing energy demands has resulted in prodigious quantities of greenhouse gasses such as carbon dioxide (CO_2) in the atmosphere (406.94 ppm in September 2017). Since the industrial revolution, our society has been primarily relying on fossil fuels to face the surging energy demand. However, their supply is dwindling and the unavoidable greenhouse gas emissions due to combustion of fossil fuels hasten atmospheric changes. In response to these abrupt emissions of CO_2 due to human activity, the average surface temperature of the planet has risen [1] (Figure 1.2). This rise in temperature has caused glaciers to retreat, sea levels to rise associated with a record number of extreme climatic events. While the natural climate change is inevitable, our current rate of greenhouse gases emission in the atmosphere is causing the climate on Earth to change 170 times faster than natural forces [3]. This alarming finding has urged human society to turn towards clean and renewable energy resources which do not contribute to additional greenhouse gas emissions, in order to eventually reverse, or mitigate, the evolution of the global climate.

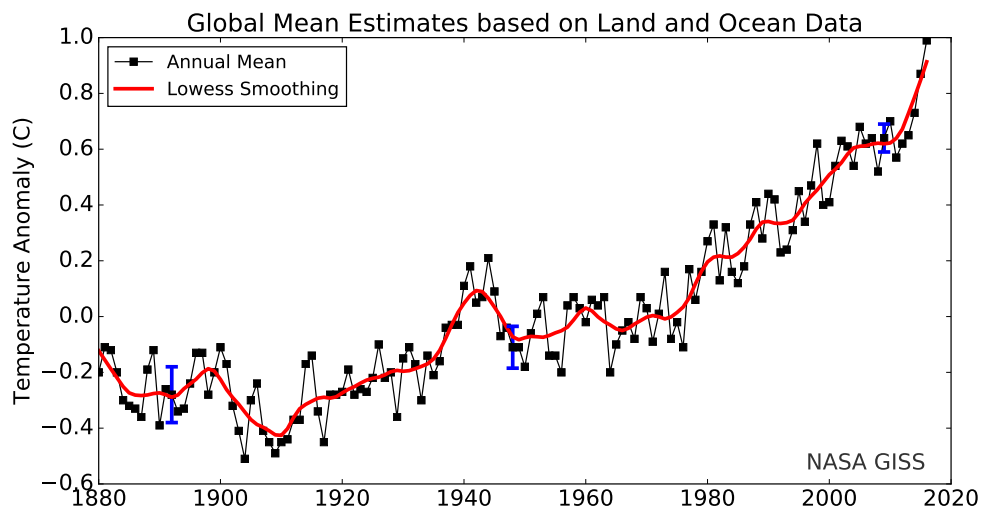


Figure 1.2: On the left, line plot of global mean land-ocean temperature index, 1880 to present. (NASA Goddard Institute for Space Studies [1])

The most abundant renewable sources are sunlight, wind, rain, waves, tides and geothermal heat. Even so fossil fuel remains the dominant source of energy powering the world economy (78.4%), renewable energies provided 19.3% of the global energy market in 2015, and are expected to triple by 2035, being the fastest growing source of energy [4] (Figure 1.3). As part of the renewable energy category, solar power, or photovoltaic energy, could exceed the current global energy demand by converting only 1% of the incident solar energy on the Earth's surface with 10% efficient photovoltaic devices [5]. However, in the latest data collected by the Renewable Energy Network (REN21), solar energy accounted for less than 1.6% of the global energy consumption.

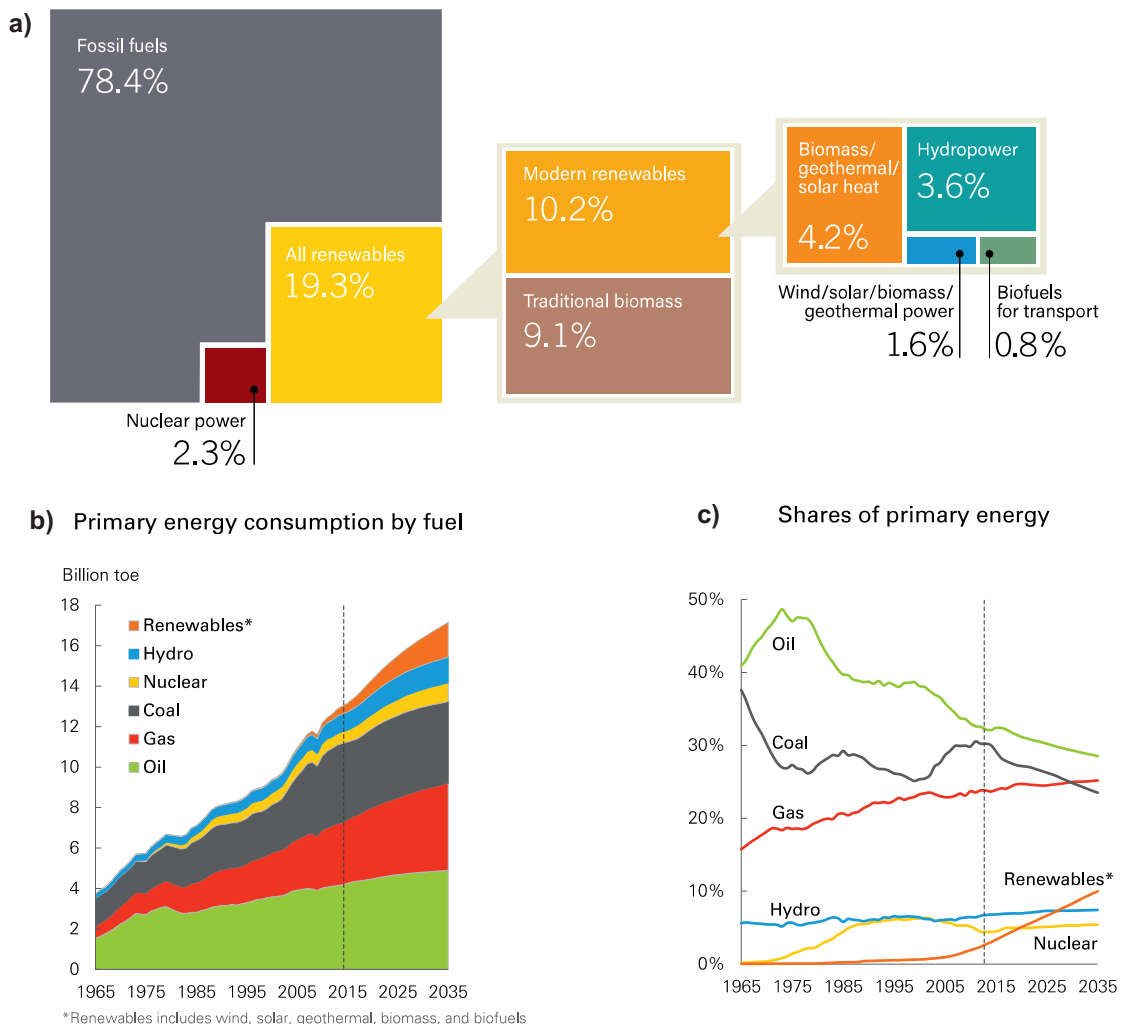


Figure 1.3: a) Estimated global energy consumption for 2015 by source, data collected by the Renewable Energy Network (REN21). (Reproduced with permission from REN21, 2017, Renewables 2017 Global Status Report, Paris, REN21 Secretariat [6]). b) and c) Trends of global energy consumption from 1965 by source and projected usage up to 2035. (Reproduced with permission from British Petroleum, 2017, BP Statistical Review of World Energy 2017 [4])

One of the major obstacles to the implementation of solar energy has been the higher cost per Watt of energy produced compared other resources. Recently, the levelised cost of electricity (LCOE) of solar power have tremendously dropped to around 0.5 \$/W making photovoltaic technology able to compete in the global energy market [7, 8]. However, most solar technologies require high initial investments which hold back manufacturers from entering the energy market at a sustainable price. In addition, conventional photovoltaic technologies, such as silicon solar cells, are not carbon-neutral due to heavy manufacturing processes. While government incentives would greatly urge the implementation of solar power, further innovations in photovoltaic solar cells are still needed in order to push the technology to be more effective and more sustainable. This involves the development of solar cells using cheap and earth-abundant materials, while limiting CO₂ emissions during the fabrication process.

One of the most promising candidates is the perovskite solar cell. Due to their outstanding optoelectronic properties, organic-inorganic lead halide perovskites have created tremendous enthusiasm in the photovoltaic community, leading to power conversion efficiency records up to 22% in merely 5 years [9, 10]. Compounds employed to create perovskite materials are abundant, cheap, and the ease of fabrication via solution or vapour process deposition methods make the technology extremely attractive. However, the major drawback of perovskite materials is their inherent instability at ambient conditions, which thus lead to further encapsulation systems with lamination foils, glass and edge sealants. These encapsulating techniques result in costly final products associated with a greater carbon emission due to additional manufacturing steps. Therefore, developing solar cells with enhanced stability should have a substantial impact on the overall carbon footprint of the technology which could push perovskite solar modules to become a major photovoltaic technology [11].

1.2 Structure and objectives of the thesis

Due to an unprecedented rise in performance, perovskite solar cells are now one of the most promising emerging photovoltaic technologies. However, pressing concerns related to the long-term operational stability of these devices remain. Indeed, the moisture sensitivity of the perovskite active layer prevents the technology from being competitive with inorganic thin-film solar cells in the global market place today. Two fundamental approaches exist for improving device stability: developing more resilient perovskite materials and shielding the sensitive absorber with protective layers. This thesis focuses on the latter, through the development of new charge-extraction layers for perovskite solar cells with the aim of enhancing the long-term stability of the devices while maintaining high power conversion efficiencies.

Chapter 2 gives a broad introduction to the fundamental concepts of photovoltaics, starting with an overview on properties of semiconductors. After having established general considerations of semiconductor physics, the general working principles of solar cells are detailed, including the absorption of a photon, charge generation and charge recombination pathways, and charge carrier separation and extraction. Particular attention is given to the description of the various types of junctions used in solar cells, followed by an outline of the typical performance parameters for quantifying the efficiency of a device. The subsequent section introduces the fundamental properties of the perovskite absorber material, and gives a short overview of the recent major developments in the perovskite solar cell field. Next, the operating mechanisms of these devices are described, followed by a thorough description of the instability challenges facing perovskite solar cells.

In Chapter 3, the materials and methods used in this body of work are described. Chapters 4, 5 and 6 contain the main experimental results which have been obtained during this work.

Chapter 4 details the development of a new composite HTM structure based on a polymer blend of P3HT nanowires and insulating PMMA. This approach is shown to substantially

reduce non-radiative recombination losses at the perovskite/HTM interface, achieving device performance comparable to common HTMs. The impact of using the inert PMMA is two-fold. It partially passivates the charge collecting interface, forcing the excited charge carriers to flow through discrete nanowires channels. As a result, non-radiative recombinations losses are significantly reduced at the *p*-type interface. Further, the polymer also acts as a barrier to water ingress which greatly enhances long-term device stability.

Most high efficiency perovskite solar cells employ a spiro-OMeTAD HTM doped with Li-TFSI salts which are highly detrimental to the long-term performance of the devices, limiting its use in future commercial applications. Due to its hygroscopic nature, Li-TFSI accelerates the permeation of water through the HTM layer resulting in a decomposition of the perovskite absorber, thus motivating the development of a more moisture resilient dopant. In Chapter 5, the Li-TFSI *p*-dopant is successfully replaced by two molybdenum complexes: molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)-ethane-1,2-dithiolene) ($\text{Mo}(\text{tfd-COCF}_3)_3$), and molybdenum tris(1-(methoxycarbonyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) ($\text{Mo}(\text{tfd-CO}_2\text{Me})_3$). Both dopants have a significantly higher doping efficacy than Li-TFSI and lead to high efficiency solar cells. Finally, the improved hydrophobicity of $\text{Mo}(\text{dt})_3$ -doped spiro-OMeTAD layers is shown to yield a significant enhancement of the long-term stability of perovskite solar cells, making molybdenum tris(dithiolene)s promising *p*-dopants candidates for HTMs with regards to both performance and stability.

Solution-processed perovskite films generally show structural defects and charge trap states at surfaces and grain boundaries. These defects are responsible for non-radiative recombination losses and limit efficient charge extraction. Chapter 6 addresses the importance of the interface between the absorber and the HTM layer and how it impacts the performance of perovskite based solar cells. In this study, the $\text{Mo}(\text{tfd-COCF}_3)_3$ molecule used in the previous chapter is studied as a surface treatment of the perovskite absorber. The treatment results in a significant improvement of the stabilised power conversion efficiency attributed to a passivation of trap states and the formation of a surface dipole at the interface, substantially improving hole extraction.

Finally, a concluding chapter briefly summarises the key findings of the thesis and gives an outlook of future developments for improving both performance and stability of perovskite solar cells.

2 | Fundamentals and background

This chapter gives an overview of the fundamental concepts and processes required to understand the results presented in this work. The key properties of semiconductors are firstly considered. Followed by an introduction to the theory and working principles of photovoltaic devices. Finally, perovskite solar cells are introduced, outlining various device architectures, materials employed and their inherent instability. For more in depth information, the reader should refer to standard textbooks [12, 13, 14, 15] from which this chapter was largely inspired.

2.1 Semiconductors

Semiconducting materials are the heart of every photovoltaic system. They are neither a good conductor nor a good insulator, but show greater electrical properties upon addition of heat, light or voltage.

2.1.1 Electrons in semiconductors

Metals, insulators, and semiconductors possess very different electrical properties, contingent on their *band structure* and *band gap*, E_g , which is given as the difference in energy between the highest energy band filled by electrons, called the *valence band* (VB), and the first available empty band, referred to as the *conduction band* (CB).

When two atoms are brought together, their respective electron orbitals *split*, defining allowed quantum energy states that an electron can occupy. In a solid with a large concentration of atoms, degenerated energy levels are not discrete anymore, but form a continuum or band of allowed energy levels. These electronic states are very close from one to another

and are separated by energy values, much smaller than the thermal energy $k_B T$ (~ 25 meV). In a crystalline material, atomic potentials are arranged on a *periodic* and practically *infinite* lattice which thus confines the distribution probability of electrons according to the atomic periodicity. In real space, a lattice can be characterised by two vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, which define the smallest possible unit cell, called primitive cell which is the smallest periodically repeated unit of the three-dimensional crystal lattice. When expressed in the reciprocal or momentum space, $\mathbf{a}_1$ and $\mathbf{a}_2$ become the reciprocal lattice vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ and define the *Brillouin zone*. The Brillouin zone is used to describe the electron energy of the band structure of crystals.

Electronic states are quantum mechanically described as electron probability distributions which are represented by a wavefunction Ψ . This wavefunction is the product of a periodic component related to the crystal lattice, and a plane wave part representing the wavefunction of an electron in free space. To determine these states for a given material, it is essential to analyse the dynamic behaviour of electrons by solving the time-independent Schrödinger equation. This thesis will not attempt to solve the Schrödinger equation in great detail, analytical solutions for crystalline systems with periodic potentials can be found in standard textbooks [13, 14]. For metal halide perovskites with a more complex crystalline structure, numerical density functional theory is employed to determine the electronic states and the band structure [16, 17, 18]. The solutions describe the relationship between an electron's energy and its momentum, giving energies as a function of k , the wave vector. This eigenstate distribution $E(k)$ is referred to as the crystal *band structure*. k varies from 0 to π/a , with a being the lattice constant which is a measure of the distance between atomic planes in that direction. For $k > \pi/a$, the energy distribution repeats itself, due to the periodic potential of the material. Furthermore, due to the symmetry of the crystal, $E(k)$ is identical to $E(-k)$. Consequently, all possible eigenstates of $E(k)$ are confined to wave vectors in the range between $0 \leq k \leq \pi/a$, which corresponds to the Brillouin zone (Figure 2.1).

When all electrons are in their lowest energy state without any additional available energy, i.e. at absolute zero ($T=0K$), the energy bands of a semiconductor are defined as

follows. The highest energy band filled by electrons is called the *valence band* (VB), and the first available empty band is referred to as the *conduction band* (CB). The two bands are separated by a gap which does not contain electron states, called the fundamental *band gap* (E_g). For a semiconducting material, the solution of the Schrödinger equation does not have solutions of the wavefunction for energies within the bandgap at $k = \pm\pi/a$. The band gap, defined the energy difference of the conduction band edge (E_C) and the valence band edge (E_V), i.e. $E_g = E_C - E_V$, corresponds to the minimum amount of energy necessary to promote an electron from the VB into the CB. When electrons are given enough energy to cross the band gap, they leave behind unoccupied states in the VB which constitute effective positive charges and are treated as quasi-particles, referred to as *holes*.

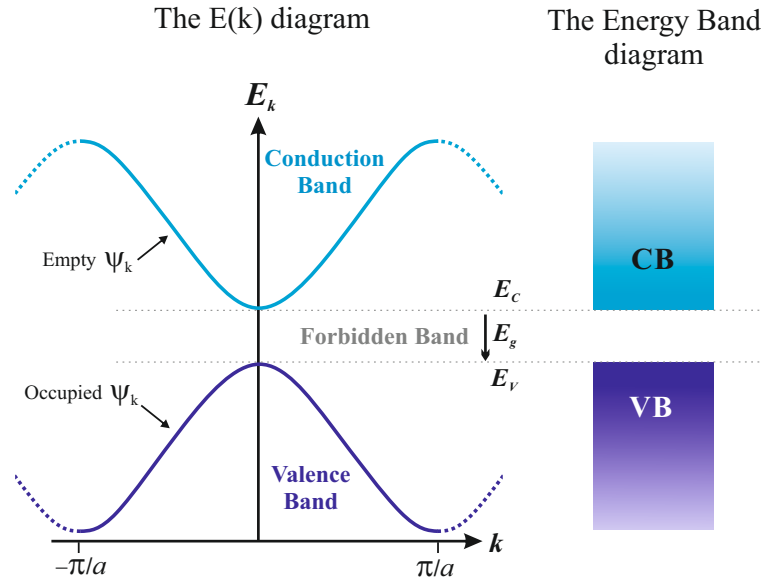


Figure 2.1: Schematic $E(k)$ diagram within a Brillouin zone for one lattice direction and its equivalent energetic band diagram. The $E(k)$ curve represents the wavefunction ψ_k and consists of many discrete points, each one them corresponding to a possible energy state. In the range E_V to E_C , corresponding respectively to the energies of the valence band (highest energy band filled by electrons) and the conduction band (the first available empty band), ψ has no solutions, giving rise to a forbidden band, E_g .

The Fermi level, denoted E_F , and associated to a chemical potential μ (a form of potential energy), is defined as the energy at which there is a 50% probability of an electronic state being filled/occupied. At thermal equilibrium, E_F lies in the centre of the band gap. The probability of an electron occupying an energetic state E at temperature T is governed by the Fermi Dirac distribution (Figure 2.2), which describes the electrons distribution of a

semiconductor:

$$f(E, T) = \frac{1}{\exp\left(\frac{E-E_F}{k_B T}\right) + 1} \quad (2.1)$$

with E_F being the Fermi energy for which $f(E_F) = 0.5$ and k_B the Boltzmann constant ($1.381 \times 10^{-23} \text{ m}^2 \text{ kg} \cdot \text{s}^{-2} \text{ K}^{-1}$). For states with an energy much smaller than the Fermi energy *i.e.* $E \ll E_F$, $f(E) \approx 1$ meaning, the probability of finding a state to be occupied is practically hundred percent. Conversely, states with energies much larger than the Fermi energy, $E \gg E_F \leftrightarrow f(E) \approx 0$, the states are almost certainly unoccupied.

Whereas the probability for the occupation of states depends only on their energy, the electron density of states (DOS) is contingent on both the momentum and energy of electrons in the studied crystal. In order to treat electrons in such complex potential landscapes, the concept of *effective mass* (m^*) is introduced. The effective mass is a parameter with the dimensions of mass, but is generally not constant. It describes the mass of a free electron taking into account the forces acting on the electron within the potential landscape of the material. It is defined by [12]:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} \quad (2.2)$$

Where $\hbar$ represents the reduced Planck constant.

Considering the states closest to an energy maximum or a minimum, *i.e.* the top of the VB or the bottom of the CB, the dispersion curve $E(k)$ can be approximated by a quadratic equation [12]:

$$E(k) = \frac{\hbar^2 k^2}{2m^*} \quad (2.3)$$

The DOS per unit crystal volume, $g(k)$, is defined as [14]:

$$g(k) d^3k = \frac{2}{(2\pi)^3} d^3k \quad (2.4)$$

Therefore, after further quantum mechanical derivations using equations 2.2, 2.3 and 2.4,

the DOS for the conduction, $g_C(E)$, and the valence band, $g_V(E)$, can be expressed as:

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_C)}}{\pi^2 \hbar^3} \quad (2.5)$$

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3} \quad (2.6)$$

with m_n^* and m_p^* being the effective masses of electrons and holes, respectively. A schematic representation of the DOS $g(E) \propto \sqrt{E}$ for an intrinsic semiconductor is shown in Figure 2.2.

For an intrinsic semiconductor, *i.e.* without added impurities, the number of electrons occupying the energy bands in equilibrium is given by the DOS $g(E)$ multiplied by the probability of occupancy $f(E)$ integrated over all possible energies (Figure 2.2). Therefore, the electron (n) and hole (p) densities are given by:

$$\begin{aligned} n &= \int_{E_C}^{\infty} g_C(E) f(E) dE \\ &= 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{\frac{3}{2}} \exp \left(-\frac{E_C - E_F}{k_B T} \right) \\ &= N_C \exp \left(-\frac{E_C - E_F}{k_B T} \right) \end{aligned} \quad (2.7)$$

$$\begin{aligned} p &= \int_{-\infty}^{E_V} g_V(E) [1 - f(E)] dE \\ &= 2 \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{\frac{3}{2}} \exp \left(-\frac{E_F - E_V}{k_B T} \right) \\ &= N_V \exp \left(-\frac{E_F - E_V}{k_B T} \right) \end{aligned} \quad (2.8)$$

where N_C and N_V define the effective density of states such that [12]:

$$N_C = 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{\frac{3}{2}}, N_V = 2 \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{\frac{3}{2}} \quad (2.9)$$

From equations 2.7 and 2.8, it is apparent that the electron and hole densities vary exponentially with the position of the Fermi level. Moreover, at a given temperature the

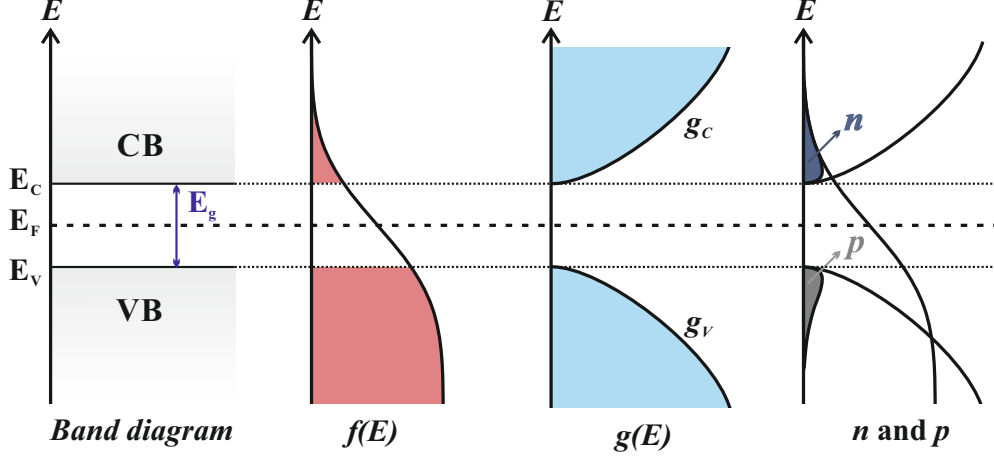


Figure 2.2: Schematic energy band diagram, Fermi-Dirac distribution $f(E)$, density of states (DOS) $g(E)$ and carrier concentrations (n and p) for an intrinsic semiconductor at thermal equilibrium. The probability that an electron occupies an energetic state E is governed by the function $f(E)$, and the number of available energy states is given by the DOS $g(E)$. The number of electrons occupying the energy bands is defined by the product of $f(E)$ and $g(E)$. For energies above E_C , the product gives the concentration of electrons in the CB, while for energies below E_V it gives the holes concentration in the valence band.

product np is constant. Thus at thermal equilibrium for an intrinsic semiconductor, *i.e.* when the number of electrons in the CB is equal to the number of holes in the VB, the intrinsic carrier concentration n_i^2 is independent of the Fermi energy and can be expressed as:

$$n_i^2 = np = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right) \quad (2.10)$$

It therefore follows the expression of the *intrinsic potential energy* E_i , which is equal to the Fermi level E_F for an intrinsic semiconductor (from Equations 2.7 and 2.8, with $n = p$):

$$E_i = E_F = \frac{1}{2}(E_c + E_v) - \frac{1}{2}k_B T \ln\left(\frac{N_C}{N_V}\right) \quad (2.11)$$

The size of the band gap and the position of the Fermi level will determine whether a material behaves as a metal, an insulator, or a semiconductor. For electrical conduction to occur, the conduction band of a material must have some of its energy states filled with mobile electrons (*i.e.* $n > 0$). Without a band gap and a large number of filled states near to the Fermi level, electrons in metals can be readily excited between states, leading to a high concentration of mobile carriers to carry current in the conduction band. In contrast,

the Fermi level in an insulator lies within a large band gap of forbidden energies ($E_g > 4 \text{ eV}$). There are no available states for electrons near the Fermi energy, which imply that $n = 0$ in the CB and electrical conduction cannot occur. In the case of semiconductors, the band gap is comparatively small ($0.5 \text{ eV} < E_g < 3 \text{ eV}$) with the Fermi level in the middle, such that the probability of an electron to occupy an energy state in the CB is non-zero for $T > 0\text{K}$. Electrons from the valence band can be thermally excited across E_g into the conduction band which will lead to an increase of mobile carriers densities. The typical band structures of these three material types are illustrated in Figure 2.3.

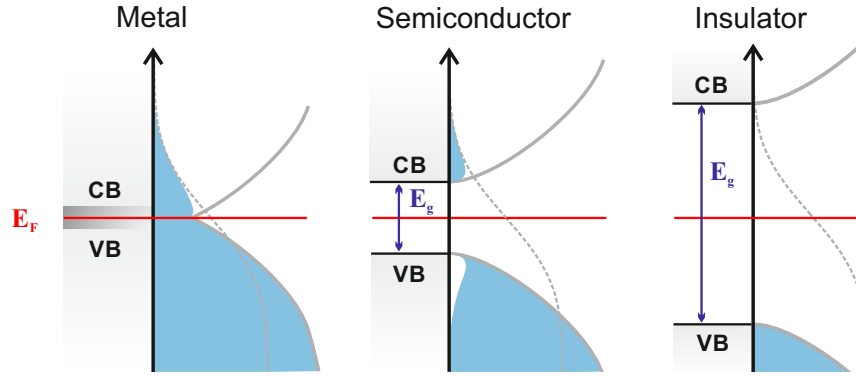


Figure 2.3: Energy band diagrams, Fermi-Dirac distribution, density of states and electron concentrations for a metal, a semiconductor and an insulator at thermal equilibrium. The Fermi level (E_F) is depicted by the red line, and the concentration of electrons n occupying an energy level is represented by the blue shaded area. In metals, the Fermi level is in the middle of a continuum of partially filled states, such that $n > 0$ which allows electrical conduction. An insulator does not conduct free charges since there are no available states for electrons near the Fermi energy. The band gap E_g is too large for electrons to be excited into the CB. In a semiconductor, the CB and VB are close enough to allow populating of the CB with mobile electrons at thermal equilibrium. When additional external energy is supplied to a semiconductor for example in the form of photons, more electrons from the VB can be excited across the E_g into the CB, thus increasing the conductivity of the semiconductor

Therefore, the classification of solid-state materials into metals, semiconductors and insulators is directly related to their electrical conductivity which is proportional to the concentration of mobile charge carriers:

$$\sigma = nq\mu \quad (2.12)$$

where n is the density of free carriers, q is the elementary charge, and μ is the charge mobility. μ quantifies the rapidity with which a charge can move through a material under an electric field, and n corresponds to the product of the density of states and the probability

of occupation (Equation 2.7).

Additionally, the position of the Fermi level E_F can be quantified by the *work function* Φ (Figure 2.4), defined as the energy required to remove one electron from the Fermi level to the vacuum level E_{vac} (a position just outside the material), such as $\Phi = E_{vac} - E_F$.

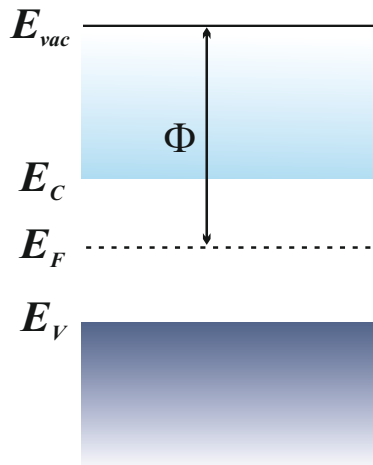


Figure 2.4: Schematic of the work function Φ on the energy band diagram.

At thermal equilibrium, intrinsic semiconductors practically behave like insulators which limits their use in electronics. Since their low conductivity is due to a limited number of free carriers, adding electrons or holes to the CB and VB, respectively, will increase the population of mobile charges and thus improve the conductivity of the material. This is called *doping*.

2.1.2 The concept of doping

Electronic doping is a powerful tool to control the conductivity of semiconductors and to adjust the position of the Fermi level in a material. It involves adding impurities (atoms or molecules) to create an excess of delocalised, or mobile, electrons or holes within the material, respectively named *n-* and *p-doping*.

Increasing the concentration of mobile carriers (either electrons or holes) causes the material to be more conductive. Based on equation 2.12 in section 2.1.1, the electrical conductivity can now be written as a function of both the densities of mobile charges (N_D

and N_A) and their respective mobilities (μ_n and μ_p), such that:

$$\sigma = q(N_D + n)\mu_n + q(N_A + p)\mu_p \quad (2.13)$$

Upon doping, the Fermi level will shift such that:

$$E_{F,n} = E_i + k_B T \ln \left(\frac{N_D}{n_i} \right) \quad (2.14)$$

$$E_{F,p} = E_i - k_B T \ln \left(\frac{N_A}{n_i} \right) \quad (2.15)$$

where N_D and N_A are the electron and hole doping densities, and $E_{F,n}$ and $E_{F,p}$ represent the respective the Fermi levels for a *n*- and *p-doped* semiconductor. Combined with equation 2.11, $E_{F,n}$ and $E_{F,p}$ can also be expressed as:

$$E_{F,n} = E_c - \frac{k_B T}{2} \cdot \ln \left(\frac{N_C}{N_D} \right) \quad (2.16)$$

$$E_{F,p} = E_v + \frac{k_B T}{2} \cdot \ln \left(\frac{N_V}{N_A} \right) \quad (2.17)$$

A complete schematic summary, illustrating the main differences between an intrinsic, *n*-type and *p*-type semiconductor, is given in Figure 2.5.

Since doping forces the Fermi level to move to a new position, the work function of the material will change. Upon *n*-doping, Φ will decrease, while *p*-doping will result in an increase in the work function such that $\Phi_n < \Phi_i < \Phi_p$. Being able to control the majority charge carriers in a solid material through doping was a major breakthrough for the semiconductor technology, as it has allowed the design of *p-n* junctions which are the fundamental building blocks of most electronic systems.

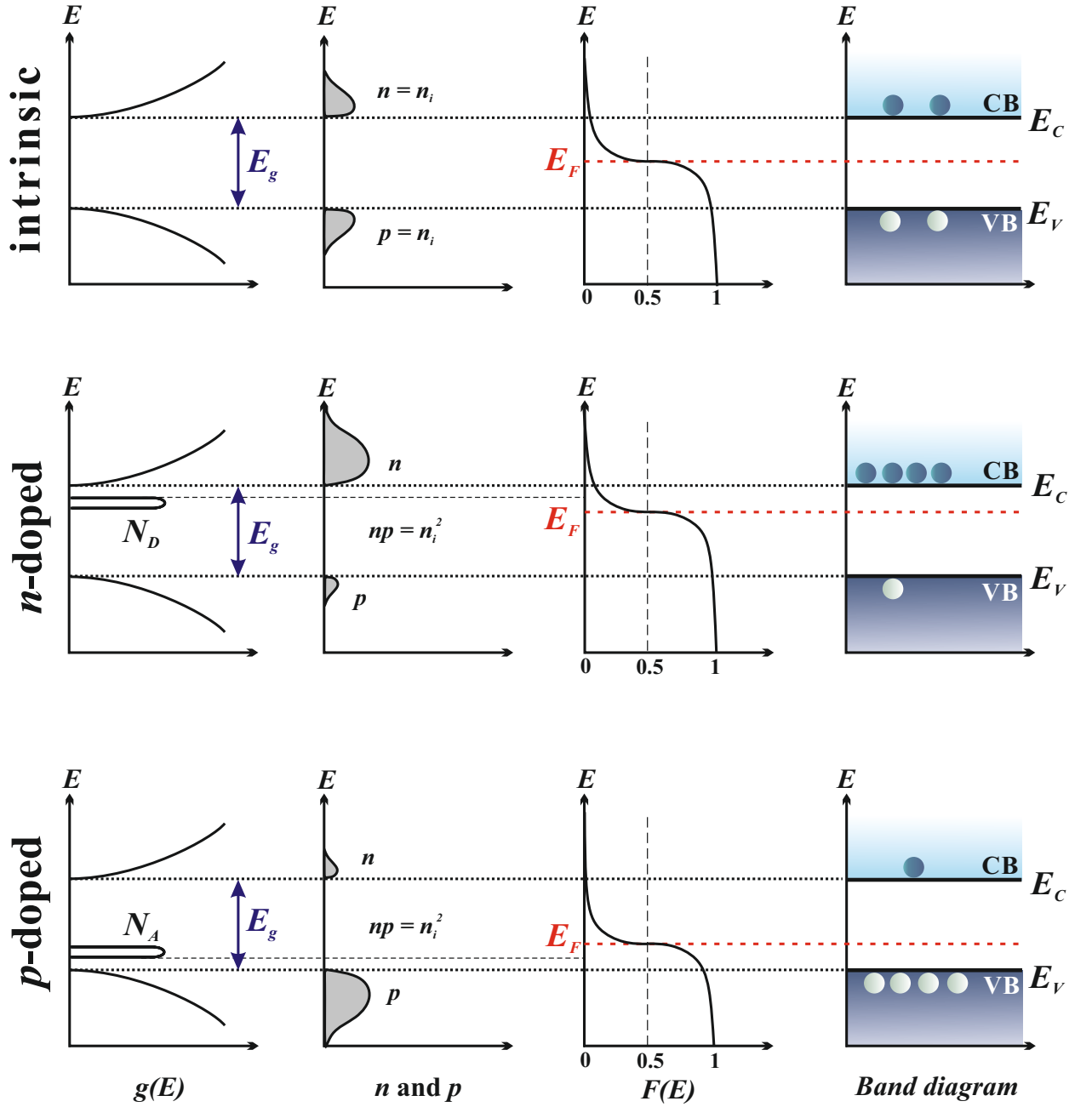


Figure 2.5: Schematic density of states, carrier concentrations, Fermi-Dirac distribution and band diagram, for an intrinsic, n -type and p -type semiconductors at thermal equilibrium.

2.1.3 Organic semiconductors

In today's optoelectronic applications, a much-noticed alternative to inorganic crystalline semiconductors are *organic semiconductors*. They mainly consist of carbon-based molecular entities, with a few heteroatoms such as sulfur, oxygen, or nitrogen, and can be divided into two main categories: *small-molecule* and *polymer* materials. Both of the two groups are extensively used as selective electron and hole conducting layers for photovoltaic applications. While polymers are exclusively processed from solution, organic small-molecules can sometimes be insoluble in organic solvents and thus are deposited through thermal evaporation.

When atoms are sufficiently close such that their electronic orbitals s and p, which are the atomic electron wavefunctions and describe the probability of finding an electron in a specific location, spatially overlap, molecular orbitals called σ and π -orbitals are formed. These molecular orbitals are associated with chemical bonds of different strength referred to as σ and π -bonds. In σ -bonds, the neighboring atoms share the electron pair located between them, thus bonding the two strongly together; while π -bonds form due to parallel orbital overlap above and below the atoms, and are therefore weaker. An illustration of the atomic s and p, and the molecular σ and π orbitals is depicted in Figure 2.6.

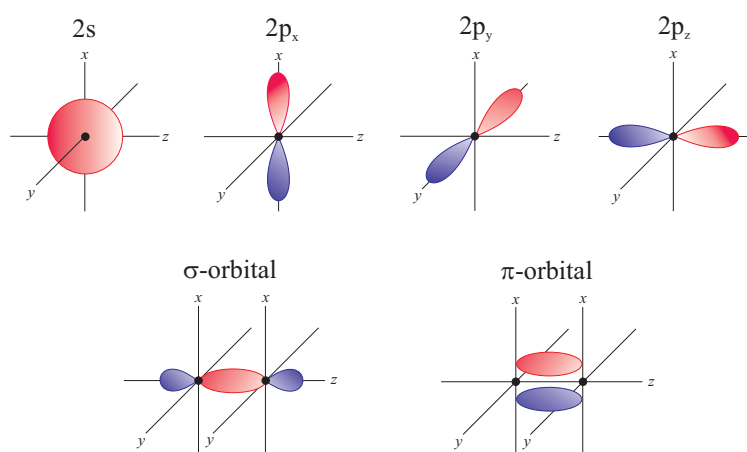


Figure 2.6: Schematic representation of the atomic s and p, and the molecular σ and π orbitals. The atomic orbitals of carbon depend on the angular momentum quantum number of electrons and are associated with a spherical charge distribution. For the s-orbital, this distribution is centered around the atom, while the p-orbital forms a figure-eight. In the case of molecular orbitals, *i.e.* when two atoms are brought together, the spatial probability density of electrons of σ -orbitals are centered around the axis joining the atoms, like a cylinder, whereas π -orbitals show delocalised electrons found above and below the axis connecting the two atoms.

As seen previously for the case of inorganic semiconductors, the presence of delocalised electrons is a fundamental prerequisite for electrical conductivity. In organic films, similarly to what happens in the electronic bands in inorganic crystalline semiconductors, the electrons are delocalised in the π -orbitals. The Lowest Unoccupied Molecular Orbital (LUMO) corresponds to the conduction band and accepts excited electrons, and the Highest Occupied Molecular Orbital (HOMO) corresponds to the valence band, separated by an energy gap without available energy states. Those orbital bands are also referred to as the ground-state bonding (π) and excited state anti-bonding (π^*) molecular orbitals. Furthermore, the HOMO level is approximately equal to the energy needed to ionise the molecule referred to as ionisation potential (IP). Upon ionisation, the molecule becomes positively charged forming a cation also called positive polaron (*i.e.* hole with associated lattice distortion). On the contrary, an anion or negative polaron (*i.e.* electron with associated lattice distortion) is formed when an electron is added to a neutral molecule and the energy gained is the electron affinity (EA) which can be approximated by the LUMO level (Figure 2.7).

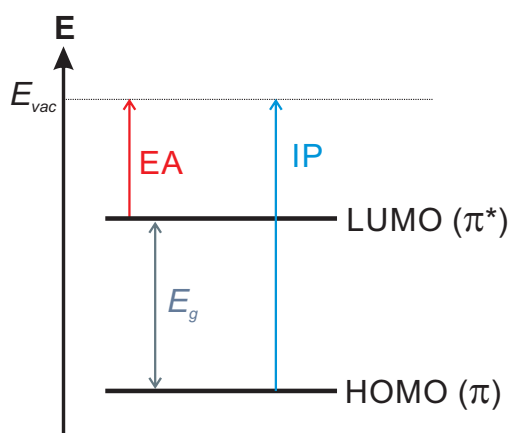


Figure 2.7: Energy diagram of an organic semiconductor. An energy gap (E_g) is created between the Highest Occupied Molecular orbital (HOMO) level and the Lowest Unoccupied Molecular Orbital (LUMO) level, also referred to as the groundstate bounding (π) and excited state anti-bonding (π^*). The HOMO and LUMO levels can also be related to the ionisation potential (IP) and the electron affinity (EA) of the molecule, respectively.

Therefore, in organic films, charges are associated with an oxidised and reduced state of the molecule and cannot be considered as free. For charge transport to occur, an activation energy is required for electrons to hop from a π -orbital to another of an adjacent molecule. In a polymer, the charge transfer process is similar since the electron delocalisation does not extend throughout the entire polymer chain and especially not between chains. Charge con-

duction in organic materials is typically strongly limited in its range. This can be attributed to the amorphous nature of the films which results in a weak overlap of the π -orbitals. Hence, the hopping of electrons between molecules is hampered which results in low charge carrier mobilities ($< 10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) compared to crystalline semiconductor ($> 1000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). Additionally, the quality of the organic layer strongly depends on processing conditions and film formation.

Similar to conventional semiconductors, it is possible to *n* or *p*-dope organic semiconductors. Molecular doping requires a close alignment of the energy levels of the matrix, or host material, and the dopant. For efficient *p*-doping (*n*-doping), the dopant molecule must be a strong electron acceptor (donor) and its LUMO (HOMO) must lie below (above) the HOMO (LUMO) of the host material (Figure 2.8). The doping process of organics is similar to inorganics. For instance, in the case of *p*-doping of a hole transporter material (HTM), an electron transfers from the host matrix to the *p*-dopant, leaving a hole in the HTM and forming ionised dopant molecules, or anions. Moreover, the Fermi energy shifts towards the LUMO and the HOMO for *n*- and *p*-doping respectively. Creation of free charges upon doping leads to increased conductivity. In addition, molecular doping results in greater mobility due to trap filling. Overall, doped organics are employed in solar cells to achieve an ohmic contact between the organic and the electrodes to guarantee efficient charge injection and extraction.

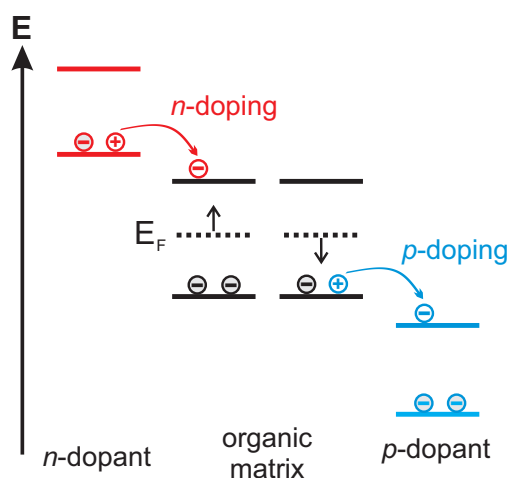


Figure 2.8: Principle of molecular doping of organic semiconductors. When the energy levels are well matched, *p*-doping (*n*-doping) occurs through the transfer of an electron from the HOMO of the host (dopant) material to the LUMO of the dopant (host) molecule.

2.2 Operating principles of solar cells

A solar cell generates electricity directly from sunlight via electronic processes occurring in a photoactive material. Such materials exhibit a property known as the *photoelectric effect* that allows them to absorb photons and release electrons with a higher electrochemical potential. These excited electrons are physically separated from the ground state by the band gap, and can be induced to travel through an electrical circuit, generating electricity.

2.2.1 Light absorption and charge carrier generation

A *light absorber* possesses a band gap E_g (defined in Section 2.1) whose width directly determines the amount of light energy which can be absorbed from the *solar spectrum*. Only the photons with an energy equal to, or greater than, the band gap can be absorbed. As seen previously, one of the most common class of materials fulfilling this condition are semiconductors. Since the solar spectrum varies depending on where and when it is measured in the world, a fixed standard terrestrial solar spectrum has been introduced, named *Air Mass 1.5 spectrum* (AM1.5), normalised so that the total integrated irradiance is equal to about $1000 \text{ W}\cdot\text{m}^{-2}$. In Figure 2.9, the AM1.5 spectrum is shown. As an example, the absorption onset of a material with a band gap $E_g = 1.1 \text{ eV}$ is represented, and the shaded part represents the photons that could be absorbed.

Upon light absorption, an electron is *photoexcited* from the occupied ground state (valence band) to an unoccupied excited state (conduction band). A photon with an energy $E < E_g$ would only promote an electron into a state located inside the band gap, and can therefore not be absorbed. Thus, photons with energies lower than the band gap are either reflected or transmitted through the material. Accordingly, photons with an energy greater than the band gap will promote an electron in a state above the band edge. The smaller the bandgap the larger is the spectral range a photoconverter can absorb. However, when excited electrons possess an excess of energy, they will relax down to the lowest available

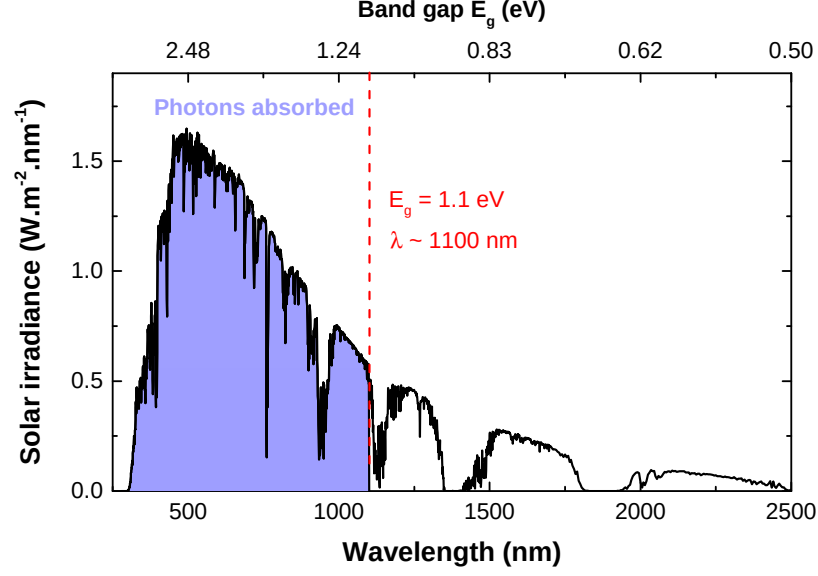


Figure 2.9: Solar spectral irradiance for the AM1.5 solar spectrum incident on the Earth's surface. For a semiconductor with a bandgap $E_g = 1.1$ eV, the corresponding wavelength λ is approximately equal to 1100 nm, hence the photons that can be absorbed have an energy higher than E_g , *i.e.* $\lambda \leq 1100$ nm (shaded in blue).

state of the conduction band through intraband transitions, dissipating their excess energy through thermal vibrations with the lattice, and scattering events with other electrons. This phenomenon is referred to as the *thermalisation* of electrons, and it occurs within a few femtoseconds. This implies that the excess energy is lost as heat and cannot be used. After thermalisation, electrons will remain at the CB band edge for a time-frame of microseconds, leaving sufficient time for the charges to be extracted into an external circuit to generate a *photocurrent*. The photocurrent corresponds to the electric current induced by light absorption in a semiconductor. A more detailed expression of the photocurrent in a solar cell is given in following sections.

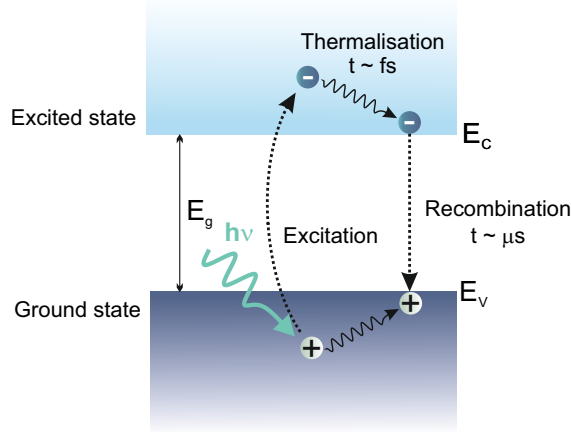


Figure 2.10: Schematic of a semiconductor material upon light excitation. Photons with an energy $E \geq E_g$ promote electrons from the valence band, or ground state, to an excited state in the conduction band. When electrons are excited to a level beyond the conduction band edge, they rapidly thermalise to the state with the lowest energy in the band through intraband transitions within femtoseconds, dissipating their excess energy as heat. In contrast, electron-hole recombination through interband transitions occurs on the order of microseconds, allowing sufficient time for the excited charges to be extracted.

For an intrinsic semiconductor in equilibrium (*i.e.* in dark conditions at a given temperature), the Fermi distribution dictates the probability of an electron occupying an energetic state, and therefore the concentration of charge carriers in the conduction and valence bands. In this case, the Fermi energy lies as its chemical potential (μ) in the middle of the band gap. When light disturbs the equilibrium, additional electrons and holes are promoted into excited states by the absorption of photons which gives rise to larger free carriers populations than in the dark state. Excited electrons and holes collide with the lattice by which phonons are emitted and absorbed. Due to these collisions and collisions with other excited electrons, the electron population in the excited state relaxes quickly by thermalisation and reaches a transient, local, thermal quasi-equilibrium. This leads to narrower distributions of both electrons and holes compared to the distribution of available states in their bands. Since a quasi-thermal equilibrium is reached, both distributions obey to mathematical Fermi distribution and are associated with quasi-Fermi energies for electrons and holes, also referred to as *quasi-Fermi levels*. Typically, the electrons' quasi-Fermi level E_{Fn} lies just below the CB, while the holes' quasi-Fermi level E_{Fp} is located just above the VB (Figure 2.11). The difference between their respective chemical potentials represents the maximum potential difference ($\Delta\mu$) of a photovoltaic device, referred to as *photovoltage*.

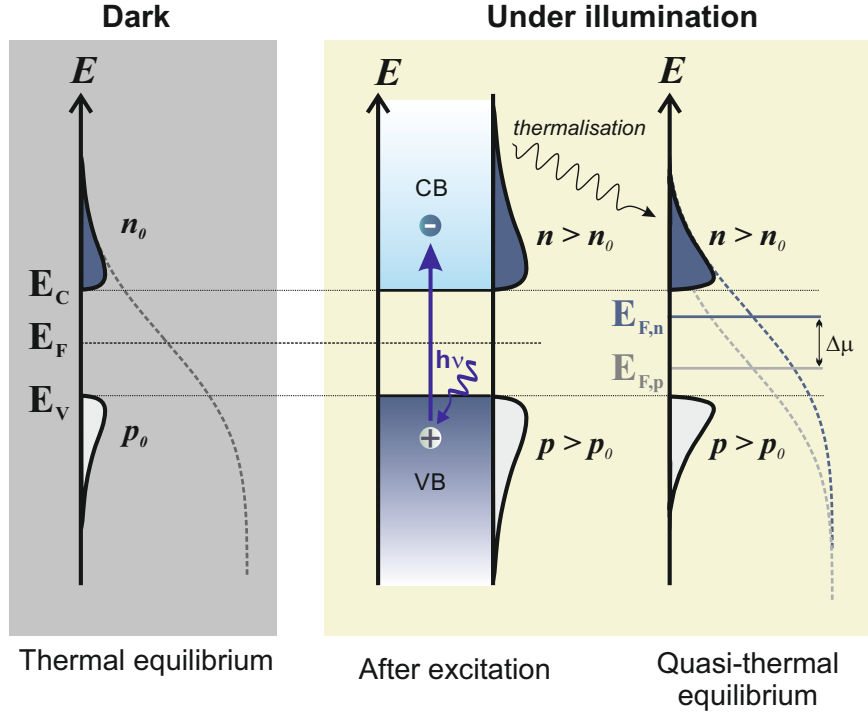


Figure 2.11: Comparison of an intrinsic semiconductor in the dark and under illumination. In the dark, a thermal equilibrium is established and the Fermi level lies in the middle of the forbidden energy gap. The concentration of electrons and holes in the CB and VB are n_0 and p_0 respectively. Under illumination, electrons are excited across the bandgap by absorption of photons, which generate greater charge carrier populations such as $n > n_0$ and $p > p_0$. The electron population in the excited state relaxes through thermalisation into a local, transient thermal equilibrium. The new distribution is described by a Fermi distribution whose Fermi energy is called the quasi-Fermi level. The difference between the electrons and holes quasi-Fermi levels $E_{F,n}$ and $E_{F,p}$ represents the maximum potential difference ($\Delta\mu$) of a photovoltaic device.

Hence, it follows that in order to maximise the power conversion efficiency of a photovoltaic device, there exists a fundamental compromise between the number of excited electrons that can be generated (related directly to the photocurrent) and their potential energy (related to the photovoltage imposed by the band gap of the material); or in short, between a high photocurrent or a high photovoltage. This fundamental physical limitation on the performance of a solar cell, known as the *principle of detailed balance*, was proposed in 1961 by Shockley and Queisser [19]. They showed that a maximum conversion efficiency of 33.7% of incident light intensity to electrical power can be achieved for an ideal absorber with a band gap of 1.34 eV under AM1.5 conditions.

In order to predict the fraction of photons absorbed for a material with a given band gap, it is essential to know its absorption coefficient at particular energies, *i.e.* how many

photons are absorbed per unit length in the material. The optical transitions allowed (for $E \geq E_g$) have specific probabilities of occurring and also depend on the wavelength. A simple way to maximise the absorption for a solid material is to increase the thickness of the layer. An increasingly thicker film of the absorber material would be a means to capture more photons. However, the intrinsic charge carrier characteristics of the absorber limit the maximal thickness of the material at which photogenerated charges can still move to the extracting electrode before recombining.

2.2.2 Radiative and non-radiative recombinations

After photoexcitation, the photogenerated species will remain in an excited state for a limited amount of time. Hence, if they are not collected by the electrodes in time, the electron in the CB will recombine with a hole in the VB. While the absorption of photons is the predominant mechanism to generate free carriers, there are three competing processes of charge carrier recombination: the spontaneous radiative band-to-band, the non-radiative trap-assisted and the non-radiative Auger recombinations (Figure 2.12). Furthermore, recombination can occur in different parts of the solar cell, for example within the absorber layer, or at the extraction contacts, or at the interface between the n and p -type materials.

The most fundamental form of recombination is the *spontaneous radiative band-to-band recombination*, which arises when an excited electron in the conduction band recombines with a hole in the valence band. Here, the excitation energy is lost in form of an emitted photon, returning the electron to its initial ground state. The process upon which a photon is emitted through electron-hole recombination is called *photoluminescence*, and will be discussed further in the following chapters. Spontaneous radiative recombination events are unavoidable since they are related to the intrinsic properties of a material.

The second inevitable recombination process is the *non-radiative Auger recombination*. In this event, instead of emitting the energy as a photon, the excess energy released by an electron recombining with a hole, is directly transferred to a second electron. While this electron gains kinetic energy of the magnitude of the band gap, the other carrier decays

across the band gap. Then, the newly excited electron relaxes back to the conduction band edge by losing its additional energy in a series of collisions with the lattice and other excited electrons. In semiconductors with very high charge carrier densities, or upon high fluences, interactions between multiple particles are more frequent and this loss mechanism becomes more important.

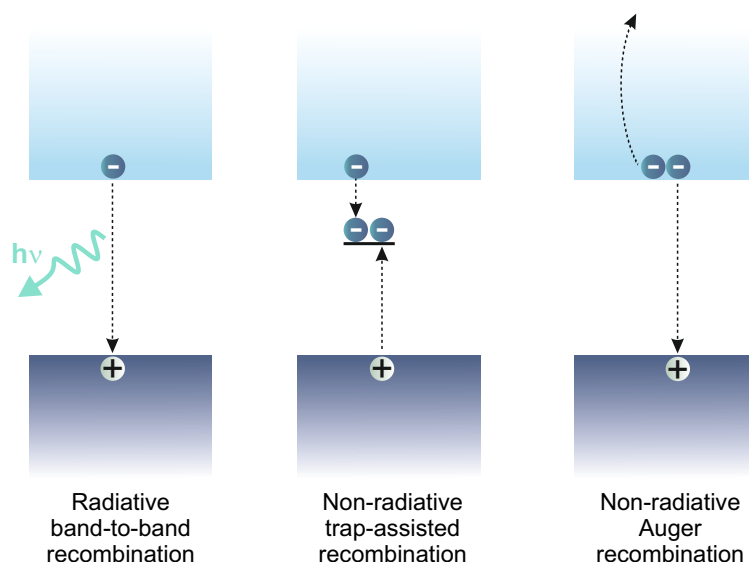


Figure 2.12: Photogenerated species can recombine through three different processes: radiative band-to-band recombination, non-radiative trap-assisted recombination and non-radiative Auger recombination.

In real applications, most solution processed materials suffer from poor crystallisation and film formation which lead to the introduction of defect sites or impurities. Often, these defects arise from under-coordinated atoms in the crystal structure, grain boundaries between crystals, or surface defects created at a junction. Such defects result in the creation of energy states within the bandgap, called *trap states*, which can exist either as electron or hole traps. Thus, an excited charge carrier can be captured by traps of different energies depending on how close they are to the band edges. Shallow traps, *i.e.* the nearest to the band edge, capture carriers that can still be thermally released to the system, nonetheless, this mechanism heavily limits the carrier mobility. In contrast, deeply trapped carriers cannot be thermally released, they are hence immobilised and tend to be lost to recombination. These deep traps are therefore often referred to as recombination centres. This constitutes another non-radiative recombination pathway, commonly referred to as *trap-assisted recombination*,

also called *Shockley-Read-Hall* recombination, which limits the extraction rate of carriers and the overall photocurrent [14].

In order to minimise recombination processes, it is useful to be able to quantify them. This can be done by estimating the charge carrier *lifetime* τ (an intrinsic property of a material). τ is defined as the average time an excited charge carrier stays in an excited state before it recombines, *i.e.* the time it takes for a charge population n to reach $1/e$, or overall corresponds to the sum of all the decay paths. Thus for the excited charges to be efficiently collected, a good solar cell should have long carrier lifetimes, small radiative rates and low trap densities. Lifetimes of perovskite materials can be obtained from photoluminescence (PL) measurements by modelling the PL decay using the general recombination rate equation [20, 21, 22, 23]:

$$\frac{dn}{dt} = -R_{rad}(n) - R_{SRH}(n) - R_{Auger}(n) \quad (2.18)$$

where $R(n)$ is the rate of spontaneous photon emission, $R_{SRH}(n)$ the rate of Shockley-Read-Hall recombination via trap states and $R_{Auger}(n)$ the rate of Auger recombination per unit volume. Each recombination rate is a function of a constant and the carrier density n such that [22, 23]:

$$R_{rad} = k_b n^2 \quad \text{Bimolecular recombination} \quad (2.19)$$

$$R_{SRH} = \beta_n N_t n \quad \text{Monomolecular recombination} \quad (2.20)$$

$$R_{Auger} = \gamma n^3 \quad \text{Trimolecular recombination} \quad (2.21)$$

with k_b the bimolecular decay constant, β_n a coefficient associated to trapped electrons, N_t the density of available traps and γ the Auger decay constant. The term monomolecular is employed to describe a recombination process which involves only one type of charge carrier, for instance trap-assisted recombination. When two, or three free carriers are involved, the recombination processes are qualified as bimolecular and trimolecular, *i.e.* respectively band-to-band and Auger recombinations.

Therefore, the recombination rate equation (2.18) can be expressed by:

$$\frac{dn}{dt} = -k_b n^2 - \beta_n N_t n - \gamma n^3 \quad (2.22)$$

When PL measurements are taken at low fluences, trapping is the most efficient recombination path for electrons and Auger recombination contributions can be ignored [22, 23]. Therefore, the decay dynamic for excited electrons can be reduced to a combination of spontaneous radiative events and non-radiative Shockley-Read-Hall recombination processes, summarised by the equation:

$$\frac{dn}{dt} = -k_b n^2 - \beta_n N_t n \quad (2.23)$$

and the average PL lifetime τ_{PL} is:

$$\tau_{PL} = \frac{1}{k_b n_0 + \beta_n N_t} \quad (2.24)$$

with n_0 being the injected carrier density.

Several models have been used over the past few years to estimate charge carrier lifetimes in perovskite materials from PL decay measurements, going from mono-exponential, double-exponential, stretched exponential fits, to more complex models [20, 24, 25]. The choice of the model strongly depends on the shape of the decay, *i.e.* when it heavily diverges from a mono-exponential more complex models are preferable. Moreover, Stranks *et al.* showed that in perovskite materials the shape of the PL decay is contingent on the fluence, and the transition between the monomolecular and bimolecular regimes is an approximation for the trap density [20]. Finally, it needs to be noted that the global PL intensity (I_{PL}) is proportional to the radiative rate $R_{rad}(n)$:

$$I_{PL} \propto R_{rad}(n) \quad (2.25)$$

The determination of the lifetime is an important parameter because it defines the average diffusion length L of a charge carrier. The latter is a measure of the distance which charges

can travel through a material without recombining. It dictates the thickness of an absorber material, which should not exceed the diffusion length if the goal is to efficiently collect the charges to generate current. The average diffusion length L of a charge carrier is defined as:

$$L = \sqrt{D\tau} \quad (2.26)$$

with D being the diffusion coefficient such that, according to the Einstein relation:

$$D = \frac{\mu k_B T}{q} \quad (2.27)$$

μ corresponds to the charge carrier mobility.

2.2.3 Charge carrier separation and extraction

When an electron is photoexcited by the absorption of a photon to an energy beyond the conduction band edge, it leaves behind an unoccupied state - a hole - in the valence band. Both photoexcited charges (electron and hole) are bound via Coulombic attraction. Such an electron-hole pair can also be considered as a quasi-particle named *exciton*. As long as the two charges remain a bound pair, they cannot be extracted into the circuit. Hence, excitons have to be dissociated so charges can move freely to create a photocurrent. The separation must happen soon after the generation of excitons, otherwise the electron and hole will eventually recombine. The strength of the Coulombic attraction, or *binding energy*, is inversely dependent on the dielectric constant of the material. For instance, crystalline inorganic semiconductors, such as silicon or germanium, possess a high dielectric constant which will result in a weak binding energy of the exciton [26, 27]. A high dielectric constant implies the availability of mobile charges which can screen the electric field between the two charges thus resulting in a weaker binding and easier dissociation of the charge pair. In contrast, due to the much lower dielectric constant of organic semiconductors, the exciton binding energy is much higher [28]. When an energy greater than the binding energy is provided to the system, excitons separate resulting in an increased concentration of free

electrons and holes. There are several ways of achieving this, for instance by applying an electric field or heat. Nonetheless, the fundamental mechanism used in a photovoltaic device relies on the creation of a *built-in asymmetry* which forces electrons and holes to flow in different directions.

Such a built-in asymmetry can be established by creating driving forces for the two charge carriers in the system. This can be achieved either by forming a gradient in the charge population density between electrons and holes, or by creating an interface such that it becomes more favourable for the transfer of only one of the two charge carriers. The extraction of charges from the absorber induced by these forces results in a net current (J_{total}) which is the sum of two types of currents, referred to as *drift* (J_{drift}) and *diffusion currents* (J_{diff}). The drift current arises due to the action of an electric field in the absorber, while the diffusion current is the result of a gradient in the charge carrier density or a selective charge carrier removal.

When two materials with different work functions are brought together, a *built-in* electric field is established which forces electrons and holes to move into opposite directions, *i.e.* the holes move in the direction of the electric field and the electrons against (Figure 2.13). The electric field can in that way pull apart or dissociate photogenerated excitons, thus producing a drift current which corresponds to the sum of both the electron drift current and the hole drift current.

A charge-selective contact allows the preferential charge carriers to flow through an interface, and blocks carriers of opposite charge. When charges flow away from an interface this leads to a non-uniform concentration of carriers, and this flow of carriers from a highly concentrated region to a lower concentrated one results in a diffusion current. To illustrate this process, a simple system can be considered with on one side, a hole-selective contact and on the other side, an electron-selective contact. Upon removal of holes, a gradient in the hole concentration arises, with the hole concentration increasing with distance away from the hole-selective interface. Thus, holes diffusing from high-concentration regions towards low-concentration constitute a hole-diffusion current ($J_{\text{p,diff}}$) towards this interface. The other

contact favours the flow of electrons, a similar density gradient arises and an electron diffusion current ($J_{n,diff}$) is created which flows in the opposite direction as $J_{p,diff}$. Similarly to the expression of the drift current, the total diffusion current is equal to the sum of both electrons and holes diffusion currents.

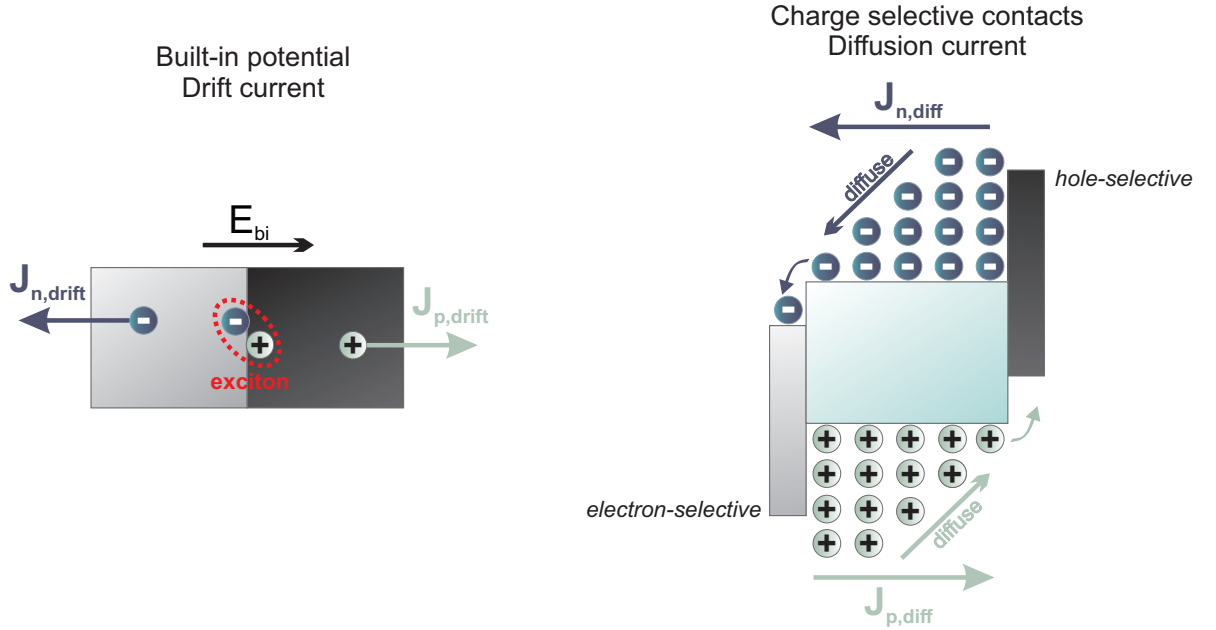


Figure 2.13: On the left, a simplified schematic of the effect a built-in electric field E_{bi} has on a photogenerated electron-hole pair. Upon contact of two materials of different work functions an electric field is created at a junction which dissociates the exciton. Drift currents are generated by electrons being driven in the direction of E_{bi} , and holes against it. On the right, a schematic representation of a system sandwiched in between two selective contacts, which exclusively allow holes, on one side, and electrons, on the other side, to leave the interfaces. These flows of carriers establish charge density gradients, which create diffusion currents for electrons and holes, both of them flowing towards their respective selective interface.

Therefore, the total photocurrent generated by a device is a combination of drift and diffusion currents created by both electrons and holes such that [14]:

$$\begin{aligned}
 J_{total} &= J_{drift} + J_{diff} \\
 &= J_{n,drift} + J_{p,drift} + J_{n,diff} + J_{p,diff} \\
 &= q(n\mu_n + p\mu_p)E_{bi} + q \left(D_n \frac{dn}{dx} + D_p \frac{dp}{dx} \right)
 \end{aligned} \tag{2.28}$$

where E_{bi} is the electric field across the material in the direction of the flow of current, n and p are the photogenerated electron and hole concentrations respectively, and x the position along the direction of current flow. μ and D are the charge carrier mobility and the diffusion

coefficient.

In real photovoltaic devices, energy cascade systems are often employed in order to create asymmetries to drive charges across the interface to a lower lying state. However, these successions of energy steps have an impact on the concentration of carriers in the device and hence lead to photovoltage losses due to non-optimal quasi-Fermi levels.

2.2.4 Junctions and contacts under applied bias

By means of consecutive built-in asymmetries, a photovoltaic device is able to separate charge carriers. These asymmetries originate from the creation of driving forces in the absorber (*i.e.* semiconductor), which can be either an electric field or a gradient in the charge density. In dark conditions without applying a bias, upon contact of two materials with different work functions, the system equilibrates which means the two Fermi levels align to form a constant energy level. This induces a gradient in the vacuum levels (*i.e.* band bending) which creates a difference in electrostatic potential across the junction. Depending on the junction, the band bending in the semiconductor is either upward or downward, which will either be favourable to the transfer of carriers or, on the contrary, lead to an accumulation of charges. Once the system reaches an equilibrium, no net current flows. In order to create a flow of charges an external potential needs to be applied. The nature of the junction and the polarity of the applied bias dictate which type of mobile charges flow through the junction to generate current. Therefore, it becomes apparent that the output current is inherently dependent on both the type of junction an absorber (*i.e.* semiconductor) forms with a contact, and the bias applied across it.

The interfaces created by contacting two materials together are referred to as junctions, which can be *homojunctions* or *heterojunctions*. A homojunction is formed by two layers of the same semiconductor at two different doping levels which can be *n*- or *p*-doped, *i.e.* electrons and holes are in excess as compared to the intrinsic material, respectively (Section 2.2.2). A heterojunction is an interface between two different semiconductors, or a metal and a semiconductor. The great majority of semiconductor devices are made of three different

types of junctions: metal-semiconductor, p - n and p - i - n junctions.

When a metal and a semiconductor are joined, two possible types of contact can occur, depending on the combination of metal and semiconductor employed. If the work function of the metal is larger than the work function of the semiconductor ($\Phi_m > \Phi_n$), the interface is referred to as a *Schottky junction*. Alternatively, when $\Phi_m < \Phi_n$, the junction is called an *Ohmic junction*. The main difference between these two types of contact is their current characteristic under applied bias: a Schottky junction is a rectifying electrical junction while an Ohmic contact is not.

- **Schottky junction ($\Phi_m > \Phi_n$) - *Rectifying behaviour***

At thermal equilibrium: A metal-semiconductor Schottky junction is shown in Figure 2.14. Upon contact, since the work function of the n -type semiconductor (Φ_n) is smaller than that of the metal (Φ_m), electrons in the conduction level of the semiconductor can flow to the empty energy states above the Fermi level of the metal. The Fermi levels of the materials will line up due to electron diffusion from energetically higher lying states in one material to energetically lower lying states in the other material. When electrons move from the semiconductor to the metal, they leave behind positive ions. Simultaneously, on the metal side, the newly arrived electrons lead to an accumulation of negative charges. Due to the relatively low electron density on the semiconductor side compared to the metal, electrons are not only removed from the surface but also from a certain depth within the semiconductor, referred to as *space charge region* also called *depletion region* (W_D). In this region, mobile charges have moved to the metal leaving behind immobile ionised atoms. A thermal equilibrium between the two materials is reached once the gradient of built-up charges is strong enough to counterbalance the charge exchange.

When both Fermi levels align, a difference in vacuum levels between the metal and the n -type semiconductor is created, which leads to a gradient in electrostatic potential. The main part of this potential drop happens within the semiconductor layer due to its greater ability to store charges, *i.e.* because of its higher dielectric constant, then the vacuum level

stabilises to its initial value further away from the interface. Therefore, an electric field (E_{bi}) is created. E_{bi} is opposed to the contact potential (V_{bi}), *i.e.* pointing from the positive to the negative charges, and is equal to zero when the vacuum level of the semiconductor stabilises (away from W_D).

Since the intrinsic properties of both materials remain unchanged upon contact, including the bandgap and electron affinities (χ the energy necessary to remove an electron from the bottom of the CB to the vacuum level), as a result, bands bend up going from the n -type semiconductor to the metal, in the direction of the electric field. The magnitude of this band bending qV_{bi} is given by the difference in work functions:

$$qV_{bi} = \Phi_m - \Phi_n \quad (2.29)$$

where V_{bi} is the built-in potential across the Schottky junction which prevents further motion of electrons to the metal once equilibrium is reached. Furthermore, the conduction band bending creates an energy barrier blocking the majority carriers (electrons) to transfer back to the semiconductor. This potential barrier, denoted as Φ_B , is referred to as *Schottky barrier*. In contrast, the bending of the valence band is energetically favourable for the holes (minority carriers) to transfer from the SC to the metal.

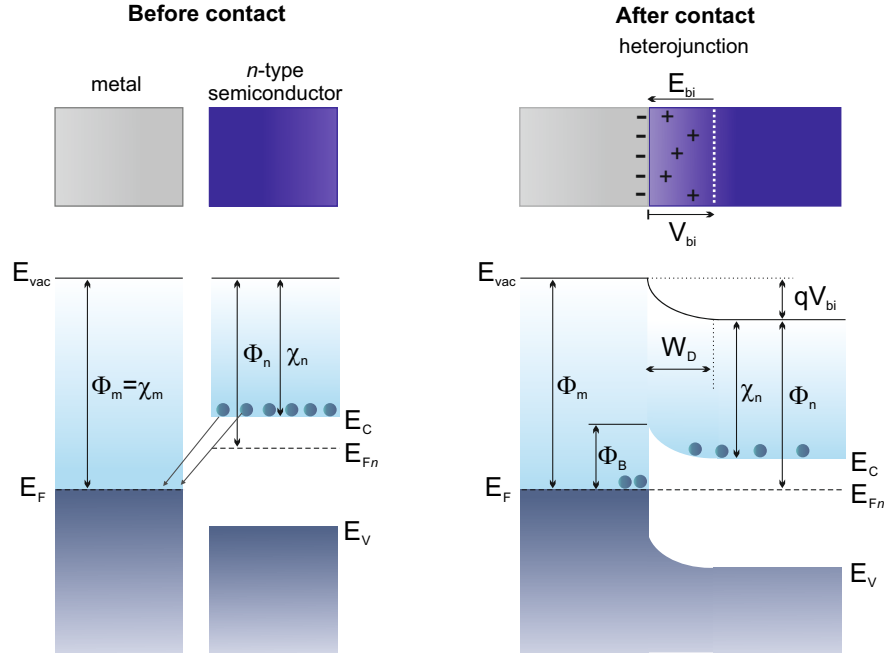


Figure 2.14: A metal and a n -type semiconductor, with a work function Φ_m and Φ_n , respectively, are brought in contact. Since $\Phi_m < \Phi_n$, electrons from the semiconductor transfer to the metal. Positive ions are left behind in the depletion region W_D , leading to the formation of a built-in potential V_{bi} . The difference in vacuum levels of the two material gives rise to the upward band bending of the semiconductor. The valence band bending is energetically favorable for the minority carriers (holes) to transfer. On the contrary, the conduction band bending creates an energy barrier preventing electrons from flowing from the semiconductor to the metal. This energetic barrier Φ_B is called the Schottky barrier.

Under applied bias in dark conditions: A junction can be biased in two different ways called *forward bias*, when a negative potential is applied to the n -terminal, and *reverse bias*, when a positive potential is applied to the n -terminal.

When a Schottky junction is forward biased, the external potential opposes the built-in potential. Considering the case where the junction is kept in the dark, electrons are pushed into the positively charged depletion region, creating a shift of the semiconductor's Fermi level towards the vacuum level. The magnitude of the shift depends on the vacuum level gradient, which is dependent on the applied voltage, *i.e.* the gradient follows the relation $q(V_{bi} - V_{ext})$. Therefore the applied voltage lowers the energy barrier at the interface, and electrons injected from the external circuit into the n -type semiconductor have a lower barrier to surmount before diffusing to the metal. This leads to the generation of a current in the circuit, named *forward current*, which increases with the decrease of the barrier height, *i.e.* higher external potentials. In the case of a reverse bias, the barrier for electrons to move

from the n -type semiconductor to the metal becomes higher according to the applied bias, suppressing any diffusion current. Hence, only a small drift current of holes referred to as *leakage current* remains, which is strongly limited by the low hole density. Much larger current will flow under forward bias than under reverse bias, a characteristic referred to as *rectifying behavior*.

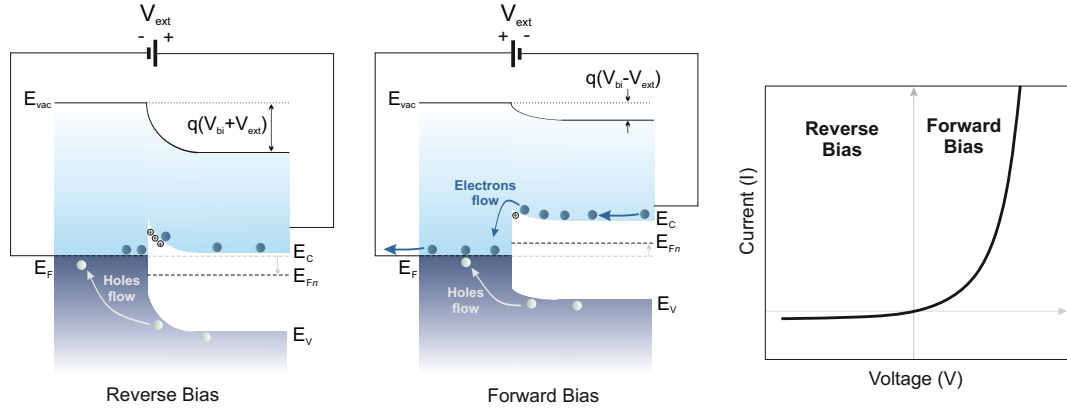


Figure 2.15: Schematic band diagrams of a Schottky junction in the dark, upon application of an external potential V_{ext} . The corresponding dark current-voltage characteristics is also sketched. Under reverse bias, the external potential augments the junction potential. The electrons (majority charge carriers) cannot surmount the higher barrier to move from the n -type semiconductor to the metal, suppressing any diffusion current. Only a low drift current of holes from the semiconductor to the metal remains. In forward bias (negative potential applied to the n -terminal), the external potential applied opposes the built-in potential. Electrons are pushed into the depletion region reducing the energy barrier allowing more and more electrons the electrons to flow across the junction. This diffusion current increases exponentially with the external potential. The junction has an asymmetric behaviour between forward and reverse current, also called *rectifying behaviour*.

Under applied bias upon illumination: The asymmetry between forward and reverse current can be exploited upon illumination in order to extract photogenerated charges and generate current, as shown in Figure 2.16.

When a Schottky junction is illuminated, photons with energy greater than the bandgap E_g of the n -type semiconductor excite electrons to the conduction band leaving behind holes in the valence band. These created holes are driven to the metal due to the electric field E_{bi} at the junction, resulting in an accumulation of electrons in the semiconductor and holes in the metal. The build-up of negative charges neutralises the positive space charge in the semiconductor (*i.e.* positive ions in W_D), and the potential difference across the interface is reduced. As defined previously in Section 2.2.1, upon illumination of a semiconductor,

electron and hole populations increase which disturbs the thermal equilibrium. Then, the new distribution of excited electrons reach a quasi-thermal equilibrium, which can be approximated by a Fermi distribution with a quasi-Fermi energy just above the Fermi level of the junction in the dark. A *photovoltage* (V) is established which corresponds to the difference between the Fermi level in the metal and the quasi-Fermi level of electrons in the *n*-type semiconductor.

The system reaches two extreme equilibrium states: one when the terminals are not connected and one when there are connected without a load. These configurations are referred to as open-circuit (OC) and short-circuit (SC) conditions respectively (more details in Section 2.2.5.). Under open-circuit condition, the system equilibrates when the electrons diffusion current is equal to the drift current of photogenerated holes. In such a configuration, there is no net current, *i.e.* $J = 0$, and the photovoltage reaches its highest value. In contrast, under short-circuit condition, there is no potential difference within the device because the chemical potential of the absorber equilibrates with the chemical potential of the metal, and a large photocurrent is generated. In reverse bias, this large photocurrent corresponds to the drift current of the photogenerated holes. The junction will perform work when the photovoltage drives the photocurrent through a load introduced into the electrical circuit, which corresponds to the forward direction in between the two extreme equilibrium states (yellow shaded zone in Figure 2.16).

In summary, by bringing a metal and an *n*-type semiconductor with a smaller work function into contact, the equilibration of the two Fermi levels gives rise to a junction which has two essential features: an electric field which drives holes from the semiconductor to the metal, and an energetic barrier inhibiting the flow of electrons in the same direction. This asymmetry is the mechanism by which the photogenerated charges are separated, and represents the key principle of a photovoltaic device.

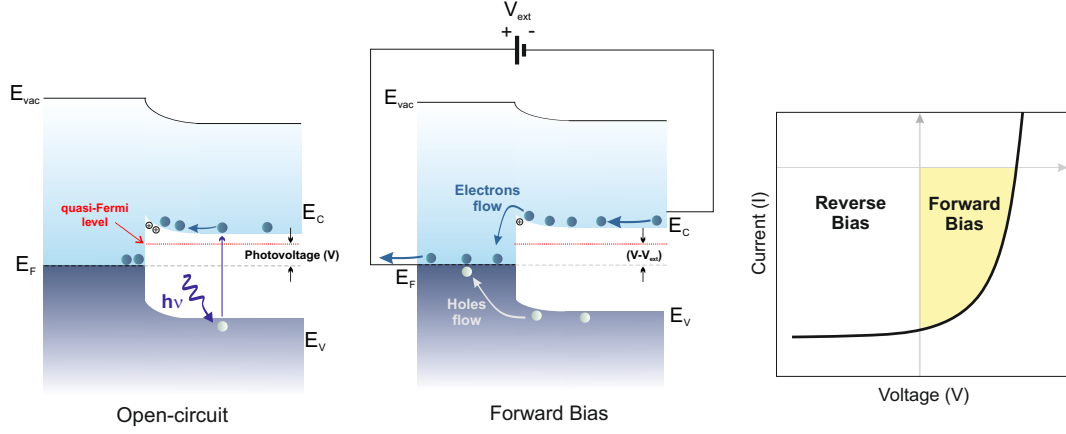


Figure 2.16: Band diagram of a Schottky junction between a n -type semiconductor and a metal, under illumination at open-circuit conditions and under forward bias. The corresponding current-voltage characteristics are also represented. When electrons in the semiconductor absorb photons, charge carrier concentrations increase leading to a new distribution of electrons and the creation of quasi-Fermi levels. A photovoltage (V) is established corresponding to the difference between the metal Fermi level and the quasi-Fermi level of electrons in the n -type semiconductor. The ability of a junction to sustain a difference in quasi-Fermi levels under illumination is essential for the power generation in a solar cell. In reverse bias, the generated photocurrent is large and corresponds to the drift current of holes. In the forward bias regime, the arising photovoltage will reduce the height of the Schottky barrier which results in the onset of the electron diffusion current attenuating the hole current. The photocurrent will therefore be inversely dependent on the photovoltage. When this photocurrent passes through a load, electrical power will be generated (shaded yellow area).

- **Ohmic junction ($\Phi_m > \Phi_n$) - *Non-rectifying behaviour***

The energy diagram of an Ohmic junction in equilibrium is shown in Figure 2.17. Upon contact, the bands of the n -type semiconductor bend downward such that the majority carriers (electrons) flow from the metal to the lower lying empty states in the semiconductor conduction band. In contrast, this downward band bending inhibits the same transfer path for the minority carriers (holes). As a result, electrons accumulate near the interface creating a region rich in majority carriers, and the contact does not form any barriers for charge carriers. Therefore, both charges can move freely across the junction due to a low resistance contact and no photovoltage can be established under illumination, unlike in a Schottky junction. When a bias is applied, the photocurrent varies linearly with the external voltage. There is no rectifying behaviour and the junction is referred to as *Ohmic contact*.

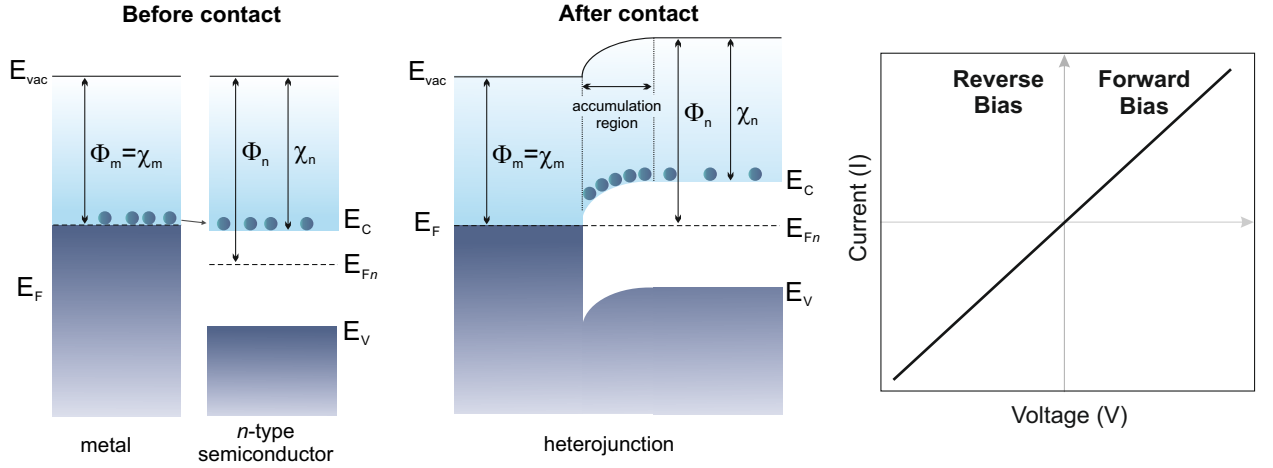


Figure 2.17: A metal and a n -type semiconductor, with a work function Φ_m and Φ_n respectively, are brought in contact. Since $\Phi_m > \Phi_n$, the bands of the semiconductor bend downward allowing electrons to flow both ways creating an accumulation region of majority carriers at the interface. Upon illumination, no photovoltage is created, the junction does not rectify and the photocurrent varies linearly with the applied voltage.

- **p - n and p - i - n junctions**

The p - n junction is the archetypal model of a solar cell. It is formed at the contact between a n -type and a p -type semiconductor with different work functions, Φ_n and Φ_p . It can either be formed by the same semiconductor (homojunction), or by two different materials (heterojunction), the former is the most commonly employed. A p - i - n junction is comparable to a p - n junction, but with an intrinsic semiconductor between the p and n -type materials. Very similarly to a p - n junction, a built-in potential is established, however, it extends over a wider distance throughout the bulk of the intrinsic region.

In a p - n junction, upon contact of the two heavily doped materials, Φ_n being smaller than Φ_p , the Fermi levels equilibrate to a constant energy which results in a band bending and the creation of an energetic gradient. The excess carriers from both sides, *i.e.* electrons on the n -side and holes on the p -side, diffuse to the interface region and recombine. Mobile charges leave behind ionised immobile dopant atoms (donors and acceptors) leading to the formation of a depletion region (positive ions in the n -type semiconductor and negative ions in the p -type semiconductor). Therefore an electric field E_{bi} is established at the interface which forces minority carriers to drift across the junction. In this process diffusion and drift currents for both electrons and holes are created, which act in opposite directions (Figure

2.18). At equilibrium, they cancel out such that no net current flows. Diffusion and drift currents are respectively limited by the height of the potential barrier and the number of minority charge carriers.

When the junction is illuminated, electron-hole pairs are generated in both the p - and n -doped semiconductor. The new distributions of both holes in the p -doped layer and electrons in the n -doped layer respectively give rise to a hole and electron quasi-Fermi level. Their difference corresponds to the photovoltage of the junction. Photoexcited charges diffuse into the depletion zone and drift across the interface by the action of the electric field. Excitons are dissociated, and the newly freed carriers can be collected to generate a photocurrent.

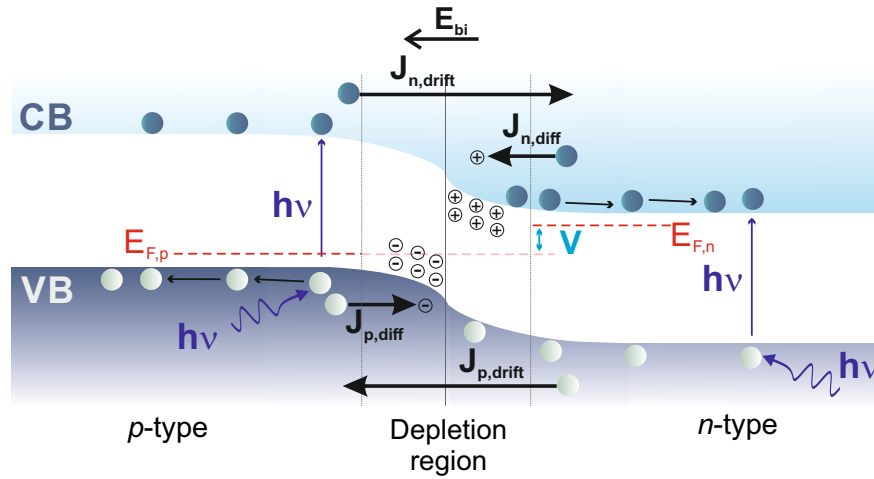


Figure 2.18: Schematic representation of a pn -junction solar cell. Upon contact of the doped materials (*i.e.* different Fermi level positions with respect to the vacuum level), both Fermi levels equilibrate to a constant energy. This creates an energetic gradient in the vacuum levels which generates an electric field. After absorption of photons, the distribution of carriers changes, which leads to the formation of a photovoltage between the newly established quasi-Fermi levels for holes and electrons. Majority carriers diffuse into the depletion region, while minority carriers drift across the junction. This creates a process for exciton separation. Once the electron-hole pair is dissociated, the free charges can be efficiently transported and collected at the appropriate electrodes.

2.2.5 Solar cell characterisation

A solar cell is able to generate a photocurrent (J) and a photovoltage (V) under illumination, which is related to the number of excited electrons and their potential energy, respectively. The electrical power generated by a solar cell is defined as the product of photocurrent and photovoltage.

$$P = J \cdot V \quad (2.30)$$

Therefore, the performance of any photovoltaic device can be characterised by the measurement of its current density upon applied bias voltage.

When no external voltage is applied across the solar cell, *i.e.* there is no load in the circuit between the two terminals, the device operates at short-circuit, and the photocurrent generated is referred to as the *short-circuit current density* (J_{SC}).

With a load present, a potential difference between the two terminals of the device creates an electric field, which generates a current flowing oppositely to the photocurrent. Such current persists in dark conditions and does not depend on the light intensity, and is known as *dark current* (J_{dark}). The dark current cannot be avoided, but can be minimised by reducing recombination pathways and by selection of appropriate selective contacts. J_{dark} can be described by the ideal diode equation:

$$J_{dark}(V) = J_0 \left[\exp \left(\frac{qV}{nk_B T} \right) - 1 \right] \quad (2.31)$$

where V is the external applied potential, J_0 is a constant named the reverse saturation current and n is the ideality factor. J_0 is closely related the recombination dynamics of the the system. The ideality factor n is introduced to account for the fact that most systems diverge from the ideal behaviour ($n = 1$).

Hence, the overall net current as a function of the applied voltage $J(V)$ under illumination can be approximated by the short-circuit current density minus the dark current from the

ideal diode equation. This gives to following expression:

$$J(V) = J_{SC} - J_0 \left[\exp \left(\frac{qV}{nk_B T} \right) - 1 \right] \quad (2.32)$$

In contrast, when a voltage is applied such that it completely cancels out the built-in electric field at the junction, no current flows ($J(V) = 0$). The two electrodes can be considered as not connected, most commonly referred to as open circuit conditions. The maximum voltage generated corresponds to the greatest potential difference between the electron and hole quasi-Fermi levels, called the *open-circuit voltage* (V_{OC}) given by:

$$V_{OC} = \frac{k_B T}{q} \ln \left(\frac{J_{SC}}{J_0} + 1 \right) \quad (2.33)$$

Both photogenerated current and photovoltage depend on the light intensity. Furthermore, the short-circuit current is contingent on the size of the bandgap, and the photovoltage is only defined in the forward bias region.

Therefore, a solar cell will produce power when the product of its photocurrent and photovoltage are both positive, *i.e.* $P = J \cdot V > 0$, equivalent to an applied voltage varying from 0 to V_{OC} . The operation of a solar cell is characterised by the measurement of its current density dependence upon applied bias and light, most commonly referred to as the *current-voltage characteristic* or *J-V curve*. A typical J-V curve is shown in Figure 2.19. The essential parameters extracted from this curve are the J_{SC} , the V_{OC} and the *maximum-power point* (MPP), the voltage when the product of current and voltage reaches its maximum value. The MPP is the operating point of the solar cell.

These parameters allow to define the fill factor (FF) which, for a given solar cell, describes the fraction of generated power in comparison to the ideal maximum power output with no internal losses. The FF is essentially a measure of the “squareness” of the J-V curve and is given by the relation:

$$FF = \frac{P_{MPP}}{P_{ideal}} = \frac{J_{MPP} \cdot V_{MPP}}{J_{SC} \cdot V_{OC}} \quad (2.34)$$

The *power conversion efficiency* (PCE or η) is given as the ratio of the generated power density (P_{MPP}) to the incident light power density P_{light} .

$$PCE = \frac{P_{MPP}}{P_{light}} = \frac{J_{MPP} \cdot V_{MPP}}{P_{light}} = \frac{J_{SC} \cdot V_{OC} \cdot FF}{P_{light}} \quad (2.35)$$

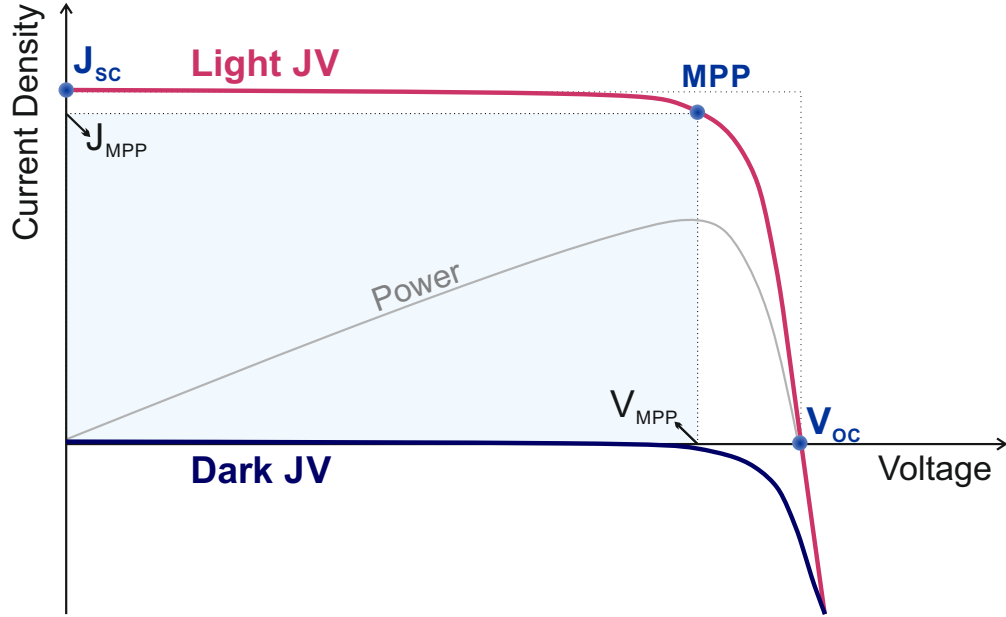


Figure 2.19: Typical current-voltage characteristics of an operational solar cell, both under illumination and in the dark. The key performance parameters are highlighted. When $V = 0$ V, *i.e.* no load applied to the circuit, the solar cell is at short-circuit conditions and the photocurrent reaches its maximum value (J_{SC}). When there is no current flowing through the device, *i.e.* the dark current matches the photocurrent, the photovoltage reaches its maximum, referred to as the open-circuit voltage (V_{OC}). The solar cell operating point corresponds to the maximum-power point (MPP) which underlies the calculation of the fill factor (FF), a metric for the “squareness” of the J-V curve.

Since the efficiency of a solar cell is heavily dependent on the incident light, for comparison purposes, the J-V curve is generally taken under standard test conditions which are a temperature of 25°C and an incident power density of 1000 W·m⁻² including the Air Mass 1.5 spectrum as described previously.

In a real device under bias, parasitic resistances have a significant impact on the current-voltage characteristics, hence on the generated power. Generally, losses occur through two types of resistance: *series resistance* and *shunt resistance*. Series resistance (R_s) arises from the addition of all contact resistances through the device, especially the contacts of the absorber. Such resistances mainly impact the J-V curve by reducing the steepness of the slope beyond the MPP. Shunt resistance (R_{sh}) describes the resistance to shunting and recombination at the selective contacts and due to pinholes. Both resistances negatively impact the FF. Hence, to limit losses, R_s must be as low as possible, while R_{sh} needs to be kept as high as possible. Therefore, adding these modifications into the diode equation (2.32) gives a more realistic current-voltage dependence such that:

$$J(V) = J_{SC} - J_0 \left[\exp \left(\frac{q(V + J \cdot AR_s)}{nk_B T} - 1 \right) \right] - \frac{V + J \cdot AR_s}{R_{sh}} \quad (2.36)$$

where A is the area of the device. This equation can be represented by an electrical circuit diagram, depicted in Figure 2.20 along with the current-voltage characteristics illustrating the effect of both types of parasitic resistances on the J-V curve.

Therefore, the power generated by a photovoltaic device can be maximised in various ways. Firstly, the absorber needs to be able to absorb a wide range of photons across the solar spectrum without suffering from intrinsic non-radiative decay losses. Then, the charge-selective contacts have to be carefully chosen. High carrier mobilities and good charge selectivity are the key to insure low series resistance and high shunt resistance, respectively.

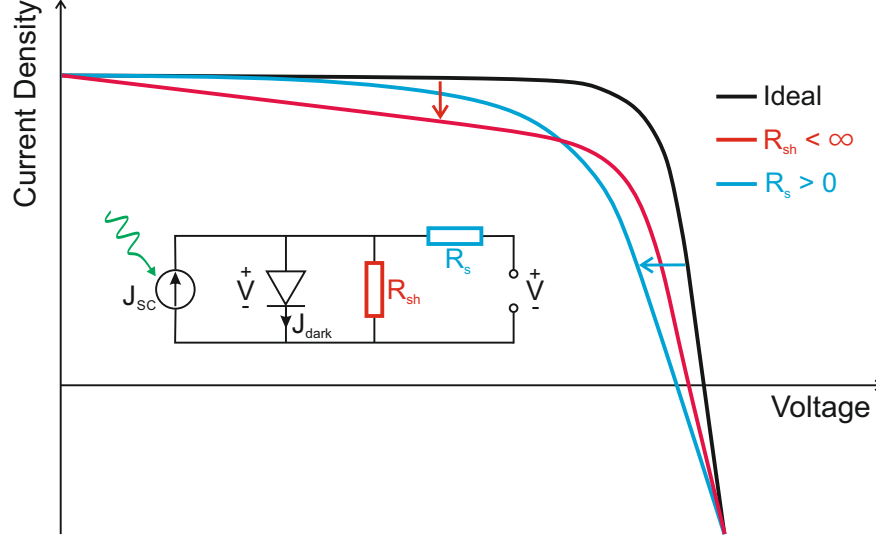


Figure 2.20: Current-voltage characteristics illustrating parasitic resistance losses (series resistance R_s and shunt resistance R_{sh}) with the associated equivalent circuit diagram. The J-V curve in black shows an ideal case where the photogenerated current follows the ideal diode equation, *i.e.* when $R_s = 0$ and $R_{sh} \rightarrow \infty$. When $R_s > 0$, the FF is reduced due to a decrease in the steepness of the J-V curve slope beyond V_{MPP} (blue curve). Leakage currents, such as recombination at the contacts or pinholes, are associated with a reduction of the shunt resistance R_{sh} and create a drop in the slope of the J-V curve between zero and V_{MPP} (red curve).

2.3 Perovskite solar cells

2.3.1 Crystal structure and fundamental properties

Perovskites are a class of materials with a crystal unit cell which is defined by the formula ABX_3 , where A is a monovalent cation, B a divalent metal cation (smaller than A) and X a monovalent halogen anion. Together, the B cations and the X anions form octahedra $[BX_6]^{4-}$, stabilised by the A cation (in between the octohedra). This structure is known as the *perovskite crystal structure*, illustrated in Figure 2.21.

In order to determine whether a combination of anions and cations can form a three-dimensional stable perovskite crystal structure, a *tolerance factor* (t) has been introduced [29]. This factor is only dependent on the ionic radii r_A , r_B and r_X of the three A, B and X elements such that:

$$t = \frac{r_A + r_X}{(R_X + R_B)\sqrt{2}} \quad (2.37)$$

A perfectly packed cubic lattice structure would correspond to $t = 1$. However, in practice, a

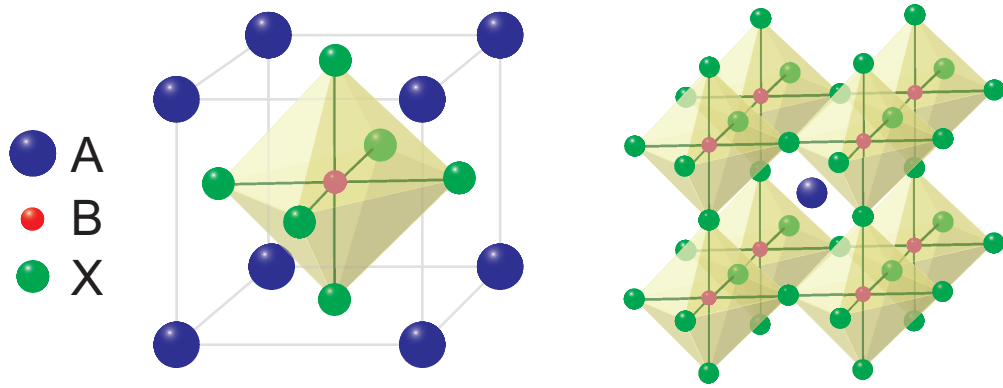


Figure 2.21: The perovskite crystal structure. On the left, the unit cell for a cubic ABX_3 perovskite lattice, where A and B are two cations of different sizes, and X is an anion. The B cation is surrounded by an octahedron of X anions. When a greater number of unit cells are assembled together (perovskite bulk), the octahedra form a cage around the A site cation, as shown on the right hand side.

three-dimensional cubic perovskite structure will likely form if $0.8 \leq t \leq 1$. When t decreases below 0.8, orthorhombic, rhombohedral, or tetragonal structures are favoured. When large A-site cations are used, such that the tolerance factor is greater than 1, layered 2D-structures form, where sheets of BX_6 -octahedra are separated by the large A-site cations.

There exists a broad class of related perovskite compounds for photovoltaic applications which all belong to the halide-based perovskite family. To form 3D-perovskites, the typical cations for the A site include the inorganic cesium (Cs^+) [30, 31], and the organic small molecules methylammonium CH_3NH_3^+ (MA) [32] and formamidinium $\text{HC}(\text{NH}_2)_2^+$ (FA) [30]. Theoretically, the B site can be occupied by any divalent metal cation, however Pb^{2+} , Sn^{2+} [33] and Ge^{2+} have shown appropriate properties for optoelectronic applications. The most commonly employed halide anions are iodide (I^-), bromide (Br^-) and chloride (Cl^-) to occupy the X site [29]. To reflect the hybrid nature of such materials, several names are employed such as metal halide, organic-inorganic, or hybrid halide perovskites. The tunability of the chemical composition and crystal structure offer the potential to design perovskites with outstanding optoelectrical properties for PV applications, including high absorption coefficients with sharp absorption onsets [34], and long charge carrier diffusion lengths [35].

One of the biggest benefits of the hybrid perovskites is the ability to tune their optical band gap over several hundreds of nanometers by ion substitution. As mentioned earlier, such chemical modifications occur through the substitution of either the halide X, the cation A, or

the metallic cation B. Since the discovery of perovskites as light absorbers, methylammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$ or MAPbI_3) with a band gap of around 1.6 eV [36], has been the most extensively studied. In this configuration, replacing the iodide by halides with larger ionic sizes, like bromide and chloride, leads to an increase of the band gap to 2.3 and 3.1 eV [37] (for polycrystalline films). The absorption band edge can also take intermediate values upon substitution of not only one, but two of these halides in different ratios [38, 39]. Another way to increase the band gap is to replace the organic methylammonium ion on the A site by the inorganic Cs^+ (smaller ionic radius), pushing its value to 1.73 eV [30, 31]. On the contrary, when the MA cation is exchanged with the slightly larger FA ion [30], the optical band gap decreases on a small scale from ~ 1.6 to ~ 1.5 eV, for MAPbI_3 and for FAPbI_3 respectively [36, 32]. Much narrower band gaps can be obtained by introducing Sn^{2+} on the B site (MASnI_3). This has been done in order to develop lead-free perovskites due to the toxicity of Pb [33, 40, 41]. However, because Sn^{2+} ion is easily oxidised to Sn^{4+} , the fabrication of Sn-based devices remains challenging.

Aside from the high optical absorbance, another characteristic which let perovskites achieve their impressive photovoltaic device performances is their excellent charge transport properties under solar illumination. Early studies reported electron-hole mobilities values in the tens of $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ for lead iodide perovskite thin films [42, 43], which is comparable to those of typical inorganic ionic semiconductors, *e.g.* GaAs [44]. In parallel to these findings, several groups measured long electronic carrier diffusion lengths on the order of 1 μm [35, 45], suggesting atypical bimolecular recombination rates below the theoretical limit set by the Langevin model [43, 46].

One more physical mechanism essential for charge generation in solar cells is the dielectric relaxation. Dielectric parameters have a strong influence on the exciton binding energy (E_B) which is directly related to the number of photogenerated free charge carriers in a semiconductor. Hence, several studies focused on the determination of the dielectric properties to determine the electron-hole binding energy in perovskite materials. This complex question has generated numerous debates in the field over the years, but has recently been answered

by Miyata *et al.* who determined the exciton binding energy to be ~ 16 meV in a polycrystalline MAPbI₃ film [47]. Despite the fact that the exact value of E_B is dependent on multiple external factors, such as composition, morphology, defect densities [48], a consensus has been reached within the community: at room temperature, metal halide perovskites for photovoltaic applications have binding energies on the order of 10 meV, thus photogenerated excitons dissociate spontaneously and transport happens predominantly through free charge carriers.

2.3.2 The rapid evolution and device architectures

The first use of metal halide perovskites in a solar cell was reported in 2009, when Kojima *et al.* employed the two perovskite absorbers MAPbI₃ and MAPbBr₃ as sensitizers in a dye-sensitised solar cell (DSSC) structure [49]. In this configuration (Figure 2.22), a thin layer of perovskite nanoparticles is anchored to a mesoporous TiO₂ scaffold, and then contacted by a liquid electrolyte which contains a redox couple. Upon illumination, excitons are generated in the perovskite, electrons are rapidly transferred into the CB of the TiO₂ *n*-type semiconductor, and holes to the electrolyte. Then, electrons and holes travel through these materials to the collection electrodes. At the time, perovskites were thought to act only as light absorber materials. In this first report, such devices delivered a power conversion efficiency of 3.8% which was then pushed further to 6.5% by Im *et al.* in 2011 [50]. However, both groups observed a very quick degradation of the solar cells within minutes, due to the dissolution of the perovskite nanoparticles in the electrolyte.

A breakthrough discovery for perovskite solar cells arrived in 2012, with the replacement of the liquid electrolyte with a solid-state hole transporting material. Almost simultaneously both groups of Snaith and Grätzel used 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), previously employed in solid-state dye sensitised solar cells (ss-DSSC) [32, 51], which unlike the liquid electrolyte does not dissolve the perovskite. The move towards ss-DSSC not only solved the degradation issue but also improved the solar cell efficiency. Kim *et al.* used sensitised mesoporous TiO₂ as the *n*-type layer and reached

a PCE of 9.7%. However, a remarkable finding was made by Lee *et al.* who discovered that replacing the mesoporous TiO_2 with an electronically inert alumina scaffold (Al_2O_3) yields an even higher efficiency (10.9%). This study provided the first evidence that metal halide perovskites are not only simple absorber materials, but are also capable of long-range electron transport similar to inorganic semiconductors. This new device architecture employing an inert Al_2O_3 scaffold was named meso-superstructured solar cell [32]. Shortly after this discovery, Etgar *et al.* replaced the spiro-OMeTAD by a thick capping layer of perovskite and such hole-transporter-free solar cells still exhibited reasonable efficiencies. Therefore, they showed that MAPbI_3 could also transport holes [52].

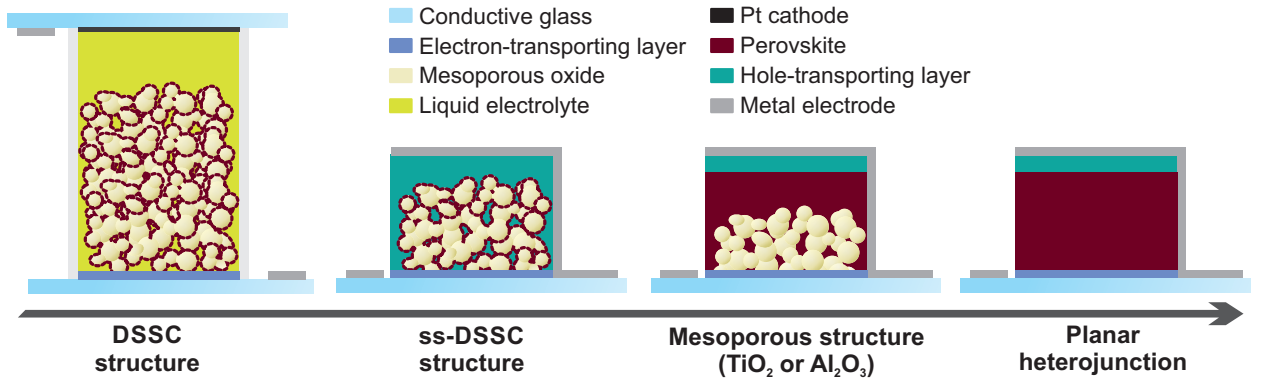


Figure 2.22: Evolution of the perovskite solar cell device architecture since its discovery. Metal halide perovskites were firstly implemented as an absorber in a traditional dye-sensitised structure solar cell (DSSC) with a liquid electrolyte. Due to rapid degradation of the perovskite upon contact with the electrolyte, solid-state perovskite sensitised solar cells (ss-DSSC) were introduced using a solid-state hole transporting material. Later on, the mesoporous TiO_2 was replaced by an inert Al_2O_3 scaffold. This breakthrough discovery that perovskite can transport electrons and holes over a micrometer led to the development of planar heterojunction solar cells.

The understanding that metal halide perovskite absorbers can effectively transport both electrons and holes over a micrometer [35, 45] allowed the development of planar heterojunction devices [53, 54]. Such devices can either be fabricated as a *n-i-p* architecture, *i.e.* with the perovskite deposited on top the electron-transporting layer (Figure 2.22), or can be inverted with the *n*-type charge collection layer on top of the device, referred to as *p-i-n* architecture [55, 56].

Over the past four years, continuous efforts have been made to, on one side, optimise the

perovskite quality through compositional tuning and deposition methods, and on the other side, to develop adequate charge extraction layers. Such improvements lead to a spectacular quick rise in power conversion efficiencies, yielding to certified values of over 22% [57, 9].

2.3.3 Processing and operating mechanism

Metal halide perovskites thin films can be deposited through various processing methods, including solution and evaporation approaches [53, 58], or combinations of thereof [59]. However, wet chemical deposition remains the most employed due to its ease of processability. It can be divided in either one-step [32, 51], or two-step sequential deposition where PbI_2 is first deposited then exposed to the organic ions, either in solution [60] or in vapour [61]. In 2014, an alternative one-step method was introduced, in which an antisolvent (a solvent which cannot dissolve the species present, *i.e.* chlorobenzene, toluene or anisole) is dripped onto the wet precursor film during spin coating [62]. This approach is known as the antisolvent method which results in a smooth layer of the absorber material. Most of the work presented in this thesis was done using this deposition technique in a planar heterojunction architecture, which has a very similar working principle to a $p-i-n$ junction as introduced in previous sections.

Upon illumination, most of the light is absorbed in the thick intrinsic perovskite bulk, where electron-hole pairs are generated. These excitonic bound-pairs immediately separate due to the low exciton binding energy and diffuse within the perovskite layer. On both sides of the absorber, charge selective contacts (n -type and p -type) facilitate electron and hole extraction into the electrodes. A simplified illustration of the operating mechanism, from light absorption to charge collection, is showed in Figure 2.23.

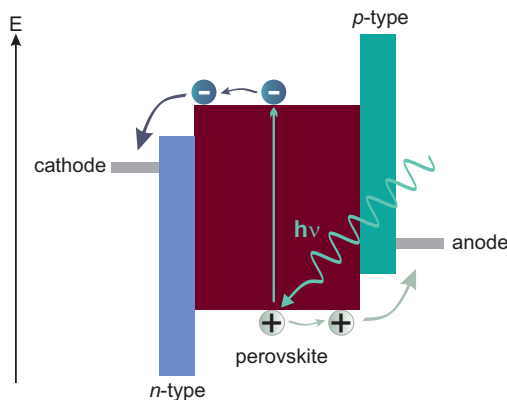


Figure 2.23: Schematic of the operating mechanism of a *p-i-n* perovskite solar cell. Light absorption, charge generation and charge transport occur in the perovskite layer. Charge selective contacts for electrons and holes are placed on both sides of the absorber in order to build an asymmetry to efficiently extract free charges to the electrodes.

2.3.4 The instability issue

In order to be commercialised, a photovoltaic device has to undergo standard stability tests set by the International Electrotechnical Commission (IEC). Such tests require the solar cell to sustain 200 thermal cycles between -40°C and $+85^{\circ}\text{C}$ with a deviation of the photocurrent smaller than $\pm 2\%$, measured at peak power above 25°C [63]. Therefore, for real-world photovoltaic applications, the metal halide perovskites employed have to show the right optoelectronic properties, and sustain sufficient structural and chemical stability towards their surrounding environment. Structural stability refers to the ability of a material to remain in one single crystalline phase across a wide range of temperature, while its capability to be resistant to reactive species such as oxygen and water relates to the chemical stability.

Upon heating perovskite materials, phase transition changes may occur. Such transitions lead to crystalline distortions which heavily impact their optoelectronic properties, *i.e.* band gap and charge carriers mobilities. Various studies showed that all the members of the methylammonium lead trihalides perovskite family (MAPbX_3) remain crystallographically stable over a wide range of temperatures [32, 42, 51]. This indicates that the structural stability is not an important concern for these materials. However, at 423 K the MAPbX_3 perovskites degrade after only 30 minutes as a result of the relatively low melting point of the methylammonium halides [30]. In order to improve the thermal stability, the volatile MA

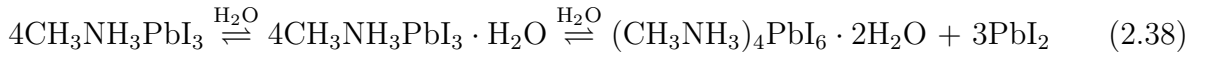
cation was successfully replaced by the slightly larger and heavier FA cation [30]. Unfortunately, in presence of moisture FAPbI_3 undergoes a phase transition at temperatures below 60°C [42, 64] into a non-perovskite structure, also called the yellow phase. Therefore, in order to operate in the adequate temperature range for photovoltaic applications, the FAPbI_3 perovskite has to remain in the black trigonal phase. This can be achieved by mixing both MA and FA organic cations especially when the MA cation is added in small concentrations ($<20\%$) [65]. The first MA/FA mixed cation perovskite solar cell was reported by Pellet *et al.*, however a certain percentage of the yellow phase remained [66]. The complete elimination of the non-perovskite yellow phase was successfully achieved by adding a percentage of MaBr to the FAPbI_3 precursor solution [67]. Such chemical modifications led to a structurally stable perovskite with enhanced performances. Further additions of caesium [68] and rubidium [69] to the A-site cation pushed the stability and efficiency even further. Despite a much improved structural stability through mixed cations and mixed halides perovskites, their inherent vulnerability to moisture poses a considerably more important challenge.

Due to the hygroscopicity of methylammonium iodide, metal halide perovskite materials suffer from a high chemical instability towards water [49, 38, 70, 71, 72] or generally to most polar solvents [49, 73]. Upon moisture exposure, the perovskite crystal readily decomposes to PbI_2 , and the mechanism behind this structural change lies in the nature of the bonds in the ionic solid. In the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal structure (Figures 2.21 and 2.24), the lead cation (Pb^{2+}) and the iodide anion (I^-) are bound together by strong ionic bonds. On the contrary, the organic cation (CH_3NH_3^+) forms hydrogen bonds to the Pb-I cage (octahedra) [74]. These weaker bonds can be disrupted by H_2O molecules, which then strongly bind to the organic cation. As a result, the perovskite crystal structure breaks down into hydrated phases and this process is particularly accelerated when the hydrogen bonds are weakened upon heat or light exposure.

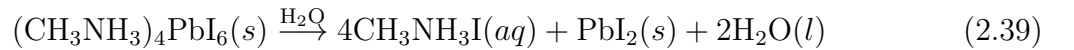
Müller *et al.* showed that MAPbI can rapidly absorb water molecules even at a relative humidity as low as 10%. Such low relative humidity exposure can have a positive effect on the solar cell performance [75], nonetheless the perovskite changes to its hydrated phases

when exposed to higher relative humidity, referred to as the monohydrate and the dihydrate phases.

The monohydrate structure $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ is the first formed when individual molecules of water infiltrate a perovskite unit cell. During this chemical transformation, the 3D-structure breaks due to H_2O intercalating into the perovskite, and each unit cell saturates with one molecule of water. Depending on the moisture level and the time of exposure, a small quantity of the dihydrate phase $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot \text{H}_2\text{O}$ is formed, which is in equilibrium with the dominant monohydrate structure [76]. Prolonged exposure to moisture leads to a complete transformation of the material into the dihydrate phase, characterised by the presence of two molecules of water per unit cell. Both hydrated structures are shown in Figure 2.24 as compared to the dehydrated perovskite crystal structure. Leguy *et al.* proposed a chemical reaction mechanism to the hydration process in the MAPbI_3 perovskite [76]:



Most interestingly, this hydration process can be reversed to a certain degree when the hydrated perovskite is exposed to dry air. If the system is dried out before the MA cation is removed, intercalated water molecules can escape from the dihydrate phase, and the perovskite goes back to its initial dehydrated structure [71, 72, 76]. However, with further exposure to moisture, the hydration progresses which results in a complete and irreversible transformation of the material into the dihydrate phase and the excess of water dissolves the organic cation CH_3NH_3^+ . This irreversible process follows the following chemical reaction:



The disintegration of MAPbI_3 into $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 with moisture, can also occur more rapidly when external factors such as heat, light or a bias are applied to the system. Under such conditions, hydrogen bonds are weakened and eventually break releasing the organic cation out of the inorganic Pb-I cage.

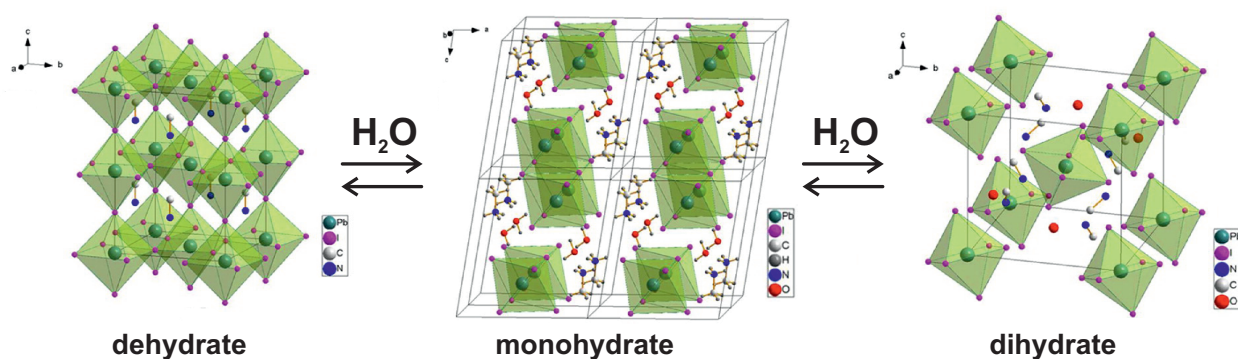


Figure 2.24: Illustration of the two hydrated structures of the MAPbI_3 perovskite as compared to its initial crystal structure. $\text{CH}_3\text{NH}_3\text{PbI}_3$ can be firstly hydrated to the monohydrate structure $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ and then to the dihydrate $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot \text{H}_2\text{O}$. Adapted with permission from A. Leguy *et al.*, Chem. Mater. 2015, 27, 3397-3407 [76]. Copyright (2015) American Chemical Society.

In a device, the hydration of the perovskite absorber is followed by a rapid drop in solar cell performance [76]. The ingress of water happens along the grain boundaries which at first leads to a segregation of individual perovskite domains [72, 76]. These domains are covered with the hydrate phase, but remain intact internally retaining their charge carrier dynamic properties [72]. Nonetheless, this isolation of grains most likely hampers long-range charge transport across several grains and inhibits the charge transfer between the perovskite and the hole-selective material which reduces the charge extraction and hence the overall performance [76]. Subsequently, the formation of the dihydrate structure due to prolonged exposure to moisture leads to a decrease in absorption across the visible range and the device can no longer generate power.

Therefore, the perovskite hygroscopicity is one of the biggest concerns to the long term operational stability of the device. In order to make this technology more resilient to water ingress, two strategies have been considered: perform compositional substitutions and additions to the perovskite structure itself to increase its chemical stability, or, suppress water infiltration by physically separating the perovskite absorber from the moist surrounding environment. In the above discussion regarding developments made to improve structural stability, MAPbI_3 can become more resilient to elevated thermal stressing by replacing CH_3NH_3^+ with the $\text{CH}(\text{NH}_2)_2^+$ cation. Unfortunately, formamidinium is also an organic compound and, similarly to methylammonium, is highly susceptible to moisture degradation. Despite strong

efforts, mixed cations and mixed halides perovskites are still to some degree vulnerable to moisture which highlights the necessity to develop moisture-blocking contacts to protect the perovskite absorber from the wet external atmosphere.

3 | Materials and Methods

This chapter gives a description of the materials and methods used, as well as a short overview over the experimental setups that have been employed throughout the experiments of this thesis.

3.1 Materials

3.1.1 Hole transporting materials

In this study, two HTMs were used: P3HT and spiro-OMeTAD.

- **Spiro-OMeTAD:** 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene, $M_w = 1225.43 \text{ g}\cdot\text{mol}^{-1}$, Luminescence Technology Corp.

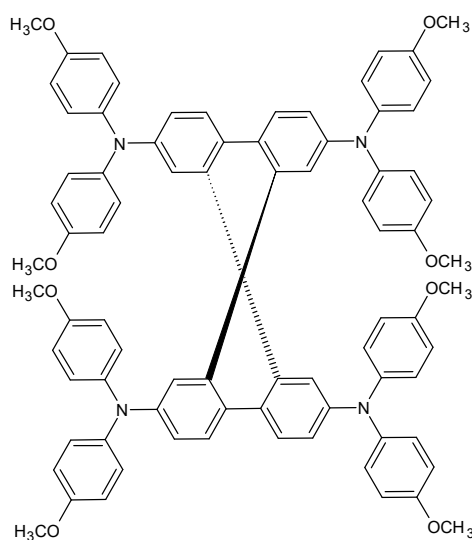


Figure 3.1: Molecular structure of Spiro-OMeTAD.

- **P3HT**: poly(3-hexylthiophene), regioregular, average molecular weight, $M_w = 50\,000$ $\text{g}\cdot\text{mol}^{-1}$, regioregularity = 95%, Rieke Metals Inc.

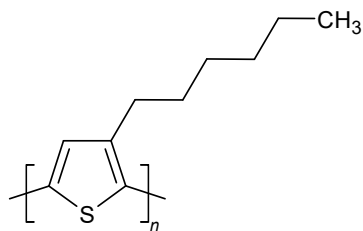


Figure 3.2: Molecular structure of P3HT.

3.1.2 Dopants

- **Li-TFSI**: lithium bis(trifluoromethanesulfonyl)imide, $M_w = 287.09$ $\text{g}\cdot\text{mol}^{-1}$, Sigma-Aldrich.

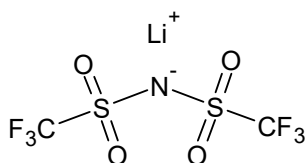


Figure 3.3: Molecular structure of Li-TFSI.

- **FK209**: tris(pyrazolylpyridine)-cobalt(III) complex, $M_w = 1503.16$ $\text{g}\cdot\text{mol}^{-1}$, Dyesol.

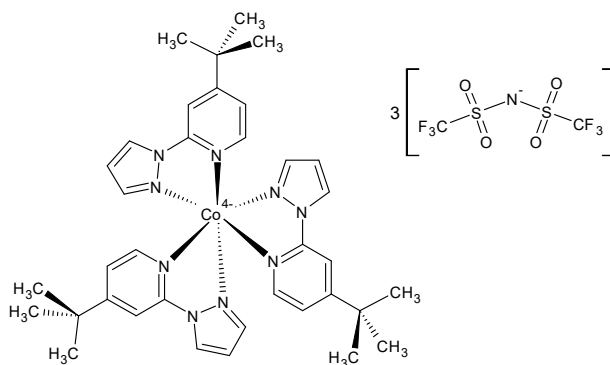


Figure 3.4: Molecular structure of FK209 complex.

- **Mo(tfd-COCF₃)₃**: Molybdenum tris-(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene), Mw = 858.44 g·mol⁻¹, synthesised according to the literature [77] by Yadong Zhang, Georgia Institute of Technology.

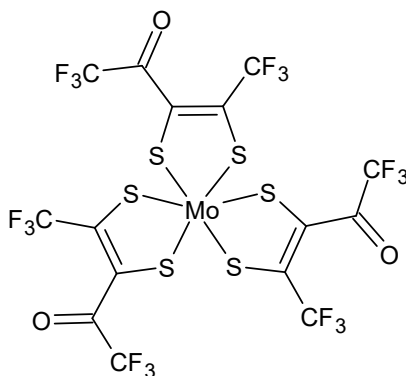


Figure 3.5: Molecular structure of Mo(tfd-COCF₃)₃.

- **Mo(tfd-CO₂Me)₃**: Molybdenum tris(1(methoxycarbonyl)2(trifluoromethyl)ethane-1,2-dithiolene), Mw = 744.54 g·mol⁻¹, synthesised according to the literature [78] by Yadong Zhang, Georgia Institute of Technology.

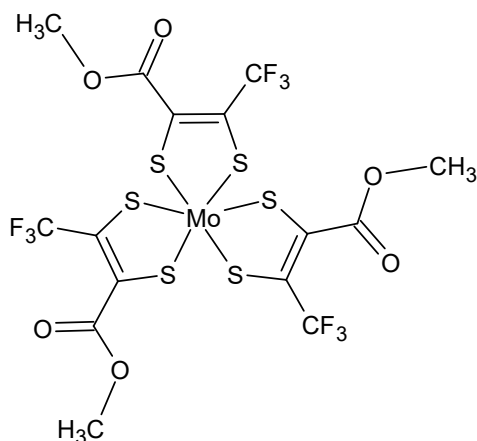


Figure 3.6: Molecular structure of Mo(tfd-CO₂Me)₃.

- **Spiro(TFSI)₂**: 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene di[bis-(trifluoromethanesulfonyl)imide], $M_w = 1785.73 \text{ g}\cdot\text{mol}^{-1}$, synthesised according to the literature [79] by Nakita Noel, University of Oxford.

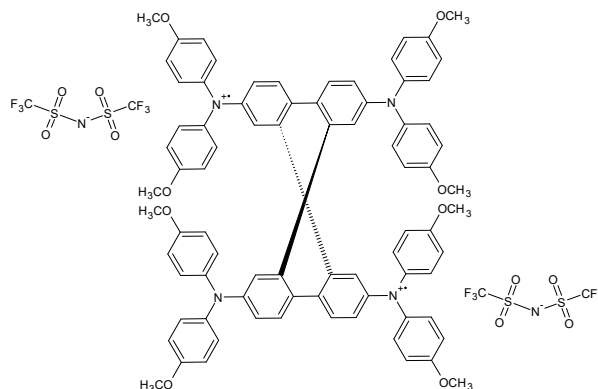


Figure 3.7: Molecular structure of Spiro(TFSI)₂.

3.1.3 Other polymers and additive

- **PMMA**: poly(methyl methacrylate), average molecular weight $M_w = 97\,000 \text{ g}\cdot\text{mol}^{-1}$, Sigma-Aldrich.

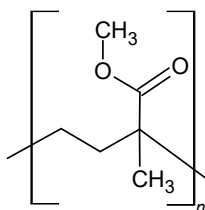


Figure 3.8: Molecular structure of PMMA.

- ***t*BP**: 4-*tert*-butyl pyridine, $M_w = 135.21 \text{ g}\cdot\text{mol}^{-1}$, Sigma-Aldrich.

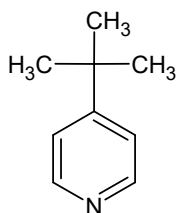


Figure 3.9: Molecular structure of *t*BP.

3.2 Perovskite solar cell fabrication

3.2.1 Substrate preparation

Fluorine-doped tin oxide (FTO) coated glass sheets ($7 \Omega \cdot \text{cm}^{-2}$ Hartford Glass) were etched with zinc powder and HCl (3M) to obtain the required electrode pattern. The sheets were first cleaned with detergent (2% Hellmanex in water), and then rinsed sequentially with deionised water, acetone, and isopropanol. The last traces of organic residues were removed by oxygen plasma cleaning for 10 min.

3.2.2 Electron Transporting Layer deposition

- *TiO₂ compact layer for mesostructured perovskite solar cells*

A 100 nm thick electron-accepting TiO₂ compact layer was spin-coated (2000 rpm for 60s) on the glass from a solution of titanium isopropoxide diluted in anhydrous ethanol, and sintered at 500°C for 45 min.

- *SnO₂/PCBM ETL for planar heterojunction perovskite solar cells*

The electron transporting layer was prepared by first spin-coating a solution of SnCl₄·5H₂O in isopropanol [80, 81] ($17.5 \text{ mg} \cdot \text{mL}^{-1}$). The substrates were then dried in air at 100°C for 10 min then annealed at 180°C for 60 min. Once the substrates were cooled down to room temperature, a solution of [6,6]-phenyl-C60-butyric acid methyl ester (PCBM) in dichlorobenzene (DCB) ($5 \text{ mg} \cdot \text{mL}^{-1}$) was dynamically spin-coated onto the substrate at 4000 rpm and dried at 100°C for 5 min.

3.2.3 Perovskite absorber deposition

- *Mesostructured perovskite solar cells*

A colloidal dispersion of 50 nm Al_2O_3 nanoparticles in isopropanol was deposited by spin-coating (2500 rpm for 60 s) and dried at 150°C for 10 min, forming the low-temperature mesostructured scaffold [82]. The $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite precursor solution (40 wt.%) was prepared according to literature methods [32], by dissolving methylammonium iodide (MAI, Dyesol) and lead(II) chloride (PbCl_2 , Sigma-Aldrich) in dimethylformamide (DMF) in a 3:1 molar ratio. Then, the perovskite precursor solution was spin-coated (2000 rpm for 40 s) on top of the scaffold, in a nitrogen-filled glovebox, and annealed at 100°C for 90 min.

- *Planar heterojunction perovskite solar cells*

The mixed-cation lead mixed-halide perovskite solution $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ was prepared from a precursor solution made of formamidinium iodide (1.25 M, Dyesol), lead iodide (1.38 M, TCI), methylammonium bromide (0.25 M, Dyesol), and lead(II) bromide (0.25 M, Sigma-Aldrich) in a 4:1 (v:v) mixture of anhydrous DMF:DMSO (Sigma-Aldrich) and stirred at 65°C for 15 min. After having cooled to room temperature, the perovskite solution was spin-coated onto the substrate in dry air. The perovskite was deposited by first spin coating the solution at 1000 rpm for 10 s, followed by 6000 rpm for 35 s. Anisole (100 μL) was dropped onto the spinning substrate 5 s before the end of the program. Films were then annealed in an oven at 100°C for 1 h.

3.2.4 Hole Transporting Layer deposition

The spiro-OMeTAD (Lumtec) was then dissolved in chlorobenzene and the solution was spin-coated onto the perovskite layer, after allowing the substrates to cool down. For the mesostructured devices, a 96 $\text{mg}\cdot\text{mL}^{-1}$ solution of spiro-OMeTAD (30 mol% of Li-TFSI and 80 mol% of *t*BP) was used. For the planar devices, a concentration of 85 $\text{mg}\cdot\text{mL}^{-1}$ was

employed, then Li-TFSI ($500 \text{ mg}\cdot\text{mL}^{-1}$ in 1-butanol), FK-209 ($230 \text{ mg}\cdot\text{mL}^{-1}$ in acetonitrile) and *t*BP, were added at $20 \text{ }\mu\text{L}\cdot\text{mL}^{-1}$, $10 \text{ }\mu\text{L}\cdot\text{mL}^{-1}$ and $35 \text{ }\mu\text{L}\cdot\text{mL}^{-1}$, respectively. Devices were left overnight in a desiccator in air.

3.2.5 Top electrode

Lastly, 80 nm-thick gold electrodes were evaporated onto the devices through a shadow mask, using a thermal evaporator.

3.3 Electrical characterisation

3.3.1 Solar cell characterisation

The current density-voltage (J-V) curves were measured (2400 Series SourceMeter, Keithley Instruments) under simulated AM 1.5 sunlight at ($100 \text{ mW}\cdot\text{cm}^{-2}$) irradiance generated by an Abet Class AAB sun 2000 simulator, with the intensity calibrated with an NREL calibrated KG5 filtered Si reference cell. The mismatch factor was calculated to be less than 1%. The solar cells were masked with a metal aperture to define the active area to be 0.0919 cm^2 .

The J-V parameters (V_{OC} , J_{SC} , FF and PCE) were found from spline interpolation of the J-V data points. Series resistance (R_S) and ideality factor (n) values were obtained by nonlinear regression of the data to the equation defined in Chapter 2 (Equation 2.36) [83].

3.3.2 Conductivity measurements

Conductivity samples were prepared by spin-coating a layer of the desired material onto glass substrates. Resistivity values were calculated by measuring the film thickness with a Dektak profilometer and multiplying it by the film's sheet resistance. The sheet resistance was measured using an in-line four-point probe with 0.635 mm tip spacing from Jandel Engineering, which was connected to a Keithley 2450 sourcemeter. Then the conductivity

was calculated as the inverse of the resistivity.

3.4 Spectroscopy

All spectroscopy samples were prepared by spin-coating the films (perovskite or HTM) on glass substrates.

3.4.1 Absorption spectroscopy

Absorption spectroscopy was carried out using a Lambda 1050 UV vis/NIR spectrometer (PerkinElmer).

3.4.2 Time-resolved photoluminescence spectroscopy

In photoluminescence (PL) measurements, species in the absorber are photoexcited with a single wavelength excitation source, they then relax to the band edge and emit light by recombining radiatively. For the mixed halide perovskite studied in this thesis, the samples were all excited at a wavelength of 505 nm, resulting in an emission ranging from 780 nm to 800 nm depending on the perovskite material used.

A schematic illustration of the time-resolved PL setup is shown in Figure 3.10. In order to record the decay of the PL signal over time, the system has to be perturbed from its equilibrium state by an optical pulse. Thus, a frequency is fixed forcing the laser to pulse light at constant intervals. This pulse is attenuated by a neutral density filter before hitting the sample. A cut-off filter is placed right after the sample position in order to filter out any scattered light. To reduce the emission of the sample to solely a single photon, an attenuator is placed just before the beam hits the photomultiplier tube (PMT) which subsequently creates a short electron pulse. The timing electronics then record the time at which the signal is received. Finally, after many repetitions, by summing all the signals a histogram of arrival time is created which depicts the PL profile over time.

Time-resolved PL measurements were acquired using a time-correlated single photon counting (TCSPC) setup (FluoTime 300, PicoQuant GmbH). Frequencies and fluences used for each experiment are cited in the main text. The PL was collected using a high resolution monochromator and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH).

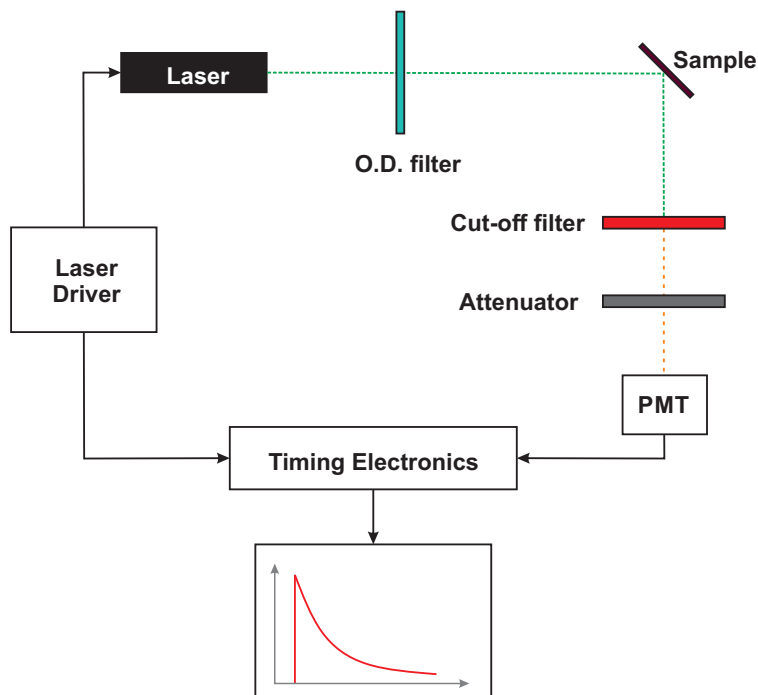


Figure 3.10: Schematic of the time-resolved photoluminescence spectroscopy setup.

3.4.3 Photoluminescence quantum efficiency

Steady-state photoluminescence quantum efficiency (PLQE) measurements were calculated as described by De Mello *et al.* [84]. The sample was illuminated using a 532 nm CW laser excitation source (Suwtech LDC-800) in an integrating sphere (Oriel Instruments 70682NS), both the scattered excitation pulse and the PL signal of the sample were collected using a fiber-coupled detector (Ocean Optics MayaPro). The excitation intensities are cited in the main text.

3.4.4 Transient photoconductivity

Transient photoconductivity was carried out on perovskite films (4 mm channel width). A Nd:YAG laser was used at the range of fluences specified in the text, with an excitation wavelength of 470 nm and pumped at 10 Hz with 7 ns pulses. A bias of 25 V was applied across the in-plane (lateral) electrodes, while the current was monitored by an oscilloscope [85, 86]. Since the contact resistance between the perovskite film and the Au electrode was fairly small compared to the resistance of the sample, two-electrodes conductivity measurements were performed. A variable resistor was placed in the circuit, in series with the sample, and was set to always be $<1\%$ of the sample resistance. The voltage drop across the variable resistor was monitored through a 1 M Ω impedance oscilloscope, to subsequently determine the potential drop across the two in-plane Au electrodes (6 mm total channel length). Films were coated with an inert layer of PMMA (200 nm) to protect samples from environmental degradation during the measurements.

3.5 Kelvin probe measurements

3.5.1 Setup

Surface photovoltage measurements were taken with a KP Technology scanning Kelvin Probe system SKP5050. Since the work function is extremely sensitive to surface conditions, the measurements were performed in a dry nitrogen atmosphere, in the dark and at room temperature in order to minimise environmental impacts on the surface. The work function data of perovskite layers deposited onto ITO-glass substrates presented in Chapter 6 were obtained by Dr Yen-Hung Lin (Imperial College, London).

3.5.2 Technique

A schematic representation of the Kelvin Probe measurement is displays in Figure 3.11. The working principle is based on the determination of a difference in work functions between a known reference *i.e.* the Kelvin Probe tip (ϕ_P), and a sample (ϕ_S). When the tip and the sample do not interact (Figure 3.11a), their Fermi levels align at the vacuum level (E_{vac}). In Figure 3.11b the two materials are connected. In the depicted case, electrons from the sample flow to the tip because $\phi_S < \phi_P$, and the Fermi levels equilibrate. Since both material were initially charge-neutral, the probe and the sample are now negatively and positively charged respectively, which gives rise to an electrostatic potential and a contact potential difference (V_{CPD}).

In the Kelvin probe measurement, the probe and the sample are never brought in contact, the magnitude of V_{CPD} can be determined by varying the current flow between the two materials upon periodic modulation of the distance, while simultaneously applying a counter voltage. When the probe vibrates vertically, the distance between the sample and the tip changes resulting in a variation of the capacitance between the two materials, and hence in a change in current through an external circuit. Then, the magnitude of the contact potential is equal to the applied counter voltage for which the current vanishes.

During the measurement, the vibrating tip is typically at a distance of 0.2 to 2.0 mm from the sample surface. Furthermore, the contact potentials obtained from a surface are typically defined by the topmost 1 to 3 layers of atoms or molecules.

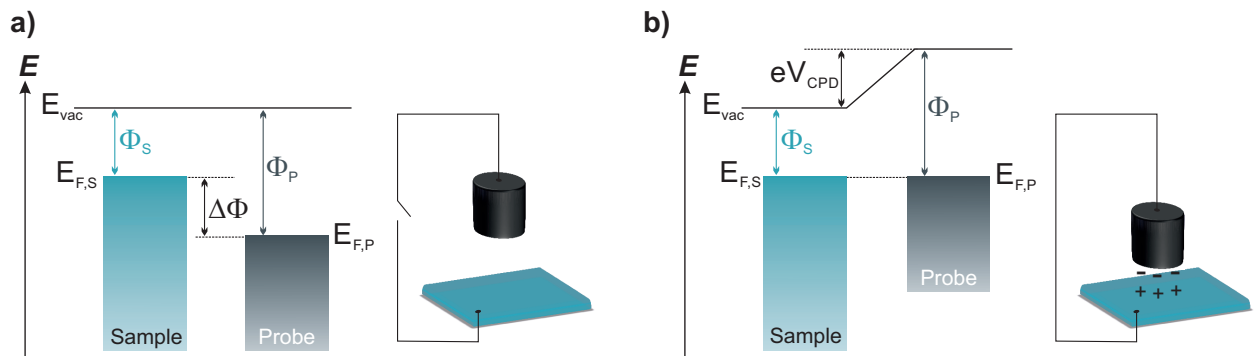


Figure 3.11: Schematic representation of a Kelvin Probe measurement between the Kelvin Probe tip, or probe (black) and a sample (blue) with different work functions ϕ_P and ϕ_S respectively. a) Before electrical contact between the probe and the sample, the Fermi levels align at the vacuum level (E_{vac}). b) When the two are connected, electrons flow and the Fermi levels equalise which gives rise to a contact potential difference (V_{CPD}).

3.6 Microscopy

3.6.1 Optical microscope imaging

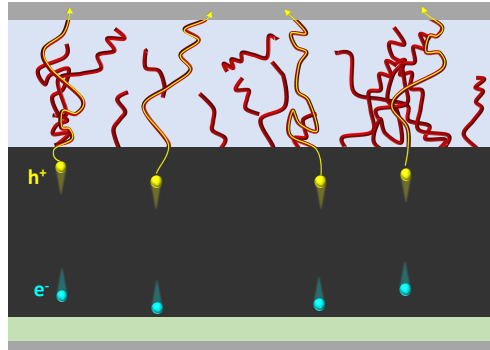
Optical microscope images were acquired in reflection and transmission mode with a Nikon Eclipse LV100 base in combination with various magnified objectives (10x, 20x, 50x and 100x). Dark field, bright field and PL modes were applied for different visualisations of the films. Measurements were performed at Oxford Photovoltaics Limited (Oxford PV).

3.6.2 Scanning Electron Microscopy

Top surface images of films were taken with a Hitachi S-4300 field emission scanning electron microscope (SEM). All samples were sputter-coated with 3 nm of Pt previous to imaging, in order to reduce charge accumulation under the electron beam and thus improve the image quality.

4 | P3HT-nanowires embedded in a PMMA matrix as a HTM composite structure

In this chapter, a new composite layer made of poly(3-hexylthiophene) (P3HT) nanowires and a poly(methyl methacrylate) (PMMA) matrix is used as the HTM in perovskite solar cell. Due to the presence of the insulating PMMA, this low-cost HTM induces contact discontinuities at the *p*-type interface which limits non-radiative recombination and enhances device performance.



4.1 Context and summary

To maximise the power output, a solar cell should generate both high photocurrent and high photovoltage. Hence, an ideal solar cell should be able to efficiently extract all excited charges at short-circuit conditions to generate a high current density. In open-circuit conditions, carriers cannot be extracted and the photoexcited charge carrier density builds up. Electrons and holes will eventually recombine by emitting a photon. In this ideal configuration, non-radiative recombinations do not exist and the solar cell is considered in its radiative limit yielding to the highest attainable V_{OC} . Therefore, the ability of a solar cell to emit light is bound to its V_{OC} and is closely linked to its power conversion efficiency under normal operating conditions [87].

With outstanding radiative efficiencies, organic-inorganic perovskite solar cells have demonstrated high open circuit voltages. Nonetheless, important non-radiative recombinations at the *p*-type interface play a major role in preventing these devices from reaching their theoretical efficiency limit. For years, silicon solar cell designers have engineered their charge collection contacts by introducing insulating material to simultaneously reduce interfacial recombinations and production costs, a technique that can be applied to perovskite solar cells as well. The inherent moisture sensitivity of the perovskite absorber remains an important obstacle to commercialisation highlighting need for new layers that can prevent or impede water from reaching the perovskite absorber.

In this chapter, a new composite HTM was developed, based on P3HT nanowires (P3HT-NW) embedded in a poly(methyl methacrylate) (PMMA) matrix. Due to improved structural ordering of the P3HT chains, P3HT-NWs have been shown to present enhanced charge mobility as compared to neat P3HT films. In solar-cells, the blend-based devices showed an increase in V_{OC} and in steady-state efficiency against the pristine P3HT, suggesting a drastic reduction of non-radiative recombination decay channels. Photoluminescence quenching experiments revealed an increase in both the PL lifetime and the PLQE when the perovskite absorber was coated with the HTM composite, strong evidence that such a

p -type interface does not introduce non-radiative recombination, unlike any other currently known HTMs employed in perovskite solar cells today. The introduction of inert PMMA, drastically reduces the area of contact between the perovskite and the P3HT-NWs resulting in extremely high hole densities and efficient charge collection. As a result, employing the P3HT-NW/PMMA composite as HTM yielded to a 3% increase in SPO as compared to the standard P3HT, with the champion device having 14.8% PCE. Furthermore, 85°C thermal stressing tests in air showed that the blend significantly enhanced the long-term stability of perovskite solar cells when compared to a spiro-OMeTAD HTM. As previously reported, the PMMA matrix acts as a barrier for water ingress, thus protecting the perovskite from moisture [88]. Finally, the P3HT-NW/PMMA blend was found 15 times less expensive than spiro-OMeTAD, making this new composite HTM highly attractive for future commercial applications.

4.2 Introduction

Solar power is the most abundant energy resource on Earth and could provide an endless energy supply. Organic-inorganic lead halide perovskite solar cells have created tremendous enthusiasm due to their impressive performance, and are now regarded as one of the most promising alternative energy conversion devices to conventional silicon-based photovoltaics. Nonetheless, the perovskite absorber remains highly sensitive to moisture which could hamper the commercial development of the technology [72, 74, 76]. Despite remarkable progress, there exists substantial parasitic non-radiative recombination losses, especially at the interfaces with the charge extraction layers, which limits the overall device performance.

From a stability point of view, an ideal hole transporting material (HTM) would protect the perovskite from water ingress while still ensuring effective charge transfer and transport. Moreover, to achieve a perfect solar cell, an optimal HTM must not induce any non-radiative decay channels. At open-circuit conditions, excited carriers have no place to go which causes charge densities build up. In an ideal scenario (*i.e.* no non-radiative recom-

bination pathways) all charges recombine radiatively and emit light. In this ideal situation, the photovoltage is maximised and any additional non-radiative recombinations will impede the carrier density build up causing a reduction in V_{OC} . Thus, a good solar cell should emit light [87]. In the case of perovskite solar cells, all contacts employed induce non-radiative decay channels at the absorber interfaces with the extraction layers [89, 21]. Holes in the HTM recombine with electrons in the perovskite, explaining the extreme photoluminescence quenching thus far observed at the perovskite/HTM interface. Hence, the ideal HTM is one that can perform the multiple tasks of being hole-selective while protecting the semiconductor from ambient conditions, without impeding but perhaps even improving radiative recombination yield in the solar cell.

To date, the small molecular 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) typically doped with lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) has exhibited the highest conversion efficiencies in perovskite solar cells when used as the HTM [10]. Unfortunately, spiro-OMeTAD remains extremely costly and presents a high sensitivity to moisture due to the presence of hygroscopic lithium salts [90], leading to an accelerated loss of device performance under stressing conditions [88]. In order for the technology to be developed at competitive prices, cheaper and more robust materials have to be used. As a cheaper alternative to small molecule HTMs, the polymeric hole-conductor poly(3-hexylthiophene) (P3HT) has appeared as highly promising. P3HT can be deposited via a broad range of coating techniques such as spin coating, spray coating, or inkjet printing, and has already yielded high power conversion efficiencies in perovskite solar cells [91, 92, 93, 94, 95]. However, P3HT was shown to induce higher non-radiative recombination rate at the perovskite/HTM interface with respect to spiro-OMeTAD [96], resulting in overall lower performance.

For the past three decades, manufacturers of silicon crystalline solar cells have managed to push the power conversion efficiency through the continual refinement of the device contacts [97, 98]. One of the oldests concept was introduced by Green *et al.* and relies on the reduction of the contact area by introducing an insulating (also referred to as "passivating")

oxide at the top contact to reduce interfacial recombinations [99]. By reducing the contact area between the emitter and the electrode, charges are forced to flow through specific channels. Such solar cell structure is named Passivated Emitter Solar Cell (PESC). The impact of the PESC structure on the industrial exploitation of solar cells is twofold. It enables manufacturers to achieve greater performance than with standard structure while reducing the amount of active material used, thus drastically lowering costs. Introducing discontinuities at the p -type interface in perovskite solar cells, similar to the PESC concept, could limit non-radiative recombination pathways and lead to greater efficiencies.

4.3 Results and discussions

4.3.1 P3HT nanowires: formation and characterisation

Conjugated polymers have aroused great interest in organic photovoltaics (OPV) and optoelectronics due to their semiconducting properties and highly tunable molecular ordering. One of the most important semiconducting polymers is poly(3-hexylthiophene) (P3HT). P3HT has been extensively used in OPV blended with PCBM as a bulk heterojunction [100, 101, 102] but also more recently in perovskite solar cells as a hole extraction layer [91, 92, 93, 94, 95]. When a solution of P3HT is spincoated on a substrate, the polymer self-assembles and crystallises with a π - π stacking of adjacent thiophene main chains as illustrated in Figure 4.1. The casted thin film formed is often highly disordered with both crystalline and amorphous domains which strongly impacts charge transport processes [103, 104, 105]. The degree of disorder is influenced by several parameters such as regioregularity, molecular weight, solvent properties and deposition methods. In P3HT thin films, transport of charge carriers can occur both along the conjugated backbone (also referred to as intra-chain transport or coherent transport), and/or *via* hopping from one chain to another (*i.e.* inter-chain transport) as shown in Figure 4.1. This anisotropic character of charge transport has been extensively reported, and the charge mobility along a single backbone chain was found to be 2-3 orders of magnitude faster than along the π - π stacking direction (between two adjacent

chains) [106, 107]. Therefore, in order to maximise the charge extraction in a solar cell, the casted film needs to be as crystalline as possible (*i.e.* reduced disorder) with preferential intra-chain transport along the P3HT fiber.

Enhancement of structural order in P3HT thin films can be obtained through post-deposition annealing at temperatures above 150°C, ranging from one to several hours [108, 109]. In a *n-i-p* solar cell structure (*i.e.* HTM on top of the perovskite), such annealing treatment is not recommended since it would thermally stress the perovskite absorber which would most likely result in degradation of the crystal structure, and hence in a performance loss. In order to avoid post-annealing, many studies in organic photovoltaics have investigated the use of self-organised 1D nanostructures of P3HT, also referred to as P3HT nanowires (P3HT-NWs) which reduce the degree of disorder and increase the mobility of charges [110, 108, 111]. P3HT-NWs are highly crystalline and can create continuous percolation pathways for charge transport contributing to enhanced carrier mobility with respect to their 2D thin film counterparts. When employed in bulk-heterojunction solar cells, P3HT-NWs have led to a remarkable improvement in the conversion efficiency of devices without subsequent annealing processes [110, 108, 111].

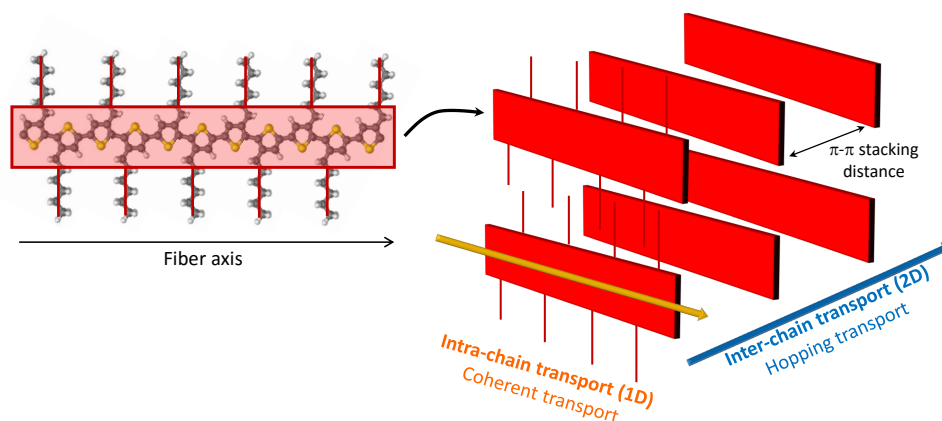


Figure 4.1: Schematic representation of a self-organised chain packing in a P3HT film. Casted P3HT films result in a lamella structure with two-dimensional conjugated sheets (in red) formed by inter-chain π - π stacking. The charge transport in the P3HT layer combines intra- and inter-chain transport, which take place along the backbone and across two adjacent chains (or lamellas), respectively. Inter-chain transport occurs *via* hopping and is therefore considerably slower than the one-directional intra-chain charge transport.

P3HT-NWs spontaneously form upon deposition, however their properties, such as crystallinity or length, are tightly dependent on P3HT's degree of solubility in the solvent em-

ployed. Numerous studies have reported enhanced intra-chain order with longer conjugation lengths and higher crystalline quality when P3HT is casted from a marginal solvent such as toluene [112, 113]. In contrast, a high solubility solvents for P3HT (*e.g.* chlorobenzene or chloroform) show both poor crystallinity and intra-chain order. P3HT-NWs can be formed either prior to deposition or during casting. In this study, the nanowires were formed by a facile self-seeded growth from a cycle of heating then cooling as proposed by Oh *et al.* [114]. In order to determine the most suitable solvent for NW growth, several solutions ($4 \text{ mg}\cdot\text{mL}^{-1}$) were prepared comparing good, intermediate and marginal solvents, corresponding to chloroform, chlorobenzene and toluene respectively. The solutions were heated on a hot plate to 100°C for 30 minutes until complete dissolution, then placed in a freezer (-20°C) for 20 minutes, and taken out to room temperature (25°C).

In order to determine whether or not the P3HT domains grown in various solvents can be characterised as P3HT-NWs, UV-vis absorption measurements were performed (Figure 4.2). UV-vis absorbance is a facile measurement which has been frequently employed to determine the degree of crystallinity of P3HT films based on the shape of the absorption spectra [112, 115, 116, 117]. The films were casted on glass immediately after the heating then cooling cycle and a film made from a fully dissolved P3HT solution in chlorobenzene was taken as reference.

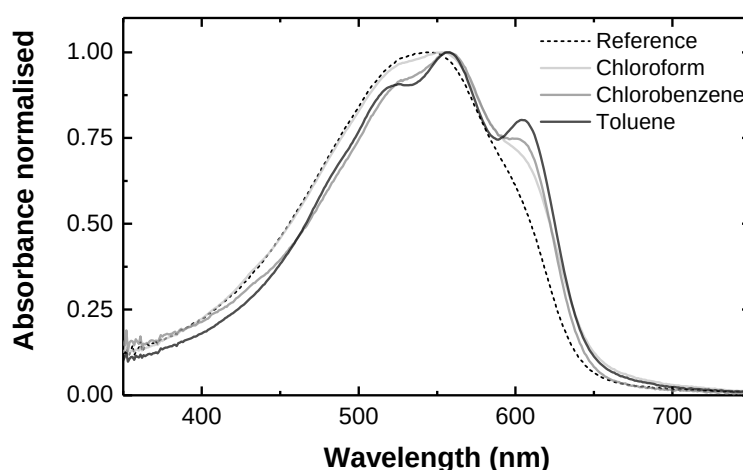


Figure 4.2: Absorption spectra of P3HT films deposited from solutions which have undergone a thermal cycle from 100°C to -20°C . Solvents with different degree of solubility are compared to a reference film casted from a fully dissolved P3HT solution in chlorobenzene.

All the spectra show an average absorption feature centered around 550 nm with no

visible peak at 450 nm (attributed to amorphous chains [112, 117]), indicating that the casted films are mostly crystalline, even the reference deposited from a dilute solution of P3HT. Nonetheless, the P3HT films that have undergone the heating then cooling treatment show a gradual red shifted absorption with the decrease in solubility (chloroform > chlorobenzene > toluene), with respect to the reference. Additionally, the vibronic features at 515, 550 and 610 nm progressively appear, corresponding to highly-conjugated π - π interactions [112, 115, 116, 117] and evidence for an enhanced crystallinity. Most particularly, the shoulder at 550 nm arises from the absorption of extended conjugation of P3HT in the solid-state, and the shoulder at 610 nm is attributed to the interchain stacking of regioregular P3HT, the intensity of which is correlated with the degree of order in the polymer [118, 119]. The absorption spectrum corresponding to formation in toluene shows the sharpest features at 550 and 610 nm suggesting the presence of extended conjugated P3HT chains and ordered inter-chain stacking which both suggest 1D nanostructures of P3HT. Therefore, the P3HT domains formed can be qualified as P3HT-NWs.

The surface morphology of films casted from fully dissolved P3HT in chlorobenzene and from preformed P3HT-NWs in toluene were examined by atomic force microscopy (AFM). The images are shown in Figures 4.3a and b. For the P3HT layer prepared from dissolved solution, no fibrillar structures are observed and the surface is homogeneous with an average root-mean-square roughness value of 0.77 nm. On the other hand, P3HT-NWs grown in toluene are shown in Figure 4.3b and have an increased film surface roughness (average root-mean-square roughness value of 11.12 nm). The fibrillar morphology is a visual indication of the structural ordering of the P3HT chains. In addition, the difference in the colour of both solutions indicates a conformational change of the P3HT chains from dissolved polymer (light orange) to nanowires (deep purple). To further characterise the P3HT-NWs grown in toluene, scanning electron microscopy (SEM) was performed (Figure 4.3c). The SEM image reveals agglomerations of P3HT-NWs with a diameter of approximately 10 nm, and a length of up to 1 μ m long. The facile self-seeded growth from a cycle of heating then cooling in a marginal solvent (toluene) is therefore a quick and efficient route to form P3HT-NWs. Furthermore, toluene is an ideal solvent since it requires high temperatures to completely

dissolve the P3HT chains, then once formed, it stabilises the NWs in the solid-state at room temperature.

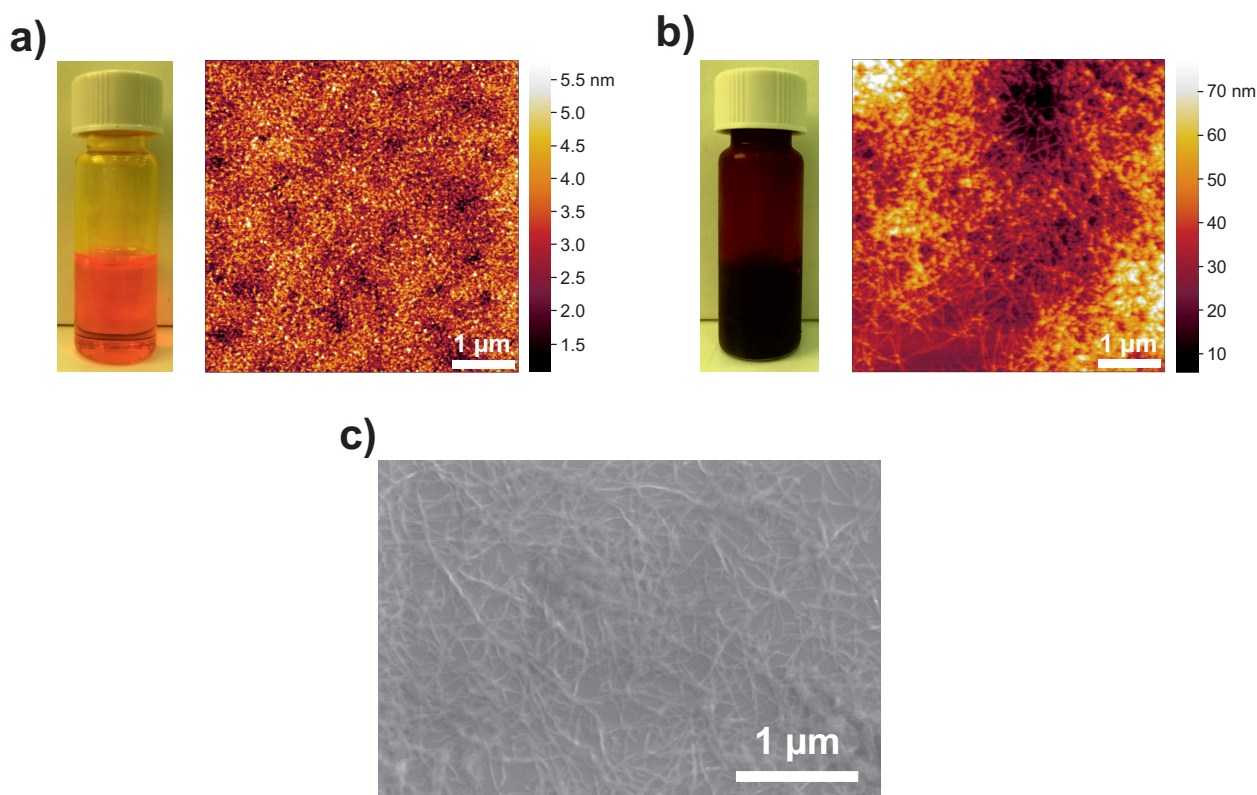


Figure 4.3: Film morphology of P3HT films determined by AFM (a and b) and SEM (c). a) P3HT film deposited from a fully dissolved solution in chlorobenzene which is characterised by a light orange colour. b) After a cycle of heating then cooling from 100°C to -20°C, the P3HT solution (toluene) becomes deep purple, a signature of a conformational change of the P3HT chains in nanowires. c) P3HT-NWs formed in toluene as deposited on glass, they have an approximate diameter of 10 nm and can be up to 1 μm long. AFM images were taken by Kelly Schutt (University of Oxford).

4.3.2 P3HT-NW/PMMA blend as a HTM composite structure

A widespread approach to improve the quality of known materials is to blend several materials with the desired properties. Following this method, semiconducting and insulating polymer blends have attracted increasing interest over the past few years. Such composite structure associates the electrical conductivity of the semiconducting polymer with the excellent mechanical properties of the insulating polymer. Several studies have reported enhanced electronic properties and improved environmental stability of organic transistor by embedding P3HT in an insulating matrix of either polystyrene (PS) or PMMA [120, 121]. More

recently, Habisreutinger *et al.* showed improved stability of perovskite solar cells by using a polymer-functionalised single-walled carbon nanotubes embedded in a PMMA insulating polymer matrix as the hole transporting layer [88]. Based on these studies, P3HT-NWs were blended with PMMA and used as a HTM composite structure in perovskite solar cells.

Meso-superstructured perovskite solar cells were prepared according to the methods described in Chapter 3, using the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite absorber and four different hole transport layers were compared. P3HT-NWs were formed as explained in Section 4.3.1. ($4 \text{ mg}\cdot\text{mL}^{-1}$ in toluene). A blend solution was obtained by mixing P3HT-NWs with a solution of PMMA ($50 \text{ mg}\cdot\text{mL}^{-1}$ in toluene) at a (1:3)(PMMA:P3HT-NW) volume ratio. Immediately prior to spin-coating, all the solutions containing P3HT-NWs were sonicated with an ultrasonic probe for 2 min at low intensity ($\sim 10\%$ of amplitude) to dissociate eventual agglomerates of P3HT-NWs without breaking the fibers. As references, both spiro-OMeTAD and pure P3HT were used at concentrations of $85 \text{ mg}\cdot\text{mL}^{-1}$ and $10 \text{ mg}\cdot\text{mL}^{-1}$, respectively, fully dissolved in chlorobenzene. 30 mol% of Li-TFSI and 80 mol% of *t*BP were added to the spiro-OMeTAD solution, while no dopants nor additives were added to the P3HT based HTM solutions. The scanned and steady-state performances of the resulting solar cell devices are reported in Figure 4.4.

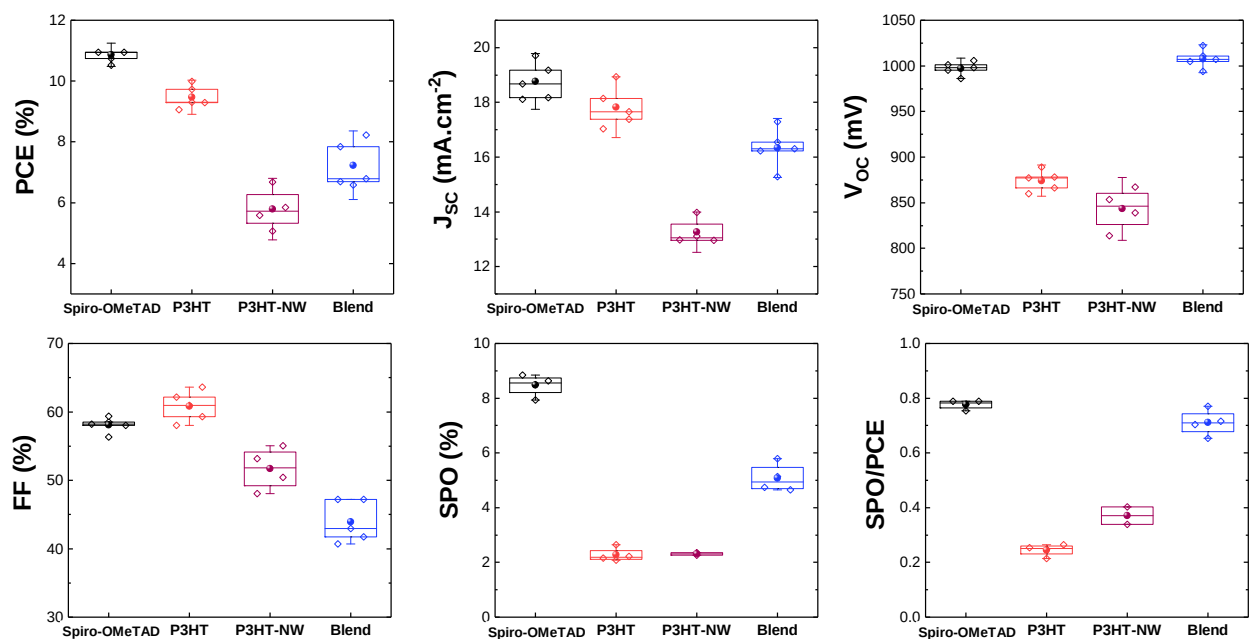


Figure 4.4: Scanned and steady-state performances for devices employing spiro-OMeTAD, P3HT, P3HT-NW and a P3HT-NW/PMMA blend as HTMs.

	J_{sc} [mA.cm ⁻²]	V_{oc} [mV]	FF [%]	PCE [%]	SPO [%]	SPO/PCE
Spiro-OMeTAD	18.8 ± 0.7	997 ± 7	58.1 ± 1.1	10.9 ± 0.3	8.5 ± 0.4	0.78 ± 0.02
P3HT	17.8 ± 0.7	874 ± 11	60.8 ± 2.2	9.5 ± 0.4	2.3 ± 0.2	0.25 ± 0.02
P3HT-NW	13.3 ± 0.5	843 ± 23	51.7 ± 3.1	5.8 ± 0.7	2.3 ± 0.1	0.37 ± 0.04
Blend	16.3 ± 0.7	1008 ± 10	43.9 ± 3.1	7.2 ± 0.8	5.1 ± 0.5	0.71 ± 0.05

Table 4.1: Average device performance parameters with standard deviation comparing devices employing spiro-OMeTAD, P3HT, P3HT-NW and a P3HT-NW/PMMA blend as HTMs. Values extracted from Figure 4.4

Clearly, spiro-OMeTAD remains the best performing HTM of all, yielding to an average scanned efficiency of $10.9 \pm 0.3\%$ and a SPO of 8.5%. While the P3HT reference shows the best scanned PCE amongst the three P3HT-based HTMs ($9.5 \pm 0.4\%$), its steady-state efficiency plummets to merely 2% which is similar to that of the neat P3HT-NWs. The P3HT/perovskite interface most likely suffers from substantial recombinations resulting in a high hysteretic behavior. In addition, the pure P3HT (which is partially crystalline and partially amorphous) shows low hole mobility inhibiting efficient charge extraction. In the P3HT-NW case, the hole mobility is most likely increased due to the enhanced crystallinity as previously established through UV-vis measurements (Figure 4.2), however the layer shows a poor surface coverage of the perovskite (Figure 4.3) which inevitably leads to shunting paths from the absorber to the electrode. As a result, the P3HT-NW devices show lower FF and V_{oc} with respect to the P3HT control. Interestingly, the P3HT-NW/PMMA composite yields a substantial reduction of the hysteresis with a SPO/PCE ratio of 0.71, almost as high as spiro-OMeTAD (0.78), resulting in an SPO of $5.1 \pm 0.5\%$ which is approximately 3% higher than the P3HT reference. While both J_{sc} and FF decrease, the most striking improvement observed with the blend is in V_{oc} , which outperforms the P3HT control by almost 200 mV, resulting in values identical to those achieved by the spiro-OMeTAD HTM (~ 1000 mV). The reduced hysteresis and the consistent increase in V_{oc} indicate that the perovskite/HTM interface has been greatly improved over all of the HTMs compared here.

Analysis of the current density-voltage characteristics at various light intensities provides information on the recombination mechanisms in a solar cell [122]. Thus, in order to compare non-radiative losses across all the devices, the dependence of the photovoltaic parameters (J_{SC} and V_{OC}) on the incident light intensity is represented in Figures 4.5a and b. J_{SC} depends linearly on light intensity as depicted experimentally in Figure 4.5a. On the other hand, the ideal diode equation predicts a logarithmic trend of V_{OC} with J_{SC} , which is in agreement with the trend shown in Figure 4.5b.

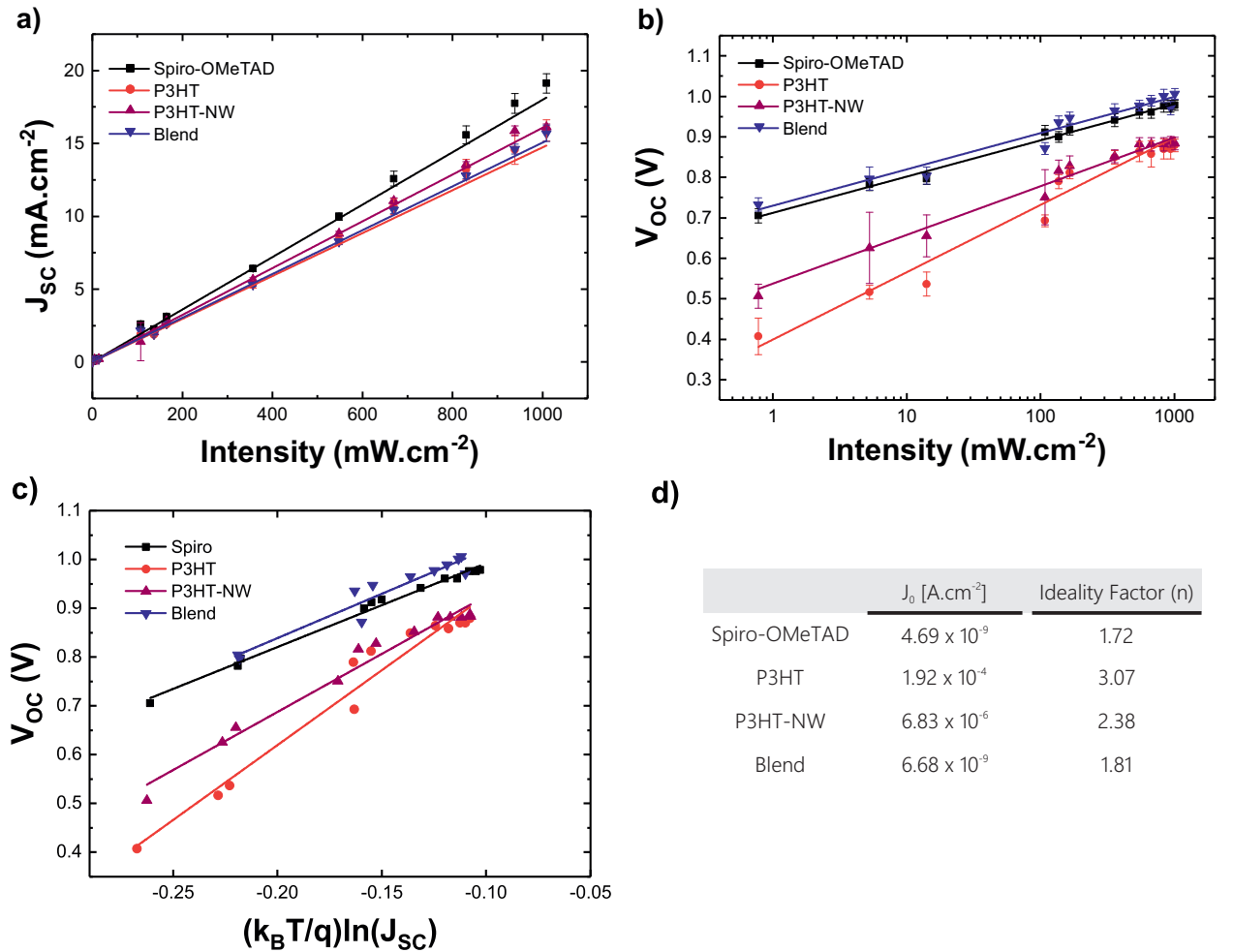


Figure 4.5: Light intensity dependence of the photovoltaic parameters. a) J_{SC} scales linearly with the fluence. b) As the light intensity increases, V_{OC} increases logarithmically. c) By plotting V_{OC} as a function of $\frac{k_B T}{q} \ln(J_{SC})$, both the reverse saturation current (J_0) and the ideality factor (n) can be extracted. d) The blend shows much reduced J_0 and n values, evidence for a reduction in non-radiative recombination losses and more efficient hole extraction with respect to the P3HT reference.

The diode ideality factor and the reverse saturation current (J_0) can be determined by plotting V_{OC} as a function of $\frac{k_B T}{q} \ln(J_{SC})$ (Figures 4.5c and d). The ideality factor corresponds

to the slope of the fit. J_0 is found from the intercept at $\frac{k_B T}{q} \ln(J_{SC}) = 0$. All the values of J_0 and n are reported Figure 4.5d. Although P3HT and P3HT-NW based devices show reverse saturation currents higher by 4 to 5 orders of magnitude with respect to spiro-OMeTAD, the blend yields a much lower J_0 value ($6.68 \times 10^{-9} \text{ A}\cdot\text{cm}^{-2}$) and an ideality factor closer to unity (1.81). The reduction of the reverse saturation current when P3HT-NWs are blended with PMMA shows an improved diode behaviour indicating that non-radiative recombination pathways are minimised. From a recombination point of view, both P3HT and P3HT-NWs form extremely poor interfaces with the perovskite, which is greatly improved by the blend. The PMMA matrix being insulating, charges are forced to flow from the perovskite to the nanowires through very few points of contact. Thus, the effective charge extraction area is significantly decreased leading to less non-radiative recombinations losses.

4.3.3 Photoluminescence quenching measurements

In a solar cell, the photoluminescence should be quenched under short circuit conditions since all carriers are extracted, but under open circuit conditions, the recombination is ideally radiative, hence no quenching should be observed. However, most conventional HTMs quench the PL emission since they were optimised solely for charge extraction with relatively little consideration for minimising recombination. Thus, photoluminescence quenching experiments were performed in order to determine how efficiently charges were extracted at the *p*-type interface (Figures 4.6 and 4.7). $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite films were coated with different HTMs and a neat film with a layer of PMMA was taken as a control.

Time-resolved PL measurements (Figure 4.6a) were taken and the decays were fitted to a monomolecular tail fit in order to estimate the lifetimes (τ_e) (Table 4.2). With such fitting procedure, the overall τ_e represents a superposition of both radiative and non-radiative decay processes. Here, the PL was measured at V_{OC} , thus a quenched emission implies that charges recombine non-radiatively across the perovskite/HTM interface. The spiro-OMeTAD, P3HT and P3HT-NW HTMs all reduce the PL decay of the perovskite from a lifetime of $231.9 \pm 1.0 \text{ ns}$ to 45 ns on average. The blend increases the PL intensity and also lead to a notably

longer decay tail, resulting in a twofold increase in lifetime (470.5 ± 2.2 ns) compared to the neat PMMA control device. Along with the PL decay measurements, the PLQE was monitored at a fluence equivalent to 1 sun. The trend in PLQE follows the change in lifetime, as reported in Figure 4.6b. All HTMs efficiently quench the emission peak with respect to the control, with the exception of the blend which doubles the PLQE from 15% to 30%.

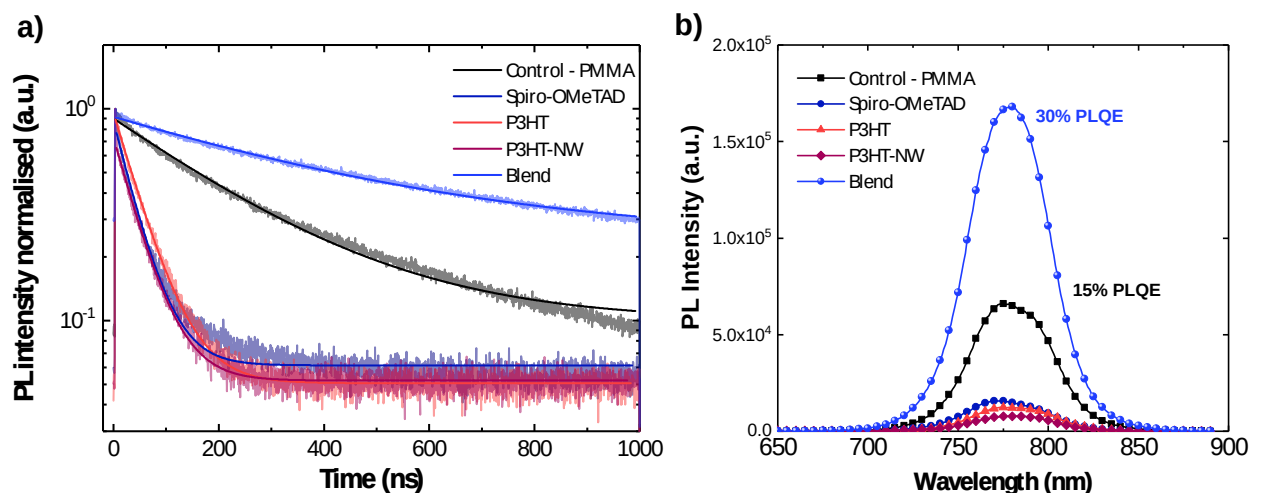


Figure 4.6: Photoluminescence quenching measurements probing the emission of samples with various HTMs. a) Time-resolved PL decays were detected at 780 nm following a pulsed (1 MHz) excitation source at 505 nm with a fluence of $30 \text{ nJ} \cdot \text{cm}^{-2}$. Solid lines are fits to the data using a monoexponential decay tail fit. b) PL peak emission measured at 1 sun illumination with the corresponding PLQE values for the control and the perovskite/blend sample.

	τ_e [ns]
Control	231.9 ± 1.0
Spiro-OMeTAD	40.5 ± 0.2
P3HT	49.7 ± 0.1
P3HT-NW	45.0 ± 0.1
Blend	470.5 ± 2.2

Table 4.2: Lifetimes τ_e corresponding to the time taken to reach $1/e$ of the initial intensity. Values extracted from monoexponential fits plotted in Figure 4.6a.

The substantial increase in both PL lifetimes and PLQE when the perovskite absorber is coated with the blend indicate a decrease in non-radiative electron-hole recombinations at the HTM-perovskite absorber interface. However, these observations would also go against the argument established by a part of the PV community which defines a good extraction layer as a good quencher [89]. Based on this hypothesis, the blend could not act as an efficient hole extracting layer, nonetheless it was previously demonstrated that devices using

the composite structure as a HTM performed as efficient solar cells and showed both a substantial increase in V_{OC} and a decrease in J_0 , both of which suggest reduced non-radiative losses. These observations are in agreement with the discussions made by Tvingstedt *et al.* in which they highlighted the fact that, in any solar cell, the PL emission of the absorber should not be quenched at the interfaces with charge extraction layers [89]. They especially demonstrated that PL quenching measurements are suited to correlate the quenching with the photocurrent generation, but a quenched emission does not necessarily imply a high V_{OC} . On the contrary, in order to bring V_{OC} closer to the radiative limit such that the solar cell performs optimally, the non-radiative recombination pathways should be minimised, *i.e.* the PLQE should remain as high as possible [87, 89, 123, 21].

To gain further insight on the photoluminescence characteristics of the films, PL imaging was performed. In Figure 4.7a, a PL image of a bare perovskite is compared to a perovskite film coated with the blend. Noticeably, the perovskite/blend sample appears much brighter with respect to the neat control indicating an increase in PL yield. However, whereas the reference shows homogeneous PL, the intensity of the absorber/blend is quite contrasted, resulting in particularly luminescent areas and much darker patches. By looking at the films separately, in both "dark" (microscope images) and "PL" mode (PL images), it becomes possible to associate the different areas with the constituent materials of the blend (Figure 4.7b). The layer of pure P3HT-NW shows aggregates ranging from 1 μm up to 30 μm across. These aggregates brighten in the PL image and can be attributed to the nanowires. When the P3HT-NWs are combined with the PMMA matrix, followed by sonication of the solution, the casted film presents much smaller and scattered aggregates of high PL corresponding to pure P3HT, and the darker zones can be attributed to the PMMA matrix with finely dispersed nanowires. When PMMA is coated onto the perovskite, the emission remains homogeneous in intensity throughout the surface at the exception of small circular dark spots which are most likely impurities. In the perovskite/blend images, the zones corresponding to finely dispersed nanowires in PMMA intensify the PL emission, while the aggregates of P3HT-NWs quench the PL. Since the zones quenched by the P3HT-NWs cover only a small part ($\sim 20\%$) of the total surface, the overall average PL intensity remains higher than the

perovskite reference, in agreement with the increase in PLQE.

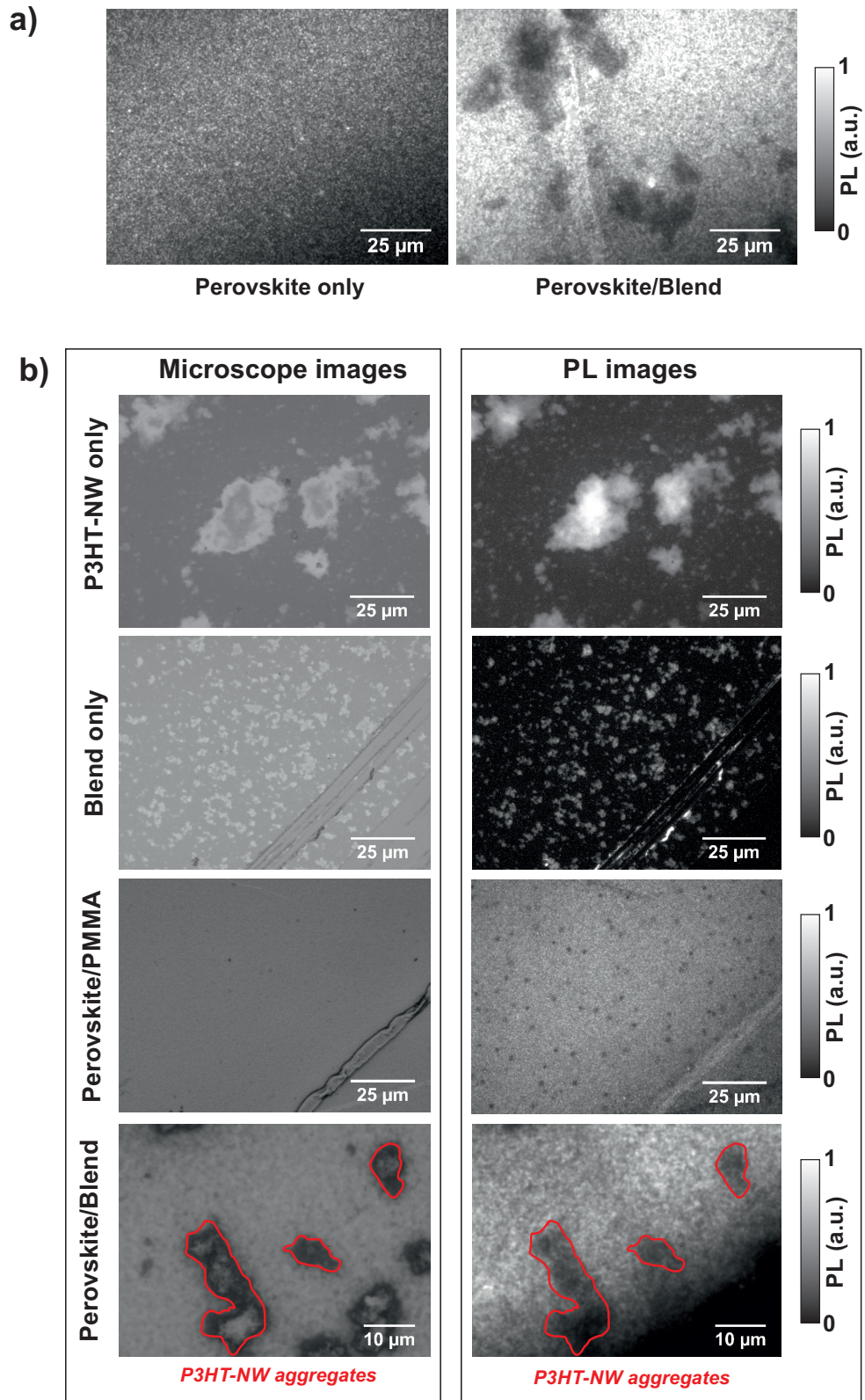


Figure 4.7: Photoluminescence imaging. a) PL images of perovskite films with and without the blend. b) Comparison between microscope images and PL images for films of P3HT-NW, blend, perovskite coated with PMMA and perovskite coated with the blend.

Nanosecond transient absorption spectroscopy (ns-TAS) was performed to reconcile this enhanced photoluminescence with the fact that the P3HT-NW/PMMA composite acts as a successful HTM in solar cells. The results are depicted in Figure 4.8 for perovskite films coated with PMMA, P3HT, P3HT-NW, and the blend.

All spectra show the expected large photo bleach at 760 nm, associated with state filling at the band edge in the perovskite semiconductor films, as well as the often observed broad absorption in the higher energy part of the spectrum [124, 125, 126]. The slight red shift of the bleaching feature in time likely corresponds to sample cooling, as the pump intensity was quite high. Upon addition of P3HT, however, the rapid (< 50 ns) growth of two additional bleaching signals at 615 nm and 560 nm can be observed, corresponding to a bleaching of the vibrational modes in crystalline P3HT, indicative of free holes in the P3HT film [127]. This is direct evidence of rapid hole transfer from the perovskite bulk to the P3HT. This occurs on the time scale of less than 50 ns, consistent with the rapid photoluminescence quenching observed for such samples (Figure 4.6a) and confirming rapid diffusion of holes through the perovskite bulk. Similar features are observed for the samples coated with P3HT-NWs. Here, the narrowness of the peaks is evidence that the P3HT nanowires are highly crystalline in nature. When the kinetics of these features are monitored at a probe wavelength of 615 nm (Figure 4.8b), it is evident that they have lifetimes on the μ s time scale, indicating several μ s recombination lifetimes. Once the NWs are blended with PMMA, the spectral features are very similar, again providing evidence of hole transfer from the perovskite to the P3HT nanowires. When the kinetics of the P3HT vibrational bleaching are monitored for the blend, it becomes evident that the recombination lifetime is massively increased to tens of μ s. The early time signal (< 100 ns) in this trace correspond to pump scatter and should hence not be considered as indicative of the hole population on the P3HT nanowires. The increased recombination lifetime also helps to rationalise the improved device performance of this architecture with respect to the P3HT control.

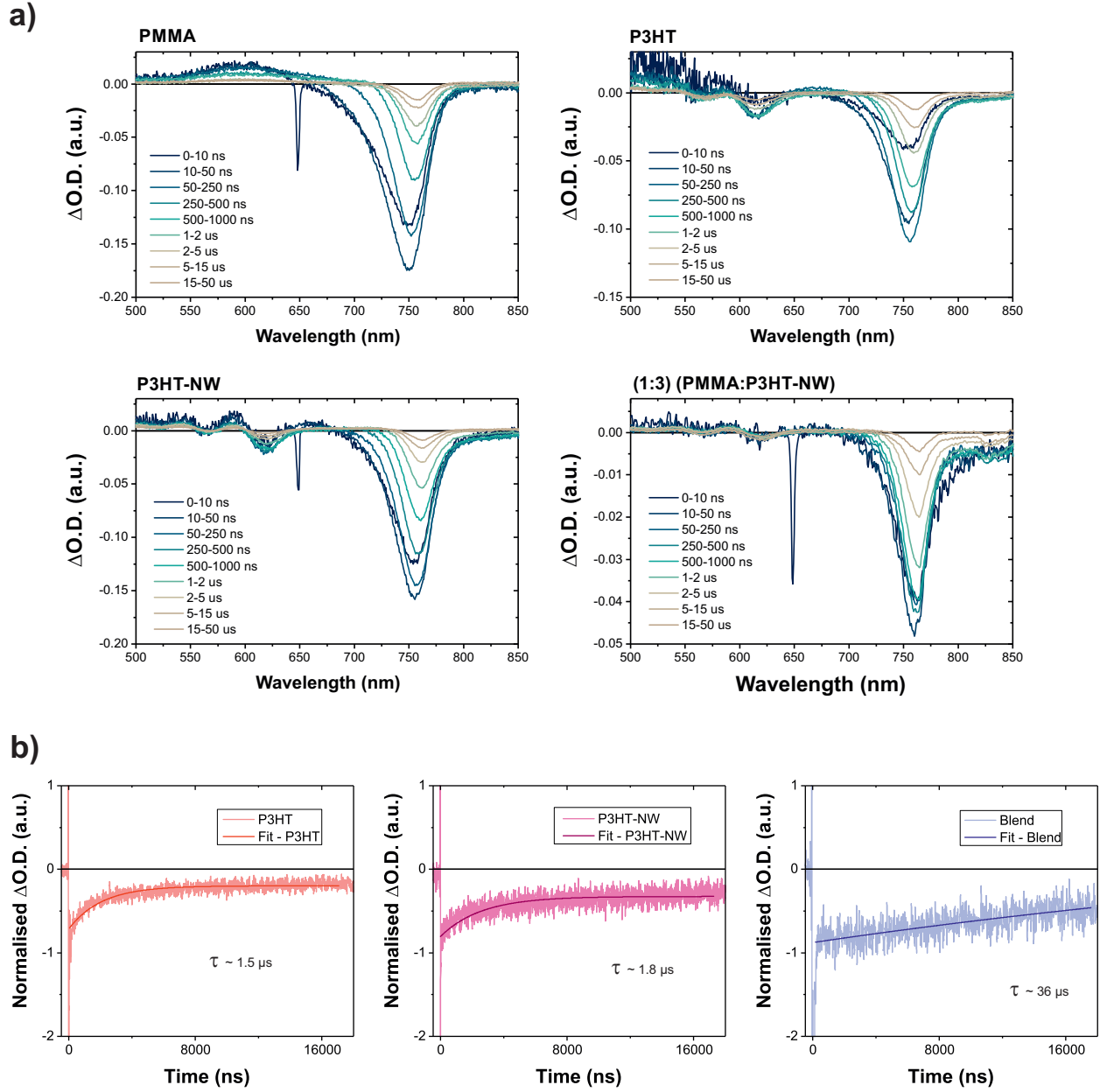


Figure 4.8: a) Transient absorption (TA) spectra for different time delays for perovskite films coated with PMMA, P3HT, P3HT-NW, and the blend. b) TA dynamics monitored at 615 nm for perovskite films coated with P3HT, P3HT-NW, and the blend. The excitation wavelength was 650 nm and the pump power $2 \text{ mW} \cdot \text{cm}^{-2}$. All samples were excited from the glass side. Measurements were taken by Dr Tomas Leijtens (Istituto Italiano di Tecnologia, Milan).

4.3.4 Correlation between V_{OC} and photoluminescence yield

At short-circuit, all the photons absorbed by the perovskite should be converted to free charges and flow in the external circuit. Thus, any recombination process (radiative and non-radiative) should be as low as possible and the solar cell should emit as little light as possible. On the contrary, at open-circuit no external current can flow and free charges must recombine. Therefore, an ideal solar cell should have an external PLQE of 0% at J_{SC} and 100% at V_{OC} [128, 129]. Complete device stacks usually show poor luminescence efficiencies due to significant non-radiative recombinations at the interfaces with the absorber. Since the previously discussed PL measurements on films revealed an increase in luminescence when the blend was deposited onto the perovskite, PL measurements of full devices at both J_{SC} and V_{OC} were taken, in order to determine whether blend-based devices were radiatively more efficient than standard devices employing P3HT as a HTM (Figure 4.9).

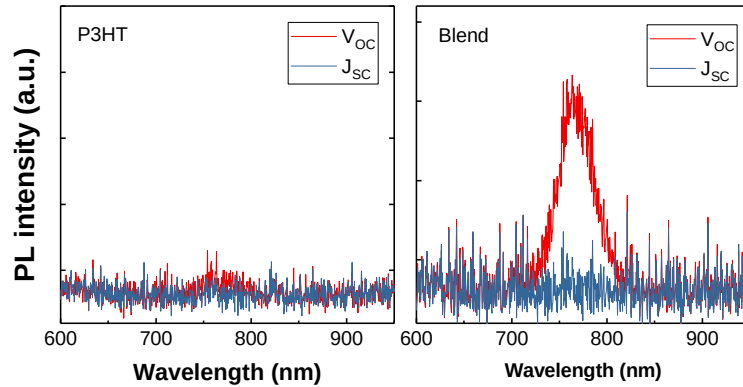


Figure 4.9: Photoluminescence of full devices employing either P3HT or the P3HT-NW/PMMA blend as a HTM, measured at V_{OC} and J_{SC} .

In the P3HT-based device, no changes in intensity can be observed between the PL measured at J_{SC} and V_{OC} , indicating that the p -type interface in this device induces substantial non-radiative losses, in line with the low V_{OC} and high J_0 observed. In the blended HTM device, the PL intensity at V_{OC} is largely enhanced over that measured at short-circuit conditions. These observations strongly suggest that non-radiative recombinations are suppressed in the blend-based device, and also highlight the fact that neat P3HT is far from being an ideal HTM since it induces recombinations at the p -type interface. This could be an explanation for the recurrent V_{OC} loss in devices (Table 4.1).

According to the Rau's reciprocity relationship which relates the generation of electron-hole pairs to the emission of light, the non-radiative V_{OC} losses of a solar cell (ΔV_{OC}^{nonrad}) scale exponentially with the EQE of the device operating as a LED (η_{LED}) [87]:

$$\Delta V_{OC}^{nonrad} \propto \frac{k_B T}{q} |\ln(\eta_{LED})| \quad (4.1)$$

Furthermore, ΔV_{OC}^{nonrad} losses can be calculated as the difference between the maximum achievable voltage obtained from the Shockley-Queisser limit V_{OC}^{rad} (*i.e.* after unavoidable thermodynamic losses where electron-hole radiative recombination is 100%), and the experimentally measured V_{OC} of a device [19, 87, 128]. Additionally, at V_{OC} conditions, η_{LED} (or ELQE) can be replaced by the PLQE [129, 130]. Hence, by measuring V_{OC} as a function of the light intensity, it is possible to estimate and correlate the non-radiative V_{OC} losses of a solar cell (ΔV_{OC}^{nonrad}) to the luminescence. Firstly, the changes in PLQE (measured at V_{OC}) and V_{OC} as a function of the light intensity were quantified and are shown in Figures 4.10a and b. Clearly, both devices show very different trends in PLQE with the incident light. While the P3HT reference shows luminescence values below 0.1%, the blend shows a gradual increase up to 1.5% which indicates that the blend-based device is an order of magnitude more radiatively efficient than the pure P3HT reference. Then V_{OC} as a function of the light intensity is represented in Figure 4.10c.

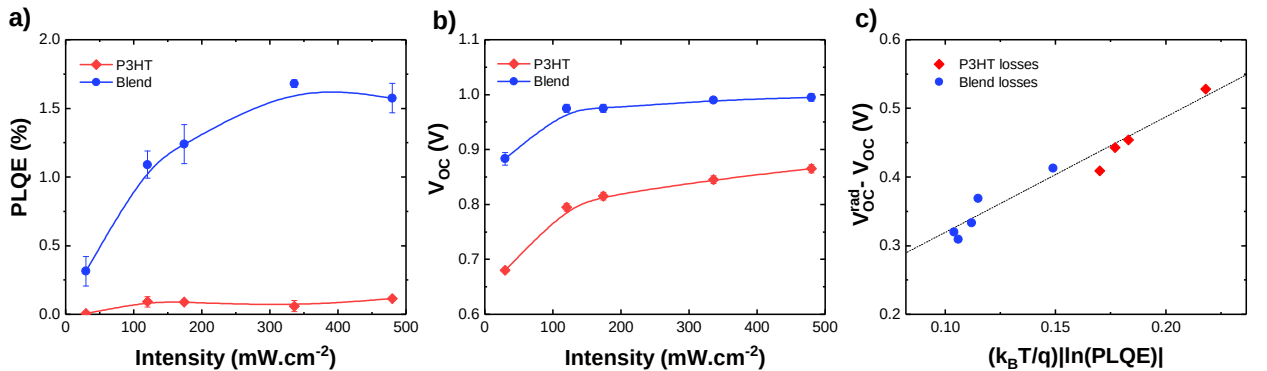


Figure 4.10: Photoluminescence efficiency of complete solar cells comparing P3HT to the blend as HTMs. a) PLQE as a function of the light intensity measured at open-circuit conditions. b) Measured V_{OC} as a function of the incident light. c) Estimation of the non-radiative V_{OC} losses and correlation to the luminescence properties of the device.

Non-radiative losses in the P3HT device are 100 mV higher than when the blend is used

as a HTM, indicating that the perovskite/blend interface is more ideal in terms of radiative efficiency. Moreover, the linear behaviour of ΔV_{OC}^{nonrad} with the luminescence of the device across the two different HTMs is clear evidence that the substantial increase in V_{OC} with the blend is directly related to the increased radiative efficiency.

4.3.5 Effect of *t*BP on the dispersion of nanowires

Despite reducing non-radiative recombinations at the *p*-type interface, devices with P3HT-NW/PMMA composite HTMs still show lower currents and fill factors than those with pure P3HT, which could indicate higher series resistances in the former. For charges to be extracted from the perovskite to the electrode, a conductive nanowire pathway through the insulating PMMA matrix must exist. If some of the nanowires are too short or lie parallel to the perovskite surface, they may become embedded into the PMMA without contributing to percolation pathways. In such a situation, those nanowires cannot take part in the charge collection process and the overall current extraction is reduced. Pyridines have been shown to help with the dispersion of nanoparticles [131], thus the commonly used additive for HTM, tert-butyl pyridine (*t*BP) might reduce NW agglomerations in solution and result in more uniformly distributed NWs in the P3HT-NW/PMMA blended films, which would lead to more wires taking part in charge transport. Additionally, *t*BP modifies the *p*-type interface by making it more selective for holes, resulting in much improved steady-state performances [132]. These two factors could greatly enhance the efficiency of the blend-based solar cells.

Here, a mixed halide perovskite, $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$, was used as the absorber, and prepared according to the antisolvent quenching method described in Chapter 3. Due to the substantial reduction in surface roughness of this perovskite as compared to $CH_3NH_3PbI_{3-x}Cl_x$, the blend content had to be reoptimised. The percolation threshold of the nanowires through the PMMA matrix was much lower on a smoother surface, thus the PMMA solution was diluted from 50 mg·mL down to 10 mg·mL. *t*BP was added to the P3HT-NW/PMMA solution in order to assess its effect on both the blend formation and the solar cell performance.

Initially, PL quenching experiments were performed on the perovskite/blend samples with *t*BP content ranging from 0 μL to 20 μL per mL of blend solution to determine whether adding *t*BP would have an influence on the quenching characteristics of the HTM. Both time-resolved PL decay and PL quantum yield were taken (Figure 4.12). As previously observed, when the blend, without *t*BP added, is coated onto the absorber layer, both the lifetime and the PLQE increase with respect to the neat PMMA coated perovskite. With increasing *t*BP concentrations, the decay lifetime is reduced and the PL quantum yield is progressively quenched. Nonetheless, the blend with the highest *t*BP content (20 $\mu\text{L}/\text{mL}$) still yields a PLQE value two orders of magnitude higher than for the P3HT control. By plotting the changes in PLQE with the *t*BP content, the volume of additive for which the PLQE remains similar to the neat PMMA control can be determined, and corresponds approximately at 5 μL of *t*BP per mL of blend solution.

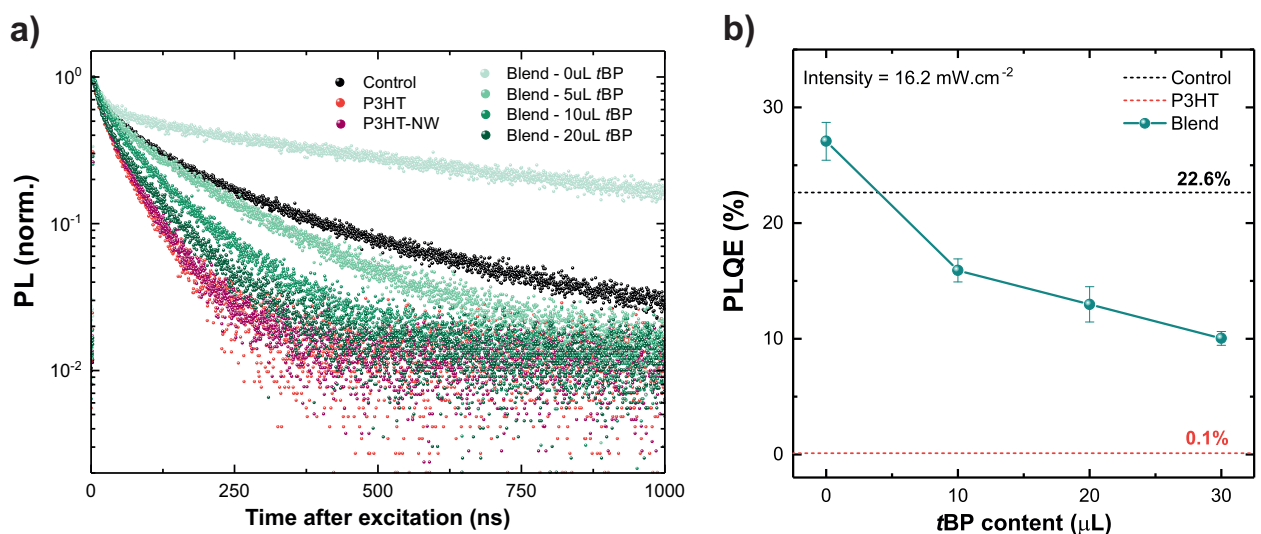


Figure 4.11: Photoluminescence quenching measurements probing the emission of perovskite films coated with the blend HTM with various *t*BP content. a) Time-resolved PL decays detected at 800 nm following a pulsed (100 kHz) excitation source at 505 nm with an initial photoexcitation density of 10^{15} cm^{-3} . b) PL quantum yield measured at a fixed intensity of $16.2 \text{ mW}\cdot\text{cm}^{-2}$.

Having shown that adding 5 $\mu\text{L}/\text{mL}$ of *t*BP to the blend marginally impacts the emission properties of the perovskite/HTM system, complete perovskite solar cells using the *n-i-p* architecture were fabricated to investigate the influence of the additive on the device performance. Since *t*BP was shown to improve the V_{OC} and the steady-state performance of devices [132], a similar volume content was added to P3HT reference. The average scanned

and steady-state performances are reported in Figure 4.12. Comparing with the P3HT reference, both blends (with and without *t*BP) boost the V_{OC} , consistent with the reduction of non-radiative recombinations previously established. When *t*BP is added to the blend, both the J_{SC} and the FF considerably increase in comparison to those of the composite HTM without the additive, resulting in a twofold increase in PCE from a mere 8% to 16% on average, bringing the blend's performance up to nearly match the P3HT control. The *t*BP-modified blend also shows a 10% reduction of the hysteresis as compared to P3HT, which manifests as an improvement of the SPO from 11.2% to 12.8%.

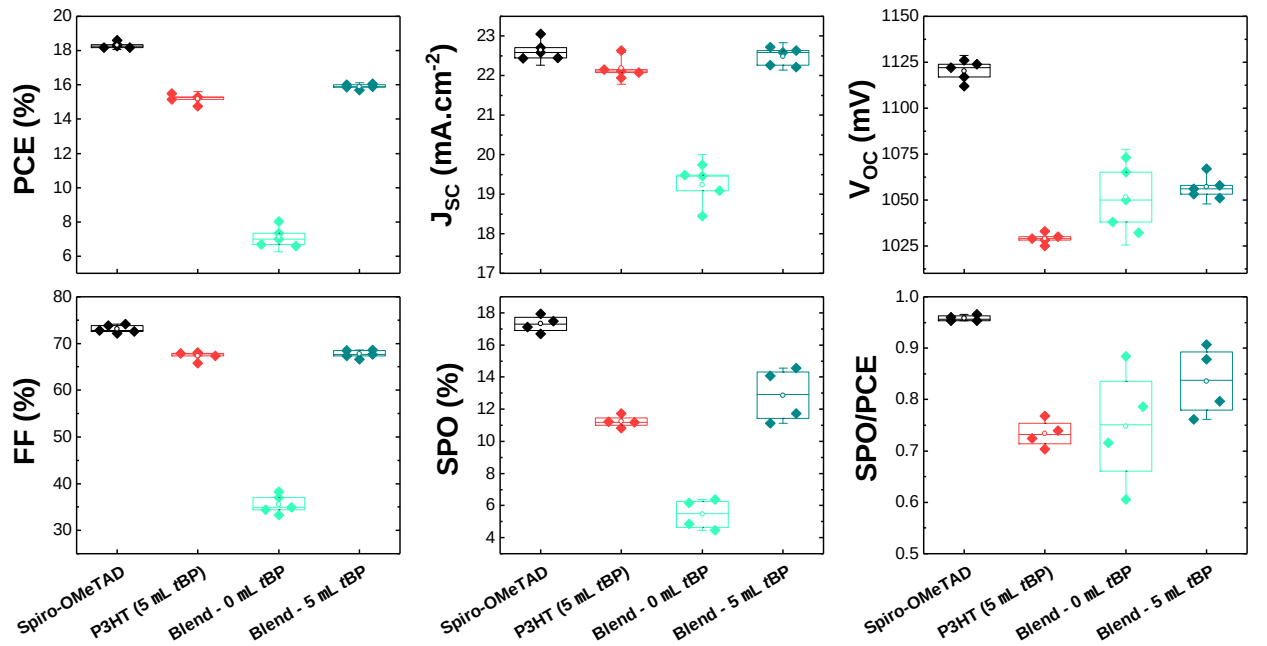


Figure 4.12: Scanned and steady-state performances of devices with and without adding *t*BP (5 μ L) to the blend. Spiro-OMeTAD was taken as a control, and the same amount of *t*BP was added to both the P3HT and the P3HT-NW solution.

Figure 4.13 depicts the current density-voltage characteristics and steady-state efficiency of the champion devices for the blend and the P3HT and spiro-OMeTAD references. The corresponding performance parameters of these champion devices are shown in the table in Figure 4.13a. Spiro-OMeTAD remains the best performing HTM of all, reaching a SPO of 18%, however both P3HT-based devices show very comparable J_{SC} , indicating that the blend is no longer limiting the extraction of charges. The P3HT-NW/PMMA composite HTM yields a slightly higher PCE than neat P3HT stemming from a 1% increase in FF and a small gain in voltage. Whereas the scanned performance of the blend is only moderately enhanced

with respect to neat P3HT, steady-state measurements show a much more significant 3% increase in SPO, bringing the best performing device using the P3HT-NW/PMMA composite HTM to 14.8%.

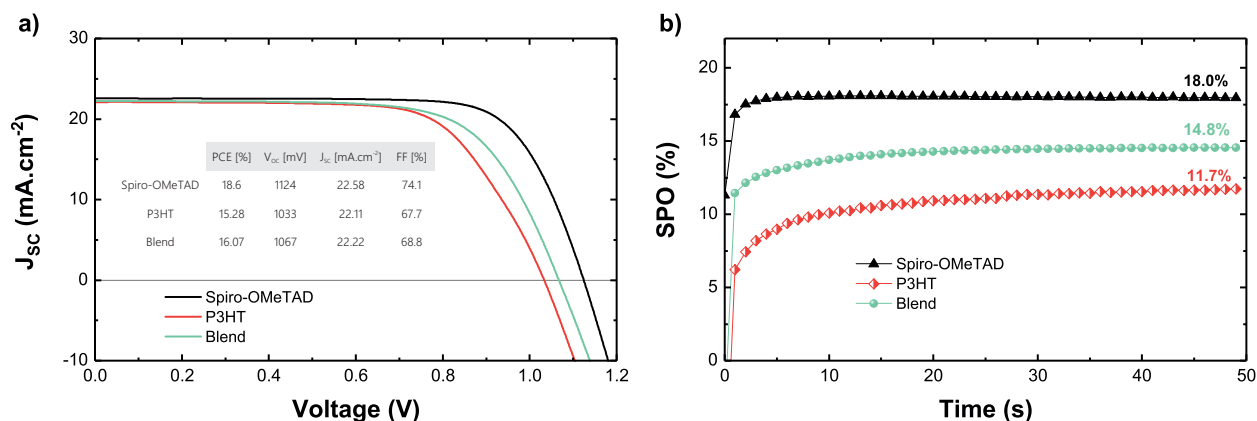


Figure 4.13: a) Current density-voltage characteristics and b) steady-state efficiencies of champion devices with different HTMs. 5 μ L of *t*BP was added to the P3HT reference and the blend solution.

In a study on polymer solar cells, pyridines have been used to facilitate the dispersion of nanorods coated with P3HT, implying that the additive somehow interacted with the polymer helping the separation of the nanoparticles [131]. A year later, Li *et al.* proposed that pyridine derivatives could bind to the thiophene ring of the P3HT, perpendicular to the polymer backbone, via the nitrogen atom [133]. With both of these findings, it becomes possible to understand why *t*BP has a strong influence on the blend formation. Since, *t*BP is a pyridine derivative, the N atom on the aromatic ring could attach to the P3HT chain with the methyl groups pointing away from the nanowire. Due to steric effects, it becomes increasingly difficult for individual P3HT-NWs to interweave, leading to the dissociation of aggregates and forcing the chains to align parallel to each other and so chances for the NWs to align vertically increase, resulting in more numerous percolation pathways. Excited charges can be efficiently extracted from the perovskite to the electrode generating more current, which is consistent with the enhancement in J_{SC} observed in devices.

4.3.6 Operating mechanism of the P3HT-NW/PMMA composite HTM

Combining the information from the PL yields and lifetimes, the TAS and device performance, it becomes possible to form an idea of the operating mechanism of these composite hole transport layers. As with any effective HTM, the holes are rapidly transferred from the perovskite to the nanowires. In solar cell operation, these holes are then transported to the collecting cathode or recombine with electrons in the perovskite. Normally, the recombination process is nonradiative, as holes in the HTM recombine with electrons in the conduction band of the perovskite. However, it seems that in the case of the composite hole transport structure, the recombination is radiative.

Upon excitation, holes migrate to the perovskite/P3HT-NW interface. Some of the NWs percolate through the PMMA matrix and efficiently transport holes to the collecting cathode. Shorter wires may contact only the perovskite while being embedded in the insulating polymer. Charges on these wires cannot be extracted and reside with long lifetimes in the NWs. Since the nanowires are extremely small (10 nm in diameter, 1 μm long at most), the hole densities in the P3HT-NWs is much greater than in a standard film of P3HT. This results in high densities of holes in the nanowires and electrons in the perovskite. These densities will be on the order of 100 times higher than for a neat perovskite film where the carrier lifetimes are on the order of 100 ns instead of tens of μs . With this large increase in charge density, it is likely that the HOMO of the nanowires becomes close to filled and the quasi-Fermi level for holes in the NWs is deepened. At this point, the quasi-Fermi level for holes in the nanowires will approach the valence band energy of the perovskite, allowing effective wavefunction overlap and promoting hole transfer between the two. Then, a back transfer process occurs via a transfer of holes from the HOMO level of the nanowires directly to the valence band of the perovskite, after which they recombine radiatively with the large density of electrons there, rather than through non-radiative recombination with electrons in the conduction band. Thus, reducing the interfacial area between the perovskite and the

HTM results in a reduction of non-radiative recombination. Since the photoluminescence is highly dependent on charge density (*i.e.* higher charge density leads to improved photoluminescence yields) [20] this mechanism results in an enhanced photoluminescence yield as compared to neat perovskite samples encapsulated with PMMA. The fact that the PL yield is so greatly enhanced is evidence that both hole transfer from the perovskite to the nanowires and the back transfer to the perovskite VB are extremely efficient processes with few loss pathways. A diagram depicting this HTM charge transfer mechanism in a perovskite solar cell with the composite P3HT-NW/PMMA blend is illustrated in Figure 4.14.

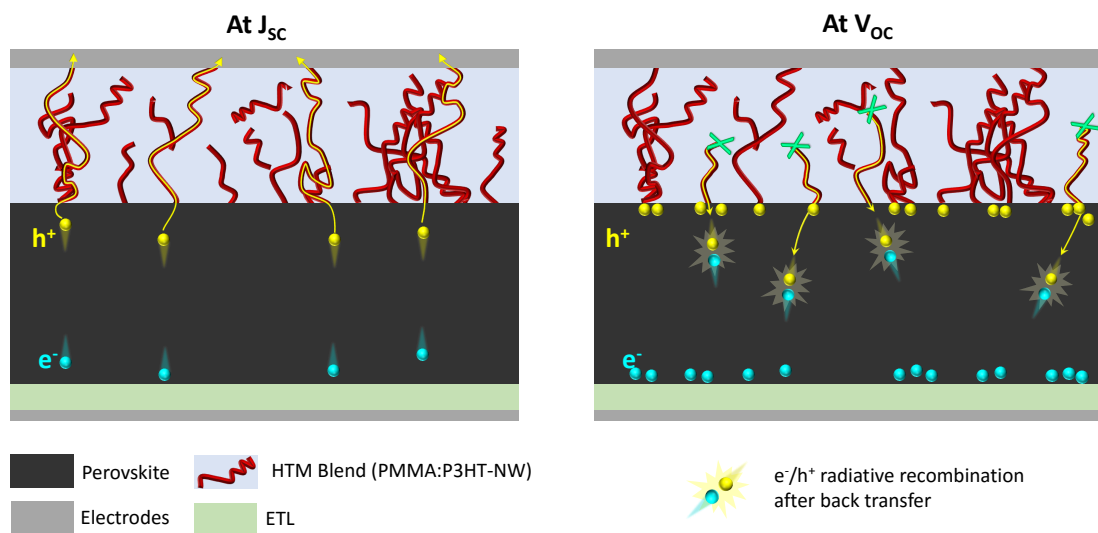


Figure 4.14: Illustration of the operating mechanism of P3HT-NW/PMMA composite structure HTM.

The contact area between the HTM and the perovskite is drastically reduced with the use of the P3HT-NWs, and so to be collected, charges are forced to flow through extremely small pathways. Hole density at the discrete NW-perovskite contact points becomes very large and non-radiative recombination is reduced resulting in better device performance, with notable enhancements in both V_{OC} and SPO. Reducing recombination by partially passivating the charge collecting interface with an insulating compound is an extensively employed technique in silicon PV, more commonly referred to as Passivated Emitter Solar Cell (PESC). This study highlights the fact that purposely introducing discontinuities at the perovskite/HTM interface, in a controlled manner, can be key in the development of a more efficient perovskite

solar cells since it inhibits non-radiative electron-hole recombination losses by forcing excited charges to travel through smaller channels before reaching the collection electrode.

4.3.7 Stability and cost

Devices employing the commonly used spiro-OMeTAD (doped Li-TFSI and FK209, with *t*BP additive) and the P3HT-NW/PMMA composite as HTMs were subjected to a thermal stress test in ambient conditions, in order to investigate the blend's impact on device stability. The solar cells were heated to 85°C on a hot plate in the dark, under ambient atmosphere with a relative humidity of 30-40% for a week without any encapsulant. Devices were then cooled down and tested at room temperature. The scanned and steady-state performances comparing spiro-OMeTAD to the blend, before and after aging, are shown in Figure 4.15.

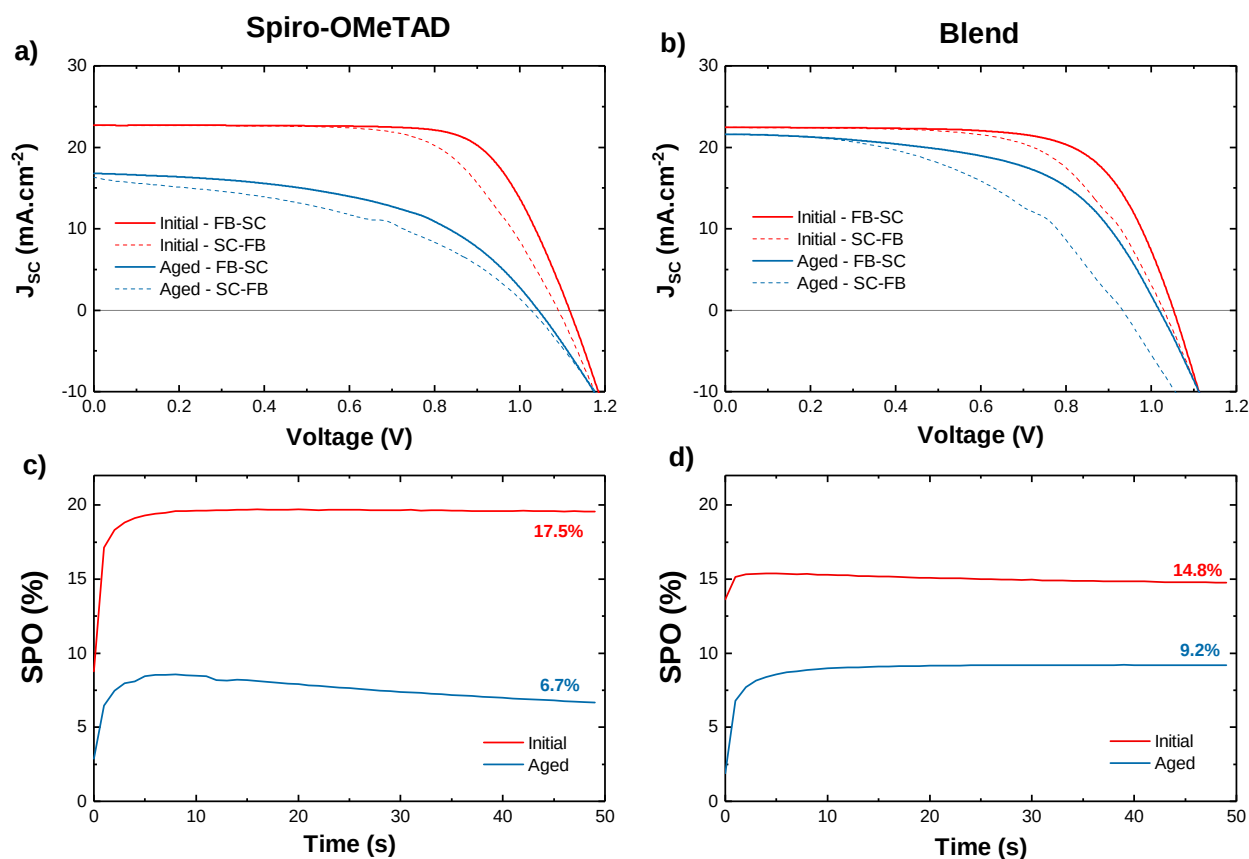


Figure 4.15: Comparison between initial and aged performances of spiro-OMeTAD and the P3HT-NW/PMMA composite HTM. The aged devices were measured after a week of aging at 85°C in the dark at 30-40% humidity without encapsulants.

Despite yielding to greater device performance initially, spiro-OMeTAD doped with lith-

ium salts degrades severely. With the blend, the solar cell retains 60% of its initial performance delivering a SPO of 9.2% after a week of aging. The fast drop in performance from 17.5% to 6.7% with spiro-OMeTAD is due to the hydration of the perovskite absorber [76] caused by the use of lithium salts. Upon oxidation of spiro-OMeTAD, lithium oxide complexes are formed which are highly hygroscopic [90] thus accelerating the permeation of water molecules through the HTM. In the composite HTM, the inert PMMA matrix acts as a barrier to water ingress. Therefore, the composite structure allows efficient charge extraction while protecting the perovskite absorber from moisture which results in greater device stability.

Besides preventing the degradation of the perovskite absorber by limiting the ingress of water, the P3HT-NW/PMMA composite HTM is significantly less costly than spiro-OMeTAD and neat P3HT. A cost analysis using the cheapest commercially available materials, comparing spiro-OMeTAD to the blend HTM is presented in Figure 4.16. The composite HTM would amount to merely $\sim 150\text{£}/\text{m}^2$ compared to spiro-OMeTAD which would cost $\sim 2300\text{£}/\text{m}^2$. Thus, the P3HT-NW/PMMA blend is 15 times cheaper than spiro-OMeTAD, making it very attractive for large-scale manufacturing. Moreover, the composite HTM solely requires *t*BP and no additional doping as compared to spiro-OMeTAD which cannot perform efficiently without *p*-dopants. The introduction of additives and dopants will increase the total production cost of the HTM layer.

	Price from Sigma-Aldrich [£/g]	HTM concentration [g/mL]	Quantity per m ² [g/m ²]	Price per m ² [£/m ²]
Spiro-OMeTAD	£270.50	0.085	7	~2300
PMMA	£156.00	0.010	1	~150
P3HT	£419.50	0.004	0.4	~170
Blend (PMMA:P3HT)(1:3)(v:v)	-	-	-	~150

Figure 4.16: Cost analysis of HTMs employed this study. Assuming a use of 100 mL of HTM solution per m².

4.4 Conclusion and outlook

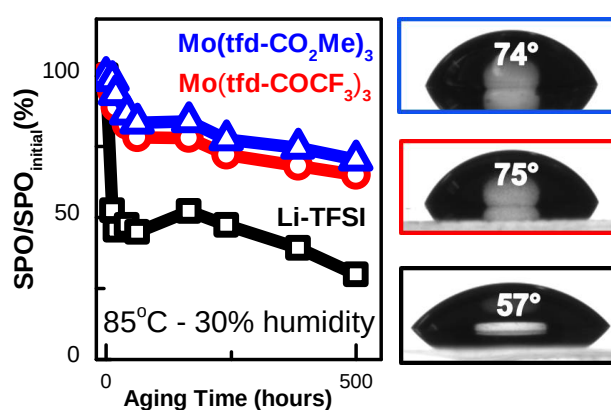
In this chapter, a novel P3HT-NW/PMMA composite structure is developed and employed as a HTM in perovskite solar cells. The P3HT polymer blend efficiently extracts holes through crystalline nanostructures, while the inert PMMA acts as a barrier to water ingress, which protects the perovskite absorber from moisture induced degradation. This results in efficient perovskite devices with enhanced stability. Interestingly, this blended HTM leads to remarkable enhancements in both V_{OC} and SPO compared to neat P3HT. Photoluminescence studies reveal that the composite structure significantly reduces non-radiative recombination losses at the interface with the absorber. In contrast to all other HTMs studied in this work, the P3HT-NW/PMMA HTM structure does not substantially quench the PL emission at open-circuit conditions which gives a high PLQE. Due to the introduction of the insulating PMMA matrix, the NW-perovskite interface is limited to discrete contact points. Hence, charges are forced to flow through extremely small channels which creates a build up of the hole density at the contact points. As a result, non-radiative recombination pathways are reduced and the device performance is improved.

Further optimisations of the P3HT-NW/PMMA blend HTM with addition of *t*BP enhances the percolation threshold of the nanowires through the PMMA matrix. The best performing device using this composite HTM yielded 14.8% SPO, which corresponds to a 3% increase with respect to a neat P3HT HTM. After exposing non-encapsulated devices to thermal stressing in air (85°C, dark 30-40% humidity), blend-based devices maintained up to 60% of their initial performance while that of solar cells using spiro-OMeTAD doped with Li-TFSI salts was severely degraded. In addition to the enhancing stability of perovskite solar cells, the P3HT-NWs/PMMA composite structure is 15 times less expensive than the spiro-OMeTAD small molecule. This chapter covers the development of composite HTM structures using PMMA, an inexpensive and inert polymer. Besides effectively extracting charges and reducing moisture ingress, such structures introduce controlled discontinuities at the perovskite/HTM interface, analogous to the extensively employed PESC technique

used in silicon photovoltaics (PESC). This opens new pathways for improving the efficiency of perovskite solar cells while shielding the absorber from moisture and drastically lowering the cost of the hole transport layer.

5 | Enhancement of the moisture resilience of perovskite solar cells using molybdenum tris(dithiolene)s as *p*-dopants for spiro-OMeTAD

The following chapter describes the use of molybdenum tris(dithiolene)s ($\text{Mo}(\text{td})_3$) as *p*-dopants for spiro-OMeTAD and their positive impact on the long-term stability of perovskite solar cells. The synthesis of both $\text{Mo}(\text{td})_3$ complexes presented in this chapter has been carried out by Yadong Zhang, Georgia Institute of Technology. The work presented has been adapted and reproduced in part with permission from: ALBA PELLARQUE, NAKITA K. NOEL, SEVERIN N. HABISREUTINGER, YADONG ZHANG, STEPHEN BARLOW, SETH R. MARDER & HENRY J. SNAITH, *ACS Energy Letters*, 2, 2044-2050 [134]. Copyright 2017 American Chemical Society.



5.1 Context and summary

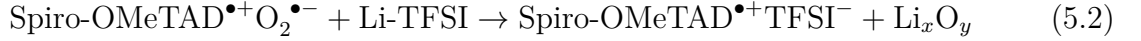
Over the years, metal halide perovskite solar cells have shown phenomenal progress and are now in a position to compete on efficiency with traditional crystalline solar cells. However, the biggest obstacle toward commercialisation of the technology lies in the instability of the absorber itself, particularly towards moisture and heat. This is due to the high affinity towards water of the organic cation, which leads to the rapid decomposition of the perovskite into a non-perovskite material PbI_2 , which is a comparatively poor absorber. This decomposition is therefore accompanied by a significant decline in device performance. To date, the most efficient perovskite solar cells have the *n-i-p* device architecture in which the hole transport material (HTM) is deposited on top of the perovskite, and hence could act as a physical barrier against moisture ingress. Several studies have focused on the development of moisture-blocking contacts to protect the perovskite absorber from the wet external atmosphere. Nonetheless, 2,2',7,7'-tetrakis(N,N'-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) typically doped with lithium bis((trifluoromethyl)sulfonyl)amide (Li-TFSI) remains the most commonly employed HTM in perovskite solar cells. Even though Li-TFSI enhances the hole transport properties of the spiro-OMeTAD, its hygroscopic nature accelerates the permeation of water molecules through the HTM, which is detrimental to the long-term performance of the solar cells and limits its practical use. In this chapter, Li-TFSI was successfully replaced by molybdenum tris(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) ($\text{Mo}(\text{tfd-COCF}_3)_3$), or molybdenum tris(1-(methoxycarbonyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) ($\text{Mo}(\text{tfd-CO}_2\text{Me})_3$). These two dopants showed stabilised power conversion efficiencies up to 16.7% and 15.7%, respectively. Furthermore, both $\text{Mo}(\text{tfd})_3$ -doped spiro-OMeTAD layers exhibited greater hydrophobicity as compared to the Li-doped HTM which lead to a significant enhancement of the long-term stability of perovskite solar cells under 85°C thermal stressing in air. Molybdenum tris(dithiolene)s are hence promising candidates as *p*-dopants for hole transporter materials with regards to both performance and stability.

5.2 Introduction

Organic-inorganic halide perovskites have now reached certified power conversion efficiencies of over 22% [57], however their ability to sustain high performance under real world conditions remains challenging which can potentially prevent the commercialisation of this technology. One of the critical concerns is the instability of iodoplumbate-based perovskite materials themselves. The organic cation, which is only bound to the Pb-I cage by weak hydrogen bonds, readily dissolves when exposed to moisture and heat [72, 74, 76], and therefore results in a breakdown of the perovskite structure. For commercial applications, solar cells are typically encapsulated with lamination foils, glass and edge sealants. These materials and encapsulation techniques are good, but can be prone to cracking, leakage and will most likely result in costly final products. Therefore, developing solar cells with an inherent resistance to moisture ingress should result in more stable and low-cost modules.

In an *n-i-p* device architecture, *i.e.* with the perovskite deposited onto the electron-transporting layer, the hole-transporting material acts as the first barrier to water since it caps the device. The most efficient perovskite solar cells employ spiro-OMeTAD or a tri-arylamine polymer (PTAA) as the hole transporting material (HTM) [69, 135, 136]. However, neat organic HTMs suffer from intrinsic low hole mobility and low conductivity [137, 138]. Therefore, *p*-doping is required to enable efficient hole extraction. This is generally accomplished by addition of both the ionic dopant lithium bis((trifluoromethyl)sulfonyl)amide (Li-TFSI) and 4-*tert*-butyl pyridine (*t*BP), often in combination with an additional *p*-dopant, typically the tris(pyrazolylpyridine)-cobalt(III) complex (FK-209) [69, 68]. The Li-TFSI salt has been shown to increase the hole mobility in spiro-OMeTAD by an order of magnitude [138], and has since been a prerequisite to obtaining a high power conversion efficiency. However, Li-TFSI does not directly oxidise spiro-OMeTAD, but rather promotes oxidation of the HTM by molecular oxygen to reach appropriate conductivities. The complete mechanism was proposed by Abate *et al.* and described as a redox reaction [90]:





Upon exposure of spiro-OMeTAD to oxygen, a weakly bound donor-acceptor complex is formed, and an electron from the O₂ molecule can transfer to the HTM matrix (Equation 4.1). When Li⁺ is added, the spiro-OMeTAD oxidises by consuming O₂ and forming lithium oxide complexes. The oxidised spiro-OMeTAD cation and the delocalised TFSI anion (Spiro-OMeTAD⁺TFSI⁻) are weakly attached, which allows generation of mobile holes in the organic matrix. While the HTM presents enhanced charge transport properties, this oxidation process comes with several drawbacks. First, the requirement for oxygen exposure makes it difficult to precisely control the exact fraction of spiro-OMeTAD that is oxidised and then may also have a detrimental effect on the overall device stability [79, 139]. Finally, according to the redox reaction, oxide complexes are also formed which are highly hygroscopic and hence accelerate the permeation of water through the spiro-OMeTAD [88, 140]. Because both device stability and reliability are crucial factors for a photovoltaic technology, it is necessary to achieve highly efficient operation without relying on the use of hygroscopic dopants such as Li-TFSI.

5.3 Current alternatives to Li-TFSI

Excluding Li-TFSI to improve stability has been achieved to recent years through several approaches. However, this has generally resulted in a significant drop in performance, for example Shin *et al.* replaced PTAA with NiO, resulting in much improved stability, but a concurrent efficiency drop from 21 to 14% [135]. Another strategy has been to use non-hygroscopic, chemically inert conductive additives such as carbon nanotubes or graphene in place of Li-TFSI [88, 141]. These additives serve to increase the conductivity of the HTM layer, while reducing its vulnerability to moisture ingress. Addition of pre-oxidised spiro-OMeTAD (spiro-TFSI₂) and related compounds can increase the conductivity of the HTM and delivers comparable performance to Li-TFSI [79, 142], while doped HTMs have also been obtained from solutions of spiro-OMeTAD that are

partially oxidised indirectly using protic species [143]. Recently, Bolink and co-workers have demonstrated some extremely efficient fully vapour deposited perovskite solar cells employing dopants developed for organic light-emitting diode applications, using 1,3,4,5,7,8-hexafluoro-9,9,10,10-tetracyano-2,6-naphthoquinodimethane (F_6 -TCNNQ) as a *p*-dopant for the HTM bis(diarylamino)terphenyl [58]. Various cobalt(III)-complexes [144, 145] and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ) [146] have also been successfully used as sole dopant for solution-processed spiro-OMeTAD films. Nonetheless, to achieve record efficiencies, cobalt(III)-complexes still require the addition of lithium salts, and F_4 -TCNQ is highly volatile, poorly soluble and prone to diffusion in some host materials [147, 148].

Molybdenum tris-(1,2-bis(trifluoromethyl)ethane-1,2-dithiolene) ($Mo(tfd)_3$) is less volatile, more soluble, and less prone to diffusion than F_4 -TCNQ and has been used to *p*-dope a variety of materials. For example, it *p*-dopes *N,N'*-di[(1-naphthyl)-*N,N'*-diphenyl]-1,1'-biphenyl-4,4'-diamine (α -NPD) when co-evaporated [149], and the $Mo(tfd)_3^-$ anion does not diffuse significantly through α -NPD at temperatures of up to 110°C [149]. Although $Mo(tfd)_3$ has reasonable solubility in organic solvents by itself, its doping products are not always very soluble in solvents suitable for spin-coating semiconductor films; hence, the more soluble analogues molybdenum tris(1(methoxycarbonyl)2(trifluoromethyl)ethane-1,2dithiolene) ($Mo(tfd-CO_2Me)_3$) and molybdenum tris-(1-(trifluoroacetyl)-2-(trifluoromethyl)ethane-1,2-dithiolene) ($Mo(tfd-COCF_3)_3$) have been developed for solution-processing [78, 150]. Both chemical structures are represented in Figure 5.1 below.

$Mo(tfd-CO_2Me)_3$ has been used to dope P3HT to improve the hole transporting material for organic photovoltaics [151], and has been found to *p*-dope spiro-OMeTAD in a study of electric-field-induced dopant drift [152]. $Mo(tfd-COCF_3)_3$ has been used in solution-processed field-effect transistors based on polymer blends with bis(triisopropylsilylethynyl)pentacene [153]. Very recently, Chang *et al.* reported a 18.5% efficient "inverted" *p-i-n* perovskite solar cell employing a solution-processed $Mo(tfd-$

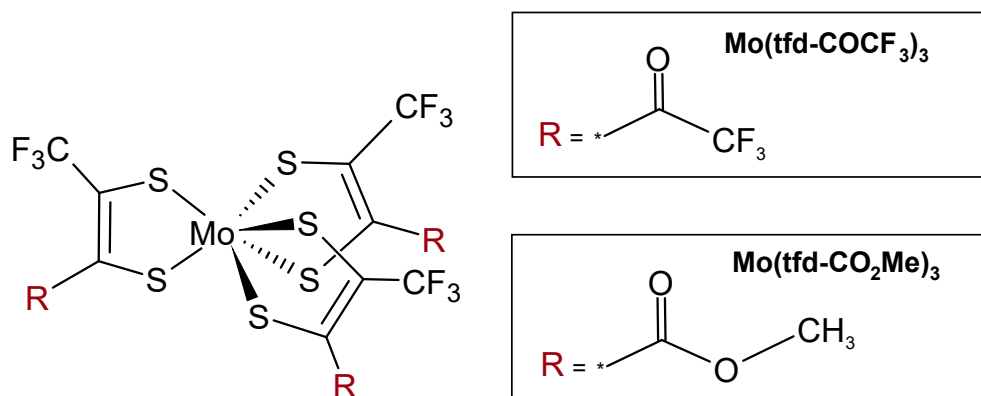


Figure 5.1: Chemical structures of both molybdenum tris(dithiolene)s used to *p*-dope spiro-OMeTAD in this study.

$\text{COCF}_3)_3$ doped poly(3,4-ethylenedioxythiophene (PEDOT) HTM [154]. All three of these molybdenum tris(dithiolene) ($\text{Mo}(\text{tfd})_3$) derivatives are air-stable in the solid state and all exhibit reversible reductions to stable monoanions at potentials (+0.12 to +0.39 V vs. ferrocene in dichloromethane) sufficient to oxidise spiro-OMeTAD [150] to its monocation (+0.05 V vs. ferrocene in dichloromethane), and both $\text{Mo}(\text{tfd-COCF}_3)_3$ and $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$ are soluble in solvents commonly used for solution processing, making them good candidates to replace Li-TFSI as a dopant for spiro-OMeTAD in perovskite-based solar cells.

5.4 Results and discussions

5.4.1 *p*-doping and conductivity

In order to confirm that $\text{Mo}(\text{tfd-COCF}_3)_3$ and $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$ can effectively dope spiro-OMeTAD, absorption spectra of doped and undoped films were taken (Figure 5.2).

For the neat films, the characteristic absorption peak of neutral spiro-OMeTAD is at 390 nm. With the addition of 1 mol% of either molybdenum dopant to the solution used to cast the film, a decrease was seen in the absorption peak at 390 nm and the appearance of two new absorption features, at ca. 500 nm and 700 nm. Further decreases at 390 nm peak, coupled with increases at 500 nm and 700 nm were observed with increased dopant concentration. The mono- and dication of spiro-OMeTAD both show absorptions in these

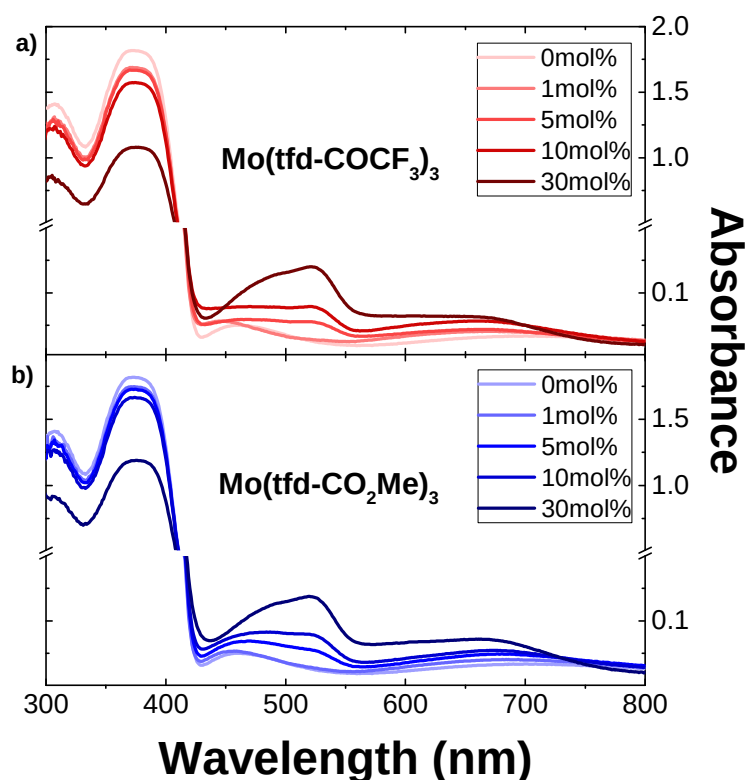


Figure 5.2: Changes in the ultraviolet-visible (UV-vis) absorption spectra of films of spiro-OMeTAD with the addition of a) Mo(tfd-COCF₃)₃ and b) Mo(tfd-CO₂Me)₃, to the casting solution, with their respective chemical structures shown as insets. Peaks at 520 nm and 690 nm can be assigned to oxidized spiro-OMeTAD (likely spiro-OMeTAD⁺, but spiro-OMeTAD²⁺ has an essentially identical spectrum) [155], with minor contributions from Mo(dt)₃⁻ absorptions.

regions [155], although presumably, it is the monocation that is formed in the presence of excess neutral spiro-OMeTAD; the monoanions of the Mo(dt)₃ dopants also absorb at similar wavelengths (ca. 490 and 670 nm in CH₂Cl₂ [150]), albeit weakly. Consistent with solution electrochemical data [79, 150] and with a previous study of dopant drift that included Mo(tfd-CO₂Me)₃-doped spiro-OMeTAD [152], the spectral changes with dopant concentration suggest that Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ are indeed capable of oxidising spiro-OMeTAD.

To correlate the evolution of absorption features to the increased availability of holes in spiro-OMeTAD upon *p*-doping, four-point probe conductivity measurements were performed. In Figure 5.3a, the conductivity of spiro-OMeTAD as a function of doping concentration is shown for both Mo(dt)₃ dopants. The measurements were made immediately after spin-coating the films in a nitrogen atmosphere and compared to the conductivity of spiro-

OMeTAD doped with Li-TFSI/FK209/*t*BP at the standard concentration, after leaving the film in dry air for 24 hours (straight line). Both Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ enhanced the conductivity by almost four orders of magnitude relative to that of undoped spiro-OMeTAD, resulting in a higher conductivity than that obtained with Li-TFSI/FK209/*t*BP. The conductivity increased exponentially with the dopant concentration. These results are consistent with effective *p*-doping of spiro-OMeTAD by both Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃. Furthermore, in contrast to Li-TFSI doping which requires oxygen [90], the Mo(dt)₃ complexes react instantly with the spiro-OMeTAD host material, consistent with a straightforward exergonic electron-transfer mechanism:



In Figure 5.3b, the absorption of neat to oxidised spiro-OMeTAD is compared, where the HTM was oxidised using either the standard concentration of Li-TFSI (50 mol%) with *t*BP (330 mol%) additive and the cobalt-complex dopant FK209 (3 mol%), or 5 mol% of either of the molybdenum tris(dithiolene) dopants in order to maintain the conductivity in the same order of magnitude. While the absorption features of oxidised spiro-OMeTAD were present for all the dopants, the Li-TFSI/FK209/*t*BP doped spiro-OMeTAD exhibited weaker features in the 500 nm and 700 nm regions, perhaps suggesting a higher efficiency of doping by the Mo dopants, although contributions by Mo(dt)₃ absorptions in the same wavelength range precluded precise quantification.

Figure 5.3c shows the absorption spectra of spiro-OMeTAD doped with Li-TFSI, FK209 and *t*BP immediately after spin-coating in inert atmosphere and after having been kept in dry air for 24 hours. With time, features attributed to oxidised spiro-OMeTAD increased in strength, consistent with the creation of additional charge carriers (holes). This led to a greater conductivity, which increased from $6.9 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ to $4.5 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ after air exposure.

Notably, these results reveal that spiro-OMeTAD films doped with only 5 mol% Mo(tfd-

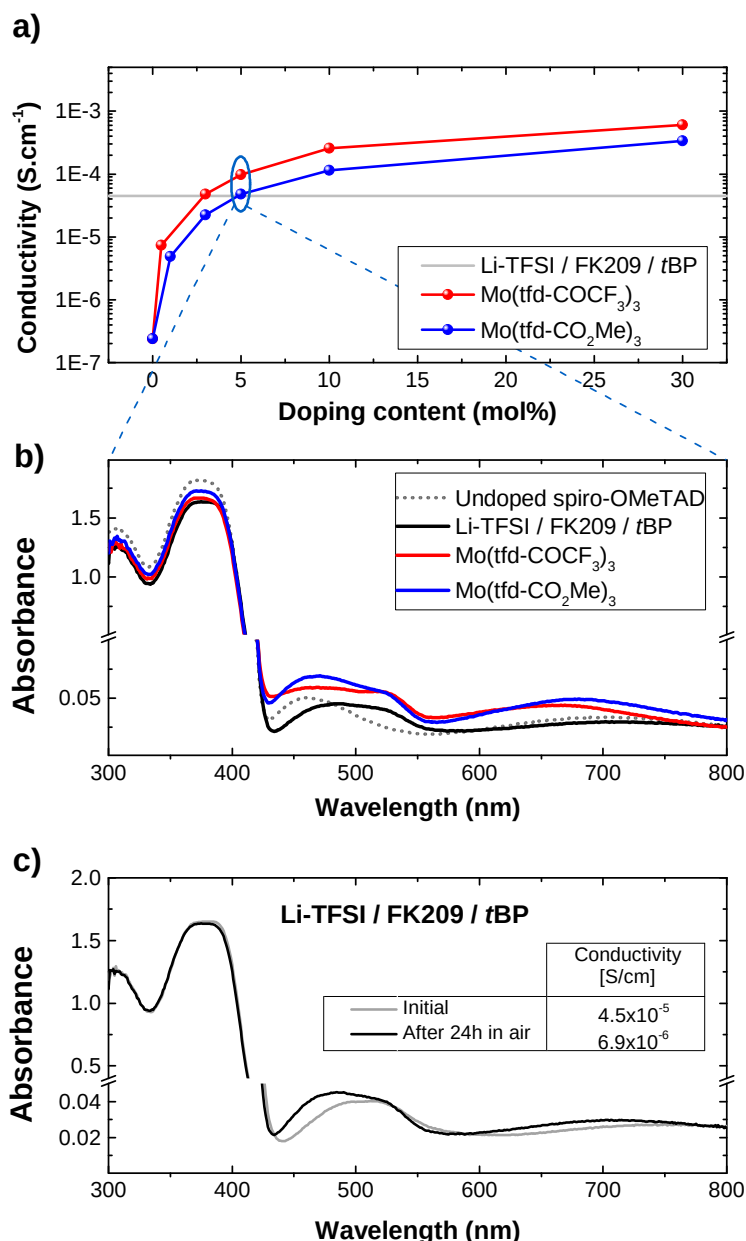


Figure 5.3: a) Conductivity of spiro-OMeTAD doped with the commonly used Li-TFSI/FK209/*t*BP after exposure to dry air for 24h (grey line), and with Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ as a function of molar doping content relative to spiro-OMeTAD. The molar concentration of the additives for the Li-doped reference with respect to spiro-OMeTAD is: 50%, 3% and 330% for Li-TFSI, FK209 and *t*BP, respectively. b) Absorption spectra of undoped spiro-OMeTAD compared to the standard Li-TFSI/FK209/*t*BP doped and molybdenum-doped spiro-OMeTAD. For both Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ a molar concentration of 5% relative to spiro-OMeTAD was chosen. The molar concentrations of additives for the Li-doped reference with respect to spiro-OMeTAD are: 50%, 3% and 330% for Li-TFSI, FK209 and *t*BP, respectively c) UV-vis absorbance spectra of Li-TFSI/FK209/*t*BP doped spiro-OMeTAD taken immediately after spin-coating in nitrogen and after air exposure for 24 h in a desiccator with corresponding film conductivities.

COCF₃)₃ and Mo(tfd-CO₂Me)₃ exhibit higher conductivities than the Li-TFSI/FK209/*t*BP doped films. At 30 mol% doping, the spiro-OMeTAD films are around one order of magnitude

more conductive. This indicates a much higher doping efficacy of the $\text{Mo}(\text{dt})_3$ dopants versus Li-TFSI, and in addition less of a negative impact upon mobility at high concentrations. Elevated dopant concentrations tend to render the organic film amorphous. This results in a greater density of traps and an increase in scattering centers for charge carriers which hamper their mobility and the overall conductivity.

5.4.2 Solar cell performance

Having shown that both $\text{Mo}(\text{tfd-COCF}_3)_3$ and $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$ can efficiently dope spiro-OMeTAD, perovskite solar cells using the *n-i-p* architecture were fabricated in order to investigate the influence of the dopants on the device performance. The mixed halide perovskite $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ was spin coated on top of a $\text{SnO}_2/\text{PC}_{60}\text{BM}$ *n*-type layer, where PC_{60}BM is [6,6]-phenyl-C60-butyric acid methyl ester, and then capped with the doped HTMs. Finally, a gold electrode was evaporated. Full experimental details are given in Chapter 3. The control devices used the commonly employed additives Li-TFSI, FK209 and *t*BP [60].

In order to determine the minimum dopant content necessary to obtain efficient devices, a concentration dependance was performed. All the scanned and steady-state performances are reported in Figure 5.4. Firstly, it was noticeable that regardless of the doping content, the reference always outperformed devices made with $\text{Mo}(\text{dt})_3$ -doped spiro-OMeTAD, mainly due to a drop in open-circuit voltage. Further for both dopants, scanned power conversion efficiencies became greater with increasing molar concentrations up to 5%. Passed 5 mol%, the scanned efficiency of the solar cell remained the same for higher dopant concentrations. Nonetheless, for $\text{Mo}(\text{tfd-COCF}_3)_3$ the steady-state performance kept improving with increasing dopant content which suggests that the molybdenum complex interacts with the perovskite. This phenomenon is explored in greater detail in Chapter 6.

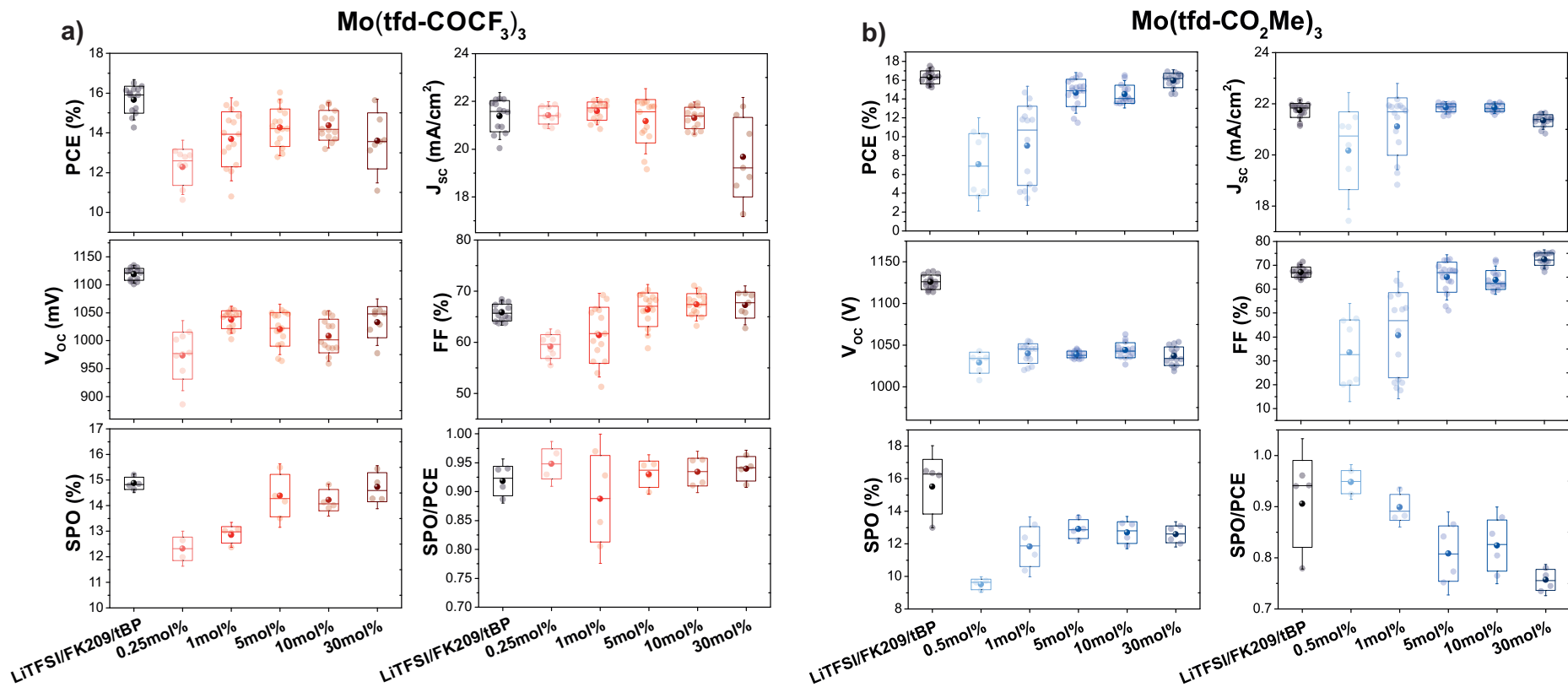


Figure 5.4: Scanned and steady-state performances for a batch of devices with different molar concentrations of: a) $\text{Mo}(\text{tfd-COCF}_3)_3$ and b) $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$. For both dopants, a concentration of 5 mol% gives the best compromise between scanned and steady-state performances.

Since a 5 mol% concentration with respect to spiro-OMeTAD gave the best trade-off between scanned and steady-state performances for both Mo(dt)₃ dopants, this doping concentration was kept constant for the rest of the study. Furthermore, by using this level of doping, the conductivity was maintained within the same order of magnitude across the various dopants, corresponding to a conductivity of $\sim 5 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ (Figure 5.3a).

Figure 5.5 depicts the current density-voltage (J-V) characteristics and steady-state efficiency of the best performing devices doped with Li-TFSI/FK209/*t*BP and both Mo(dt)₃ *p*-dopants, recorded under simulated AM1.5, 1 sun irradiance. The corresponding performance parameters of these champion devices are shown in Table 5.1. With the use of the molybdenum complexes the open-circuit voltage (V_{OC}) decreased from 1.13V to 1.07V and 1.06V for Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃, respectively, for the best performing device. Losses in voltage were compensated to some degree by an increase in fill factor (FF), attributed to the lower series resistance of the Mo(dt)₃-doped HTMs due to their increased hole conductivities (Figure 5.3a). As a result, Mo(dt)₃-doped devices achieved J-V determined power conversion efficiencies (PCE) surpassing 17% for the champion devices.

In a statistical analysis across four batches of devices (Table 5.2), Mo(dt)-doped devices showed similar short circuit current (J_{SC}), lower V_{OC} by 100 mV on average, and higher FF compared to the Li-TFSI/FK209/*t*BP control devices. Furthermore, the ratio of steady-state to scanned performance was on average 10% lower for Mo(dt)₃-doped spiro-OMeTAD compared to Li-based HTM, but remained remarkably high considering the absence of *t*BP additive which has been proven to be a prerequisite for high SPOs [132]. This observation indicated that the molybdenum molecules might have a similar role than *t*BP at the perovskite/HTM interface, yet probably not as effective.

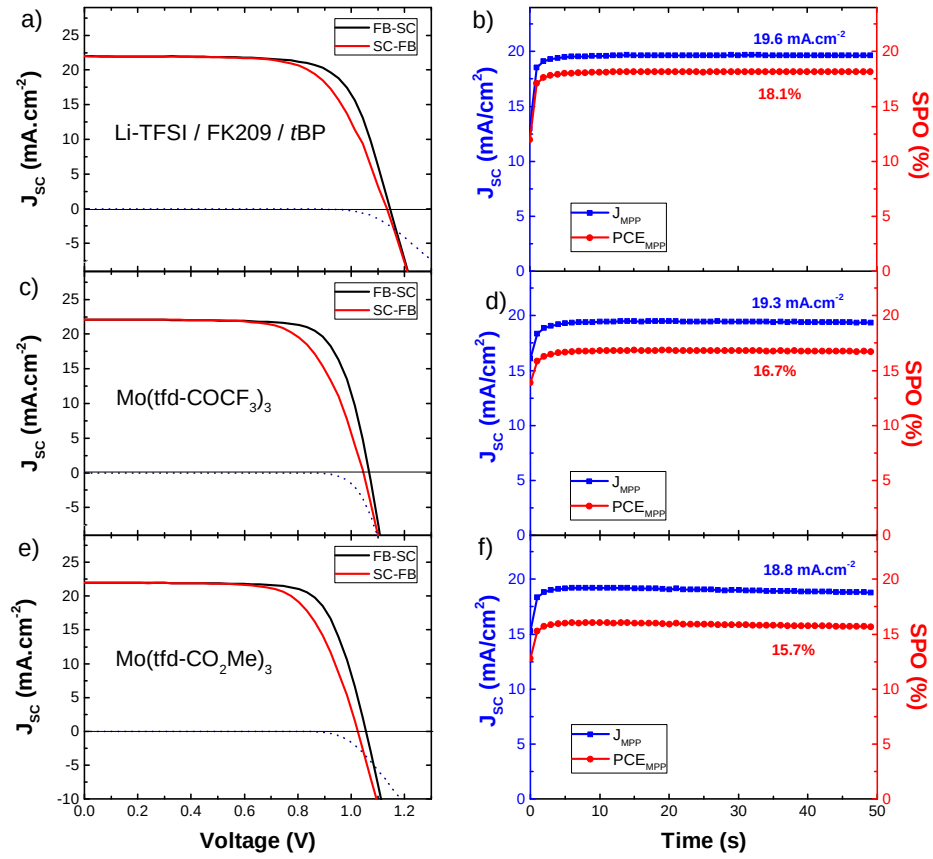


Figure 5.5: Current density-voltage characteristics of the champion devices using spiro-OMeTAD doped with a) Li-TFSI/FK209/tBP, c) $\text{Mo}(\text{tfd-COCF}_3)_3$ and e) $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$. b), d) and f) show the stabilised photocurrent densities and efficiencies of the devices presented in a), c) and e) respectively, measured by holding the devices at their J-V determined maximum power point for 50 seconds.

	J_{sc} [$\text{mA}\cdot\text{cm}^{-2}$]		V_{oc} [V]		FF		PCE [%]		R_s [$\Omega\cdot\text{cm}^{-2}$]		SPO [%]	SPO/PCE
	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB		
Li-TFSI/FK209/tBP	21.97	21.96	1.11	1.11	0.73	0.68	18.2	16.8	4.33	6.42	18.1	0.99
$\text{Mo}(\text{tfd-COCF}_3)_3$	22.11	22.12	1.07	1.04	0.76	0.68	17.8	15.6	2.47	4.77	16.7	0.94
$\text{Mo}(\text{tfd-CO}_2\text{Me})_3$	21.98	21.98	1.06	1.02	0.74	0.69	17.2	15.4	3.78	6.01	15.7	0.92

Table 5.1: Device performance parameters of champion devices. FB-SC: Forward-Bias to Short-Circuit; SC-FB: Short-Circuit to Forward-Bias.

	J_{sc} [$\text{mA}\cdot\text{cm}^{-2}$]	V_{oc} [mV]	FF [%]	PCE [%]	R_s [$\Omega\cdot\text{cm}^{-2}$]	SPO [%]	SPO/PCE
Li-TFSI/FK209/tBP	21.8 ± 0.3	1121 ± 24	67 ± 3	16.4 ± 0.9	6.4 ± 1.8	16.2 ± 1.3	0.96 ± 0.06
$\text{Mo}(\text{tfd-COCF}_3)_3$	21.6 ± 0.5	1023 ± 40	70 ± 5	15.5 ± 1.5	5.8 ± 2.3	14.8 ± 1.1	0.89 ± 0.05
$\text{Mo}(\text{tfd-CO}_2\text{Me})_3$	21.5 ± 0.4	1039 ± 41	69 ± 5	15.4 ± 1.4	4.3 ± 1.5	14.4 ± 1.2	0.88 ± 0.05

Table 5.2: Device performance statistics - Average device performance parameters with standard deviation measured across 4 batches of devices.

5.4.3 Influence of *t*BP

In a study by Habisreutinger *et al.*, it was reported that *t*BP has a highly beneficial effect on the steady-state performance of perovskite solar cells and also lead to higher V_{OC} [132]. The HTM additive directly interacts with the perovskite making it more charge selective for holes. Furthermore, when Li-TFSI salts are used to *p*-dope spiro-OMeTAD, *t*BP prevents phase segregation between the HTM and the dopant which results in a homogeneous hole transporting layer [156]. In order to improve the stabilised power output (SPO) and the V_{OC} of devices using $Mo(dt)_3$ *p*-dopants, the influence of *t*BP on scanned and steady-state performances is studied. The results are represented in Figure 5.6.

At very low concentrations, *t*BP has a beneficial effect on device performance for $Mo(tfd-COCF_3)_3$ -doped spiro-OMeTAD (Figure 5.6a). The introduction of *t*BP leads to an increase in V_{OC} and stabilised power output, while also improving the ratio of steady-state to scanned performance. However, with the addition of *t*BP at greater concentrations than 2 μ L per mL of spiro-OMeTAD solution (equivalent to 20 mol%), the device performance plummets due to an abrupt drop in FF. A similar effect is observed for $Mo(tfd-CO_2Me)_3$ -doped spiro-OMeTAD (Figure 5.6b). However, in the latter case *t*BP does not lead to any clear improvement in the device performances. This decrease in device performance upon *t*BP addition is attributed to the “de-doping” of spiro-OMeTAD as shown in Figure 5.7. The absorption spectra of Mo-doped spiro-OMeTAD taken before and after the addition of *t*BP shows an increase in the intensity of the ground state absorption of spiro-OMeTAD at 390 nm, and a decrease in the absorption features at both 520 nm and 690 nm. This clearly indicates a reduction of oxidised spiro-OMeTAD within the films. Since $Mo(dt)_3$ -based devices without the use of *t*BP still deliver SPOs of 16.7% for $Mo(tfd-COCF_3)_3$ and 15.7% for $Mo(tfd-CO_2Me)_3$, *t*BP is not added to the HTM for the following stability studies.

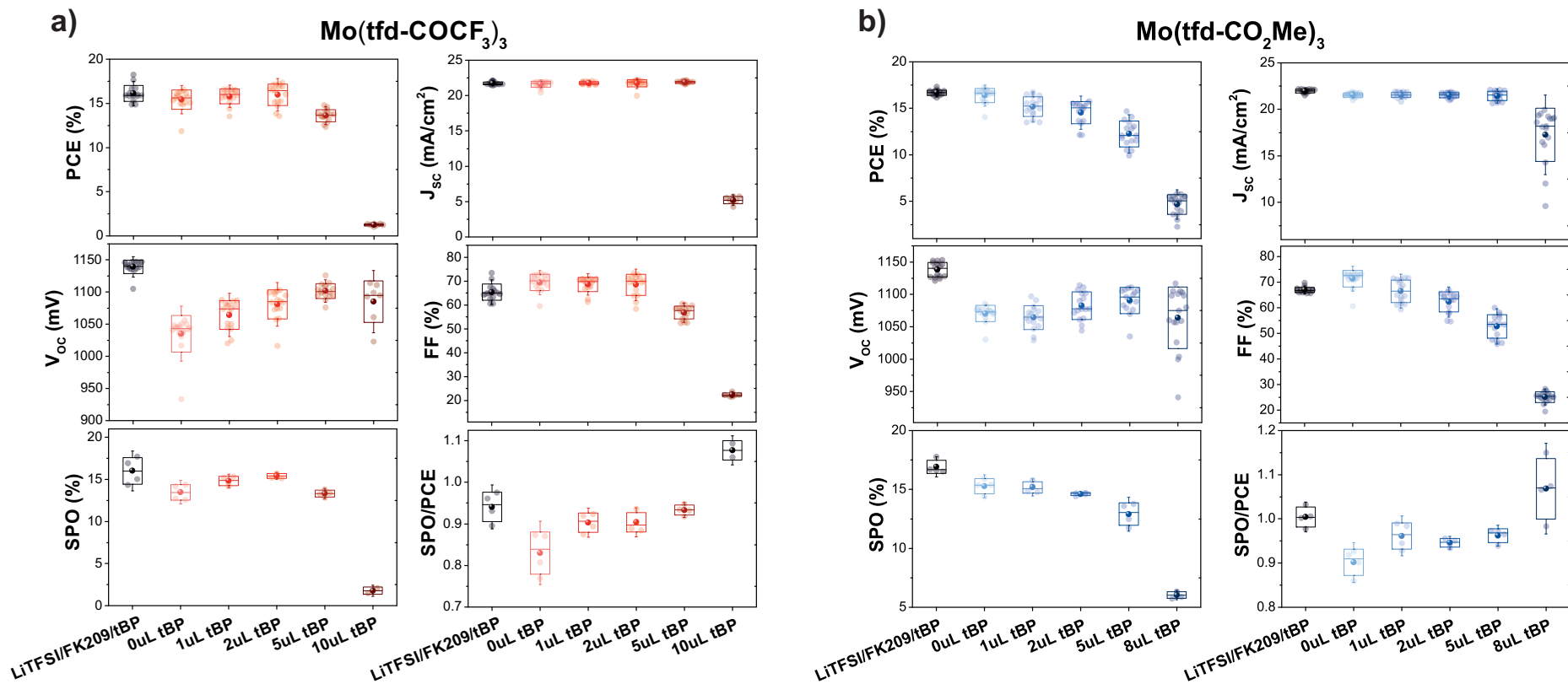


Figure 5.6: Scanned and steady-state performances for devices with various volumes of *t*BP added per mL of doped spiro-OMeTAD solution: a) $\text{Mo}(\text{tfd-COCF}_3)_3$ and b) $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$. For both dopants, a concentration of 5 mol% relative to spiro-OMeTAD is fixed.

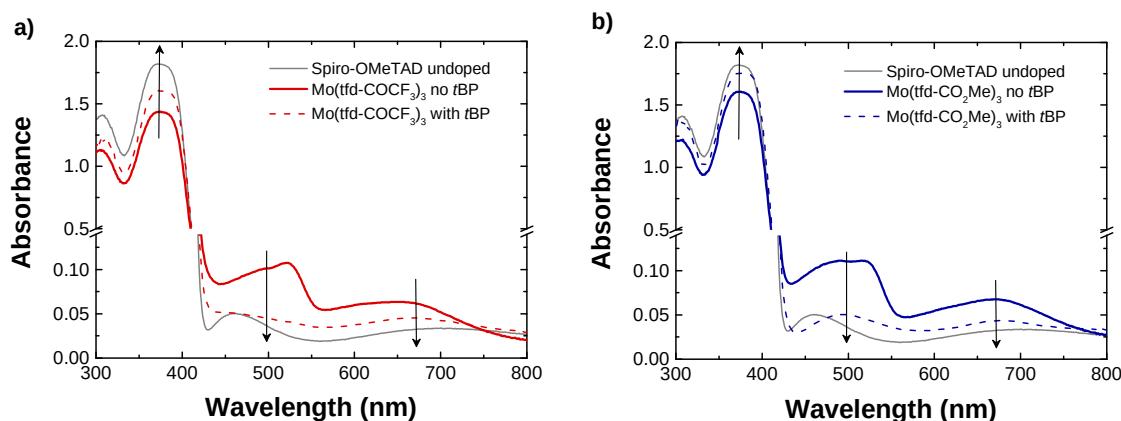


Figure 5.7: Absorption spectra of undoped and $\text{Mo}(\text{dt})_3$ -doped spiro-OMeTAD. The dopants used are: a) $\text{Mo}(\text{tfd-COCF}_3)_3$ and b) $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$. Upon addition of *t*BP, the characteristic peak of undoped spiro-OMeTAD at 390 nm increases and both absorption features at 520 and 690 nm diminish, which indicate a reduction of oxidised spiro-OMeTAD within the films.

5.4.4 Thermal stability in air with ambient humidity

To investigate whether the replacement of lithium salts with $\text{Mo}(\text{dt})_3$ -based complexes has an impact upon device stability, the complete non-encapsulated devices are subjected to a thermal stress test at 85°C on a hot plate in the dark, under ambient atmosphere (relative humidity of 30-40%) for 500 h. The cells are periodically removed from the hotplate and tested at room temperature under simulated AM1.5 (100 $\text{mW}\cdot\text{cm}^{-2}$) sun light. Therefore, the devices also undergo 10 thermal cycles from room temperature to 85°C.

The evolution of the photovoltaic performance parameters and the average stabilised efficiencies of a batch of eight devices per parameter, measured by holding the devices at their J-V determined maximum power point for 60 seconds, are shown in Figure 5.8. Notably, devices fabricated with $\text{Mo}(\text{dt})_3$ doped HTM layers show significantly slower deterioration than devices made using the typically employed Li-TFSI/FK209/*t*BP additives. After 500 h of aging, devices employing HTMs doped with both $\text{Mo}(\text{tfd-COCF}_3)_3$ and $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$ still yield SPOs greater than 10%, while the SPOs of their Li-TFSI/FK209/*t*BP based counterparts plummet from 17.1% to 5.1% on average (Table 5.3). As previously reported [157], all cells suffer from a fast deterioration or “burn-in” over the first 40 h and thereafter degrade at a much slower, linear rate. Within 24 h, devices with lithium-doped HTMs degrade by

50% while both Mo(dt)₃-doped HTMs retain 65-70% of their initial device performance after 500 h of aging, as shown in Figure 5.8b and Table 5.3.

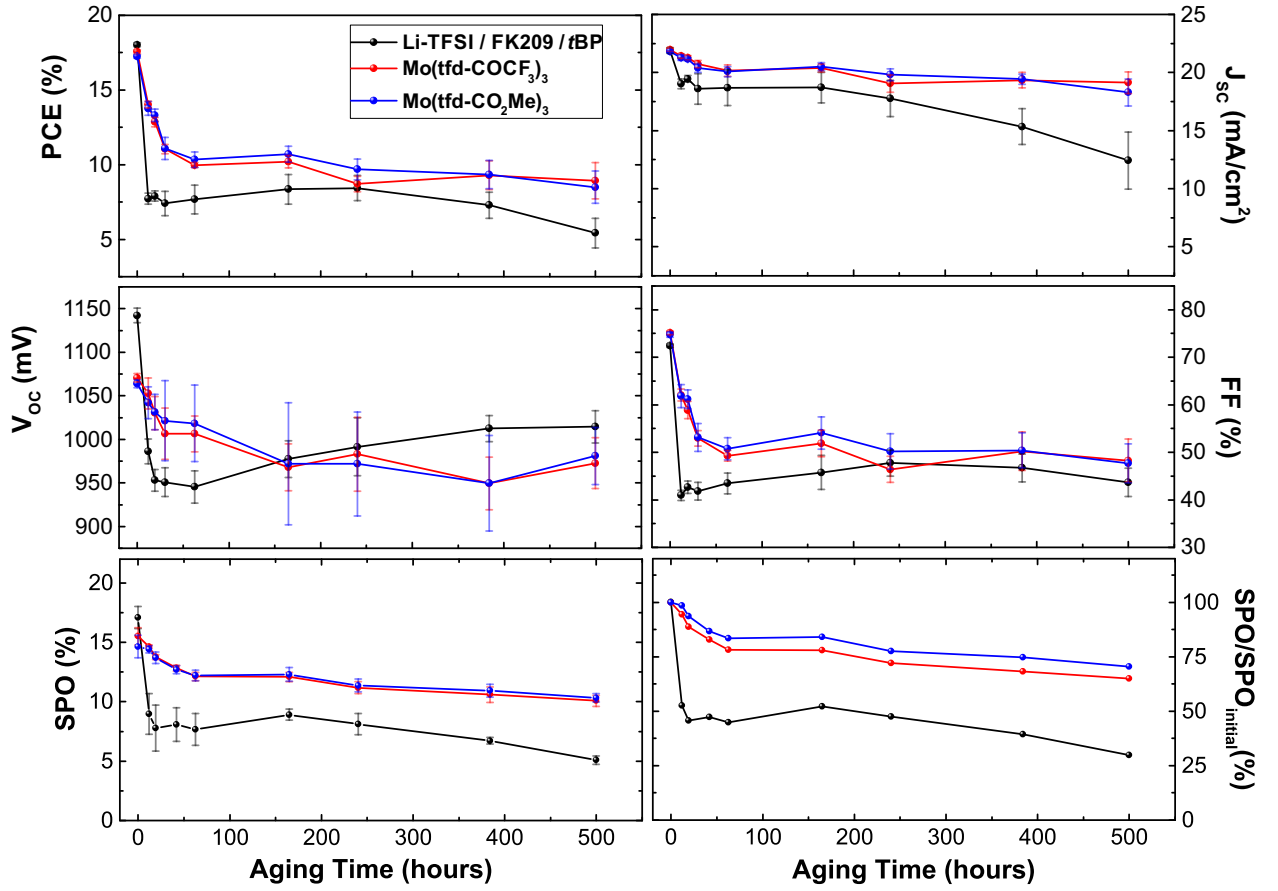


Figure 5.8: Aging for 500 h at 85°C in the dark at 30-40% humidity of non-encapsulated high-performance perovskite solar cells comparing Li-TFSI/FK209/tBP and Mo(dt)₃-doped spiro-OMeTAD. The evolution over time of the photovoltaic performance parameters determined from the J-V curves and the average SPO of eight solar cells measured by measuring the photocurrent while holding them at their maximum power voltage for 60 seconds. Furthermore, the average stabilised efficiencies over the initial stabilised power output is depicted in order to quantify the performance loss. Within 24 h, lithium-doped devices deteriorate by 50% while both Mo(dt)₃-doped devices sustain 70% of their initial performance after 500 h of aging.

	SPO _{initial} [%]	SPO _{500h} [%]	SPO _{500h} /SPO _{initial} [%]
Li-TFSI/FK209/tBP	17.1 ± 0.9	5.1 ± 0.3	30%
Mo(tfd-COCF ₃) ₃	15.5 ± 0.7	10.0 ± 0.4	65%
Mo(tfd-CO ₂ Me) ₃	14.6 ± 0.9	10.3 ± 0.4	70%

Table 5.3: Comparison between initial and aged steady-state efficiencies, measured after 500 h of aging at 85°C in the dark at 30-40% humidity of non-encapsulated perovskite solar cells.

In order to isolate the underlying cause for the improved stability of the solar cells when using Mo(dt)₃-doped spiro-OMeTAD, X-ray diffraction (XRD) on aged perovskite films coated with differently doped HTMs were performed (Figure 5.9a and b). Tracking the PbI₂ peak intensity by XRD measurements is a straightforward technique to follow the decomposition of the perovskite structure. As a control, a PMMA-coated perovskite film was taken. The PMMA layer protects the ionic crystal from moisture and hence inhibits its decomposition [88]. Noticeably, lithium-doped spiro-OMeTAD promoted a very fast increase of the PbI₂ signal over time suggesting a rapid degradation of the perovskite layer due to water ingress through the HTM. On the contrary, both Mo(dt)₃ dopants, similarly to PMMA, showed a slight increase of the PbI₂ peak intensity during the first 6 days of moisture and heat exposure, then stabilised indicating that the crystal structure did not undergo further changes from infiltration of water molecules. After three months of aging in similar conditions, the perovskite films coated with the Mo(dt)₃-doped spiro-OMeTAD sustained their dark brown colour unlike the lithium-doped sample which showed a clear discolouration (Figure 5.9c).

To confirm the hypothesis that replacing Li-TFSI with molybdenum complexes dopants enhances the stability of the perovskite due to a greater resistance to water, contact angle measurements were performed by depositing droplets of water onto films of undoped and doped spiro-OMeTAD in order to compare the surface wettability of the HTMs (Figure 5.10). For both Mo(dt)₃-doped spiro-OMeTAD, contact angle measurements were similar to the undoped HTM ($\sim 75^\circ$), whereas the addition of the hygroscopic lithium dopant caused a decrease of the contact angle by almost 20° . Therefore, by adding Mo(dt)₃ complexes to the spiro-OMeTAD the hydrophobicity of the film increased as compared to Li-doped HTM, which minimised the ingress of water molecules through the spiro-OMeTAD and drastically slowed down the structural degradation of the perovskite crystal. Hence, Mo(dt)₃ dopants are extremely promising candidates for replacing the current state-of-the-art dopants employed to *p*-dope the hole-transporting layer.

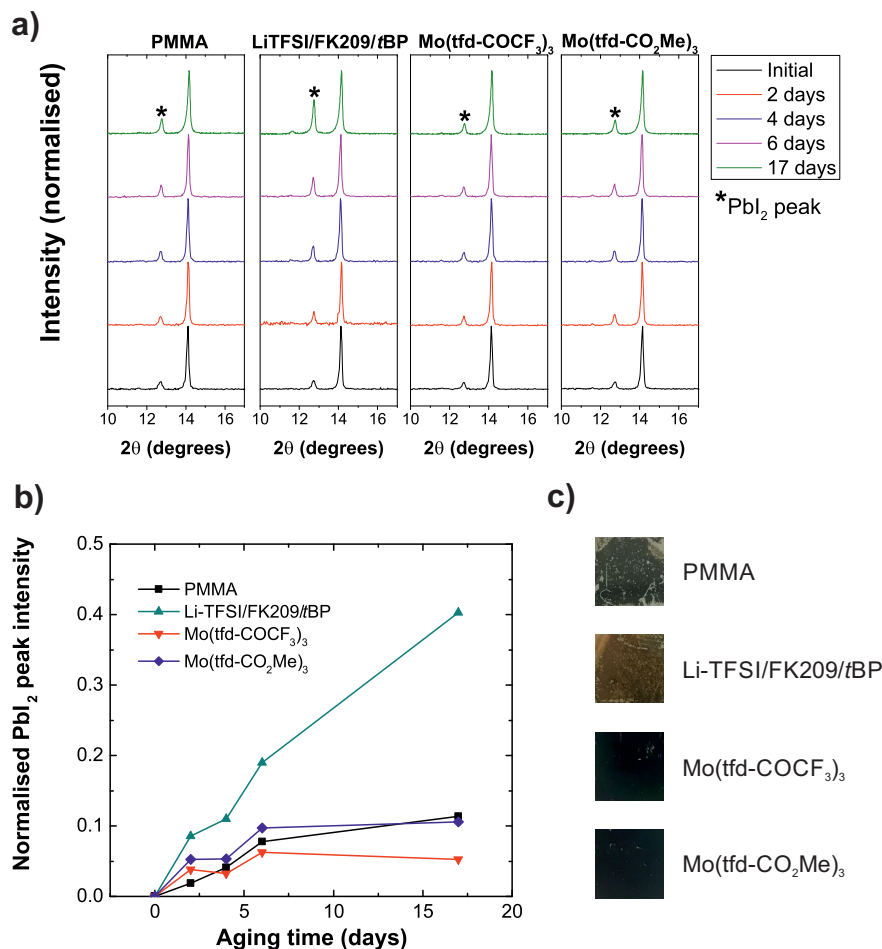


Figure 5.9: X-ray diffraction (XRD) measurements of FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})₃ perovskite films coated with differently doped spiro-OMeTAD. a) XRD patterns comparing freshly made to aged films at 85°C in ambient atmosphere in the dark up to 17 days. A perovskite film coated with PMMA was taken as reference. b) Evolution of the PbI₂ peak intensity at 12.7°, signature of perovskite degradation. c) Photographs of the aged perovskite films after 3 months of aging.

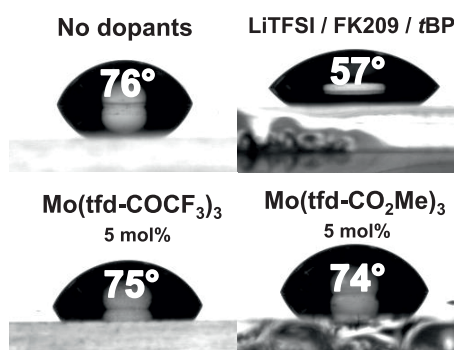


Figure 5.10: Contact angle measurements of water droplets on spiro-OMeTAD doped with various dopants and undoped. Li-doped spiro-OMeTAD showed a greater wettability compared to the undoped and Mo(dt)₃-doped films, indicating the enhanced hydrophobicity of the HTM upon addition of molybdenum dopants.

5.5 Conclusion and outlook

In summary, this study shows that $\text{Mo}(\text{dt})_3$ complexes which are strong electron-acceptor materials can be used to efficiently *p*-dope spiro-OMeTAD. Unlike Li-TFSI which requires air exposure to oxidise spiro-OMeTAD, the $\text{Mo}(\text{dt})_3$ dopants react instantly with the HTM matrix *via* a simple electron-transfer mechanism. Thus, the conductivity of the *p*-type layer was increased by up to four orders of magnitude compared to undoped spiro-OMeTAD. Moreover, a 5 mol% doping of either $\text{Mo}(\text{dt})_3$ complexes exhibited higher conductivities than the commonly employed doping cocktail Li-TFSI/FK209/*t*BP (50 mol%/3 mol%/330 mol%), which emphasise the much higher doping efficacy of the molybdenum compounds versus Li-TFSI.

The effectiveness of the *p*-doping by the $\text{Mo}(\text{dt})_3$ dopants translated into high device performances, with champion steady-state efficiencies of 16.7% and 15.7% for $\text{Mo}(\text{tfd-COCF}_3)_3$ and $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$, respectively. These efficiencies remained slightly lower than the Li-doped control mainly due to a loss in V_{OC} by 100 mV on average. In order to recover this loss in voltage the influence of *t*BP on device performance was studied. *t*BP has been shown to induce a local *p*-doping at the absorber/HTM interface thus allowing high V_{OC} and enhanced steady state efficiencies [132]. Unfortunately, the additive negatively impacted the photovoltaic performance by dedoping the HTM. Further investigations are required in order to elucidate the incompatibility of *t*BP with these new *p*-dopants. However, with only a 5 mol% doping of $\text{Mo}(\text{dt})_3$ complexes and without addition of *t*BP high SPOs were achieved remarkably, suggesting that the molybdenum molecules most likely have a similar role than the commonly used additive at the perovskite/HTM interface. In addition, these findings stress the reliance of spiro-OMeTAD on *t*BP to achieve high V_{OC} values which indicates the necessity of surface modification to sufficiently suppress surface recombination or improve the energy band alignment at the perovskite/HTM interface when employing spiro-OMeTAD.

Simultaneously, the $\text{Mo}(\text{dt})_3$ dopants made the spiro-OMeTAD much more hydrophobic

which minimised the water ingress *via* the hole transporting layer and slowed down the decomposition of the perovskite crystal structure into PbI_2 . This resilience against moisture lead to a significantly enhanced long-term device stability. After exposing non-encapsulated devices to 85°C in air and dark for 500 h, Mo(dt)_3 -doped spiro-OMeTAD devices maintained up to 70% of their initial performance while steady state efficiencies of the solar cells fabricated using lithium salts quickly declined from 17.1% to 5.1%.

Overall, this study revealed that despite moderately lower photovoltaic performances, Mo(dt)_3 complexes a remarkable positive impact on the long-term stability of perovskite solar cells and are thus promising alternatives to the hygroscopic Li-TFSI.

6 | Modification at the *p*-type interface in perovskite solar cells *via* Mo(tfd-COCF₃)₃ surface treatment

This chapter outlines the effect of Mo(tfd-COCF₃)₃ at the absorber/HTM interface in perovskite solar cells. The molybdenum complex has the ability to passivate structural defects at the surface and *p*-dope the perovskite/HTM interface, which results in more favourable energetics between the perovskite and the HTM, and enhances device performance. The synthesis of Mo(tfd-COCF₃)₃ presented in this chapter has been carried out by Yadong Zhang, Georgia Institute of Technology.

6.1 Context and summary

Organic-inorganic perovskite solar cells have undergone rapid development and surged to the forefront of photovoltaics research. Tremendous effort has been placed on perfecting the optoelectronic properties of the bulk perovskite material itself through modification of the chemical composition and notable improvements in fabrication methods, which lead to impressively long photocarrier diffusion lengths [35, 45]. After years of continuous increases in the record efficiencies, the race for the new peak performance appears to have slowed, indicating that perovskite absorber might be approaching its attainable thermodynamic limit. To further improve the performance of perovskite based devices, attention must shift towards perfecting its interfaces with the charge extraction layers. Since solution-processed perovskite films are polycrystalline materials with mixed ionic and covalent character, structural defects and charge trap states are inevitably created especially at the surface and the grain boundaries. These defects are responsible for trap-assisted, non-radiative recombination losses. Moreover, most commonly employed charge extraction materials exhibit a non-ideal alignment of the energy levels at the interfaces with the perovskite, which limits the attainable V_{OC} and emphasizes the importance of interfacial engineering and design for the future development of perovskite solar cells.

In this chapter, the molybdenum tris(dithiolene) complex $\text{Mo}(\text{tfd-COCF}_3)_3$, previously used to *p*-dope spiro-OMeTAD, was employed as a surface treatment of the perovskite absorber. The deposition of the molecule onto the surface of the perovskite film, causes a reduction in non-radiative electron-hole recombination, and significantly shifts the work function of the perovskite away from vacuum. The implications of the results obtained in this study are twofold. On the one hand, the improvement in the photoluminescence lifetimes and quantum efficiencies suggest that the $\text{Mo}(\text{tfd-COCF}_3)_3$ molecule can be used to passivate the surface of perovskite films. This can possibly occur through interaction with under-coordinated Pb atoms, thus effectively removing Coulomb traps responsible for trap mediated recombination losses. On the other hand, the molecule also appears to *p*-dope

the perovskite surface, thus facilitating improved hole extraction. These changes resulted in an enhancement of the stabilised power conversion efficiencies from 15.1% to 17.2% after treatment with $\text{Mo}(\text{tfd-COCF}_3)_3$.

6.2 Introduction

Over the past few years, lead halide perovskite solar cells have received a tremendous amount of attention which rapidly lead their photovoltaic performances soaring to only a few percent lower than the best single-crystalline silicon solar cell [9]. Much attention has been focused on understanding the chemical and physical properties of the perovskite material in order to fully explore and exploit its potential for photovoltaic applications, while also focusing on the development of a wide range of deposition methods. Such extensive optimisation has enabled the preparation of better quality perovskite layers with remarkable optoelectronic properties, close to their attainable limit. Nonetheless, the ionic, polycrystalline nature of hybrid perovskites makes them prone to exhibiting under-coordinated ions which are responsible for numerous defects and vacancies within the bulk material, and particularly at the grain boundaries. Such defects are well known to act as recombination centers for charges which limits the power conversion efficiency [158, 159, 160]. Moreover, in a complete device several challenges such as stability [161, 162] and hysteresis [163] remain issues closely correlated with the quality of the interfaces. In order to achieve higher efficiencies and improve the stability of perovskite solar cells, future research needs to focus on understanding and controlling interfacial energetics between the perovskite absorber and the charge extraction layers.

The detrimental effect of trap states on the photovoltaic performance of perovskite solar cells is a well-documented fact, and is generally attributed to trap-mediated recombination losses of photogenerated carriers [159, 160, 164, 165, 166, 167]. While both electrons and holes can be trapped, Leijtens *et al.* have recently presented evidence that electrons are more likely to be trapped than holes [168]. Several methods have been employed to pas-

sivate undesirable surface and bulk defects to reduce trap states in the perovskite and at the interface with the electron transport layer (ETL) and hole transport layer (HTL). For example, fullerenes have been shown to efficiently passivate defects at the perovskite/ETL interface [55, 166, 169, 170, 171]. More recently, Tan *et al.* demonstrated that treating the TiO₂ ETL with chlorine mitigates interfacial recombination by passivating deep trap states in the perovskite, resulting in improved power conversion efficiency and device stability. At the perovskite/HTL interface, undercoordinated halide ions (X⁻) can form supramolecular halogen bonds with iodopentafluorobenzene (IPFB), resulting in a reduction of trapped holes and improving the cell performance [165]. Moreover, under-coordinated Pb ions result in the formation of a δ^+ charge which can act as an electron trap. These defects were successfully passivated using Lewis bases, such as thiophene and pyridine, which possess a lone pair of electrons available able to create a covalent bond with under-coordinated Pb atoms, resulting in enhancements in both solar cell performance and photoluminescence lifetimes [159, 164, 160]. Very interestingly, Song *et al.* showed that carrier losses could be reduced by introducing a layer of F₄TNCQ at the perovskite/HTL interface [172]. Their work demonstrated that the well known *p*-dopant for organic HTMs can also chemically interact with the perovskite absorber by simultaneously passivating trap states and *p*-doping the surface of the MAPbI₃ perovskite layer. Such *p*-doping effect at the perovskite/HTL interface has also been reported by Habisreutinger *et al.* who investigated the role of *t*BP additive and its positive influence on the steady-state performance of perovskite solar cell [132].

In the previous chapter, it was noticed that molybdenum tris(dithiolene)s not only effectively *p*-dope spiro-OMeTAD, but also have a highly beneficial effect on the steady-state performance of the perovskite solar cells. As previously mentioned, the reasons for enhanced stabilised power conversion efficiencies may come from a reduction of non-radiative trap-assisted recombination losses *via* the passivation of surface defects [165, 159, 166, 160, 167, 173], and/or a greater selectivity for electrons and holes at the perovskite interfaces with the electron and hole transport layers respectively [174, 132, 172]. In this chapter, the perovskite layer was directly treated with the Mo(tfd-COCF₃)₃ complex in order to study in greater detail its direct interaction with the perovskite surface. In this chapter the focus has been

placed solely on $\text{Mo}(\text{tfd-COCF}_3)_3$ as it yielded the highest device improvement of the two complexes investigated (Chapter 5). Moreover, the p -doping of the perovskite surface would be more likely to occur with $\text{Mo}(\text{tfd-COCF}_3)_3$ since it is a stronger electron acceptor than $\text{Mo}(\text{tfd-CO}_2\text{Me})_3$ [150]. After treating the surface of the perovskite with $\text{Mo}(\text{tfd-COCF}_3)_3$, photoluminescence studies revealed increases in both the PL lifetime the PLQE consistent with passivation of non-radiative recombination sites at the surface. In addition, shifts of the workfunction away from vacuum, measured using a Kelvin probe, indicated effective p -doping of the surface by the dopant. In devices, $\text{Mo}(\text{tfd})_3$ -treated perovskite resulted in an improvement of the average power conversion efficiencies increasing from 14.7 ± 0.5 to 16.8 ± 0.4 , with a champion device of 17.2%.

6.3 Results and discussions

6.3.1 Film morphology of $\text{Mo}(\text{dt})_3$ -treated perovskites

The mixed halide perovskite $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ was deposited using the antisolvent quenching method as described in Chapter 3. $\text{Mo}(\text{tfd-COCF}_3)_3$ was dissolved in chlorobenzene at a concentration of 0.1 wt.%, and the solution was spincoated onto the perovskite immediately after it was annealed and cooled down to room temperature. At higher concentrations, the molecule aggregated upon deposition resulting in discontinuous films. After spincoating, the treated film was annealed at 100°C for 5 min in order to drive off any remaining solvent.

Firstly, to ensure that the $\text{Mo}(\text{dt})_3$ treatment does not alter the perovskite film, SEM images and UV-Vis absorption spectra were taken (Figure 6.1). As clearly shown by the images in Figure 6.1a, treating the perovskite with the molybdenum molecule did not noticeably affect the surface morphology. Both the treated and the untreated film exhibit the morphology typical of perovskite films fabricated through the antisolvent quenching method; a polycrystalline film with grain sizes ranging from tens of nanometers to around 400 nm.

Additionally, no shift in the absorption spectra was observed (Figure 6.1b) suggesting that the $\text{Mo}(\text{dt})_3$ molecule does not affect the perovskite band structure. Since both the surface topology and the absorption band edge of the treated perovskite were similar to the control, it is likely that the dopant is distributed at the surface of the film or at the grain boundaries without impacting the properties of the bulk.

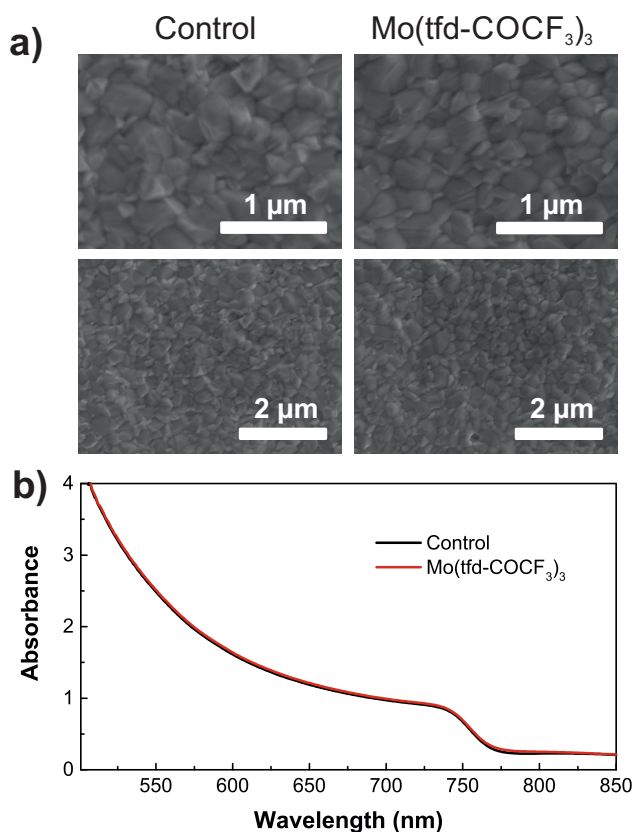


Figure 6.1: a) Scanning electron microscopy (SEM) images and b) absorption spectra of a neat perovskite film, and one treated with $\text{Mo}(\text{tfd-COCF}_3)_3$ at a concentration of 0.1 wt.%.

6.3.2 Passivation of surface trap states

A consequence of solution processing is the polycrystallinity of thus prepared thin films. Polycrystalline films are prone to having a high density of defect states due to the abundance of grain boundaries and surfaces, where lattice vacancies and dangling bonds can form and act as very effective electronic trap states. Their presence leads to strong quenching of PL emission due to the non-radiative loss of photogenerated carriers. Both under-coordinated Pb ions due to the presence of halide vacancies, as well as excess halides in the film have been

identified as major contributors to these defect sites [175, 158, 176, 159]. Noel *et al.* have reported that under-coordinated Pb ions results in the formation of δ^+ charges at the surface which can effectively bond with electron-rich molecules. They postulate that the lone pair of electrons on the sulphur atom of thiophene can compensate for the net positive charge of the iodide vacancy by forming a dative covalent bond with the lead atom thus delocalising the positive charge within the molecule. Similarly to thiophene, Mo(tfd-COCF₃)₃ possesses sulfur atoms with two sets of lone pair electrons which can potentially bond to the positively charged Pb. On the other hand, it was demonstrated that undercoordinated halides, such as iodide, can interact with IPFB [165, 177] and F₄TCNQ [172] through halogen bonding. A halogen bond is a non-covalent intermolecular interaction between an electrophilic region and a nucleophilic region [178, 179]. A good halogen bond donor molecule should present an anisotropic delocalisation of charge density. This delocalisation results in the creation of a positive electrostatic potential away from the electronegative atoms (*e.g.* fluorine). This electropositive region will then be attracted to electron-rich sites such as iodide anions. In the case of Mo(tfd-COCF₃)₃, the strong electron-withdrawing substituents (CF₃ groups [180]), could eventually pull electrons away from the aromatic ring leaving an electropositive charge which then might bind with the negatively charged defects.

In order to investigate the influence of the Mo(tfd-COCF₃)₃ surface treatment and determine whether the molecule does in fact passivate the crystal surface, the photoluminescence properties of untreated and treated films were studied (Figures 6.2 and 6.3). The mixed halide perovskite FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})₃ was coated with Mo(tfd-COCF₃)₃ dissolved in CB at concentrations varying from 0.0001 wt.% to 1 wt.%. For the sake of protecting the samples from degradation during photoluminescence measurements the perovskite films were covered with PMMA, which was spincoated dynamically in order to avoid the molybdenum molecule from being washed off the perovskite surface.

At first, photoluminescence quantum efficiency (PLQE) was measured (Figure 6.3). Both samples showed a similar evolution of the PLQE with the fluence in that there is an initial increase followed by a plateau. With increasing fluences, traps are filled and the bimolecular recombination becomes faster resulting in a greater fraction of the excited charges recombining radiatively [20, 22, 124]. Thus, the PLQE reaches a maximum value when the trap states responsible for Shockley-Read-Hall non-radiative losses are for the most part filled. For the lowest concentration of $\text{Mo}(\text{tfd-COCF}_3)_3$ (0.0001 wt.%), the treated perovskite showed higher PLQE than the control at all fluences, providing evidence that trap-mediated recombination losses were reduced. With increasing concentrations, the PLQE is gradually quenched indicating that charges preferentially recombine non-radiatively. This quenching in PLQE may indicate a degradation of the perovskite when treated with highly concentrated solutions of $\text{Mo}(\text{tfd-COCF}_3)_3$, however the exact mechanism behind these observations remains unknown and is subject to further investigation. In addition, due to the large size of the $\text{Mo}(\text{tfd})_3$ molecule, highly concentrated solutions will most likely result in a relatively thick layer of dopant on top of the perovskite, which in a complete solar cell could induce series resistance at the perovskite/HTM interface and inhibit charge extraction due to steric hindrance.

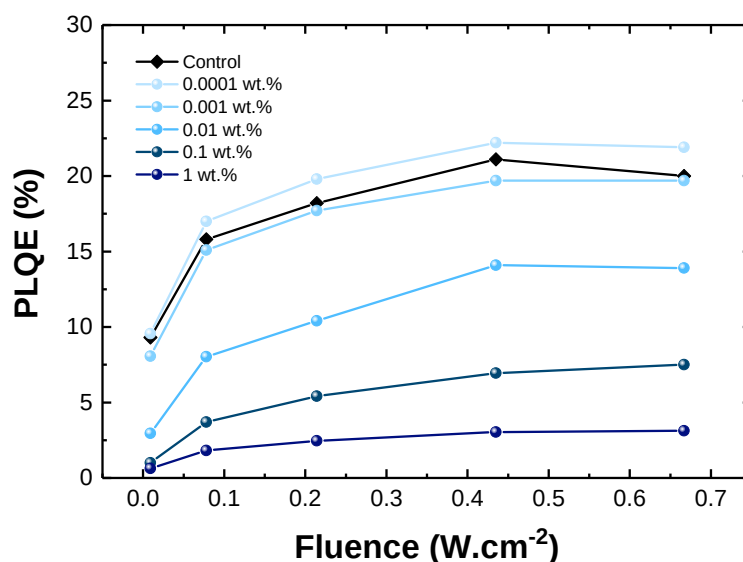


Figure 6.2: Photoluminescence quantum efficiency of untreated and $\text{Mo}(\text{tfd})_3$ -treated films at concentrations ranging from 0.0001 wt.% to 1 wt.%. Measurements were taken by Dr. Bernard Wenger (Department of Physics, University of Oxford).

Time-resolved photoluminescence decay measurements were taken on neat and Mo(dt)₃-treated perovskite films in order to estimate the PL lifetime of the samples (Figure 6.3). The fluence was kept constant corresponding to a injected carrier density (n_0) of 10^{15} cm^{-3} . Since concentrations higher than 0.01 wt.% substantially quenched the PLQE, only the samples treated with the lowest concentrations of dopant were considered (*i.e.* 0.0001, 0.001 and 0.01 wt.%). The decays were globally fitted to a kinetic trap model employed by Zhang *et al.* which follows the time dependent PL intensity using the expression [181]:

$$I_{PL}(t) = \alpha \cdot \frac{\exp(-\gamma n_T \cdot t)}{\left(1 + \frac{n_0}{n_T} \cdot (1 - \exp(-\gamma n_T \cdot t))\right)^2} + \beta \quad (6.1)$$

with α accounting for the fast PL decay at short times, β representing the noise level of the instrument, γ being the bimolecular recombination constant and n_T equivalent to the filled trap concentration.

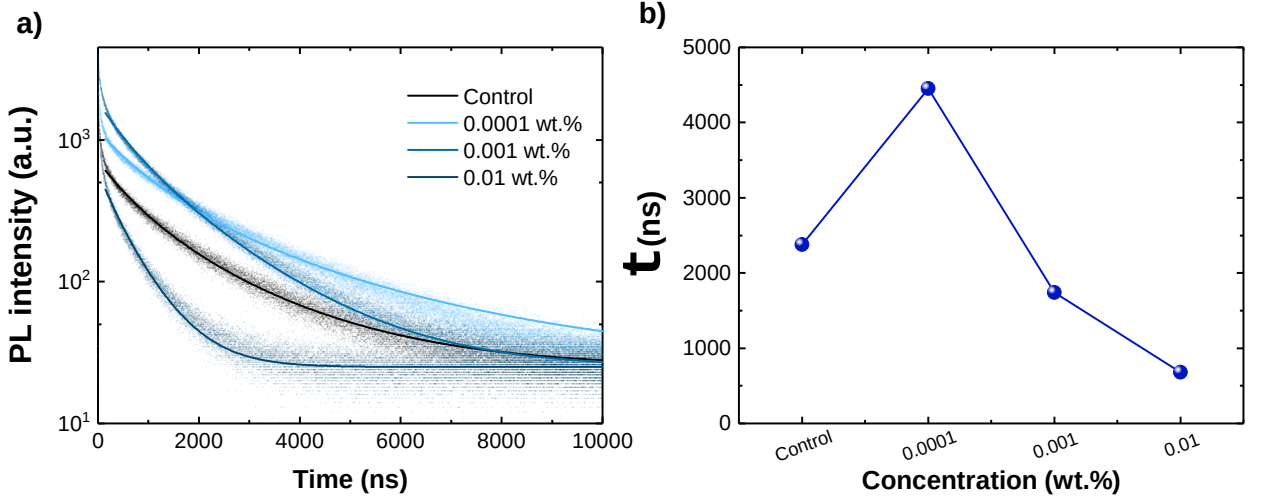


Figure 6.3: Time resolved PL measurements of untreated and treated perovskite films with Mo(tfd-COCF₃)₃ at different concentrations (0.0001, 0.001 and 0.01 wt.%). a) The PL decays were detected at 800 nm following pulsed excitation (505 nm, 100 kHz repetition rate) with an initial photoexcitation density of 10^{15} cm^{-3} . Solid lines are fits to the data using a decay model employed by Zhang *et al.* [181] which is a reformulation of the model initially introduced by Stranks *et al.* [20]. Fits were done by Dr. Bernard Wenger (Department of Physics, University of Oxford). b) Lifetime τ extracted from the fits.

A global fit of the four decays was performed. As compared to a monomolecular tail fit, this kinetic trap model gives accurate fits for a greater part of the decay, thus a more reliable

lifetime ($\tau = \frac{1}{\gamma n_T}$) can be extracted (Figure 6.3b). At 0.0001 wt.%, the PL lifetime of the perovskite films increased almost twofold from 2376 ns to 4454 ns with respect to the control. With increasing concentrations, the lifetime became progressively shorter consistent with the quenched PLQE. Nonetheless, perovskite treated with the more Mo(tfd)₃-concentrated solution (*i.e.* 0.01 wt.%) still exhibited a relatively long decay tail with a lifetime of 680 ns. The increases in both PLQE and PL lifetime indicate a reduction of non-radiative losses, giving evidence of an effective passivation of trap sites acting as recombination centers at the perovskite surface.

After establishing that Mo(tfd-COCF₃)₃ might passivate trap states at the surface of the perovskite film, transient photoconductivity measurements were performed in order to see whether or not the treatment has an influence on the bulk properties (Figure 6.4). The extracted values correspond to the bulk photoconductivity (σ_{ph}) taken across a film of perovskite, therefore if the molybdenum molecule diffuses through the grain boundaries and passivates defects located deeper within the film, an increase in photoconductivity is expected. For the two perovskite films treated with different concentrations of the dopant, the photoconductivity remained comparable to the control. On average, σ_{ph} increased from $6 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ to $0.1 \text{ S}\cdot\text{cm}^{-1}$ for carrier densities corresponding approximately to 10^{17} and 10^{19} cm^{-3} , respectively. Hence Mo(tfd-COCF₃)₃ does not appear to penetrate into the bulk at the grain boundaries and predominantly remains at the perovskite surface.

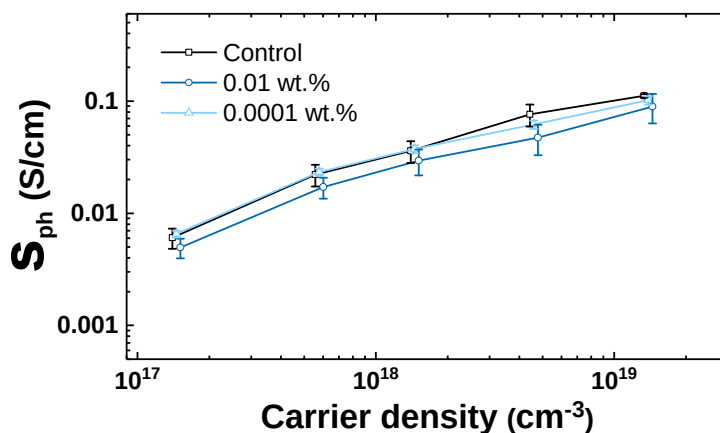


Figure 6.4: Transient photoconductivity measurements of neat and Mo(dt)₃-treated perovskite. Measurements were performed by Dr Jongchul Lim (University of Oxford).

As initially postulated, one potential passivation mechanism may arise from the formation of a dative covalent bond between the lone pair electrons on the sulfur atom in $\text{Mo}(\text{tfd-COCF}_3)_3$ and the net positive charge (δ^+) on the under-coordinated lead cation. This eventual passivation mechanism proposed is illustrated in Figure 6.5. This study does not exclude halogen bonding as a potential route to defect passivation with $\text{Mo}(\text{tfd})_3$ complex, nonetheless by comparing the molecular structure of the dopant studied with molecules used in previous works on passivation at the *p*-type interface [159, 165, 172], the likelihood of forming a covalent bond between the lone pair electrons of the sulfur and the under-coordinated Pb atom should be higher. Indeed, in $\text{Mo}(\text{tfd-COCF}_3)_3$ the three CF_3 groups pull electrons away from the aromatic ring leaving an electropositive charge. However here, due to the symmetrical shape of the molecule, the delocalisation of charge density is not as pronounced as for instance in IPFB [165], and halogen bonding of $\text{Mo}(\text{tfd-COCF}_3)_3$ with I^- anions seems unlikely.

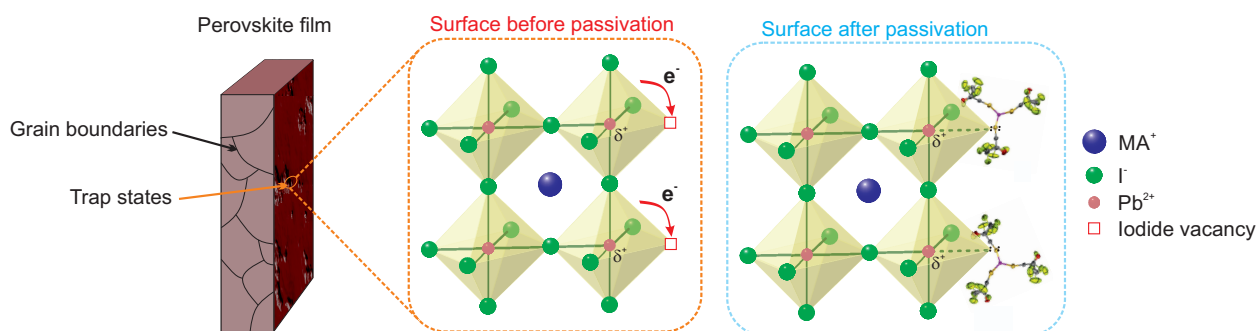


Figure 6.5: Illustration of a solution-processed perovskite film before and after surface passivation treatment. Solution-processing leads to multi-faceted polycrystalline films which tend to exhibit numerous surface defects such as under-coordinated lead. In addition, the latter is caused by high temperature annealing steps in which the iodide ions can be driven off as iodine. As a result of this under-coordination, the positive charge of the divalent lead cation is not fully compensated by the neighboring anions leading to a small net positive charge (δ^+) in the vicinity of the lead. This constitutes an effective Coulomb trap for electrons (red hollow box). The $\text{Mo}(\text{tfd-COCF}_3)_3$ complex possesses sulfur atoms with two sets of lone pair electrons (yellow spheres) whose negative charge can compensate for the δ^+ by forming a dative bond while delocalising the positive charge within the Mo molecule.

6.3.3 Creation of a dipole at the perovskite surface

In order to investigate the effect of the molybdenum complex on the surface of the absorber, Kelvin Probe (KP) photovoltage measurements were performed to determine the work function of the perovskite (Figure 6.6 and Table 6.1). The films were prepared similarly to PL samples however, because KP measurements rely on the surface potential of the probed material, no PMMA coating was deposited onto the perovskite.

Measuring the work function of perovskite before and after treatment reveals a significant shift of the Fermi energy away from the vacuum, which is typically considered as "*p*-doping" the surface. The work function of treated the perovskite decreased by -300 meV at 0.0001 wt.% as compared to the control (-4.62 eV), then gradually shifted down to -5.12 eV for the highest concentration. As a strong electron-acceptor, due to the presence of electron-withdrawing CF₃ groups [180], the Mo(tfd-COCF₃)₃ complex could remove electrons from the perovskite surface leading to an excess of holes at the treated interface. When the work function of the Mo(tfd-COCF₃)₃ is measured independently of the perovskite, its Fermi energy lies at -5.44 eV. Therefore, the deeper work function of the dopant would allow an energetically favorable transfer of electrons from the perovskite to the molybdenum complex, consistent with the observed *p*-doping of the surface. When the Mo(tfd-COCF₃)₃ withdraws electrons from the perovskite, holes are left behind and accumulate at the surface of the perovskite. Here, holes remain in the perovskite close to the interface while Mo(tfd-COCF₃)₃ anions lie at the surface forming an interfacial dipole layer at the perovskite/Mo(tfd-COCF₃)₃ interface. A gradient of charges is created which results in an enhanced electric field in this region. Consequently, the bands bend upwards thus improving hole extraction at the interface.

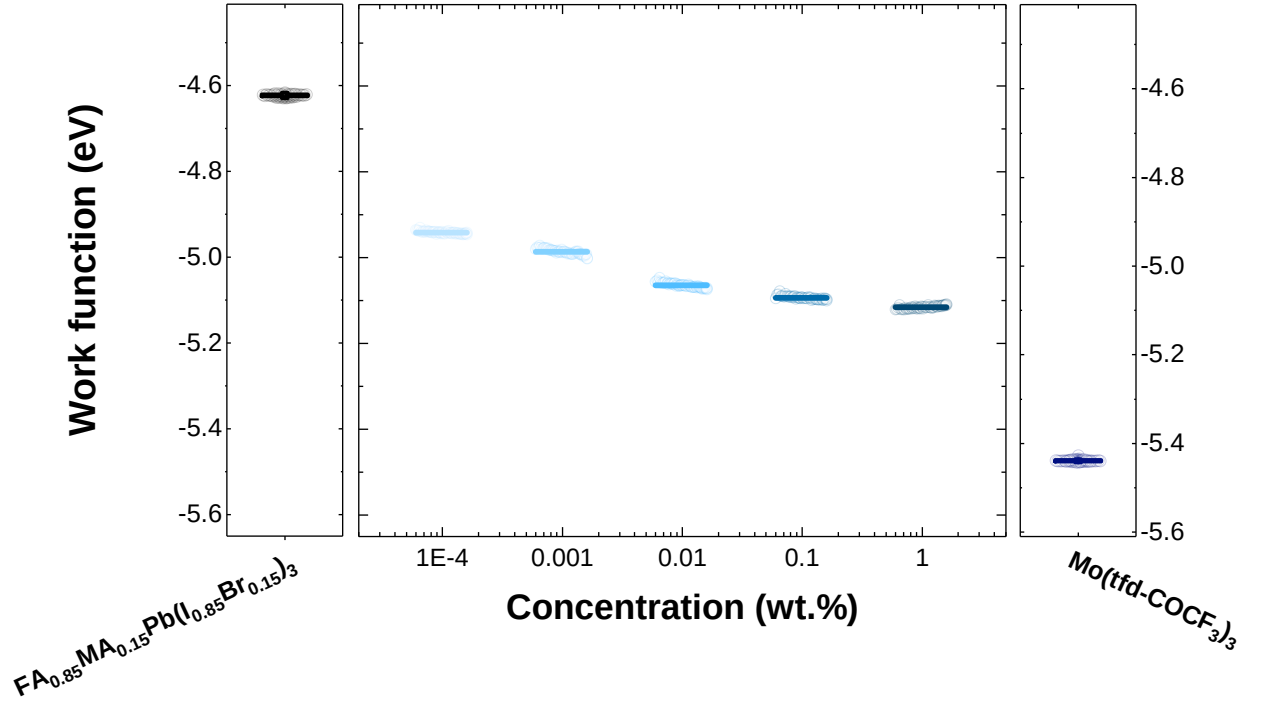


Figure 6.6: Work function determination by Kelvin probe measurements. A bare perovskite film was taken as the reference on which neat chlorobenzene was spincoated on top in order to account for solvent washing effect. Upon treatment, the work function of the perovskite shift towards its valence band providing evidence for *p*-doping at the interface. Measurements were taken by Dr Yen-Hung Lin (Imperial College London).

	Concentration [wt.%]	Work function [eV]
$\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$	-	-4.62
$\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ treated with $\text{Mo}(\text{tfd-COCF}_3)_3$	0.0001	-4.94
	0.001	-4.99
	0.01	-5.06
	0.1	-5.09
	1	-5.12
$\text{Mo}(\text{tfd-COCF}_3)_3$	0.1	-5.44

Table 6.1: Values of the work function measured by Kelvin probe extracted from Figure 6.6.

6.3.4 Diode characteristics

To assess the impact of $\text{Mo}(\text{tfd-COCF}_3)_3$ on the charge extraction in devices, the current-voltage characteristic of devices without charge selective contacts were investigated. In this configuration, the perovskite absorber was directly sandwiched between the FTO and a gold electrode. The JV-characteristics were measured after stabilising the devices in forward and

reverse biased for 5 seconds, under both illumination and dark conditions (Figure 6.7).

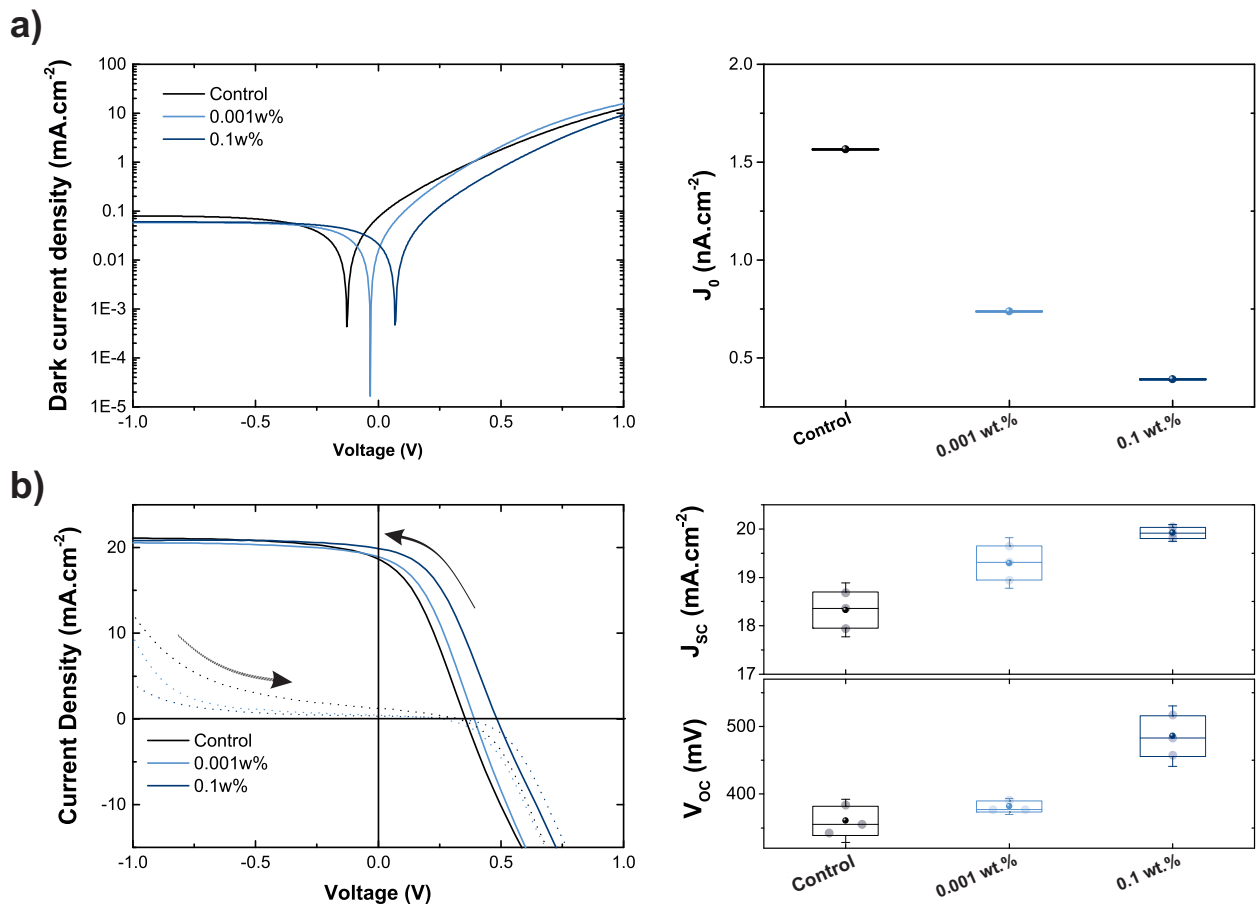


Figure 6.7: Comparison of untreated and $\text{Mo}(\text{dt})_3$ -treated perovskite devices without charge selective contacts. a) Under dark conditions, treated perovskite showed a reduction of the reverse saturation current (J_0), evidence of lower recombination losses and/or a enhanced selectivity for holes. b) Current-voltage characteristics taken under light revealed an enhancement of both J_{SC} and V_{OC} after surface treatment.

The dark current density as a function of the applied voltage is represented in Figure 6.7a. The dark current characteristics were fitted to the ideal diode equation (2.31) introduced in Chapter 2 in order to extract the reverse saturation current (J_0). $\text{Mo}(\text{dt})_3$ -treated perovskite yielded to J_0 values of 7.4×10^{-10} and $3.9 \times 10^{-10} \text{ A}\cdot\text{cm}^{-2}$ for 0.001 wt.% and 0.1 wt.% respectively, values lower than the untreated control for which $J_0 = 1.4 \times 10^{-9} \text{ A}\cdot\text{cm}^{-2}$. This reduction of the reverse saturation current showed that either the recombination pathways were minimised, the treated interface became more selective for holes, or a combination of both, which should result in an improved diode behaviour.

Under illumination, all devices showed good rectification, nonetheless an increase in both J_{SC} and V_{OC} was observed for $\text{Mo}(\text{dt})_3$ -treated devices. The lowest concentration had a

greater impact on the J_{SC} , consistent with a passivation of trap states, while higher dopant concentration significantly boosts the V_{OC} , evidence for a more efficient hole extraction at the treated interface. These findings agree with both PL and KP measurements, overall indicating that treating the perovskite with $Mo(tfd-COCF_3)_3$ simultaneously minimises trap-mediated recombination centers and locally shifts the Fermi energy of the perovskite away from vacuum due to the high electron affinity of the complex. Upon removing electrons from the valence band of the perovskite the Mo-anion becomes electrostatically bound to the surface, thus an interfacial dipole is created which leads to a local enhancement of the electric field and an upward band bending. Accordingly, a greater fraction of generated charges can be extracted (*i.e.* increased J_{SC}), and the charge selectivity at the p -type interface is enhanced (*i.e.* increased V_{OC}).

6.3.5 Solar cell performance

Having shown that $Mo(tfd-COCF_3)_3$ had a positive impact in devices without selective contacts, full perovskite solar cells using the $n-i-p$ architecture were fabricated in order to investigate the influence of the surface treatment on the device performance. Devices were prepared according to the methods described in Chapter 3, using the mixed halide perovskite $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ as the absorber. After formation of the perovskite layer, the solution of $Mo(tfd-COCF_3)_3$ was deposited as previously explained in Section 6.3.1. Three concentrations were chosen: 0.00001 wt.%, 0.0001 wt.% and 0.1 wt.%. An untreated device was kept as a control. In order to rule out the doping effect of the $Mo(tfd-COCF_3)_3$ complex on the spiro-OMeTAD, the HTM was oxidised prior to deposition with a dicationic salt of spiro-OMeTAD (Spiro(TFSI)₂) [79] to a concentration of 5 mol%. After addition of the TFSI salts, the solution was kept stirring at room temperature for 12 hours to fully oxidise the spiro-OMeTAD, then spin-coated dynamically to minimise losses of the $Mo(dt)_3$ at the treated interface. Furthermore, since the commonly employed tBP additive has been showed to affect the steady-state charge-collection efficiency of perovskite solar cells by making the HTM/perovskite interface more selective for holes [132], in this study, tBP was not added

to the HTM solution to observe solely the effect of the molybdenum complex. Finally, the devices were completed with evaporation of gold electrodes. The scanned and steady-state performances are reported in Figure 6.8 and Table 6.2.

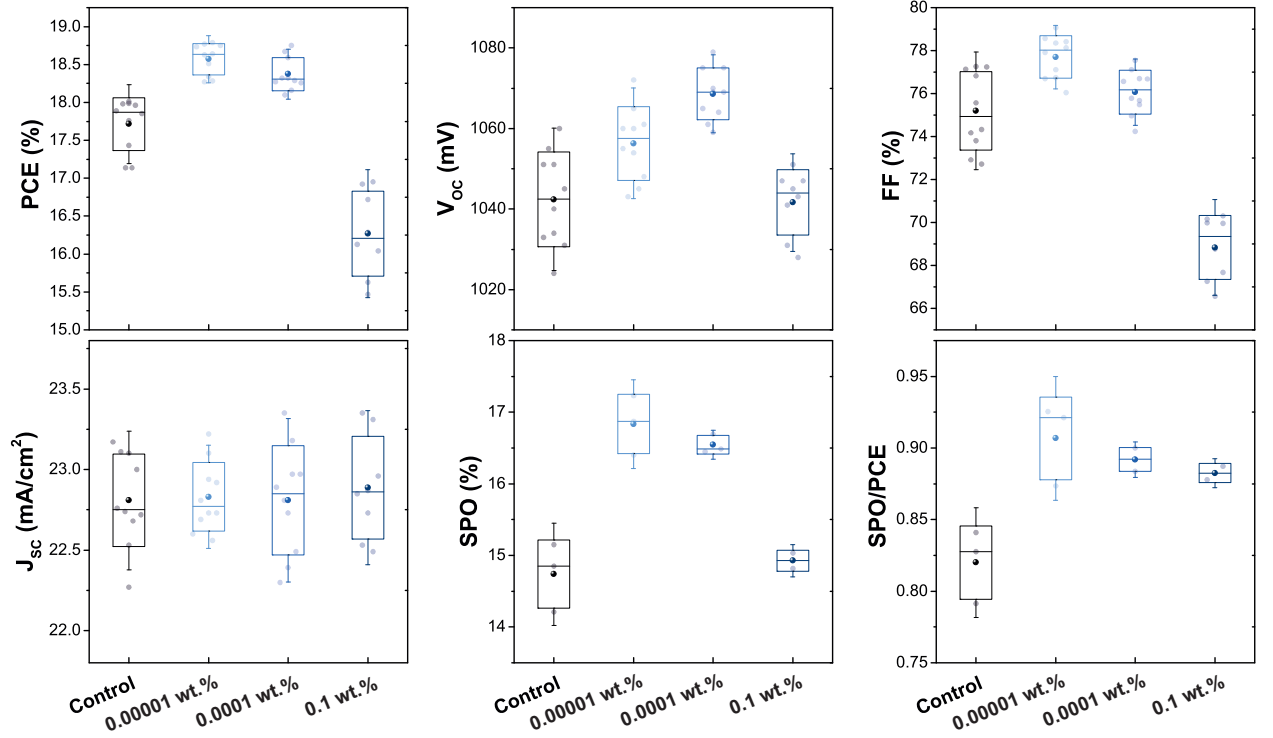


Figure 6.8: Scanned and steady-state performances for devices with untreated (control) and treated perovskite with Mo(tfd-COCF₃)₃ at various concentrations.

	Concentration [wt.%]	J _{sc} [mA·cm ⁻²]	V _{oc} [mV]	FF [%]	PCE [%]	R _s [Ω·cm ⁻²]	SPO [%]	SPO/PCE
Control	-	22.8 ± 0.3	1042 ± 12	75.2 ± 1.8	17.7 ± 0.3	3.2 ± 0.7	14.7 ± 0.5	0.82 ± 0.03
	0.00001	22.8 ± 0.2	1056 ± 9	77.7 ± 1.0	18.6 ± 0.2	2.3 ± 0.3	16.8 ± 0.4	0.91 ± 0.03
Mo(tfd-COCF ₃) ₃	0.0001	22.8 ± 0.3	1069 ± 6	76.1 ± 1.0	18.4 ± 0.2	3.0 ± 0.6	16.5 ± 0.1	0.89 ± 0.01
	0.1	22.9 ± 0.3	1042 ± 8	68.8 ± 1.5	16.3 ± 0.6	3.0 ± 0.5	14.9 ± 0.1	0.88 ± 0.01

Table 6.2: Average device performance parameters with standard deviation comparing untreated and Mo(dt)₃-treated devices. Values extracted from Figure 6.8

At low concentrations, while the scanned efficiencies of Mo(tfd)₃-treated devices only show a slight increase in performance (1% on average) compared to the untreated control devices, the steady-state efficiencies consistently outperformed those of the control. Both 0.00001 wt.% and 0.0001 wt.% lead to SPOs close to 16.5% on average, which corresponds to a 2% increase in performance from the untreated control which stabilises at 14.7%. Since the J_{sc} remains constant across all the samples (22.8 mA·cm⁻²), the enhancement in performance arises from and increase in both the V_{oc} and the FF. These observations would suggest

that in devices when a HTM is deposited on top of the treated perovskite, the "*p*-doping" of the interface might predominate over the passivation effect leading to an increased charge selectivity at the perovskite/HTM interface. Increasing concentrations of dopant lead to the formation of thicker layers at the interface which creates an energy barrier and hampers the charge transfer from the perovskite to the HTM. Overall, this results in a drop in FF and thus, poorer device performance.

The current-voltage characteristics and the stabilised efficiencies of the champion devices are shown in Figure 6.9. Both devices produce scanned efficiency close to 18%, however show current-voltage hysteresis with and without treatment. Nonetheless, in the case of the treated perovskite (0.00001 wt.%), the SPO is noticeably improved with respect to the untreated control. With a steady-state efficiency of 17.2%, Mo(tfd)₃-treated devices yield to an increase of 2% in SPO with respect to the control. The hysteretic behaviour is substantially decreased in treated devices which can be explained by the enhanced charge separation at the perovskite/HTM interface consistent with the local shift of the work function determined by KP measurements.

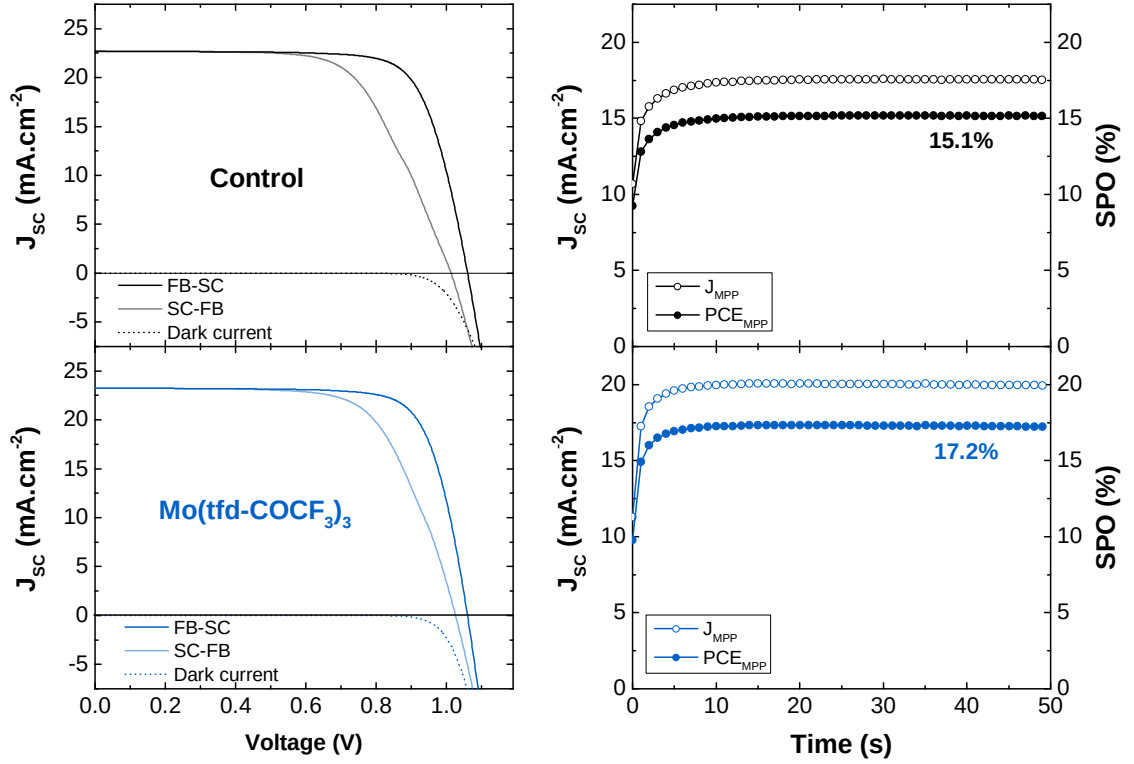


Figure 6.9: Current density-voltage characteristics of the champion devices with their respective stabilised photocurrent densities and efficiencies measured by holding the devices at their J-V determined maximum power point for 50 seconds. An untreated control device is compared to a Mo(tfd)₃-treated device at a concentration of 0.00001 wt.%.

	PCE [%]		V_{oc} [mV]		J_{sc} [mA.cm ⁻²]		FF [%]		R_s [Ω .cm ⁻²]		SPO [%]	SPO/PCE
	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB	FB-SC	SC-FB		
Control	18.0	14.7	1060	1013	22.7	22.7	0.76	0.64	3.0	4.9	15.1	0.84
Mo(tfd-COCF ₃) ₃	18.7	15.9	1060	1026	23.2	23.2	0.77	0.67	2.2	4.1	17.2	0.92

Table 6.3: Device performance parameters of champion devices presented in Figure 6.9. FB-SC: Forward-Bias to Short-Circuit; SC-FB: Short-Circuit to Forward-Bias.

6.4 Conclusion and outlook

In summary, a $\text{Mo}(\text{tfd-COCF}_3)_3$ layer was introduced at the *p*-type interface in perovskite solar cells to directly study its interaction with the perovskite surface. At an optimised concentration, the molybdenum complex appears to reduce the density of electronic trap sites at the surface of the perovskite, and also modifies the absorber/HTM interface, such that there is an increase in hole selectivity. These modifications result in greatly improved steady-state efficiencies, underscoring the importance of the charge-selective interfaces for charge extraction.

Photoluminescence measurements show increases in both the PL quantum yield and the PL lifetime when the perovskite was treated with the $\text{Mo}(\text{dt})_3$ molecule at low concentrations (0.0001 wt.%) with respect to an untreated perovskite. These results provide evidence for a reduction in non-radiative losses, indicating an effective passivation of trap sites at the surface of the perovskite. One potential explanation for this passivation could be the formation of a dative covalent bond between the lone pair electrons on the sulfur atoms of the $\text{Mo}(\text{tfd-COCF}_3)_3$ acting to neutralise a delta positive charge on the under-coordinated Pb atoms.

Kelvin probe studies reveal a shift of the Fermi level away from vacuum when the perovskite surface is treated with $\text{Mo}(\text{dt})_3$, evidence for an interfacial *p*-doping. As a result, devices without charge selective contacts show a reduction of the reverse saturation current and an enhancement in both J_{SC} and V_{OC} after the treatment of the perovskite surface. In complete *n-i-p* perovskite solar cells, $\text{Mo}(\text{dt})_3$ -treated devices show an important reduction of the hysteresis leading to an enhancement of the steady-efficiency from 15.1% to 17.2%. As a strong electron acceptor molecule, $\text{Mo}(\text{tfd-COCF}_3)_3$ can remove an electron from the valence band of the perovskite. This electron transfer can result in the formation of the Mo-anion which would then remain electrostatically bound to the perovskite creating a surface dipole. Consequently, the bands bend upwards inhibiting the diffusion of electrons and improving the extraction of holes extraction at the treated interface.

These findings demonstrate that a slight chemical modification of the interface between

the perovskite and the HTM can improve the device performance, and highlights the crucial importance of the charge-selective interfaces on the steady-state performances of perovskite solar cells.

7 | Conclusion and Outlook

The work presented in this thesis has been focused on the development of new hole-extracting layers which increase the stability of the device while maintaining high efficiencies. Perovskite based photovoltaic solar cells have the potential to revolutionise the energy market in the near future however, important challenges related to the long-term stability persist, most particularly due to the inherent moisture vulnerability of these materials. In order for the technology to be commercially viable, solar cells have to undergo stressing tests such as thermal cycles, atmospheric moisture, UV irradiation and others, with a minimal loss in performance. While such harsh real-life tests can eventually be passed successfully by using existing encapsulation techniques, these encapsulants are costly and their use should be reduced in order to keep costs to a minimum. Thus, a low-cost strategy to enhance the moisture resilience of the devices, is to develop hole-extracting layers which fulfill the role of extracting carriers and serving as a physical barrier to water ingress. The work presented here has shown two new HTM structures which inhibit the moisture induced degradation of the perovskite absorber, and also shows an interfacial treatment technique to improve the performance of the solar cell.

In Chapter 4, the commonly employed spiro-OMeTAD HTM doped with Li-TFSI salts was successfully replaced by a composite HTM structure which contains P3HT nanowires (P3HT-NWs) embedded in an inert PMMA matrix. P3HT-NWs were formed by a process of heating then cooling in toluene, resulting in one-dimensional crystalline nanowires. In devices, the blend composite outperformed the neat P3HT HTM caused by an enhancement in V_{OC} and a reduction of the hysteresis. This yielded SPOs as high as 14.8% which corres-

ponds to an increase of 3% with respect to the neat P3HT HTM. In depth photoluminescence studies reveal a high luminescence of perovskite samples coated with the blends, which was attributed to a substantial reduction of non-radiative losses at the perovskite/HTM interface. Unlike any other contact so far employed in perovskite solar cells, this blend HTM does not induce substantial non-radiative decay channel. This was attributed to the discontinuities at the *p*-type interface which force holes to flow through extremely small pathways at the discrete NW-perovskite contact. Voluntarily reducing the contact area of the charge extracting layers has been extensively used in silicon photovoltaics, however no significant progress in that regard, has been made in perovskite solar cell technology. New lost-cost HTMs adopting this concept could be developed in the future, in order to increase the efficiency of perovskite solar cells. Moreover, the addition of inert compounds in HTM layers has a dual impact: it drastically reduces cost while improving the long-term stability of the devices, which makes conducting/insulating composite HTMs particularly attractive for industrial prospects.

With the goal of enhancing moisture resilience, the hygroscopic Li-TFSI *p*-dopant for spiro-OMeTAD, was substituted with two molybdenum tris(dithiolene)s complexes. As strong electron-acceptor materials, both Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ directly oxidise spiro-OMeTAD, unlike Li-TFSI which requires air exposure, leading to an increase in conductivity by up to four orders of magnitude compared to undoped spiro-OMeTAD. Mo(tfd-COCF₃)₃ and Mo(tfd-CO₂Me)₃ yielded 16.7% and 15.7% SPO, respectively, however these efficiencies remained slightly lower than the spiro-OMeTAD doped with Li-TFSI. This loss in performance mainly arose from a lower V_{OC} . In an attempt to recover this loss in voltage, the commonly employed *t*BP additive was added to the doped-HTM solutions. Indeed, *t*BP has been shown to have a highly beneficial impact on both the steady-state performance and the V_{OC} [132]. Adding *t*BP resulted in a dedoping of the HTM and hence reduced the photovoltaic performances. Thus, Mo(dt)₃ complexes were found to be incompatible with *t*BP, and searching alternative additives remains necessary in order to bring these dopants to a comparable level with lithium doping with regard to performances. Nonetheless, molybdenum tris(dithiolene)s remarkably improve the hydrophobicity of the HTM

layer which significantly enhanced the long-term stability of Mo(dt)₃-doped spiro-OMeTAD devices after exposure to thermal stressing in moist atmosphere for 500h. Therefore, it can be concluded that Mo(dt)₃ complexes are extremely promising candidates for replacing the current state-of-the-art dopants employed to *p*-dope the HTM. Coupled with more thermally stable perovskite absorber, these dopants should deliver further improvements in overall stability and promote the technology at an industrial level.

When used as a *p*-dopant for spiro-OMeTAD, the molybdenum tris(dithiolene)s complexes lead to impressive high steady-state performances without the need for the *t*BP additive. In Chapter 6, the effect of Mo(tfd-COCF₃)₃ on the perovskite's surface was studied in an attempt to elucidate the impact of the molecule on the charge extraction properties at the perovskite/HTM interface. Through photoluminescence measurements of perovskite treated with the molybdenum complex, a reduction of non-radiative recombination losses was observed associated with longer PL decay lifetimes and greater PL quantum yields. This findings suggested an effective passivation of trap states by the molybdenum molecule, possibly via covalent bonding as previously reported by Noel *et al.* [159]. In addition, a significant shift of the workfunction away from vacuum indicates a *p*-doping of the perovskite surface. Consequently, treating the perovskite/HTM interface with Mo(tfd-COCF₃)₃ resulted in improved device performance from 15.1% to 17.2%. The work presented in this chapter stresses that despite tremendous efforts to perfect the perovskite absorber itself, one of the main limitation to high performance lies at the interfaces with charge extraction layers. Thus, understanding and controlling interfaces are expected to play a crucial role in the future development of perovskite solar cells.

A | Publications

SANDEEP PATHAK, NOBUYA SAKAI, FLORENCIA W. R. RIVAROLA, SAMUEL D. STRANKS, JIEWEI LIU, GILES E. EPERON, CATERINA DUCATI, KONRAD WOJCIECHOWSKI, JAMES T. GRIFFITHS, AMIR A. HAGHIGHIRAD, ALBA PELLAROQUE, RICHARD H. FRIEND, HENRY J. SNAITH, Perovskite Crystals for Tunable White Light Emission, *Chemistry of Materials*, 27, 23, (2015) 8066-8075

ALBA PELLAROQUE, NAKITA K. NOEL, SEVERIN N. HABISREUTINGER, YADONG ZHANG, STEPHEN BARLOW, SETH R. MARDER & HENRY J. SNAITH, Efficient and Stable Perovskite Solar Cells Using Molybdenum Tris(dithiolene)s as *p*-Dopants for Spiro-OMeTAD *ACS Energy Letters*, 2, (2017) 2044-2050

B | Conferences

B.1 Oral presentations

Use of new molybdenum complexes to *p*-dope spiro-OMeTAD in perovskite solar cells, *Hybrid & Organic Photovoltaics (HOPV)*, Swansea, UK, 2016

Improved stability of perovskite solar cells using Molybdenum Tris(dithiolene)s as *p*-dopants for spiro-OMeTAD, *International Conference on Perovskite Solar Cells and Optoelectronics (PSCO)*, Genova, Italy, 2016

B.2 Posters

Limiting non-radiative pathways in organic-inorganic perovskite solar cells, *Hybrid & Organic Photovoltaics (HOPV)*, Rome, Italy, 2015

Molybdenum Tris(dithiolene)s as *p*-dopants for spiro-OMeTAD, *International Conference on Perovskite Solar Cells and Optoelectronics (PSCO)*, Genova, Italy, 2016

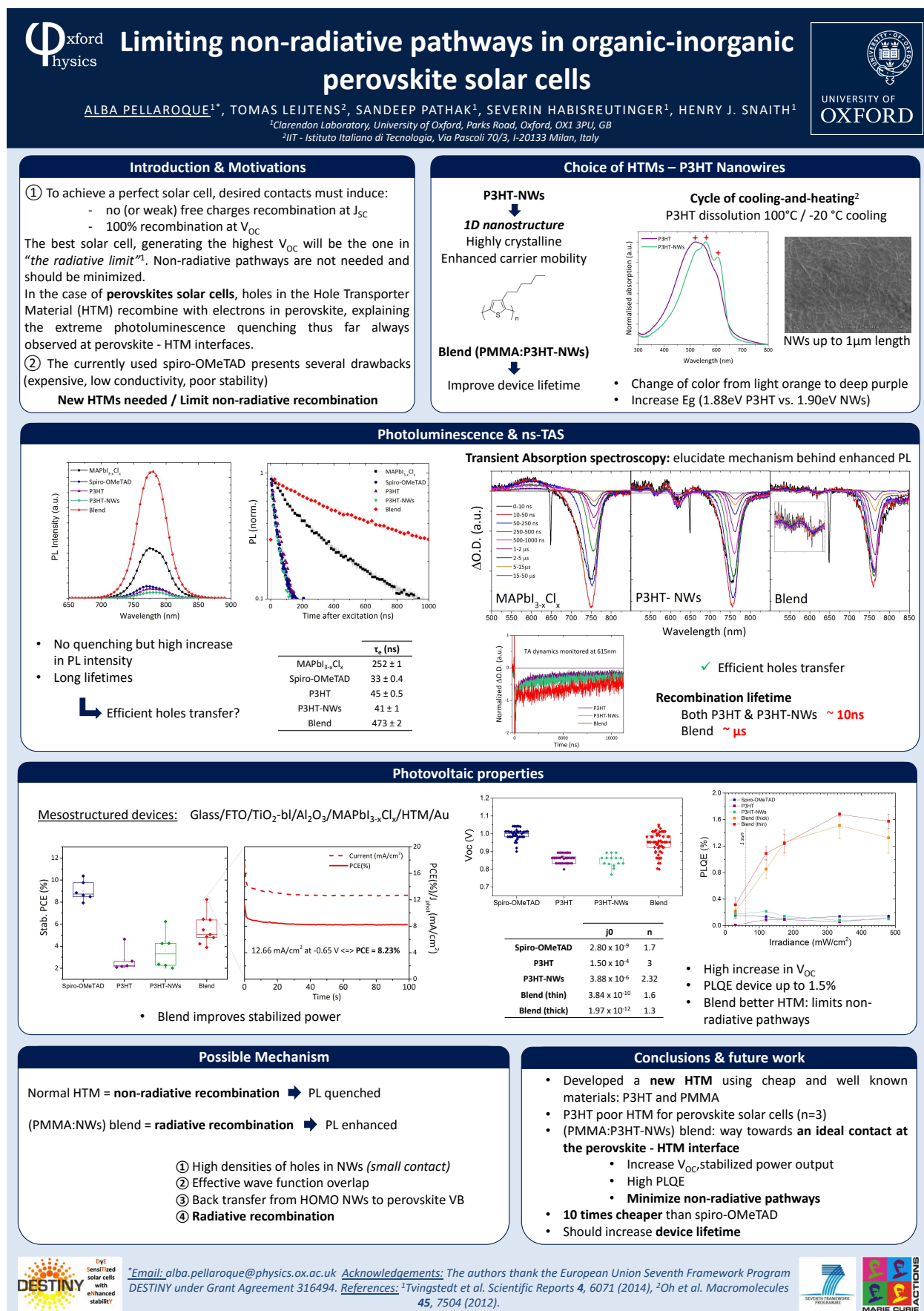


Figure B.1: Poster based on work described in Chapter 4. Presented at the international conference for Hybrid & Organic Photovoltaics (HOPV15), 2015, Rome, Italy.

Bibliography

- [1] GISTEMP-Team.
- [2] United Nations. ISSN 10187081.
- [3] Owen Gaffney & Will Steffen. *The Anthropocene Review*, **4**, 1 (2017) 53–61. ISSN 2053-0196.
- [4] BP. *British Petroleum*, , 66 (2017) 1–52. ISSN 1098-6596.
- [5] Nathan S. Lewis, George Crabtree, Arthur J Nozik, Michael R Wasielewski & Paul Alivisatos. *Basic Energy Sciences Workshop on Solar Energy Utilization*, page 276.
- [6] REN 21. “Renewables 2017: global status report” (2017). ISBN 9783981810769.
- [7] Ran Fu, Donald Chung, Travis Lowder, David Feldman, Kristen Ardani, Ran Fu, Donald Chung, Travis Lowder, David Feldman & Kristen Ardani. *NREL Technical Report*, , September.
- [8] Martin Schachinger. “Module price index” (2017).
- [9] National Renewable Energy Laboratory. “NREL Efficiency Chart”.
- [10] Qi Jiang, Zema Chu, Pengyang Wang, Xiaolei Yang, Heng Liu, Ye Wang, Zhigang Yin, Jinliang Wu, Xingwang Zhang & Jingbi You. *Advanced Materials*, **1703852** (2017) 1703852. ISSN 09359648.
- [11] Jian Gong, Seth B. Darling & Fengqi You. *Energy Environ. Sci.*, **8**, 7 (2015) 1953–1968. ISSN 1754-5692.
- [12] Simon M. Sze & Kwok K. Ng. “Physics of semiconductor devices”. Wiley-Interscience, 3rd editio edition (2006). ISBN 978-0-471-14323-9.
- [13] Peter Wurfel. “Physics of Solar Cells”. Wiley-VCH Verlag GmbH (2009). ISBN 978-3-527-40857-3.
- [14] Jenny Nelson. “The Physics of Solar Cells”. Imperial College Press (2003). ISBN 978-1-86094-340-9.

-
- [15] Wolfgang Tress. “Organic Solar Cells”, volume 208 of *Springer Series in Materials Science*. Springer International Publishing, Cham (2014). ISBN 978-3-319-10096-8.
- [16] Paolo Umari, Edoardo Mosconi & Filippo De Angelis. *Scientific Reports*, **4** (2014) 4467. ISSN 2045-2322.
- [17] Giacomo Giorgi, Jun-Ichi Fujisawa, Hiroshi Segawa & Koichi Yamashita. *The Journal of Physical Chemistry Letters*, **4**, 24 (2013) 4213–4216. ISSN 1948-7185.
- [18] Lucy D. Whalley, Jarvist M. Frost, Young-Kwang Jung & Aron Walsh. *The Journal of Chemical Physics*, **146**, 22 (2017) 220901. ISSN 0021-9606.
- [19] William Shockley & Hans J. Queisser. *Journal of Applied Physics*, **32**, 3 (1961) 510–519. ISSN 0021-8979.
- [20] Samuel D. Stranks, Victor M. Burlakov, Tomas Leijtens, James M. Ball, Alain Goriely & Henry J. Snaith. *Physical Review Applied*, **2**, 3 (2014) 034007. ISSN 2331-7019.
- [21] Samuel D. Stranks. *ACS Energy Letters*, **2**, 7 (2017) 1515–1525. ISSN 2380-8195.
- [22] Michele Saba, Michele Cadelano, Daniela Marongiu, Feipeng Chen, Valerio Sarritzu, Nicola Sestu, Cristiana Figus, Mauro Aresti, Roberto Piras, Alessandra Geddo Lehmann, Carla Cannas, Anna Musinu, Francesco Quochi, Andrea Mura & Giovanni Bongiovanni. *Nature Communications*, **5**, May (2014) 5049. ISSN 2041-1723.
- [23] Alison Walker, Henry Snaith, Filippo De Angelis & Enrico Da Como. “Unconventional Thin Film Photovoltaics”. Royal Society of Chemistry, Cambridge (2016). ISBN 978-1-78262-293-2.
- [24] Wei Zhang, Sandeep Pathak, Nobuya Sakai, Thomas Stergiopoulos, Pabitra K. Nayak, Nakita K. Noel, Amir A. Haghighirad, Victor M. Burlakov, Dane W. DeQuilettes, Aditya Sadhanala, Wenzhe Li, Liduo Wang, David S. Ginger, Richard H. Friend & Henry J. Snaith. *Nature Communications*, **6** (2015) 10030. ISSN 2041-1723.
- [25] Dane W. DeQuilettes, Wei Zhang, Victor M. Burlakov, Daniel J. Graham, Tomas Leijtens, Anna Osherov, Vladimir Bulović, Henry J. Snaith, David S. Ginger & Samuel D. Stranks. *Nature Communications*, **7**, May (2016) 11683. ISSN 2041-1723.
- [26] D. E. Aspnes, A. A. Studna & E. Kinsbron. *Physical Review B*, **29**, 2 (1984) 768–779. ISSN 0163-1829.
- [27] J. S. Blakemore. *Journal of Applied Physics*, **53**, 10 (1982) R123–R181. ISSN 0021-8979.
- [28] Christoph Brabec, Ullrich Scherf & Vladimir Dyakonov. “Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies” (2014). ISBN 978-3-527-33225-0.
- [29] David B. Mitzi. “Synthesis, Structure, and Properties of Organic-Inorganic Perovskites and Related Materials”. In “Progress in inorganic chemistry”, volume 47, pages 1–121 (2007).

-
- [30] Giles E. Eperon, Samuel D. Stranks, Christopher Menelaou, Michael B. Johnston, Laura M. Herz & Henry J. Snaith. *Energy & Environmental Science*, **7**, 3 (2014) 982. ISSN 1754-5692.
- [31] Giles E. Eperon, Giuseppe M. Paternò, Rebecca J Sutton, Andrea Zampetti, Amir Abbas Haghighirad, Franco Cacialli & Henry J. Snaith. *J. Mater. Chem. A*, **3**, 39 (2015) 19688–19695. ISSN 2050-7488.
- [32] Michael M Lee, Joël Teuscher, Tsutomu Miyasaka, Takuro N Murakami & Henry J Snaith. *Science*, **338**, 6107 (2012) 643–647. ISSN 0036-8075.
- [33] Nakita K. Noel, Samuel D. Stranks, Antonio Abate, Christian Wehrenfennig, Simone Guarnera, Amir-abbas Haghighirad, Aditya Sadhanala, Giles E. Eperon, Sandeep K. Pathak, Michael B. Johnston, Annamaria Petrozza, Laura M. Herz & Henry J. Snaith. *Energy Environ. Sci.*, **7**, 9 (2014) 3061–3068. ISSN 1754-5692.
- [34] Stefaan De Wolf, Jakub Holovsky, Soo-Jin Moon, Philipp Löper, Bjoern Niesen, Martin Ledinsky, Franz-Josef Haug, Jun-Ho Yum & Christophe Ballif. *The Journal of Physical Chemistry Letters*, **5**, 6 (2014) 1035–1039. ISSN 1948-7185.
- [35] Samuel D Stranks, Giles E Eperon, Giulia Grancini, Christopher Menelaou, Marcelo J P Alcocer, Tomas Leijtens, Laura M Herz, Annamaria Petrozza & Henry J Snaith. *Science (New York, N. Y.)*, **342**, 6156 (2013) 341–344. ISSN 1095-9203.
- [36] T. Jesper Jacobsson, Juan-Pablo Correa-Baena, Meysam Pazoki, Michael Saliba, Kurt Schenk, Michael Grätzel & Anders Hagfeldt. *Energy Environ. Sci.*, **9**, 5 (2016) 1706–1724. ISSN 1754-5692.
- [37] Aditya Sadhanala, Shahab Ahmad, Baodan Zhao, Nadja Giesbrecht, Phoebe Pearce, Felix Deschler, Robert L.Z. Hoyer, Karl C Goedel, Thomas Bein, Pablo Docampo, Siân E. Dutton, Michael De Volder & Richard H. Friend. *Nano Letters*, page 150803110321002. ISSN 1530-6984.
- [38] Jun Hong Noh, Sang Hyuk Im, Jin Hyuck Heo, Tarak N Mandal & Sang Il Seok. *Nano letters*, **13**, 4 (2013) 1764–9. ISSN 1530-6992.
- [39] Dong Myung Jang, Kidong Park, Duk Hwan Kim, Jeunghye Park, Fazel Shojaei, Hong Seok Kang, Jae-Pyoung Pyung Ahn, Jong Woon Lee & Jae Kyu Song. *Nano Letters*, **15**, 8 (2015) 5191–5199. ISSN 1530-6984.
- [40] Feng Hao, Constantinos C Stoumpos, Duyen Hanh Cao, Robert P H Chang & Mercuri G Kanatzidis. *Nature Photonics*, **8**, 6 (2014) 489–494. ISSN 1749-4885.
- [41] Feng Hao, Constantinos C. Stoumpos, Robert P H Chang & Mercuri G. Kanatzidis. *Journal of the American Chemical Society*, **136**, 22 (2014) 8094–8099. ISSN 15205126.
- [42] Constantinos C. Stoumpos, Christos D. Malliakas & Mercuri G. Kanatzidis. *Inorganic Chemistry*, **52**, 15 (2013) 9019–9038. ISSN 00201669.

-
- [43] Christian Wehrenfennig, Giles E. Eperon, Michael B. Johnston, Henry J. Snaith & Laura M. Herz. *Advanced Materials*, **26**, 10 (2014) 1584–1589. ISSN 15214095.
- [44] Thomas M. Brenner, David A. Egger, Andrew M. Rappe, Leeor Kronik, Gary Hodes & David Cahen. *The Journal of Physical Chemistry Letters*, **6**, 23 (2015) 4754–4757. ISSN 1948-7185.
- [45] Guichuan Xing, Nripan Mathews, Shuangyong Sun, Swee Sien Lim, Yeng Ming Lam, M. Gratzel, Subodh Mhaisalkar & Tze Chien Sum. *Science*, **342**, 6156 (2013) 344–347. ISSN 0036-8075.
- [46] Michael B. Johnston & Laura M. Herz. *Accounts of Chemical Research*, **49**, 1 (2016) 146–154. ISSN 0001-4842.
- [47] Atsuhiko Miyata, Anatolie Mitioglu, Paulina Plochocka, Oliver Portugall, Jacob Tse-wei Wang, Samuel D Stranks, Henry J Snaith & Robin J Nicholas. *Nature Physics*, **11**, 7 (2015) 582–587. ISSN 1745-2473.
- [48] Giulia Grancini, Ajay Ram Srimath Kandada, Jarvist M Frost, Alex J Barker, Michele De Bastiani, Marina Gandini, Sergio Marras, Guglielmo Lanzani, Aron Walsh & Annamaria Petrozza. *Nat Photon*, **9**, 10 (2015) 695–701. ISSN 1749-4885.
- [49] a Kojima, K Teshima, Y Shirai & T Miyasaka. *Private Communication*, **1** (2009) 1. ISSN 0002-7863.
- [50] Jeong-Hyeok Im, Chang-Ryul Lee, Jin-Wook Lee, Sang-Won Park & Nam-Gyu Park. *Nanoscale*, **3**, 10 (2011) 4088. ISSN 2040-3364.
- [51] Hui-Seon Kim, Chang-Ryul Lee, Jeong-Hyeok Im, Ki-Beom Lee, Thomas Moehl, Arianna Marchioro, Soo-Jin Moon, Robin Humphry-Baker, Jun-Ho Yum, Jacques E Moser, Michael Grätzel & Nam-Gyu Park. *Scientific Reports*, **2**, 1 (2012) 591. ISSN 2045-2322.
- [52] Lioz Etgar, Peng Gao, Zhaosheng Xue, Qin Peng, Aravind Kumar Chandiran, Bin Liu, Md K. Nazeeruddin & Michael Grätzel. *Journal of the American Chemical Society*, **134**, 42 (2012) 17396–17399. ISSN 0002-7863.
- [53] Mingzhen Liu, Michael B Johnston & Henry J Snaith. *Nature*, **501**, 7467 (2013) 395–398. ISSN 0028-0836.
- [54] Giles E. Eperon, Victor M. Burlakov, Pablo Docampo, Alain Goriely & Henry J. Snaith. *Advanced Functional Materials*, **24**, 1 (2013) n/a–n/a. ISSN 1616301X.
- [55] Zhengguo Xiao, Cheng Bi, Yuchuan Shao, Qingfeng Dong, Qi Wang, Yongbo Yuan, Chenggong Wang, Yongli Gao & Jinsong Huang. *Energy Environ. Sci.*, **7**, 8 (2014) 2619–2623. ISSN 1754-5692.
- [56] Pablo Docampo, James M Ball, Mariam Darwich, Giles E Eperon & Henry J Snaith. *Nature Communications*, **4** (2013) 2761. ISSN 2041-1723.

- [57] Ruoxi Yang, Jonathan M. Skelton, E. Lora da Silva, Jarvist M. Frost & Aron Walsh. *Journal of Physical Chemistry Letters*, **8** (2017) 4720–2726. ISSN 1948-7185.
- [58] Cristina Momblona, Lidón Gil-Escrig, Enrico Bandiello, Eline M. Hutter, Michele Sessolo, Kay Lederer, Jan Blochwitz-Nimoth & Henk J. Bolink. *Energy Environ. Sci.*, **9**, 11 (2016) 3456–3463. ISSN 1754-5692.
- [59] Yanbo Li, Jason K. Cooper, Raffaella Buonsanti, Cinzia Giannini, Yi Liu, Francesca M. Toma & Ian D. Sharp. *The Journal of Physical Chemistry Letters*, **6**, 3 (2015) 493–499. ISSN 1948-7185.
- [60] Julian Burschka, Norman Pellet, Soo-Jin Moon, Robin Humphry-Baker, Peng Gao, Mohammad K Nazeeruddin & Michael Grätzel. *Nature*, **499**, 7458 (2013) 316–319. ISSN 0028-0836.
- [61] Qi Chen, Huanping Zhou, Ziruo Hong, Song Luo, Hsin-Sheng Duan, Hsin-Hua Wang, Yongsheng Liu, Gang Li & Yang Yang. *Journal of the American Chemical Society*, **136**, 2 (2014) 622–625. ISSN 0002-7863.
- [62] Nam Joong Jeon, Jun Hong Noh, Young Chan Kim, Woon Seok Yang, Seungchan Ryu & Sang Il Seok. , July (2014) 1–7.
- [63] Regan Arndt & R Puto. *TUV America*, , 978 (2010) 1–15.
- [64] Teck Ming Koh, Kunwu Fu, Yanan Fang, Shi Chen, T. C. Sum, Nripan Mathews, Subodh G. Mhaisalkar, Pablo P. Boix & Tom Baikie. *Journal of Physical Chemistry C*, **118**, 30 (2014) 16458–16462. ISSN 19327455.
- [65] Andreas Binek, Fabian C. Hanusch, Pablo Docampo & Thomas Bein. *The Journal of Physical Chemistry Letters*, **6**, 7 (2015) 150316103833007. ISSN 1948-7185.
- [66] Norman Pellet, Peng Gao, Giuliano Gregori, Tae Youl Yang, Mohammad K. Nazeeruddin, Joachim Maier & Michael Grätzel. *Angewandte Chemie - International Edition*, **53**, 12 (2014) 3151–3157. ISSN 15213773.
- [67] Nam Joong Jeon, Jun Hong Noh, Woon Seok Yang, Young Chan Kim, Seungchan Ryu, Jangwon Seo & Sang Il Seok. *Nature*, **517**, 7535 (2015) 476–480. ISSN 0028-0836.
- [68] Michael Saliba, Taisuke Matsui, Ji-Youn Seo, Konrad Domanski, Juan-Pablo Correa-Baena, Mohammad Khaja Nazeeruddin, Shaik M. Zakeeruddin, Wolfgang Tress, Antonio Abate, Anders Hagfeldt & Michael Grätzel. *Energy Environ. Sci.*, **9**, 6 (2016) 1989–1997. ISSN 1754-5692.
- [69] Michael Saliba, Simonetta Orlandi, Taisuke Matsui, Sadig Aghazada, Marco Cavazzini, Juan-Pablo Correa-Baena, Peng Gao, Rosario Scopelliti, Edoardo Mosconi, Klaus-Hermann Dahmen, Filippo DeAngelis, Antonio Abate, Anders Hagfeldt, Gianluca Pozzi, Michael Graetzel & Mohammad Khaja Nazeeruddin. *Nature Energy*, page 15017. ISSN 2058-7546.

- [70] Tom Baikie, Yanan Fang, Jeannette M. Kadro, Martin Schreyer, Fengxia Wei, Subodh G. Mhaisalkar, Michael Graetzel & Tim J. White. *Journal of Materials Chemistry A*, **1**, 18 (2013) 5628. ISSN 2050-7488.
- [71] Jinli Yang, Braden D Siempelkamp, Dianyí Liu & Timothy L Kelly. *ACS Nano*, **9**, 2 (2015) 1955–1963. ISSN 1936-0851.
- [72] Jeffrey A. Christians, Pierre Alexander Miranda Herrera & Prashant V. Kamat. *Journal of the American Chemical Society*, **137**, 4 (2015) 1530–1538. ISSN 0002-7863.
- [73] Yixin Zhao & Kai Zhu. *Chemical Communications*, **50**, 13 (2014) 1605. ISSN 1359-7345.
- [74] Christian Müller, Tobias Glaser, Marcel Plogmeyer, Michael Sendner, Sebastian Döring, Artem A. Bakulin, Carlo Brzuska, Roland Scheer, Maxim S. Pshenichnikov, Wolfgang Kowalsky, Annemarie Pucci & Robert Lovrinčić. *Chemistry of Materials*, **27**, 22 (2015) 7835–7841. ISSN 0897-4756.
- [75] Giles E. Eperon, Severin N. Habisreutinger, Tomas Leijtens, Bardo J. Bruijnaers, Jacobus J. van Franeker, Dane W. DeQuilettes, Sandeep Pathak, Rebecca J. Sutton, Giulia Grancini, David S. Ginger, Rene A. J. Janssen, Annamaria Petrozza & Henry J. Snaith. *ACS Nano*, **348**, 6235 (2015) 150806144801005. ISSN 1936-0851.
- [76] Aurélien Leguy, Yinghong Hu, Mariano Campoy-Quiles, M. Isabel Alonso, Oliver J. Weber, Pooya Azarhoosh, Mark van Schilfgaarde, Mark T. Weller, Thomas Bein, Jenny Nelson, Pablo Docampo & Piers R.F. Barnes. *Chemistry of Materials*, **27**, 9 (2015) 3397–3407. ISSN 0897-4756.
- [77] An Dai, Yinhua Zhou, Andrew L. Shu, Swagat K. Mohapatra, He Wang, Canek Fuentes-Hernandez, Yadong Zhang, Stephen Barlow, Yueh-Lin Loo, Seth R. Marder, Bernard Kippelen & Antoine Kahn. *Advanced Functional Materials*, **24**, 15 (2014) 2197–2204. ISSN 1616301X.
- [78] Sergio a. Paniagua, Jose Baltazar, Hossein Sojoudi, Swagat K. Mohapatra, Siyuan Zhang, Clifford L. Henderson, Samuel Graham, Stephen Barlow & Seth R. Marder. *Mater. Horiz.*, **1**, 1 (2014) 111–115. ISSN 2051-6347.
- [79] William H. Nguyen, Colin D. Bailie, Eva L. Unger & Michael D. McGehee. *Journal of the American Chemical Society*, **136**, 31 (2014) 10996–11001. ISSN 0002-7863.
- [80] Weijun Ke, Guojia Fang, Qin Liu, Liangbin Xiong, Pingli Qin, Hong Tao, Jing Wang, Hongwei Lei, Borui Li, Jiawei Wan, Guang Yang & Yanfa Yan. *Journal of the American Chemical Society*, **137**, 21 (2015) 6730–6733. ISSN 15205126.
- [81] Elham Halvani Anaraki, Ahmad Kermanpur, Ludmilla Steier, Konrad Domanski, Taisuke Matsui, Wolfgang Tress, Michael Saliba, Antonio Abate, Michael Grätzel, Anders Hagfeldt & Juan-Pablo Correa-Baena. *Energy Environ. Sci.*, **9**, 10 (2016) 3128–3134. ISSN 1754-5692.

-
- [82] James M. Ball, Michael M. Lee, Andrew Hey & Henry J. Snaith. *Energy & Environmental Science*, **6**, 6 (2013) 1739. ISSN 1754-5692.
- [83] M. Christoforo, Eric Hoke, Michael McGehee & Eva Unger. *Photonics*, **2**, 4 (2015) 1101–1115. ISSN 2304-6732.
- [84] J. C. de Mello, H. F. Wittmann & Richard H. Friend. *Advanced Materials*, **9**, 3. ISSN 09359648.
- [85] Tomas Leijtens, Jongchul Lim, Joël Teuscher, Taiho Park & Henry J Snaith. *Advanced Materials*, **25**, 23 (2013) 3227–3233. ISSN 09359648.
- [86] Annamaria Petrozza, Chris Groves & Henry J Snaith. *Journal of the American Chemical Society*, **130** (2008) 12912–12920. ISSN 1520-5126.
- [87] Uwe Rau. *Physical Review B*, **76**, 8 (2007) 085303. ISSN 1098-0121.
- [88] Severin N Habisreutinger, Tomas Leijtens, Giles E Eperon, Samuel D Stranks, Robin J Nicholas & Henry J Snaith. *Nano Letters*, **14**, 10 (2014) 5561–5568. ISSN 1530-6984.
- [89] Kristofer Tvingstedt, Olga Malinkiewicz, Andreas Baumann, Carsten Deibel, Henry J. Snaith, Vladimir Dyakonov & Henk J. Bolink. *Scientific Reports*, **4**, 1 (2015) 6071. ISSN 2045-2322.
- [90] Antonio Abate, Tomas Leijtens, Sandeep Pathak, Joël Teuscher, Roberto Avolio, Maria E Errico, James Kirkpatrick, James M Ball, Pablo Docampo, Ian McPherson & Henry J Snaith. *Physical Chemistry Chemical Physics*, **15**, 7 (2013) 2572. ISSN 1463-9076.
- [91] Francesco Di Giacomo, Stefano Razza, Fabio Matteocci, Alessandra D’Epifanio, Silvia Licoccia, Thomas M. Brown & Aldo Di Carlo. *Journal of Power Sources*, **251** (2014) 152–156. ISSN 03787753.
- [92] F Matteocci, S Razza, F Di Giacomo, S Casaluci, G Mincuzzi, T M Brown, A D’Epifanio, S Licoccia & A Di Carlo. *Physical Chemistry Chemical Physics*, **16**, 9 (2014) 3918. ISSN 1463-9076.
- [93] Hisham A. Abbas, Ranjith Kottokkaran, Balaji Ganapathy, Mehran Samiee, Liang Zhang, Andrew Kitahara, Max Noack & Vikram L. Dalal. *APL Materials*, **3**, 1 (2015) 016105. ISSN 2166-532X.
- [94] Yuchen Zhang, Mohammed Elawad, Ze Yu, Xiaoqing Jiang, Jianbo Lai & Licheng Sun. *RSC Adv.*, **6**, 110 (2016) 108888–108895. ISSN 2046-2069.
- [95] Narges Yaghoobi Nia, Fabio Matteocci, Lucio Cina & Aldo Di Carlo. *ChemSusChem*, **10**, 19 (2017) 3854–3860. ISSN 18645631.
- [96] Dongqin Bi, Lei Yang, Gerrit Boschloo, Anders Hagfeldt & Erik M J Johansson. *The Journal of Physical Chemistry Letters*, **4**, 9 (2013) 1532–1536. ISSN 1948-7185.

-
- [97] Andrew W Blakers, Aihua Wang, Adele M Milne, Jianhua Zhao & Martin A Green. *Applied Physics Letters*, **55**, 13 (1989) 1363–1365. ISSN 0003-6951.
- [98] Martin A. Green. *Solar Energy Materials and Solar Cells*, **143** (2015) 190–197. ISSN 09270248.
- [99] Martin A Green. *Applied Physics Letters*, **27**, 5 (1975) 287–288. ISSN 0003-6951.
- [100] G. Yu, J. Gao, J. C. Hummelen, F. Wudl & A. J. Heeger. *Science*, **270**, 5243 (1995) 1789–1791. ISSN 0036-8075.
- [101] Neil D. Treat, Alessandro Varotto, Christopher J. Takacs, Nicolas Batara, Mohammed Al-Hashimi, Martin J. Heeney, Alan J. Heeger, Fred Wudl, Craig J. Hawker & Michael L. Chabinyc. *Journal of the American Chemical Society*, **134**, 38 (2012) 15869–15879. ISSN 0002-7863.
- [102] Jin Young Oh, Minkwan Shin, Tae Il Lee, Woo Soon Jang, Yu-Jeong Lee, Chang Su Kim, Jae-Wook Kang, Jae-Min Myoung, Hong Koo Baik & Unyong Jeong. *Macromolecules*, **46**, 9 (2013) 3534–3543. ISSN 0024-9297.
- [103] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig & D. M. de Leeuw. *Nature*, **401**, 6754 (1999) 685–688. ISSN 0028-0836.
- [104] H. Yang, Tae Joo Shin, Lin Yang, Kilwon Cho, Chang Y. Ryu & Zhenan Bao. *Advanced Functional Materials*, **15**, 4 (2005) 671–676. ISSN 1616-301X.
- [105] Robert a. Street. *Nature Materials*, **5**, 3 (2006) 171–172. ISSN 1476-1122.
- [106] Yi-Kang Lan, Cheng Han Yang & Hsiao-Ching Yang. *Polymer International*, **59**, 1 (2010) 16–21. ISSN 09598103.
- [107] Yi-kang Lan & Ching-i Huang. *The Journal of Physical Chemistry B*, **113**, 44 (2009) 14555–14564. ISSN 1520-6106.
- [108] Jong Soo Kim, Ji Hwang Lee, Jong Hwan Park, Chiyeoung Shim, Myungsun Sim & Kilwon Cho. *Advanced Functional Materials*, **21**, 3 (2011) 480–486. ISSN 1616301X.
- [109] Feng Liu, Yu Gu, Jae Woong Jung, Won Ho Jo & Thomas P. Russell. *Journal of Polymer Science Part B: Polymer Physics*, **50**, 15 (2012) 1018–1044. ISSN 08876266.
- [110] Joo-Hyun Kim, Jong Hwan Park, Ji Hwang Lee, Jong Soo Kim, Myungsun Sim, Chiyeoung Shim & Kilwon Cho. *Journal of Materials Chemistry*, **20**, 35 (2010) 7398. ISSN 0959-9428.
- [111] Joo-Hyun Kim, Min Kim, Hiroshi Jinnai, Tae Joo Shin, Haena Kim, Jong Hwan Park, Sae Byeok Jo & Kilwon Cho. *ACS Applied Materials & Interfaces*, **6**, 8 (2014) 5640–5650. ISSN 1944-8244.
- [112] John D. Roehling, Ilke Arslan & Adam J. Moulé. *J. Mater. Chem.*, **22**, 6 (2012) 2498–2506. ISSN 0959-9428.

-
- [113] Longjian Xue, Xinhong Yu & Yanchun Han. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **380**, 1-3 (2011) 334–340. ISSN 09277757.
- [114] Jin Young Oh, Minkwan Shin, Tae Il Lee, Woo Soon Jang, Yuho Min, Jae-min Myoung, Hong Koo Baik & Unyong Jeong. *Macromolecules*, **45**, 18 (2012) 7504–7513. ISSN 0024-9297.
- [115] Gavvalapalli Nagarjuna, Mina Baghgar, Joelle A Labastide, Dana D Algaier, Michael D Barnes & Dhandapani Venkataraman. *ACS Nano*, **6**, 12 (2012) 10750–10758. ISSN 1936-0851.
- [116] Seong-Min Cho, Jin-Hyuk Bae, Eunje Jang, Min-Hoi Kim, Changhee Lee & Sin-Doo Lee. *Semiconductor Science and Technology*, **27**, 12 (2012) 125018. ISSN 0268-1242.
- [117] S. Berson, R. DeâBettignies, S. Bailly & S. Guillerez. *Advanced Functional Materials*, **17**, 8 (2007) 1377–1384. ISSN 1616301X.
- [118] Linlin An, Yongxin Duan, Yuan Yuan, Lijuan Zhou & Jianming Zhang. *Vibrational Spectroscopy*, **68** (2013) 40–44. ISSN 09242031.
- [119] Peter J. Brown, D. Steve Thomas, Anna K  hler, Joanne S. Wilson, Ji-Seon Kim, Catherine M. Ramsdale, Henning Sirringhaus & Richard H. Friend. *Physical Review B*, **67**, 6 (2003) 064203. ISSN 0163-1829.
- [120] Longzhen Qiu, Wi Hyoung Lee, Xiaohong Wang, Jong Soo Kim, Jung Ah Lim, Donghoon Kwak, Shichoon Lee & Kilwon Cho. *Advanced Materials*, **21**, 13 (2009) 1349–1353. ISSN 09359648.
- [121] Loig Kergoat, Nicolas Battaglini, Luciano Miozzo, Benoit Piro, Minh-Chau Pham, Abderrahim Yassar & Gilles Horowitz. *Organic Electronics*, **12**, 7 (2011) 1253–1257. ISSN 15661199.
- [122] Zhiyong Liu, Shengli Niu & Ning Wang. *Solar Energy*, **155** (2017) 1044–1051. ISSN 0038092X.
- [123] Wolfgang Tress. *Advanced Energy Materials*, **7**, 14 (2017) 1602358. ISSN 16146832.
- [124] Felix Deschler, Michael Price, Sandeep Pathak, Lina E. Klintberg, David-Dominik Jarausch, Ruben Higler, Sven H  ttner, Tomas Leijtens, Samuel D. Stranks, Henry J. Snaith, Mete Atat  re, Richard T. Phillips & Richard H. Friend. *The Journal of Physical Chemistry Letters*, **5**, 8 (2014) 1421–1426. ISSN 1948-7185.
- [125] Carlito S Ponseca, Tom J Savenije, Mohamed a Abdellah, Kaibo Zheng, Arkady Petrovich Yartsev, Tobj  rn Pascher, Tobias Harlang, Pavel Chabera, Tonu Pullerits, Andrey Stepanov, Jean-pierre Wolf & Villy Sundstrom.
- [126] Jan C. Brauer, Yong Hui Lee, Mohammad Khaja Nazeeruddin & Natalie Banerji. *The Journal of Physical Chemistry Letters*, pages 3675–3681. ISSN 1948-7185.

-
- [127] R. Alex Marsh, Justin M. Hodgkiss, Sebastian Albert-Seifried & Richard H. Friend. *Nano Letters*, **10**, 3 (2010) 923–930. ISSN 1530-6984.
- [128] Owen D Miller, Eli Yablonovitch & Sarah R Kurtz. *IEEE Journal of Photovoltaics*, **2**, 3 (2012) 303–311. ISSN 2156-3381.
- [129] Martin A. Green. *Progress in Photovoltaics: Research and Applications*, **20**, 4 (2012) 472–476. ISSN 10627995.
- [130] Martin A. Green & Stephen P. Bremner. *Nature Materials*, **16**, 1 (2016) 23–34. ISSN 1476-1122.
- [131] W U Huynh. *Science*, **295**, 5564 (2002) 2425–2427. ISSN 00368075.
- [132] Severin N. Habisreutinger, Nakita K. Noel, Henry J. Snaith & Robin J. Nicholas. *Advanced Energy Materials*, **7**, 1 (2017) 1601079. ISSN 16146832.
- [133] Yi Li, Kaori Kamata, Sadayuki Asaoka, Takamichi Yamagishi & Tomokazu Iyoda. *Organic & Biomolecular Chemistry*, **1**, 10 (2003) 1779–1784. ISSN 14770520.
- [134] Alba Pellaroque, Nakita K. Noel, Severin N. Habisreutinger, Yadong Zhang, Stephen Barlow, Seth R. Marder & Henry J. Snaith. *ACS Energy Letters*, pages 2044–2050. ISSN 2380-8195.
- [135] Seong Sik Shin, Eun Joo Yeom, Woon Seok Yang, Seyoon Hur, Min Gyu Kim, Jino Im, Jangwon Seo, Jun Hong Noh & Sang Il Seok. *Science*, **356**, 6334 (2017) 167–171. ISSN 0036-8075.
- [136] Hairen Tan, Ankit Jain, Oleksandr Voznyy, Xinzheng Lan, F. Pelayo García de Arquer, James Z. Fan, Rafael Quintero-Bermudez, Mingjian Yuan, Bo Zhang, Yongbiao Yicheng Zhao, Fengjia Fan, Peicheng Li, Li Na Quan, Yongbiao Yicheng Zhao, Zheng-Hong Lu, Zhenyu Yang, Sjoerd Hoogland & Edward H. Sargent. *Science*, **355**, 6326 (2017) 722–726. ISSN 0036-8075.
- [137] Udo Bach, P Comte, J E Moser, F Weisso & M Gra. *Nature*, **395**, October (1998) 583–585.
- [138] Henry J. Snaith & Michael Grätzel. *Applied Physics Letters*, **89**, 26 (2006) 262114. ISSN 0003-6951.
- [139] Andrew J. Pearson, Giles E. Eperon, Paul E. Hopkinson, Severin N. Habisreutinger, Jacob Tse-Wei Wang, Henry J. Snaith & Neil C. Greenham. *Advanced Energy Materials*, **6**, 13 (2016) 1600014. ISSN 16146832.
- [140] Jiewei Liu, Sandeep Pathak, Thomas Stergiopoulos, Tomas Leijtens, Konrad Wojciechowski, Stefan Schumann, Nina Kausch-Busies & Henry J. Snaith. *The Journal of Physical Chemistry Letters*, **6**, 9 (2015) 1666–1673. ISSN 1948-7185.
- [141] Junyan Xiao, Jiangjian Shi, Huibiao Liu, Yuzhuan Xu, Songtao Lv, Yanhong Luo, Dongmei Li, Qingbo Meng & Yuliang Li. *Advanced Energy Materials*, **5**, 8 (2015) 1401943. ISSN 16146832.

-
- [142] Tomas Leijtens, Tommaso Giovenzana, Severin N. Habisreutinger, Jonathan S. Tinkham, Nakita K. Noel, Brett A. Kamino, Golnaz Sadoughi, Alan Sellinger & Henry J. Snaith. *ACS Applied Materials & Interfaces*, **8**, 9 (2016) 5981–5989. ISSN 1944-8244.
- [143] Antonio Abate, Derek J Hollman, Joël Teuscher, Sandeep Pathak, Roberto Avolio, Gerardino D’Errico, Giuseppe Vitiello, Simona Fantacci & Henry J Snaith. *Journal of the American Chemical Society*, **135**, 36 (2013) 13538–13548. ISSN 0002-7863.
- [144] Julian Burschka, Amalie Dualeh, Florian Kessler, Etienne Baranoff, Ngoc-Lê Cevey-Ha, Chenyi Yi, Mohammad K Nazeeruddin & Michael Grätzel. *Journal of the American Chemical Society*, **133**, 45 (2011) 18042–18045. ISSN 0002-7863.
- [145] Julian Burschka, Florian Kessler, Mohammad Khaja Nazeeruddin & Michael Grätzel. *Chemistry of Materials*, **25**, 15 (2013) 2986–2990. ISSN 0897-4756.
- [146] Junsheng Luo, Chunyang Jia, Zhongquan Wan, Fei Han, Bowen Zhao & Ruilin Wang. *Journal of Power Sources*, **342** (2017) 886–895. ISSN 03787753.
- [147] Priyanka Tyagi, Manas Kumar Dalai, C. K. Suman, Suneet Tuli & Ritu Srivastava. *RSC Advances*, **3**, 46 (2013) 24553. ISSN 2046-2069.
- [148] Jun Li, Chris W. Rochester, Ian E. Jacobs, Stephan Friedrich, Pieter Stroeve, Moritz Riede & Adam J. Moulé. *ACS Applied Materials & Interfaces*, **7**, 51 (2015) 28420–28428. ISSN 1944-8244.
- [149] Yabing Qi, Tissa Sajoto, Michael KroÛlger, Alexander M. Kandabarow, Wonjun Park, Stephen Barlow, Eung-Gun Kim, Leszek Wielunski, L. C. Feldman, Robert a. Bartynski, Jean-Luc BreÛadas, Seth R. Marder & Antoine Kahn. *Chemistry of Materials*, **22**, 2 (2010) 524–531. ISSN 0897-4756.
- [150] Swagat K. Mohapatra, Yadong Zhang, Bhupinder Sandhu, Marina S. Fonari, Tatiana V. Timofeeva, Seth R. Marder & Stephen Barlow. *Polyhedron*, **116** (2016) 88–95. ISSN 02775387.
- [151] Marcel M. Said, Yadong Zhang, Raghunath R. Dasari, Dalaver H. Anjum, Rahim Munir, Hanlin Hu, Aram Amassian, Stephen Barlow & Seth R. Marder. *Organic Photonics and Photovoltaics*, **4**, 1 (2016) 1–16. ISSN 2299-3177.
- [152] Lars Müller, Seon-young Rhim, Vipilan Sivanesan, Dongxiang Wang, Sebastian Hietzschold, Patrick Reiser, Eric Mankel, Sebastian Beck, Stephen Barlow, Seth R Marder, Annemarie Pucci, Wolfgang Kowalsky & Robert Lovrincic. *Advanced Materials*, **1701466** (2017) 1701466. ISSN 09359648.
- [153] James Belasco, Swagat K. Mohapatra, Yadong Zhang, Stephen Barlow, Seth R. Marder & Antoine Kahn. *Applied Physics Letters*, **105**, 6 (2014) 063301. ISSN 0003-6951.
- [154] Chih-Yu Chang, Bo-Chou Tsai & Yu-Cheng Hsiao. *ChemSusChem*, **10**, 9 (2017) 1981–1988. ISSN 18645631.

-
- [155] Simona Fantacci, Filippo De Angelis, Mohammad K. Nazeeruddin & Michael Grätzel. *The Journal of Physical Chemistry C*, **115**, 46 (2011) 23126–23133. ISSN 1932-7447.
- [156] Emilio J. Juarez-Perez, Matthew R. Leyden, Shenghao Wang, Luis K. Ono, Zafer Hawash & Yabing Qi. *Chemistry of Materials*, **28**, 16 (2016) 5702–5709. ISSN 0897-4756.
- [157] Zhiping Wang, David P. McMeekin, Nobuya Sakai, Stephan van Reenen, Konrad Wojciechowski, Jay B. Patel, Michael B. Johnston & Henry J. Snaith. *Advanced Materials*, **29**, 5 (2017) 1604186. ISSN 09359648.
- [158] James M. Ball & Annamaria Petrozza. *Nature Energy*, **1**, October (2016) 16149. ISSN 2058-7546.
- [159] Nakita K. Noel, Antonio Abate, Samuel D. Stranks, Elizabeth S. Parrott, Victor M. Burlakov, Alain Goriely, Henry J. Snaith & Noel E T Al. *ACS Nano*, **8**, 10 (2014) 9815–9821. ISSN 1936-0851.
- [160] Dane W. DeQuilettes, Susanne Koch, Sven Burke, Rajan K. Paranji, Alfred J. Shropshire, Mark E. Ziffer & David S. Ginger. *ACS Energy Letters*, **1**, 2 (2016) 438–444. ISSN 2380-8195.
- [161] Tomas Leijtens, Giles E. Eperon, Nakita K. Noel, Severin N. Habisreutinger, Annamaria Petrozza & Henry J. Snaith. *Advanced Energy Materials*, **5**, 20 (2015) 1500963. ISSN 16146840.
- [162] Severin N. Habisreutinger, David P. McMeekin, Henry J. Snaith & Robin J. Nicholas. *APL Materials*, **4**, 9 (2016) 091503. ISSN 2166-532X.
- [163] Henry J. Snaith, Antonio Abate, James M. Ball, Giles E. Eperon, Tomas Leijtens, Nakita Kimberly Noel, Samuel David Stranks, Jacob Tse-Wei Wang, Konrad Wojciechowski & Wei Zhang. *The Journal of Physical Chemistry Letters*, **5**, 9 (2014) 1511–1515. ISSN 1948-7185.
- [164] Dane W. de Quilettes, Sarah M Vorpahl, Samuel D Stranks, Hirokazu Nagaoka, Giles E Eperon, Mark E Ziffer, Henry J Snaith & David S Ginger. , April.
- [165] Antonio Abate, Michael Saliba, Derek J. Hollman, Samuel D. Stranks, Konrad Wojciechowski, Roberto Avolio, Giulia Grancini, Annamaria Petrozza & Henry J. Snaith. *Nano Letters*, **14**, 6 (2014) 3247–3254. ISSN 15306992.
- [166] Ting Zhao, Chu-Chen Chueh, Qi Chen, Adharsh Rajagopal & Alex K.-Y. Jen. *ACS Energy Letters*, **1**, 4 (2016) 757–763. ISSN 2380-8195.
- [167] Cong-Cong Zhang, Meng Li, Zhao-Kui Wang, Yu-Rong Jiang, Hai-Rui Liu, Ying-Guo Yang, Xing-Yu Gao & Heng Ma. *J. Mater. Chem. A*, **5**, 6 (2017) 2572–2579. ISSN 2050-7488.

-
- [168] Tomas Leijtens, Giles E. Eperon, Alex J. Barker, Giulia Grancini, Wei Zhang, James M. Ball, Ajay Ram Srimath Kandada, Henry J. Snaith & Annamaria Petrozza. *Energy Environ. Sci.*, **9**, 11 (2016) 3472–3481. ISSN 1754-5692.
- [169] Jixian Xu, Andrei Buin, Alexander H. Ip, Wei Li, Oleksandr Voznyy, Riccardo Comin, Mingjian Yuan, Seokmin Jeon, Zhijun Ning, Jeffrey J. McDowell, Pongsakorn Kanjanaboos, Jon-Paul Sun, Xinzheng Lan, Li Na Quan, Dong Ha Kim, Ian G. Hill, Peter Maksymovych & Edward H. Sargent. *Nature Communications*, **6**, c (2015) 7081. ISSN 2041-1723.
- [170] Xiaodong Liu, Weixiang Jiao, Ming Lei, Yi Zhou, Bo Song & Yongfang Li. *J. Mater. Chem. A*, **3**, 17 (2015) 9278–9284. ISSN 2050-7488.
- [171] Yuchuan Shao, Zhengguo Xiao, Cheng Bi, Yongbo Yuan & Jinsong Huang. *Nature Communications*, **5** (2014) 5784. ISSN 2041-1723.
- [172] Dandan Song, Dong Wei, Peng Cui, Meicheng Li, Zhiqiang Duan, Tianyue Wang, Jun Ji, Yaoyao Yingfeng Li, Joseph Michel Mbengue, Yaoyao Yingfeng Li, Yue He, Mwenya Trevor & Nam-Gyu Park. *J. Mater. Chem. A*, **4**, 16 (2016) 6091–6097. ISSN 2050-7488.
- [173] Stephan van Reenen, Martijn Kemerink & Henry J. Snaith. *The Journal of Physical Chemistry Letters*, **6**, 19 (2015) 3808–3814. ISSN 1948-7185.
- [174] Tomas Leijtens, Samuel D Stranks, Giles E Eperon, Rebecka Lindblad, Erik M J Johansson, James M Ball, Michael M Lee, Henry J Snaith & Ian J Mcpherson. *ACS nano*, , 7 (2014) 7147–7155. ISSN 1936086X.
- [175] Jongseob Kim, Sung-Hoon Lee, Jung Hoon Lee & Ki-Ha Hong. *The Journal of Physical Chemistry Letters*, **5**, 8 (2014) 1312–1317. ISSN 1948-7185.
- [176] Robert J. Stewart, Christopher Grieco, Alec V. Larsen, Grayson S. Doucette & John B. Asbury. *The Journal of Physical Chemistry C*, **120**, 23 (2016) 12392–12402. ISSN 1932-7447.
- [177] Lei Zhang, Xiaogang Liu, Jing Su & Jingfa Li. *Journal of Physical Chemistry C*, **120**, 41 (2016) 23536–232541. ISSN 19327455.
- [178] Lydia C. Gilday, Sean W. Robinson, Timothy A. Barendt, Matthew J. Langton, Benjamin R. Mullaney & Paul D. Beer. *Chemical Reviews*, **115**, 15 (2015) 7118–7195. ISSN 0009-2665.
- [179] Gabriella Cavallo, Pierangelo Metrangolo, Roberto Milani, Tullio Pilati, Arri Priimagi, Giuseppe Resnati & Giancarlo Terraneo. *Chemical Reviews*, **116**, 4 (2016) 2478–2601. ISSN 0009-2665.
- [180] Pierangelo Metrangolo, Jane S. Murray, Tullio Pilati, Peter Politzer, Giuseppe Resnati & Giancarlo Terraneo. *Crystal Growth & Design*, **11**, 9 (2011) 4238–4246. ISSN 1528-7483.

- [181] Wei Zhang, Sandeep Pathak, Nobuya Sakai, Thomas Stergiopoulos, Pabitra K. Nayak, Nakita K. Noel, Amir a. Haghighirad, Victor M. Burlakov, Dane W. DeQuilettes, Aditya Sadhanala, Wenzhe Li, Liduo Wang, David S. Ginger, Richard H. Friend & Henry J. Snaith. *Nature Communications*, **6**, May (2015) 10030. ISSN 2041-1723.